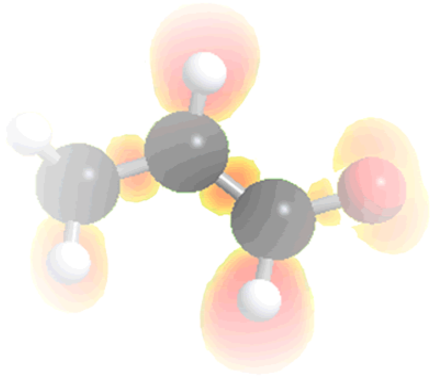
31st August - 4th September 2009
Lyon, France

13th International Conference on the Applications of Density Functional Theory in Chemistry and Physics

Book of Abstracts



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13th edition of the International Conference on the Applications of
DENSITY FUNCTIONAL THEORY
in Chemistry and Physics

August 31st to September 4th, 2009

– Lyon, France –

Topics:

1. **P**roperties
2. **D**ensity **M**atrices, **c**urrent **f**unctionals and **d**ensity **f**unctionals
3. **L**inear **s**caling **m**ethods
4. **V**an der **W**aals **i**nteractions
5. **T**ime-**d**ependent DFT
6. **C**atalysis, **r**eactivity and **s**urface **p**roperties
7. **L**arge **s**ystems and **b**iosystems
8. **N**ano and **m**olecular **d**evices
9. **C**onceptual DFT

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Foreword

On behalf of the Organizing Committee and the International Scientific Committee we wish to welcome you to the 13th in the series of the European Conferences on the Applications of Density Functional Theory to chemistry and physics. This series started in 1984 in San Miniato (Italy) with 13 participants, and since then visited many major European cities with an uninterruptedly growing number of participants, becoming a unique international, biennial, gathering of scientists interested in fundamental and applied Density Functional Theory.

The last edition was held in Amsterdam (2007), following the meetings in Geneva (2005) and Brussels (2003). Arles (1988) and Paris (1995) were the previous French stops. More than 440 participants from 40 countries are expected in Lyon for the DFT09.

DFT is now widely recognized as an unavoidable tool for the simulation and modeling in chemistry and physics. Although mature, DFT still constitutes an area in continuous and rapid expansion both from the point of view of new fields of application (new domains, increasingly larger systems), and of developments (new functionals, new algorithms, systems out of equilibrium). Failures of the method and inaccuracies in some domains of application represent a stimulus for deeper understanding of the fundamental theory, and for new developments both in chemistry and physics.

We wish that the DFT09 conference will provide a fruitful environment for scientific exchange to all participants, and we also hope that you will also find the time to enjoy the richness of the cultural patrimony of Lyon.

Welcome to Lyon and to DFT09!

Henry Chermette, chair
Carlo Adamo, vice-chair

DETAILED PROGRAMME

DFT09 - DETAILED PROGRAM - August 31st to September 2nd, 2009

MONDAY, AUGUST 31ST, 2009	
14:00 - 16:00	**Arrival & Welcome of the Participants: Registration Desk & Poster installations**
16:00 - 18:00	**Opening Ceremony: Welcome Talks & Musical Interludes:** * Sandro Bencini by Claude Daul (5') *Music: Aria "Erbarme dich" n°47 de la Mattäuspassion BWV 244, JS. Bach* * Sandro Bencini and DFT09 by PierCarlo Fantucci (30') *Music: Sonate en sol majeur pour violoncelle et basse continue, D. Gabrielli* * UCBL Welcome by Pierre Lanteri (5') *Music: «Et è pur dunque vero» -extrait des «Scherzi Musicali», C. Monteverdi* * ICL / ENSL Welcome by David Loffreda (5') *Music: « Meine Seele hört im Sehen » (German arias N°6), GF. Haendel* * Lyon Welcome (5') *Music: Sonate 5 pour violon et Basse continue de l' Opera Quinta, A. Corelli* * History of DFT conferences (5') *Music: « Die ihr aus dunkeln Grüften » (German arias N°7), GF. Haendel*
18:00 - 19:45	**Cocktails - Welcome reception**

TUESDAY, SEPTEMBER 1ST, 2009	
9:00 - 10:10	**Conference & Oral Presentation** (Jacques Weber, chairman) * Axel BECKE, *A density-functional approximation for relativistic kinetic energy* (40') * Ann MATTSSON, *The subsystem functional scheme: the Armiento-Mattsson 2005 (AM05) functional and beyond* (30')
10:10 - 10:40	***Coffee Break***
10:40 - 12:10	**Oral Presentations** (David J. Tozer, chairman) * Yingkai ZHANG, *Born oppenheimer DFT QM/MM molecular dynamics simulations of enzyme reactions* (30') * Marcel SWART, *A new DFT functional based on spin-states and Sn2 barriers* (30') * Fabio DELLA SALA, *The role of exact-exchange in organic-metal interfaces* (30')
12:10 - 14:00	***Lunch***
14:00 - 15:40	**Conference & Oral Presentations** (Eberhard K.U. Gross, chairman) * Evert Jan BAERENDS, *Excitation energies with time-dependent density matrix functional theory* (40') * Julien TOULOUSE, *Adiabatic-connection fluctuation-dissipation density functional theory based on range separation* (30') * Wenjian LIU, *New generation relativistic theories for eletronic structures and magnetic properties* (30')
15:40 - 16:10	***Coffee Break***
16:10 - 16:40	**Oral Presentation** (Agnes Nagy, chairwoman) * Gustavo SCUSERIA, *New models for mixing wavefunctions with density functional theory* (30')
16:40 - 19:00	**Poster Session I**

WEDNESDAY, SEPTEMBER 2ND, 2009	
9:00 - 10:10	**Conference & Oral Presentation** (Jose M. Garcia de la Vega, chairman) * Matthias SCHEFFLER, *DFT and beyond: a discussion of exact exchange plus local- and nonlocal-density approximations to the correlation functional* (40') * Georg KRESSE, *The random phase approximation to the correlation: successes and failures* (30')
10:10 - 10:40	***Coffee Break***
10:40 - 12:10	**Oral Presentations** (Miguel Moreno, chairman) * Alessandro LAIO, *Computer simulation of rare events in material science and computational chemistry* (30') * Patrizia CALAMINICI, *Metal cluster heat capacities from first-principle molecular dynamics simulations* (30') * Angel RUBIO *GW renormalization of DFT molecular electronic levels at the vicinity of a surface: The image charge effect* (30')
12:10 - 14:00	***Lunch***
14:00 - 15:40	**Conference & Oral Presentations** (Annick Goursot, chairwoman) * Mark CASIDA, *Defining and going beyond the limits of conventional time-dependent density functional theory for photochemical modeling* (40') * Paul DAY, *Prediction of two-photon absorption spectra by applying time-dependent density functional theory* (30') * Denis JACQUEMIN, *TD-DFT calculations for organic dyes* (30')
15:40 - 16:10	***Coffee Break***
16:10 - 16:40	**Oral Presentation** (Andreas K. Theophilou, chairman) * Kimihiko HIRAO, *Towards linear scaling density functional theory* (30')
16:40 - 19:00	**Poster Session II**
19:30 - 21:00	**Cocktails at the Rhône County Council**

DFT09 - DETAILED PROGRAM - September 3rd to September 4th, 2009

THURSDAY, SEPTEMBER 3RD, 2009 !!! Parallel sessions all morning long	
9:00 - 10:00	
Room A	**Oral Presentations** (Claude A. Daul , chairman)
	* Lars PETTERSSON, *Liquid water structure from X-Ray spectroscopy and DFT simulations* (30')
	* Tomasz WESOLOWSKI, *Orbital-free embedding potential: exact properties, approximations and applications* (30')
Room B	**Oral Presentations** (Roman Nalewajski, chairman)
	* Alberto VELA, *Non-empirical GGAs under scrutiny (30')*
	* Eliseo RUIZ, *Theoritical studies of magnetic properties in single-molecule magnet* (30')
10:00 - 10:30	***Coffee Break***
10:30 - 12:00	
Room A	**Oral Presentations** (Karlheinz Schwarz, chairman)
	* Julian GALE, *Using density functional theory to design a viable material for hydrogen storage* (30')
	* Bartolomeo CIVALLERI, *DFT augmented with an empirical dispersion term as applied to solids* (30')
	* Francesco MAURI, *Stability, chemical structure, and Clar's aromatic sextets of hydrogen terminated graphene ribbons* (30')
Room B	**Oral Presentations** (Paul Geerlings, chairman)
	* Alejandro TORRO LABBE, *Characterizing the mechanism of chemical reactions from the perspective of conceptual DFT* (30')
	* Jans MOENS, *Application of conceptual DFT descriptors in the field of redox chemistry and the spectrochemical series* (30')
	* Christophe MORELL, *Characterization of the chemical behaviour of the first excited state through a local chemical potential* (30')
12:00 - 14:00	***Lunch***
14:00 - 19:00	**Social Program: Touristic visits**
	* Lyon Renaissance district and its "traboules"
	* From Fourvière to the Old Lyon
	* When the Court of France lived in Lyon
19:00 - 23:00	**Gala Dinner in the "Abbaye de Collonges" at Bocuse**

FRIDAY, SEPTEMBER 4TH, 2009	
9:00 - 10:10	**Conference & Oral Presentation** (Paola Gori-Giorgi, chairwoman)
	* Marcus ELSTNER, *The approximate SCC-DFTB method: performances and challenges* (40')
	* Luigi GENOVESE, *Ab initio simulations of large systems in complex environments: daubechies wavelets for eletronic structure calculations* (30')
10:10 - 10:40	***Coffee Break***
10:40 - 11:40	**Oral Presentations** (Dennis R. Salahub, chairman)
	* Jean-Sébastien FILHOL, *Ab initio electrochemistry at the metal interface: from ultra-vacuum to the water* (30')
	* Michael SPRIK, *Computation of absolute ionization potentials and electron affinities of simple aqueous species using DFT based molecular dynamics* (30')
11:40 - 12:15	**Closing Ceremony**

CONTENTS

ORAL PRESENTATIONS

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Excitation energies with time-dependent density *matrix* functional theory

Evert Jan Baerends[a], Klaas J. H. Giesbertz[a], Oleg V. Gritsenko[a], Katarzyna Pernal[a,b]

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Time-dependent density functional theory in its current adiabatic implementations exhibits three striking failures: a) totally wrong behavior of the excited state surface along a bond-breaking coordinate [1]; b) lack of doubly excited configurations, affecting again excited state surfaces; c) much too low charge transfer excitation energies. We address these problems with time-dependent density *matrix* theory (TDDMFT) [2.3].

First, a brief introduction into density matrix functional theory will be given, reviewing the current state-of-the-art of functional development in an application to *E* vs *R* curves for bond dissociation of A-H bonds of the first row 10-electron hydrides [4].

For two-electron systems the exact exchange-correlation functional is known in DMFT, hence exact response equations can be formulated. This affords a study of the performance of TDDMFT in the TDDFT failure cases mentioned (which are all strikingly exhibited by prototype two-electron systems such as dissociating H_2 and HeH^+). At the same time, adiabatic approximations, which will eventually be necessary, can be tested without being obscured by approximations in the functional. We find [5.6]: a) In the fully non-adiabatic (ω-dependent, exact) formulation of linear response TDDMFT, it can be shown that LR-TDDMFT is able to provide exact excitation energies; in particular the first order (linear response) formulation does not prohibit the correct representation of doubly excited states; b) Within previously formulated simple adiabatic approximations [3] the bonding-to-antibonding excited state surface as well as charge transfer excitations are described without problems, but not the double excitations; c) An adiabatic approximation is formulated in which also the double excitations are fully accounted for.

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[2] K. Pernal, O. V. Gritsenko, E. J. Baerends, *Phys. Rev.* **A 75**, 012506 (2007)
[3] K. Pernal, K. J. H. Giesbertz, O. Gritsenko, E. J. Baerends, *J. Chem. Phys.* **127**, 21401 (2007)
[4] D. Rohr, K. Pernal, O. Gritsenko, E. J. Baerends, *J. Chem. Phys.* **129** (2008) 164105
[5] K. J. H. Giesbertz, E. J. Baerends, O. V. Gritsenko, *Phys. Rev. Lett.* **101** (2008) 033004
[6] K. J. H. Giesbertz, K. Pernal, O. V. Gritsenko, E. J. Baerends, *J. Chem. Phys.* **130** (2009) ...

13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

A Density-Functional Approximation for Relativistic Kinetic Energy

Axel D. Becke

Department of Chemistry, Dalhousie University, Halifax NS, Canada B3H 4J3

A density-functional approximation, of meta-GGA type, for the relativistic kinetic energy of a system of particles will be introduced. The resulting (single-component) equation for the orbitals resembles Schroedinger’s non-relativistic equation but incorporates mass-velocity effects. Spin-orbit effects are not included. Preliminary calculations of relativistic orbital contractions and orbital energies in atomic systems have been carried out. The results are encouraging.

Metal Cluster Heat Capacities from First-Principle Molecular Dynamics Simulations

P. Calaminici[1,*] A. M. Köster,[1] J. M. Vásquez-Pérez[1], G. U. Gamboa Martinez[1]

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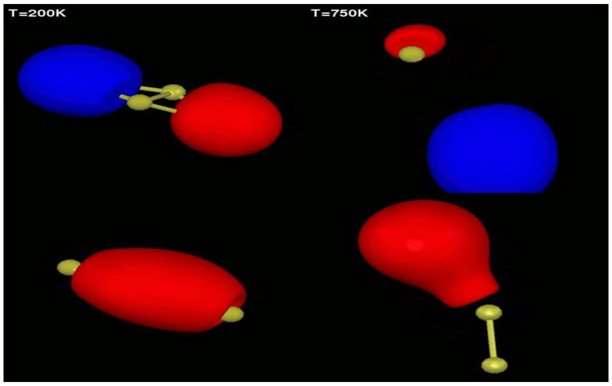
Density functional theory Born-Oppenheimer molecular dynamics (BOMD) simulations [1] of metal clusters are presented. The heat capacities of the clusters are calculated from these BOMD trajectories by the multiple histogram method. Characteristic changes in the caloric curves with respect to cluster size are discussed.



Welcome to Lyon!

Keywords: Heat Capacity, Metal Clusters, First-Principle Molecular Dynamics Simulations

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Pushing the Limits of Conventional Time-Dependent Density-Functional Theory for Photochemical Modeling

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Although traditional Hohnberg-Kohn-Sham density-functional theory (DFT) is formally restricted to (time-independent) ground-state energies and charge densities, interesting molecular properties are neither restricted to time-independent situations nor to the ground state, and this is particularly true if one is interested in modeling photochemistry. About a decade after Runge and Gross provided a firm foundation for future developments of time-dependent DFT (TDDFT), [1] linear response TDDFT (LR-TDDFT) was introduced for the calculation of molecular electronic excitation spectra, and “Casida’s equations” [2] were rapidly implemented in the TDDFT “adiabatic approximation” in most Quantum Chemistry and many Solid-State Physics packages, thus defining “conventional TDDFT.” TDDFT used in this way has now become one of the inevitable tools to be found in the photochemical modeler’s toolbox, but its range of applicability is now widely recognized to be limited by at least two problems: (i) underestimated charge transfer excitations, and (ii) the lack of explicit many-electron excitations. In this talk I will address problem (ii), which arises from the use of the TDDFT adiabatic approximation and which is relevant, for example, for the description of biradicaloïd structures, and hence for the description of conical intersections (CXs) found along photochemical pathways. We have explored this issue for the ring opening of oxirane (CH_2OCH_2). [3, 4, 5] Based upon this work, my presentation will address the questions of how TDDFT behaves in practice around CXs, how we think exact TDDFT should behave around CXs, and some ideas for how to make TDDFT behave better around CXs.

Keywords: Time-Dependent Density-Functional Theory, Double Excitations, Conical Intersections

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[3] F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, C. Filippi, and A. Vela, *J. Chem. Phys.* **127**, 164111 (2007). “Troubleshooting Time-Dependent Density-Functional Theory for Photochemical Applications: Oxirane.”

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DFT augmented with an empirical dispersion term as applied to solids

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Density functional theory (DFT) methods have been widely used in the ab initio modelling of solids but it has been shown that they often fail to adequately describe dispersive interactions. Recently, there has been a renewed interest in the use of pair-wise attraction terms of the form -$f(R)\frac{C_n}{R_n}$ $(n = 6, 7, 8,)$. The proposed corrections differ in the adopted damping function $f(R)$ and the atom-atom dispersion coefficients C_n.

In this work, we focus on the inclusion of the empirical -$s_6 f(R)\frac{C_6}{R_6}$ correction to DFT methods recently proposed by Grimme [1] for molecular systems. Grimme [1] has defined a general set of parameters and used an optimized scaling factor to adjust the dispersion correction for each DFT method. Here, we use the Grimme's empirical model in combination with the B3LYP hybrid method (hereafter referred as B3LYP-D) and assess the transferability of such a model to solids. To this purpose, the Grimme's empirical model has been implemented in the CRYSTAL code [2]. CRYSTAL is an ab-initio periodic program that computes the properties of periodic systems at HF, DFT and hybrid HF/DFT levels of theory by adopting a linear combination of atom-centered Gaussian-type orbitals.

The B3LYP-D model has been tested in the prediction of the cohesive energy and structure of a set of molecular crystals ranging from hydrogen bonded to dispersion bonded crystals [3], structure and vibrational properties of layered materials [4] (e.g. hydroxides and clays) and graphitic-like structures, adsorption of small molecules on surfaces (e.g. CO on MgO(001) surface) and in microporous materials (e.g. H_2, CO, CO_2 in metal-organic frameworks). Particular attention has been devoted to the basis set dependence and the role of the basis set superposition error (BSSE). The inclusion of the empirical correction is crucial to reach a reasonable agreement with experiment, as in the correct prediction of structural features. For molecular crystals, a modification of the original parameterization (denoted as B3LYP-D*) is needed to obtain a better agreement for both cohesive energies and structures, and a better balance between hydrogen bonded and dispersion bonded molecular crystals. Some deficiencies have also been observed for semi-ionic systems for which the C_6 parameters tabulated by Grimme [1] are not properly adequate and have to be re-parameterized. Also, a correct balance between the dispersion term and the damping function is needed to avoid artifacts.

Overall, results are very promising and the application of the B3LYP-D method for solids is successful and cost effective.

Keywords: B3LYP, Dispersion energy, Solid-state

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[2] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco and M. Llunell, *CRYSTAL06 User's Manual*, 2006, Università di Torino, Torino

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Prediction of Two-Photon Absorption Spectra by Applying Time-Dependent Density Functional Theory

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Linear response (LR) time-dependent density functional theory (TDDFT) has been well validated to calculate the excitation energies and oscillator strengths of one-photon absorption (OPA). In two-photon absorption (TPA), a nonlinear process in which two photons are absorbed simultaneously, the rate of light absorption is proportional to the square of the light intensity. TPA is of interest in a variety of applications, including fluorescence imaging, microfabrication, optical memory, and photodynamic therapy. TPA cross-sections can be obtained using quadratic response (QR) TDDFT either to obtain the excited-states transition dipole moments needed in the sum-over-state (SOS) formalism or, more directly, from the residue of the QR function. By applying QR TDDFT to a series of coumarin derivatives [1] using an appropriate exchange-correlation (X-C) functional and including the effects of the solvent, good agreement with measured TPA spectra was obtained. TDDFT has been used to calculate the OPA and TPA of substituted stilbene and fluorene [2], and of porphyrins and porphyrin dimers [3]. In some of these systems, significant charge transfer occurs in getting to the excited state, and using asymptotically corrected exchange-correlation (X-C) functionals is important.

The coulomb attenuated model (CAM) [4] functional was developed in order to include a larger fraction of exact exchange in the asymptotic regions without using such a large fraction of exact exchange everywhere. Two versions of the CAMB3LYP X-C functional are compared to the B3LYP and PBE0 functionals in the calculation of OPA and TPA for these compounds. In comparing substituted stilbene and fluorene, we show the importance of including varying exchange contributions in order to obtain accurate OPA and TPA spectra.

Furthermore, using QR TDDFT with the CAMB3LYP functional yielded qualitative agreement with measured TPA properties for porphyrins, including the successful prediction of the larger than 100-fold enhancement of the TPA cross-section for the porphyrin dimer in comparison to the monomer. Obtaining quantitative agreement is difficult due to the sensitivity of the calculated cross-section to the excited-state energy levels. This sensitivity to the state energies can be explained by resonance effects, which are predicted in the SOS formula for the TPA cross-section derived from perturbation theory.

Keywords: two-photon absorption, quadratic response, porphyrin

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The role of exact-exchange in organic-metal interfaces

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Organic-metal interfaces play a key role in different nanoscience research area, such as molecular electronics and organic (opto-)electronic devices. When a metal surface is covered by a self-assembled monolayer (SAM) of organic molecules, its workfunction changes. This workfunction-shift is related to the formation of an interface-dipole which can be divided into two contributions [1,2]: the dipole of the isolated SAM and the bond-dipole, related to the electronic charge reorganization at the interface. Density Functional Theory (DFT) investigations (see e.g. Refs. 1-5) of the SAM-induced workfunction-shift usually employ plane-waves and thus they are limited to the conventional exchange-correlation(XC) functionals, such as the Local Density Approximation (LDA) or the Generalized Gradient Approximation (GGA).

To investigate the role the of exact-exchange in complex interfaces, we present a gaussian basis-set study of different thiolated oligo-phenyls chemisorbed on a gold (111) surface, which is modeled as a finite cluster [6].

We compare conventional functionals with hybrid methods and orbital-dependent functionals based on the Localized Hartree Fock (LHF) method [7,8]. We analyze both the dipole of the isolated SAM, including depolarization effects [1], and the bond-dipole.

We show that the LHF method, as conventional XC-functionals, can correctly describe the Fermi-level position and the density-of-states of the metal cluster. On the molecular side, the LHF method solves two of the main shortcomings of the conventional XC-functionals in which:

i) the energy of the highest-occupied molecular-orbital (HOMO) largely underestimates the negative of ionization potential and thus a bond-dipole much smaller than LHF and hybrid methods is predicted. [9]

ii) dipoles and polarizabilites of oligomers, with different chain-length and functional groups, are incorrectly described [10]. We show that the LHF can accurately describe the SAM depolarization in agreement with ab-initio wavefunction methods [9].

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The approximate SCC-DFTB method: performance and challenges

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In the last years, we have developed an approximate Density Functional Theory Method (SCC-DFTB), which can be derived from DFT by a second order expansion of the total energy expression with respect to the charge density [1]. Improvements of the original scheme include a modification of the treatment of electron-electron repulsion terms for a better description of hydrogen bonded systems and inclusion of third order terms in the density fluctuations, which become important for the treatment of highly charged systems. Recently, we have used a new scheme to derive repulsive potentials, which increases the accuracy substantially, but also shows the limits of the current method. Since common DFT-GGA functionals lack the description of dispersion forces, which is inherited by SCC-DFTB, we have included them empirically because of their crucial role for the stability of protein and DNA structures [2]. SCC-DFTB has been further implemented into combined quantum mechanical molecular mechanical (QM/MM) algorithms [3] and has been widely applied to biological systems, in particular to proton transfer reactions. The scheme has been extended into various mutlti-scale approaches, where the QM/MM method is coupled to an electrostatic treatment of the environment. Excited state energies are calculated in the framework of time dependent density functional linear response theory [4].

Keywords: SCC-DFTB, approximate DFT, dispersion, excited states, QM/MM

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Ab initio electrochemistry at the metal interface: from ultra-vacuum to water.

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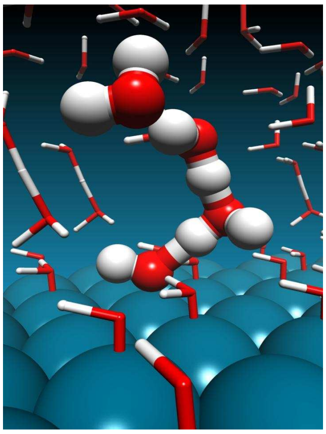
The need to reduce CO_2 production and to find more powerful and lighter batteries for our always more demanding electronic devices necessitates to design more efficient electrochemical systems. Furthermore, in surface science, the biased of a surface by mean of a STM tip is still not fully understood and is not clearly linked to electrochemistry. There is, then, a great need to model these electrochemical systems at the atomic scale using *ab initio* methods. We present a method that allows using DFT to add the electrochemical dimension [1,2]. In particular, we can model at the DFT level the electrochemical behaviour of a metal-water interface that would allow to understand and improve systems like fuel cells, corrosion protection layers or water electrolyse.

In the case of the Pd/H2O, we have studied the stability as a function of the applied electrochemical potential and for different water thicknesses. The interface structure is not only dependant on the applied biased, but also on the number of water layers leading to different structures and electrochemical reactivity. For a thick water layer, our calculations reproduce the electrochemical experimental behaviour: the water molecules can dissociate for a large (or low) enough potential into adsorbed proton or hydroxyl and the corresponding hydronium and hydroxide ions solvated in the water layers [1]. For thin layers, the water behaviour is completely different, as water never dissociate in the studied potential range, but still shows an electrochemical behaviour linked with the water reorientation on the surface [3]. The modification of the STM images can be computed and corresponds to what was experimentally observed.

Finally, we show that all the electrochemical behaviour observed can be rationalized by the usual tools of quantum chemistry.



Keywords: electrochemistry, surface, interface

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Using density functional theory to design a viable material for hydrogen storage

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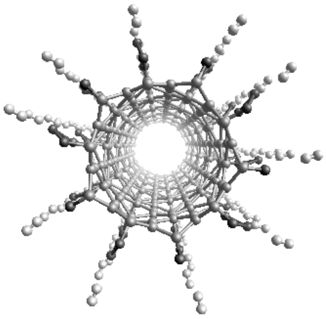
With the need to urgently address climate change there has been a strong driver to try to create a viable hydrogen economy as the basis for mobile energy. One of the key barriers to the practical deployment of hydrogen has been the need to store this substance at high density without the use of high pressures. Consequently, there has been considerable effort to identify materials that may adsorb hydrogen with the "ideal" binding strength that balances the conflicting needs of high density with ease of desorption during consumption [1]. Density functional calculations are already playing a valuable role in the identification and design of materials for this purpose [2]; the present work describes how DFT-based calculations can be used to identify nanomaterials that have the potential to meet the target binding energy.

Carbon based materials have attracted considerable interest as potential candidates, due to their light weight and high surface areas. Although there was initial optimism that carbon nanotubes may represent a viable candidate absorbent, the pure material is now believed to be inadequate, regardless of whether chemisorption occurs [3]. Despite this, theoretical calculations have suggested that metal decorated forms have the potential to strongly adsorb hydrogen [2], though again a weakness was subsequently highlighted in that the metal is found to preferentially agglomerate leading to loss of function [4].



Based on the linear-scaling SIESTA methodology [5], we have used density functional calculations to design a new form of functionalized carbon nanomaterial that exhibits a binding strength for hydrogen close to that proposed as ideal, while avoiding the potential problems identified with other theoretical candidates. Results are validated against post-Hartree-Fock methods for a representative cluster, and estimates of the likely hydrogen storage capacity made.

Keywords: DFT, hydrogen storage, carbon nanotubes

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Ab initio simulation of large systems in complex environments : Daubechies wavelets for electronic structure calculations

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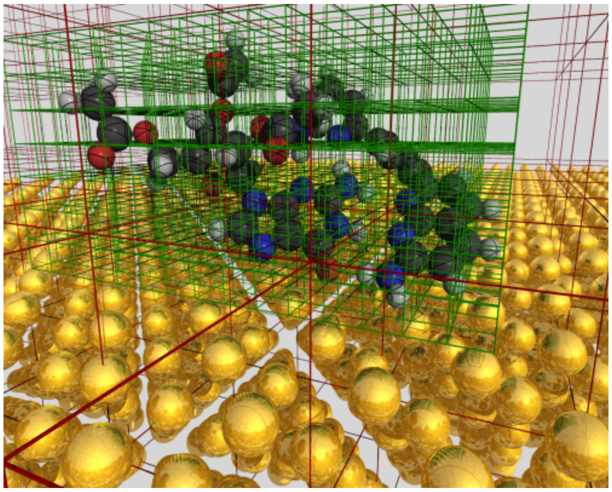
The european BigDFT project has developed an ab initio Density Functional Theory code based on Daubechies wavelets[1]. Such functions have features which make them a powerful and promising basis set for application in materials science. These are a compact support multiresolution basis, and form one of the few examples of systematic real space basis sets. For these reasons they are an optimal basis for expanding localised information. The real space description they provide allows to build an efficient, clean method to treat systems in complex environments, like surfaces geometries[2] or system with a net charge[3]. The mathematical properties of the formalism are optimal to build a robust, highly optimised code, conceived for systems of few hundred atoms, with excellent efficiency on parallel computers. This code is at present available under GNU-GPL license and integrated in ABINIT software package.

In this presentation we will illustrate the main features of the code, its actual performances and capabilities, together with the ongoing applications. We will then conclude by outlining the planned developments and the potentialities of this powerful formalism in the context of electronic structure calculations of systems in complex environments.



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Towards Linear-Scaling Density Functional Theory

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With the emergence of peta-scale computing platforms we are entering a new era of modeling. The computer simulations can be carried out for larger, more complex, and more realistic systems than ever before.

DFT may be the only tool that enables us to carry out accurate simulations for larger systems with reasonable computational cost. Recently, there has been considerable interest toward the development and assessment of new hybrid functional based on the long-range correction (LC) scheme [1-3]. In the original LC scheme, the exchange functional is partitioned with respect to the inter-electronic separation into long-range and short-range parts using a standard error function. Only the short-range part is retained, while the long-range part is replaced with an exact orbital expression using Hartree-Fock exchange integrals. The LC approach was shown to clearly solve many of the problems which conventional DFT confronted. Moreover, the LC approach successfully provided a good description of van der Waals interactions [4] as well as accurate reaction enthalpies and barrier heights. The variants of range separated functional, LCgau and LC2gau, will also be discussed.

Coulomb integral evaluation part is very often the most time consuming step in particular with GGA functional. Recently we have developed a new implementation of a novel approach to treating the Coulomb problem, which is rigorously linear scaling. The Gaussian and finite element Coulomb (GFC) method [5] evaluates the Coulomb potential by direct solution of the Poisson equation. Unlike traditional real-space methods which discretize the Poisson equation on a grid using finite-difference, finite-element, or wavelet basis functions, in our approach we use a mixture of finite-element and Gaussian functions to describe the Coulomb potential. This is the key to the efficiency of the GFC since the Gaussian functions allow for an extremely compact representation of the potential near the nuclei. We have also developed the linear-scaling spectral-element method [6] for computing electrostatic potentials, in which we used a simple real-space partitioning of the systems into cubic cells and a spectral-element representation of the density in a tensorial basis of high-order Chebyshev polynomials. The preliminary results are very encouraging.

Keywords: Linear scaling, LC, GFC

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TD-DFT Calculations for Organic Dyes

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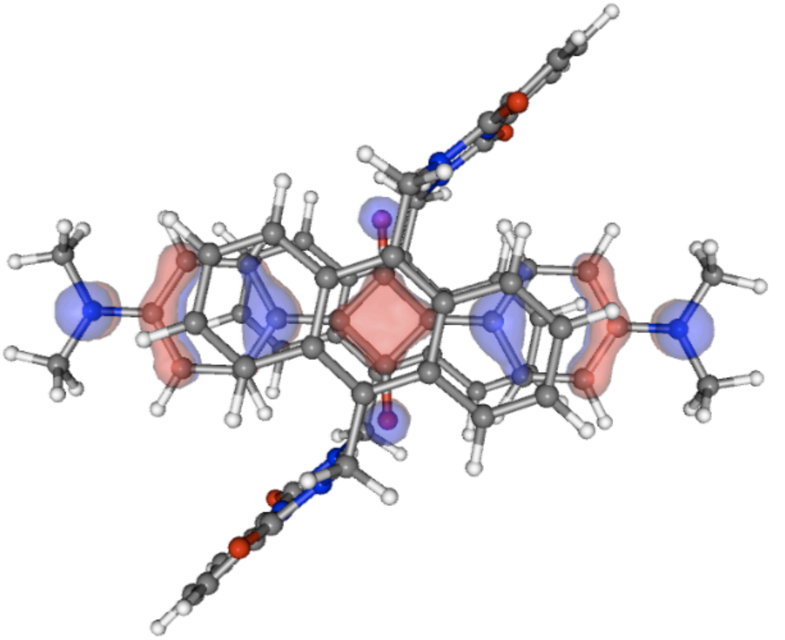
The structures and UV/Vis spectra of a very large panel of organic dyes have been evaluated using a TD-DFT approach explicitly taking bulk solvent effects into account by means of the Polarizable Continuum Model. First, we discuss methodological aspects : choice of appropriate basis sets, DFT functionals (with extensive benchmarking), importance of solvent effects, ... [1,2]. In a second stage, comparisons between experimental and theoretical values are carried out, and it is demonstrated that TD-DFT results can be sufficiently accurate to allow practical dye design [2,3]. In a third stage, fluorescent dyes as well as cage-like effects are tackled [4,5]. The efficiency of statistical treatment of the raw theoretical data is also assessed.



Keywords: Time-Dependent Density Functional Theory, Organic Dyes, Benchmark Calculations, Range-Separated Hybrids

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The random phase approximation to the correlation: Successes and failures

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For extended systems, density functional theory currently possesses the optimal balance between computational efficiency and accuracy. Thus its wide spread acceptance and application in quantum chemistry, materials science, and computational catalysis is in no way astonishing.

Despite this success, challenging problems remain: even for simple chemical reactions involving small molecules, reaction energies are wrong by up to one eV, some semiconductors are predicted to be metals, many oxides, in particular, correlated oxides are not well described, equilibrium volumes and elastic constants are generally wrong by several percent, and, finally, van der Waals like forces are not properly accounted for. There is now emerging evidence that an improved description will require the evaluation of non-local exchange and a compatible correlation functional constructed by many electron Greens function methods or many electron perturbation theory.

In this talk, exact exchange is complemented by the random-phase approximation (RPA) to the correlation energy [1]. For solids, this approximation has long been used with great success for the prediction of quasiparicle energies [2,3], but fairly little is known about total energies. We show that exact exchange+RPA yields excellent lattice constants, bulk moduli, and reasonable atomization energies for many prototypical solids [4,5]. Setting out from this observation, we apply the method to more challenging problems, such as surface energies, adsorption energies of small molecules on surfaces, and van der Waals bonded systems. The results suggest that energies from exact exchange and RPA generally outperform the available density functionals, accounting equally well for van der Waals bonding, ionic, covalent, and metallic bonding. A slight tendency towards underbinding is observed, making accurate predictions (chemical accuracy) not yet possible. Possible solutions to this problem are discussed briefly.

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Computer simulation of rare events in material science and computational chemistry.

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The realistic simulation of complex reactions in chemistry and condensed matter is one of the biggest challenges in computational science. Metadynamics [1,2] is an approach that seems to provide a manner to cope with the complexity of these systems, greatly enhancing the probability to observe rare events in a short computational time. In this approach the finite temperature dynamics of one or more collective variables (Cvs) is biased by a history-dependent potential constructed as sum of Gaussians centered on the trajectory of the CVs. After a transient period, the free energy as a function of the CVs can be estimated as the negative of the bias potential.

We will present some recent extensions of the technique that could be useful for predicting the reaction pathway in chemical reactions, discussing their advantages/limitations:

- Using the total energies as a CV for metadynamics: this allows predicting the thermodynamic properties in a wide range of temperatures performing the simulation at a single T [3].
- Using the gap, estimated by the empirical valence bond approach [4], as a CV: this allows predicting the reaction pathway in an unbiased manner, using only information about the bond structure in the reactant and in the product states [5].
- Bias-exchange metadynamics: in this approach, multiple metadynamics simulations of the same system are performed, biasing each replica with a time-dependent potential constructed in a different CV. Exchanges between the bias potentials in the different variables are periodically allowed according to a replica exchange scheme. This allows the parallel reconstruction of the free energy as a function of a several CVs [6,7]

Keywords: metadynamics, reaction mechanism, enhanced sampling techniques

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New Generation Relativistic Theories for Electronic Structure and Magnetic Properties

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Accurate quantum chemical calculations on electronic structure and typical core properties such as NMR shielding tensor should include both relativistic and correlation effects. Relativity is in the Hamiltonian whereas correlation is in the wave function described by the method.

(1) Electronic structure

It is clear that the best Hamiltonian is something between the Dirac and Schrödinger equations. Here we propose an exact two-component Hamiltonian (X2C), viz. the symmetrized elimination of the small component (SESC)[1-3], which is conceptually simple, numerically accurate, and computationally efficient, and in addition serves a seamless bridge between the Dirac and Schrödinger equations. It outperforms any approximate quasi-relativistic theories.

(2) Magnetic properties

Four-component relativistic theory on second order magnetic properties such as NMR shielding tensor is formally very simple: It consists only of a single term. Yet, this imposes two fundamental issues. Conceptually, the diamagnetism known from the non-relativistic counterpart is 'missing'. Computationally, such a standard formulation is very demanding on basis functions of high angular momentum. Even worse, the non-relativistic limit (nrl) cannot be obtained correctly with a finite basis. Attempts to find solutions to these problems started since 1962[4] but no real success has been achieved until 2003[5]. Herewith we propose several strictly equivalent approaches [6-8] based on the generic ansatz of orbital decomposition. The diamagnetism arises naturally so as to guarantee the correct nrl. The computation is consequently simplified greatly: Standard basis sets optimized for electronic structure calculations are already sufficient for reliable NMR data. The methods can be combined with any level of theory for electron correlation.

Without any exaggeration, it can now be claimed that relativity in chemistry has been solved, 80 years after Dirac though. The remaining task is to combine the X2C Hamiltonian with know-how many-body theories to generate a new generation of relativistic electronic structure theories for the whole periodic table.

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The subsystem functional scheme:
The Armiento-Mattsson 2005 (AM05) functional and beyond

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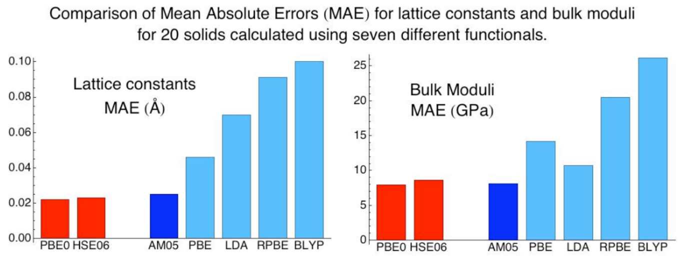
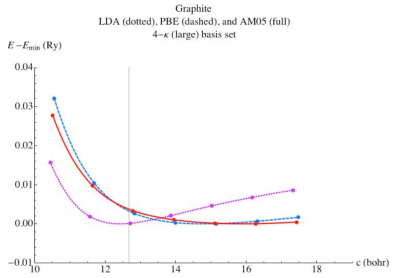
The sub-system functional scheme [1,2] is a recently proposed framework for constructing exchange-correlation density functionals for use in density-functional theory based calculations. The fundamental principle is to describe the physics in a real material by mapping onto model systems that exhibit the characteristic physics in each separate part of the real system. The LDA functional can be seen as a sub-system functional: in all part of the real material the assumption is that the needed physics is well described by the uniform electron gas model system. It is well known that this assumption is less valid in certain cases but it holds for surprisingly large classes of materials. The AM05 [3,4] functional takes this a step further by distinguishing between two separate types of regions in a real material, one type that is assumed to be well described by the uniform electron gas, and the other type of region assumed to be well described by a surface model system. I will discuss fundamental concepts of the sub-system functional scheme, such as model systems and compatibility.

One important consequence of the sub-system functional scheme is that it is known what physics is included in a functional. From the performance of AM05 for solid-state systems, it is clear that including a surface reference system into the functional cures the over-binding problem of LDA (see the left of the figure below) [5]. As expected, including physics from a single surface is not enough for describing regions where van der Waals forces dominate the physics (see the right of the figure). I will present AM05 results and discuss where the model systems included are enough and when additional physics need to be included in a new functional.


Comparison of Mean Absolute Errors (MAE) for lattice constants and bulk moduli for 20 solids calculated using seven different functionals.


Graphite
LDA (dotted), PBE (dashed), and AM05 (full)
4-κ (large) basis set

Improvement of AM05 is possible by fine-tuning the details in the construction. But a new major step in accuracy improvement is only expected if new physics is integrated in a functional via an additional model system. I will discuss what type of physics would be needed and what model systems could be used for this next step beyond AM05.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Keywords: Exchange-Correlation functionals, Density Functional Theory, Surfaces

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Stability, chemical structure, and Clar's aromatic sextets of hydrogen-terminated graphene ribbons

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Université Pierre et Marie Curie, Paris

The fine control of the chemical and electronic structure of graphene edges is a fundamental step for the use of graphene in nanoelectronics.

Here we use density functional theory to determine the stability, the geometric, the electronic and magnetic structure of hydrogen-terminated graphene-nanoribbons edges as a function of the hydrogen content of the environment [1]. Antiferromagnetic zigzag ribbons are stable only at extremely-low ultra-vacuum pressures. Under more standard conditions, the most stable structures are the mono- and di-hydrogenated armchair edges and a zigzag edge reconstruction with one di- and two mono-hydrogenated sites. The stability and the existence of exotic edge electronic-states and/or magnetism is rationalized in terms of simple concepts from organic chemistry, the Clar's aromatic sextets. Finally we show that the Clar's aromatic sextets have also a clear signature in the STM images, that can be used to identify the edge termination.

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Application of Conceptual DFT descriptors in the field of redox chemistry and the spectrochemical series

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In the field of structure and reactivity, concepts such as electronegativity, hardness and softness became cornerstones. These widespread concepts however turned out to be rather vaguely defined. A theoretical framework for these indices was provided by conceptual DFT,[1] ensuring their computability and their quantitative use for a variety of organic and inorganic reactions. The main interest in this talk is on the application of DFT descriptors in redox reactions and their utility to recover the well-known spectrochemical series.

In a first attempt to tackle the redox problem, the chemical environment of the oxidized species was simulated by a perfect electron donor. The electrophilicity descriptor,[2] here describing the energy change with maximum electron uptake, was shown to correctly predict the redox characteristics of transition metal ions in aqueous solution.[3] Its local counterpart made it possible to identify different reactive regions in the whole metal-aqua complex. In a second approach, the chemical environment was simulated by an external reservoir at constant chemical potential within the grand canonical ensemble theory. By minimizing the grand potential, an equation was derived for the chemical potential of the electrode composed of the chemical potentials of oxidized and reduced species and their hardness values.[4] The derived equation is analogous to the result of the electronegativity equalization method (EEM). For a large collection of 44 organic and inorganic systems, convincing results were found for reactions in different solvents modelled by implicit and explicit solvation models.

The spectrochemical series is known to order ligands with increasing field strength within a metal complex. The first construction of a quantitative scale goes back to the sixties when Jørgensen attempted to divide the ligand field strength in a field factor f of the ligand and g of the metal.[5] In this talk, a new approach to a non-empirical scale is introduced within the spin-polarized conceptual DFT field. Of particular interest was the spin-philicity descriptor which can be seen as the SP-DFT analogue of the electrophilicity. For a series of different ruthenium complexes, the local spin-philicity condensed on the metal ion showed a remarkable analogy with the well-known spectrochemical series while the local Fukui function $f_{SS,Metal}^{+}$ could be linked to the nephelauxetic effect.

Keywords: Conceptual DFT, redox chemistry, spectrochemical series

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Characterization of the Chemical Behaviour of the First Excited State through a Local Chemical Potential

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So far, excited state reactivity and selectivity have been scarcely studied within the paradigm of conceptual DFT. Among those few papers, one of the most original approaches has been proposed by Ayers *et al.* [1], in which through a Molecular Orbital picture the Woodward-Hoffmann rules have been rationalized only using the opposite of the dual descriptor [2]:

$$\Delta f_{excited\ state}(\vec{r}) = -\Delta f_{ground\,state}(\vec{r}) \tag{1}$$

In the present work, a theoretical justification of this chemical intuition is proposed. As the excited state Density Functional Theory still has to be tightened up, it has been preferred to overcome the problem by considering the electronic density of any excited state as a trial density for the well known ground state DFT. The consequence is the likely locality of the associated chemical potential:

$$\lambda(\vec{r}) = \frac{\delta E}{\delta \rho_{e.s}(\vec{r})} = v(\vec{r}) + \frac{\delta F}{\delta \rho_{e.s}(\vec{r})} \tag{2}$$

A Taylor's development of the electron-electron self-repulsion potential leads to a relation between the local first excited state chemical potential, the global ground state chemical potential and the dual descriptor:

$$\lambda_1(\vec{r}) \approx \mu_0 + \int \frac{\Delta f(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\,' \tag{3}$$

Exploiting the selectivity information provided by the second term of the right hand side of the previous expression, the preferred regioselectivity of some photocycloadditions can be predicted.

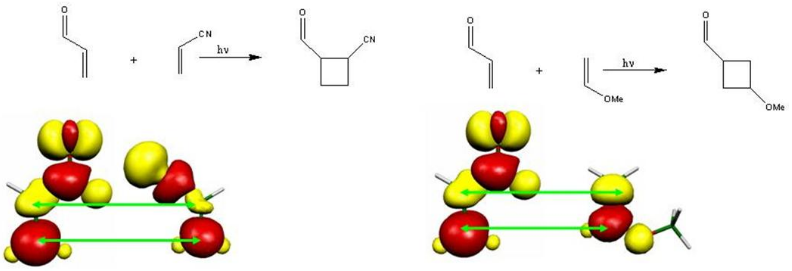

Figure 1: Regioselectivity of some photocycloadditions [2+2]

Keywords: conceptual DFT, excited states, dual descriptor, local chemical potential

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Liquid Water Structure from X-ray Spectroscopy and DFT Simulations

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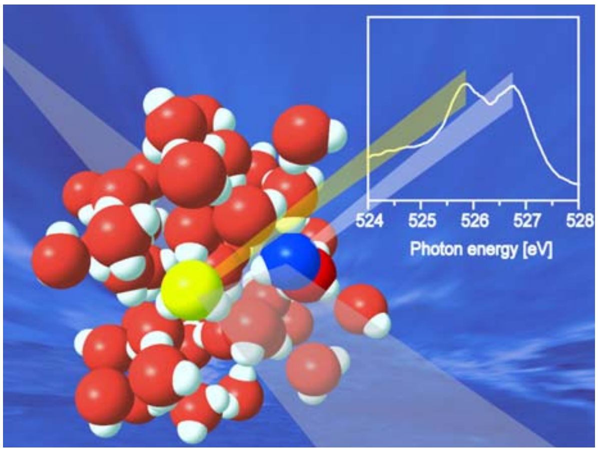
The past few years have seen the rapid introduction of resonant soft x-ray absorption spectroscopy (XAS or Near-Edge X-ray Absorption Fine Structure, NEXAFS, or XANES) as well as high-energy x-ray Raman scattering (XRS), both using synchrotron radiation, to the study of ambient liquid water. The conclusion from ref. [1] that a dominant fraction of the molecules in the liquid are very asymmetrically hydrogen-bonded with only two well-defined H-bonds, one donating and one accepting, is in strong contrast to the accepted picture of liquid water as being near-tetrahedrally H-bonded. Very recently also x-ray emission spectroscopy (XES) was applied at high resolution to liquid water [2], arriving at similar conclusions as Wernet *et al*. [1] with a predominance of strongly H-bond distorted configurations. Based on comparison with gas phase and ice, isotope substitution as well as the temperature and excitation energy dependence, in conjunction with theoretical simulations, we interpret the observed splitting of the lone-pair state into two sharp features as evidence of a bimodal distribution of local structures in the liquid: either strongly tetrahedral or highly disordered, which interconvert discontinuously with temperature [2]. From Small-Angle X-ray Scattering (SAXS) studies we furthermore find evidence for density inhomogeneities on a length-scale of 1-2 nm indicating that the two components are spatially separated on the time-scale of the experiment [3].



In the talk I will describe the experimental results and discuss techniques and challenges to theoretical simulations of these spectroscopies and data for water. In particular, the XES must include the femtosecond time-scale dynamics induced through the creation of the core-hole.

Keywords: Water, x-ray spectroscopy, spectrum calculations

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GW renormalization of DFT molecular electronic levels at the vicinity of a surface: The image charge effect

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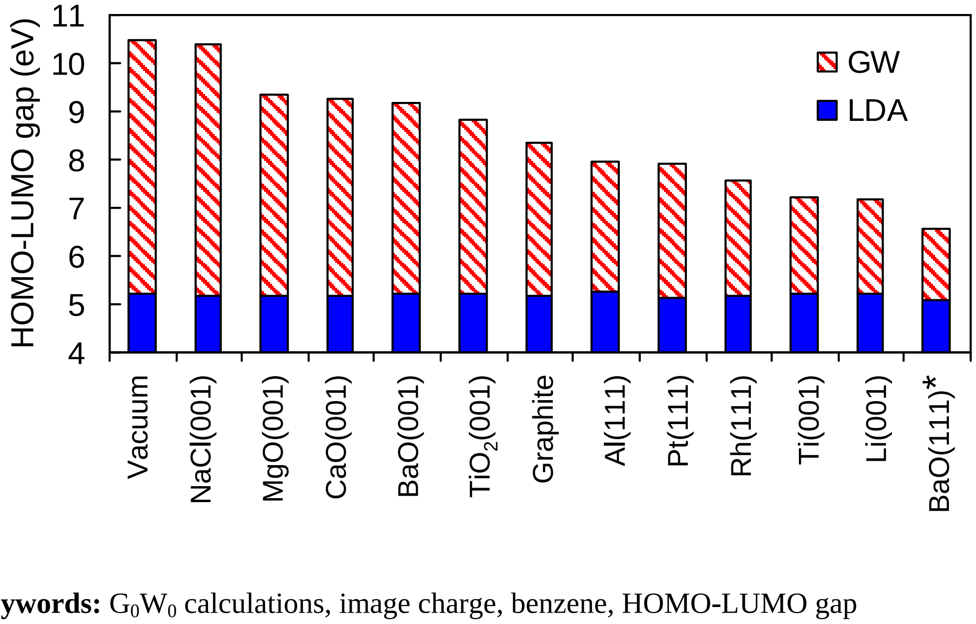
Recently Neaton et al. [1] have computed, on the basis of first-principles G_0W_0 calculations, how the HOMO-LUMO gap of the benzene molecule adsorbed on graphite is renormalized. In the present work we have extended the study for a range of metallic and semiconducting substrates in the physisorption limit, investigating how the electronic levels are renormalized by dynamic image charge effects, which are not present in the Kohn-Sham calculations. We find that a classical image charge model [2] can account qualitatively for the observed level shifts; however, the effective dielectric constant and image plane position entering the model are sensitive to the atomistic details of the surface. Using many-body perturbation theory, we express the electron self-energy in terms of the substrate joint density of states weighted by electron-hole transition matrix elements [3]. This provides a microscopic explanation of general trends in the first-principles results.



Keywords: G_0W_0 calculations, image charge, benzene, HOMO-LUMO gap

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Theoretical Studies of Magnetic Properties in Single-Molecule Magnets

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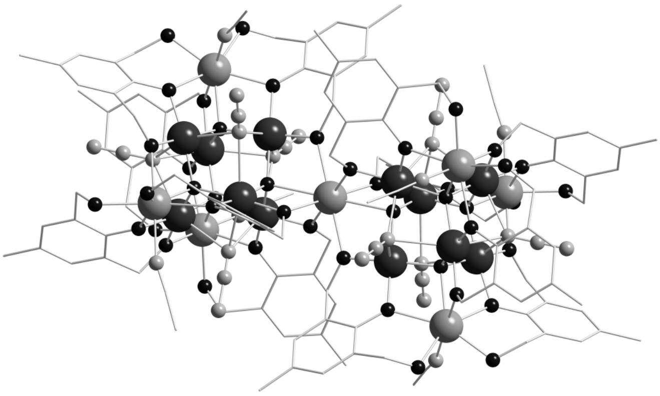
Some polynuclear transition metal complexes, usually known as single molecule magnets (SMM), show a slow relaxation of the magnetization and, as a result, each individual molecule behaves as a magnet.[1] The main requirement for a polynuclear complex to show such property is to present large spin and a large negative magnetic anisotropy. However, due to the difficulty of the prediction of these two magnetic properties the experimental search is basically a serendipitous process. The calculation of such magnitudes using Density Funtional Theory (DFT) allows to use the theoretical methods not only to compare the results with known complexes also to predict values for not-yet-synthesized systems and to understand to dependence of these two magnitudes with the structure of the complexes, helping for a rational search of improved SMMs.[2,3] If the slow relaxation of the magnetization could be extended to high temperatures, such molecules would become good candidates for the storage of information at the molecular level. Thus, such small molecules could replace the metallic particles employed in storage information devices, such as hard drives or memories allowing a considerably larger integration and faster electronic processes than the actual technology.

In this communication, we will show the results corresponding to the Mn_{19} (see Figure, large dark and light grey spheres correspond to Mn^{III} and Mn^{II} cations, respectively) and Mn_{10} complexes. The Mn_{19}.complex is the molecule with a largest spin known $S = 83/2$.[3] The use of DFT methods allow to calculate all the exchange coupling constants for such system, and to establish some correlations with structural parameters. The second family of studied complexes are those Mn_6 complexes showing the largest known anisotropic barrier. In this case, we have performed a completed study of the exchange coupling constants for such complexes and also the calculation of the magnetic anisotropy parameters using a DFT approach including perturbatively the spin-orbit effects.



Keywords: single-molecule magnets, exchange interactions, transition metal complexes

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DFT and beyond: A discussion of exact exchange plus local- and nonlocal-density approximations to the correlation functional

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Local- and semilocal-density approximations (LDA/GGA) to density functional theory, although tremendously successful for describing the properties of many molecules and materials, suffer from, amongst others, self-interaction errors and the absence of long-range van der Waals interactions. One at present most systematic approach for handling the xc functional appears to be exact exchange combined with the random phase approximation for correlation. We show that significant insight can be obtained by this approach, e.g. for studying the interaction between two graphene sheets [1] or the adsorption of CO on close-packed transition metal surfaces [2]. For both systems the LDA and GGA give an even qualitatively wrong description. -- Despite the success for the mentioned systems we also identify shortcomings of the approach, in particular for molecules.

A second route discussed in this talk concerns the linkage of LDA+U and many-body perturbation theory: G0W0@LDA+U. We discuss results for the 4f lanthanide-oxide series [3] as well as for 3d transition metal oxides.

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New models for mixing wavefunctions with density functional theory

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The recent realization that the ground-state correlation energy of the random phase approximation (RPA) is intimately connected to an approximate coupled cluster doubles (CCD) model [1], opens interesting avenues for mixing RPA with DFT [2].

I will also present a two-particle density matrix ansatz that seems particularly well-suited for describing static (and only static) correlation [3]. Dynamical correlation functionals for this model are non-trivial and I will discuss progress on this front.

Keywords: RPA, range-separation, static correlation

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Computation of absolute ionization potentials and electron affinities of simple aqueous species using DFT based molecular dynamics

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Recent progress in Photo Electron Spectroscopy (PES) of liquids has made it possible to determine vertical ionization potentials of aqueous species[1]. Adiabatic ionization free energies can obtained from absolute experimental electrode potentials (i.e. work functions). It would be clearly of interest to use these experimental data to validate the performance of density functional theory (DFT) methods in condensed aqueous systems. Such a computation must not only reproduce the absolute values of the ionization energies but also the large difference between vertical and adiabatic ionization energies ($\approx$ 3eV[1]) due to the reorganization of the aqueous solvent. We have approached this problem using DFT based molecular dynamics simulation (DFTMD) of fully atomistic model systems under periodic boundary conditions. Ionization energies (electron affinities) are computed, just as in vacuum, as the relative total energy of two systems with one electron less (or more). While this method in principle offers a rigorous way of treating solvent effects (entropy contributions and relaxation), it also introduces two serious technical problems. The first is the question of how to relate ionization energies in a periodic model systems to vacuum. This problem was addressed by the applications of finite size corrections and using as energy reference the solvation free energy of the proton computed by a recently developed method for reversible insertion of protons in bulk aqueous systems[2]. Replacing the free energy of solvation of the proton by the experimental value converts the computed relative ionization energies to an absolute vacuum scale[3]. The second problem is the well-known tendency of approximate density functionals to delocalize unpaired electrons which in a fully atomistic model of aqueous radicals such as $OH^\bullet$ can lead to formation of spurious three electron bonds with a solvent molecule[3,4]. Hemi-bond formation was discouraged by extending the BLYP functional with an empirical self interaction (SIC) correction applied only to the singly occupied orbital in a restricted Kohn-Sham scheme[3,4]. Model reactions discussed in some detail are the aqueous $OH^-/OH^\bullet$ and $Cl^-/Cl^\bullet$ oxidations. Vertical and adiabatic ionization energies could be reproduced within an error margin of 0.5 eV. We also make a prediction of the energy for vertical attachment of an electron to $OH^\bullet$(aq). Analysis of the results indicates that the sizable deviations form experiment are mostly due to the limited accuracy (and validity) of our SIC scheme rather than our implementation of the computation of vertical and adiabatic ionization energies in small periodic DFTMD model systems, confirming that this methodology indeed opens up a new way of testing the performance of DFT in aqueous systems. If time permits we will also discuss some preliminary results on the application of this method to the electronic structure of a titania (TiO_2) water interface.

Keywords: Ionization energies, aqueous solution, open shell systems

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A new DFT functional based on spin-states and S_N2 barriers

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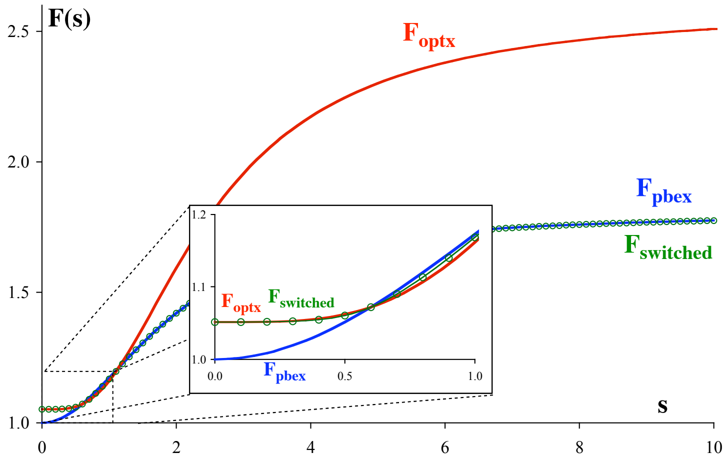
We recently reported a study into what causes the dramatic differences between OPBE and PBE for reaction barriers, spin-state energies, hydrogen-bonding and π-π stacking energies. [1] It was achieved by smoothly switching from OPBE to PBE at a predefined point P of the reduced density gradient *s*. By letting the point P run as function of the reduced density gradient *s*, with values from *s*=0.1 to *s*=10, we could determine which part of the exchange functional determines its behavior for the different interactions. Based on the thus obtained results, we created a new exchange functional that showed the good results of OPBE for reaction barriers and spin-state energies, and combined it with the good (H-bonds) and reasonable (π-stacking) results of PBE for weak interactions. In other words, it combined the best of OPBE with the best of PBE.

Encouraged by these good results, we have further improved the new exchange functional and fine-tuned its parameters. [2] Similar to the switched functional from ref. [1], our new SSB functional [2] works well for both S_N2 barriers (see e.g. ref. [3]), spin states and H-bonding interactions. Moreover, by including Grimme's dispersion corrections it also works well for π-π stacking interactions. [2]



In summary, we have constructed a new GGA exchange functional that when combined with the sPBE correlation functional [4] gives the correct spin ground-state of iron complexes, and small deviations for S_N2 barriers (2.7 kcal·mol^{-1}), geometries (0.005 Å), H-bond distances (0.012 Å), weak interactions (S22 set, 0.5 kcal·mol^{-1}), and transition-metal ligand distances (0.008 Å).

Keywords: S_N2 barriers, weak interactions, spin states

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C28

13th International Conference on the Application of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Characterizing the Mechanism of Chemical Reactions from the Perspective of Conceptual DFT: The Reaction Force and Reaction Electronic Flux.

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In this talk it is shown how the mechanism of chemical reactions can be understood using the reaction force concept that, through a fragmentation of the reaction coordinate, defines three *reaction regions* featuring specific and unique characteristics (see Figure 1). It has been observed in different kinds of chemical reactions that in the *reactant region*, prior to the reaction force minimum, what occurs are primarily structural distortions of the reactants which are a preparation for subsequent steps. In the *transition state region*, from the force minimum to its maximum, is where takes place the rapid and extensive changes in electronic properties, such as chemical potential, hardness and electronic populations; here new bonds may begin to form. At the force maximum, the system has reached what can be described as distorted (or activated) states of the products. The *product region* involves primarily structural relaxation of the system to its final state. The general pattern, then, is that while structural changes occur throughout a process, they are the dominant factors in the first and the third regions. Variations in electronic properties, on the other hand, tend to be slow and gradual in these regions, and much more rapid and extensive in the intervening transition-to-products region.

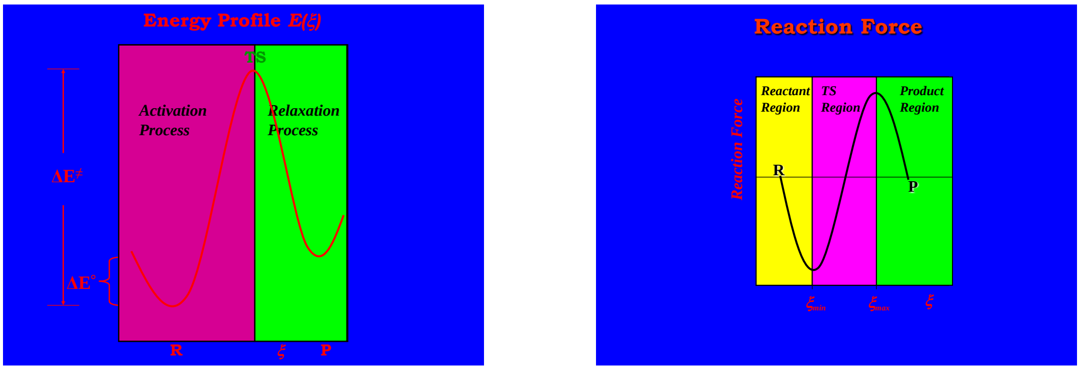

Figure 1. Typical profiles of energy and reaction force along the reaction coordinate ξ. Note that the critical points of the later defines three reaction regions along the reaction coordinate.

The reaction force also provides a rational way for partitioning the activation energy into two contributions, which are associated to structural and electronic effect, it will be shown how this partition helps identify the physical nature of the activation energy and characterize the effect of solvents or catalysts on energy barriers. Within this context, the reaction electronic flux (REF) is introduced to characterize the electronic activity observed during the reaction and that takes place mainly at the transition state region (see Figure 1). The REF, defined as the negative of the chemical potential gradient, is a global property of the reaction and is used to identify the regions along the reaction coordinate where electronic polarization and/or transfer are the main effects that drive the reaction. For a physical interpretation, the REF is partitioned into intra and intermolecular contributions, characterized in terms of polarization effects on each reactant and a net charge transfer between them. The polarization flux takes into account the deformation of the electronic cloud of a given fragment in response to the external field created by the other(s) fragment(s); this effect takes place generally in the preparation and relaxation steps of the reaction. The intermolecular charge transfer includes the charge transfer between the fragments. With this decomposition at hand, a very detailed characterization of the electronic activity is obtained, this gives a complete picture of the bond formation, dissociation and polarization effects that takes place during the reaction.

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Adiabatic-Connection Fluctuation-Dissipation Density-Functional Theory Based on Range Separation

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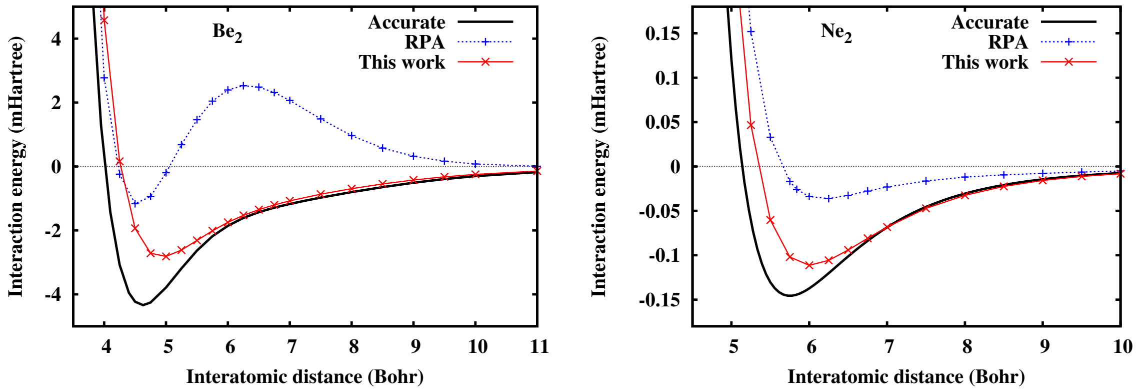
One difficulty in the Kohn-Sham formulation of density functional theory using local density and generalized-gradient approximations is the description of nonlocal correlation effects, such as those involved in weak van der Waals complexes, bound by London dispersion forces [1]. Adiabatic-connection fluctuation-dissipation theorem (ACFDT) approaches, such as the random phase approximation (RPA), are one the most promising ways of constructing highly non-local correlation functionals [2]. In a similar spirit as in the work of Kohn *et al.* [3], we propose an ACFDT approach based on a range separation of electron-electron interactions [4]. It involves a rigorous combination of a short-range density functional with one of the possible long-range generalizations of the RPA. This method corrects several shortcomings of the standard RPA and it is particularly well suited for describing weakly-bound van der Waals systems, as demonstrated on several chemical systems. This method is expected to supersede a previously-proposed approach based on long-range second-order perturbation theory [5] for systems with small electronic gap.



Keywords: range separation, random phase approximation, van der Waals

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DFT Europe 2009

Non-empirical GGAs under scrutiny

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By locally tightening the Lieb-Oxford bound and through an analysis of the behavior of the exchange enhancement function, $F_X(s)$, for large values of the dimensionless reduced gradient s, $s(\mathbf{r}) = \left| \nabla\rho \right| / 2\ \mathrm{k_F}\ \rho(\mathbf{r})$, it is shown that one can improve the prediction of atomization energies of the molecules contained in the G2 set while the structural parameters (bond distances, bond angles and dihedrals) are marginally changed. Two asymptotic limits of F_X are discussed. One, where the uniform electron gas limit is recovered, $F_X(s) \xrightarrow[s\to\infty]{} 1$, and another where the exact condition $\lim\limits_{s\to\infty} s^{1/2}\ F_{XC}(s) < \infty$. Results for a non-empirical exchange-correlation as well as with an empirical combination with the LYP correlation functional are presented. As a motivation of this work, and very briefly, it will be shown that by modifying the parameter of the quadratic contribution of s in the exchange one can improve the ordering (branched versus linear) of n-alkane isomers and the description of the isodesmic protobranching reaction. Some comments towards an incorporation of this switching between the gradient expansion limit and the semiclassical limit will be presented.

Orbital-free embedding potential: exact properties, approximations, and applications

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The orbital-free effective potential introduced by Wesolowski and Warshel [1,2] is a local potential which is expressed by means of an universal functional depending on two electron-densities: that of the given density of the environment (ρ_B) and that of the "to-be-found" electron density of the investigated system (ρ_A) such as a solvated molecule for instance:

$$V_{eff}^{emb}[\rho_A,\rho_B](\vec{r}) = -\sum_{\alpha}^{N_B}\frac{Z_\alpha^B}{|\vec{R}_\alpha^B-\vec{r}|}+\int\frac{\rho_B(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}dr' \qquad (1)$$

$$+\left.\frac{\delta E_{xc}[\rho]}{\delta\rho}\right|_{\rho=\rho_A+\rho_B}-\left.\frac{\delta E_{xc}[\rho]}{\delta\rho}\right|_{\rho=\rho_A}+\left.\frac{\delta T_s[\rho]}{\delta\rho}\right|_{\rho=\rho_A+\rho_B}-\left.\frac{\delta T_s[\rho]}{\delta\rho}\right|_{\rho=\rho_A\;\rho_1=\rho_A}$$

where $T_s[\rho]$ and $E_{xc}[\rho]$ are density functionals defined in the Levy constrained search [3,4] for the kinetic energy of non-interacting electrons and the exchange-correlation energy, respectively. This potential can be used, as proposed in the original work, to embed a Kohn-Sham system. Recently, it was shown that the same form of the embedding potential expressed as the density functional given in Eq. (1) is the exact embedding potential also for other cases where the embedded system is described using other descriptors such as: an *embedded wavefunction* of a CI form [5] or an *embedded one-particle density matrix* [6].

In the first part, we overview our recent work on the exact properties of this potential [7,8] and the strategies to enforce these exact properties on approximate analytic expressions needed in practical calculations. In the second part, recent applications of the orbital-free embedding potential in multi-level type of numerical simulations targeting electronic structure in condensed phase will be reviewed.

Keywords: kinetic energy functional, multi-level simulations, electronic structure, condensed phase

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Born-Oppenheimer DFT QM/MM Molecular Dynamics Simulations of Enzyme Reactions

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To simulate enzyme reactions, extensive sampling on a reasonably accurate potential energy surface is needed to obtain reliable results. We are pushing the envelope of on-the-fly Born-Oppenheimer MD simulations with DFT QM/MM methods and umbrella sampling to determine free energy profiles of chemical reactions in complex systems. At each time step, the atomic forces as well as the total energy of the QM/MM system are calculated with the pseudobond ab initio QM/MM approach on-the-fly, and Newton equations of motion are integrated. This direct ab initio QM/MM BO-MD approach provides an ab initio description of chemical bond formation and breaking process, properly and explicitly models the rest of the system, and takes accounts of dynamics of reaction center and its environment on an equal footing. Very recently, we have demonstrated it to be feasible and successful in elucidating the catalytic power of histone lysine methyltransferase SET7/9 [1], providing insights into the methylation state specificity of histone lysine methylation [2]. and characterizing the Sir2 catalyzed nicotinamide cleavage reaction [3]. In the latter case, 720 ps B3LYP(6-31G*) QM/MM BO-MD simulations have been employed to study the SIR2 enzyme, in which the QM subsystem has 65 QM atoms and 560 basis functions while the MM sub-system has more than 9000 atoms. This would represent a typical application that we would be able to carry out with the currently available computational resources. In addition, I will also present our most recent efforts to advance the frontier of the DFT QM/MM MD approach in its feasibility and applicability to simulate metalloenzymes.

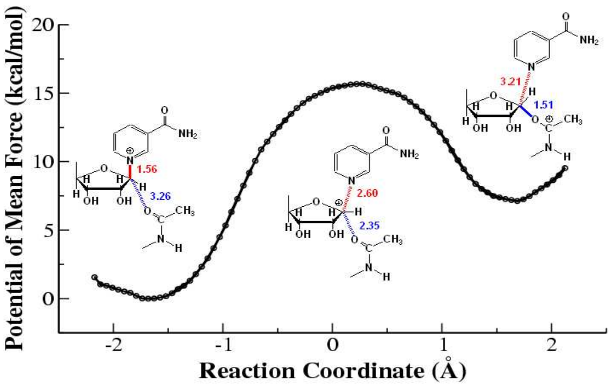

Figure 1: Free energy profile for the Sir2Tm catalyzed nicotinamide cleavage reaction determined with B3LYP(6-31G*) QM/MM MD simulations.

Keywords: ab initio QM/MM method, Born-Oppenheimer molecular dynamics simulation, enzyme reaction

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POSTER PRESENTATIONS

Topic 1.

Properties

DFT calculations of ^{1}H chemical shifts and spin-spin coupling constants for prostate polyamines

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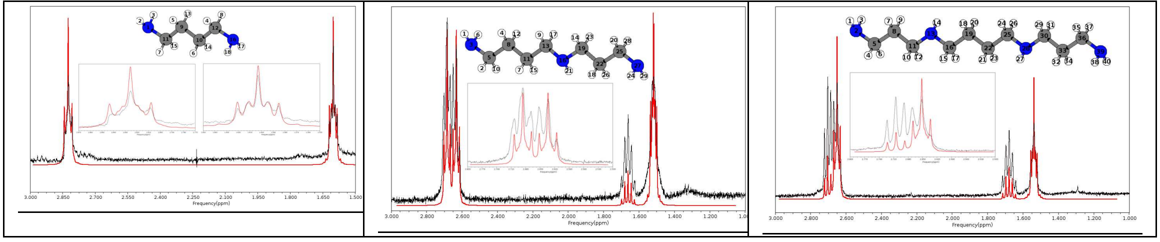
In ^{1}H HR-MAS spectra [1], concentration of the three polyamines: putrescine, spermidine and spermine was seen to be significantly reduced in the presence of prostate cancer, as compared to healthy glandular tissue. Quantitation of metabolites in prostate tissue requires *a priori* knowledge of the ^{1}H NMR spectra of these polyamines, which can be measured from solutions or simulated from the NMR spin Hamiltonian parameters: chemical shifts δ and spin-spin coupling constants J. Spin-spin coupling constants are difficult to determine from spectra of solutions, and to the best of our knowledge, no J values are yet at disposal for the three polyamines present in prostate tissue. In this study, we have 1) calculated δ and J values for isolated and solvated polyamines using DFT methods, 2) simulated the corresponding NMR spectra that we compared to the experimental spectra we obtained in D_2O at 400MHz.

DFT calculations are performed with three functionals: B3LYP, PBE and OPBE and twelve basis sets: 6311+G*, 6311++G**, 6311++G(2d,2p), 6311++G(3df,3pd) and {pcn, pcJn, n=0-3}. Chemical shifts are calculated using the GIAO method to ensure gauge independence and TMS is chosen as reference. Spin-spin coupling constants J are also estimated. Solvent effects are taken into account through the Polarisable Continuum Model. Contributions to δ and J values from the numerous isomers lying in a relative energy range of some kcal/mol are taken into account assuming Boltzmann distributions. All calculations have been carried out using Gaussian03 [2] and the graphical interface Gabedit [3]. From δ and J values, the NMR spectra of each isolated and solvated polyamine have been simulated using a home-made code handling up to 12 ^{1}H spins, recently implemented in Gabedit.

Here are only presented our final results, by comparing simulated (in red) and experimental (in black) NMR spectra for each solvated polyamine. Full results will be presented in the poster.



We have demonstrated that DFT calculations provide reliable spin-spin coupling constants for the three polyamines: putrescine, spermidine and spermine. These data can be considered as good starting values for further quantitation methods of metabolites in prostate tissue.

Keywords: DFT calculations, simulated NMR spectra, putrescine, spermidine, spermine

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A First Principle Calculation of the Magnetic Exchange Coupling and Zero Field Splitting in Trinuclear Chrom^{III} Complexes using LF-DFT.

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LF-DFT is a new, non-empirical, multi-determinant, Density Functional Theory (DFT) based Ligand Field (LF) model. A LF-DFT calculation involves two steps: (i) an Average Of Configuration (AOC), with equal occupation of the d- or f-orbitals is carried out, (ii) with these orbitals kept frozen, the energies of all Single Determinants (SD) within the whole LF-manifold is performed. These energies are then used to estimate all the Racah- and LF-parameters needed in a conventional LF-calculation. The results of this first-principle prediction are in very good agreement with the experimental values. In this communication we will calculate the Zero Field Splitting and the magnetic exchange coupling in a trinuclear Chrom^{III} complex and compare it with the experimental findings. The prediction is in good agreement with des experimental data. We will perform a benchmarking of the various functionals and various computer codes mainly on the well established and broadly used Dmol, ADF and DeMon program packages and will compare their performance using three nuclear Cr^{III} complexes that have been well characterized by magnetic susceptometry, by optical spectroscopy and using inelastic neutron scattering.

Keywords: LF-DFT, Zero Field Splitting

13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Metal to insulator phase transition in $(EDO\text{-}TTF)_2PF_6$ driven by anion displacements

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$(EDO\text{-}TTF)_2PF_6$ is an organic salt consisting of electron donors D (D=EDO-TTF) stacked against each other and electron acceptors A ($A=PF_6$). The high temperature phase is metallic with a (3/4)-filled band (0.5 hole is found on each molecule). It undergoes a metal to insulator phase transition at a high critical temperature (T_c=278 K) [1]. The doubling of the unit cell in the low temperature phase is accompanied by an intriguing charge ordering phenomenon schematically depicted as $\cdots D^0D^{+1}D^{+1}D^0\cdots$ where the charged and neutral molecules are respectively flat and bent. It has been recently found that a new phase sharing some resemblance with the metallic phase can be photoinduced when irradiating the insulating phase with an ultrashort laser pulse[2, 3]. The melting of the charge order on a subpicosecond time scale paves the way for new applications in molecular commutation.

In this work, we focus on the thermal phase transition and use the all-electron projector-augmented-wave method method[4] to investigate the electronic structure and optical properties[5] of both phases within the density-functional theory (DFT). Our calculated optical spectras at the RPA level, where local field and excitonic effects are neglected, show a good agreement with experiments. We also developped a simple tight binding model including on-site hubbard terms to reproduce the band structure and magnetic properties of the metallic phase and found that this model captures most of the physics since it is able to reproduce the plasmon frequencies and the reflectivity spectra of the metallic phase. This model when extended to include the effect of the electrostatic potential due to the PF_6 anions allows to explain qualitatively the *ab-initio* results for the insulating phase and shows that the displacement of the anions from their high symetry position plays a very important role to understand the nature of the thermal phase transition[6].

Keywords: DFT calculation, metal-insulator phase transition, optical properties, hubbard model

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Stability of point defects and volatile elements in uranium and silicon carbides

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The scope of this study is to shed light on the behavior of point defects and volatile impurities in two types of carbide materials of interest for the future of nuclear industry, silicon carbide and uranium carbide. Actinide carbides are potential nuclear fuels for Generation IV reactors, whereas silicon carbide could be used as cladding for these fuels.

The study of point defects and volatile impurities is central in order to get some comprehension in the behaviour of the materials under irradiation. We have calculated and compared the formation energies of the various types of point defects that can be found in SiC and UC. Vacancies, interstitials, dumbbells, Frenkel pairs, anti-site defects and small vacancy clusters are considered. Then the behaviour of impurities in UC and SiC is studied: volatile fission products Kr, Xe and I, as well as O which could be incorporated by oxidation. The most stable location of these elements in the lattice is determined and their incorporation energies are compared in the SiC and UC matrices.

All calculations are done using the *ab initio* PAW method (Projector Augmented Waves) based on the DFT as implemented in the VASP code. Exchange-correlation interactions are taken into account within the GGA approximation.

Keywords: point defects, impurities, carbides

Relativistic effects and Reaction Profiles from Electron Density Functions and Information Theory

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We present two studies where functionals, borrowed from information theory and complexity, are employed to surface chemical properties of atoms and molecules, based on the shape function (the one normalized density function) of the involved system alone.

In the first study atomic Dirac-Fock density functions are used to evaluate two complexity measures for all atoms: i) the C^s_{LMC} form of the statistical complexity measure due to López-Ruiz, Mancini, and Calbet and ii) the simple two parameter complexity measure, $\Gamma_{\alpha,\beta}$, proposed by Shiner, Davison and Landsberg. A comparison with the non-relativistic Hartee-Fock results is carried out to ascertain the influence of the relativistic effects on complexity. Unlike the non-relativistic Hartree-Fock results, which lead to the non-increasing C^s_{LMC} , the Dirac-Fock calculations lead to both C^s_{LMC} and $\Gamma_{\alpha,\beta}$ clearly displaying an increasing trend in complexity as the atomic number increases.

The second study is concerned with an analysis of the Kullback–Liebler information deficiency, evaluated along molecular internal rotational or vibrational coordinates and along the intrinsic reaction coordinate for several reactions (intra- and intermolecular proton transfer and S_N2 reaction). The results are consistent with the Hammond postulate. A local version of the information deficiency is defined by considering Hirshfeld's partitioning of atoms in molecules. The analysis of the local information profiles permits the identification of the atoms taking part in the electron reorganization processes [4].

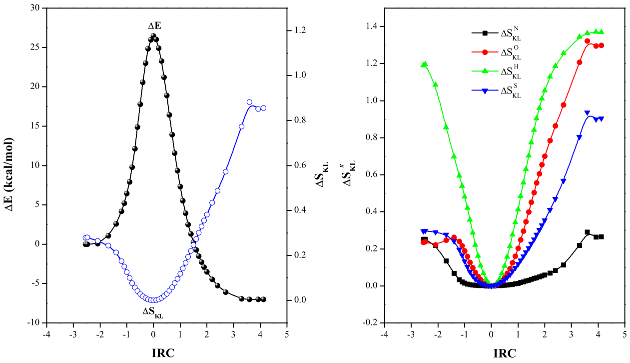

Figure 1: The reaction profile of the Kulllback–Leibler information along the IRC. The global property to the left and the atomic contributions to the right.

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P106

How 5f electrons could drive structural, electrochemical and magnetic properties of uranium complexes. A relativistic DFT study.

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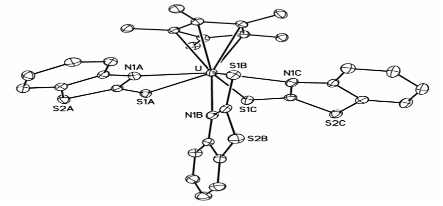
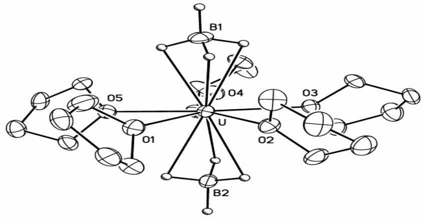
On several examples making use of Relativistic DFT, it is shown how 5f metal orbitals could be responsible for peculiar structures and properties encountered in actinide organometallic chemistry.

First, in the context of Ln(III)/Ac(III) differentiation, comparison of the crystal structures of the pentagonal bipyramidal complexes $[M(Cp^*)(SBT)_3]^-$ (Cp* = pentamethylcyclopentadienyl, SBT = 2-mercapto benzothiazolate, M = U(III) or Ln(III) Ln = La, Ce, Nd) reveals that the $M–N_{ax}$ distances are shorter than the $M–N_{eq}$ distances, the phenomenon being enhanced in the U(III) compound versus the Ln(III) analogues. We show that this structural peculiarity is due to the uranium 5f orbital–ligand mixing, which is greater that the lanthanide 4f orbital–ligand one [1]. A second example is given by the structural data obtained for $[M(BH_4)_2(18\text{-crown-}6)]^+$ (M = U, Ce) via Relativistic DFT calculations which are indicative of a covalent character of the B–H–U three-center two-electrons bond. Three MOs represent the π bonding interactions between U(III) and the three H_b atoms with significant 6d and 5f orbital contributions. These MOs in the Ce(III) complex exhibit a much lesser metallic weight with practically no participation of the 4f orbitals [2].





Second, the investigation of the electron affinity (EA) of a series of triscyclopentadienyl uranium complexes $(C_5H_5)_3UX$ (X = Cl, BH_4, SPh, S^iPr and O^iPr) related to the U(IV)/U(III) redox system which implies 5f electrons brings to light the importance of spin-orbit coupling and solvent effects. Under such conditions a very nice correlation ($r^2 = 0.99$) is found between the computed EA values and experimental half-wave potentials [3].

Third, metal-metal communication and ferro and anti-ferromagnetic interactions in several binuclear U(IV)-U(IV) uranium complexes investigated using the broken symmetry approach, show the driving role of the metal 5f orbitals.

Keywords: uranium, 5f orbitals, Ln-An differentiation

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DFT Investigation of the Thermal and Electrical Conductivities in Mg_2Si

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In recent years thermoelectricity has regained interest because of present energetic and environmental challenges. In effect, thermoelectricity could be used for the recovery of the waste heat.

Currently, best practice thermoelectric materials have maximum ZT values near one. However, efficient thermoelectric devices require materials with ZT at least as large as 2. Hence, the quest for new thermoelectric materials with higher figure of merit is a subject of intensive research.

Nowadays, the only known way to discover new materials is the experimental investigation. Computational methods could be used to predict the thermoelectric properties of materials. Calculations have already been performed on existing materials by using the Boltzmann classical transport equation. We propose to go beyond this approximation by using the Density-Functional Pertubation Theory (DFPT)[1,2].

Mg2Si has been identified as an interesting materials for its thermoelectric properties in the temperature range 500-800K. So far, only structural, electronic and vibrational (phonons) properties of Mg2Si have been reported from DFT calculations[3]. In this poster we presente DFPT calculations on the transport properties (electrical and thermal conductivities, Seebeck coefficient) of Mg2Si.

Keywords: Density-Functional Theory, transport properties in thermoelectric materials

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P108

Vibrational Averaging of Spectroscopic Molecular Properties

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Vibrational averaging is important for exact modelling of molecular properties, understanding the dynamics and conformational equilibria. Somewhat different numerical techniques have to be used to account for soft molecular motions characterized by vibrational frequencies comparable with the Boltzmann quantum, and for higher-frequency vibrations. The former case is typically treated semi-classically and provides information about conformational equilibria. In an analysis of the Raman and Raman optical activity spectra we introduced new decomposition methods that revealed more precise information about the dynamics of peptides [1] or sugar derivatives in solution [2].

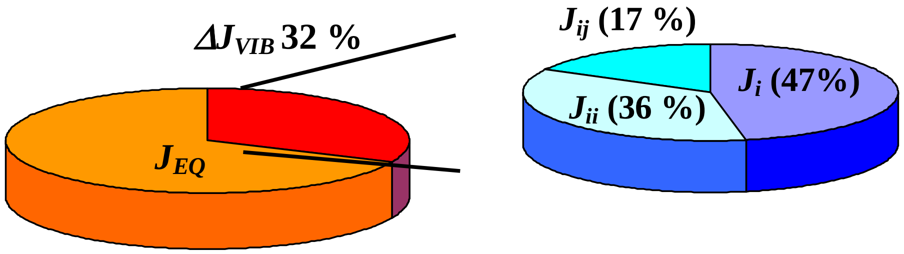

Figure 1. Calculated averaged equilibrium and vibrational parts of spin-spin coupling constants in the alanine zwitterion are plotted on the left. For the vibrational part, average relative ratios of the first ("i"), diagonal ("ii") and off-diagonal ("ij") second derivatives are plotted at the right hand side.

The averaging over the higher-frequency modes is relatively independent on the temperature, but in general requires a difficult anharmonic treatment. Yet for model systems we found that it may be very beneficial for nuclear magnetic resonance (NMR) chemical shifts, and *J*-coupling constants [3]. In most cases the harmonic vibrational function combined with the property second derivatives provided the largest correction of the equilibrium values, while anharmonic corrections (third and fourth energy derivatives) were found less important. The vibrational corrections of NMR shifts were small and yielded a convincing improvement only for very accurate wavefunction calculations. For the indirect spin-spin coupling constants the averaging significantly improved already the equilibrium values obtained at the density functional theory (DFT) level. Both first and complete second shielding derivatives were found important for the shift corrections, while for the *J*-coupling constants the vibrational parts were dominated by the diagonal second derivatives.

Keywords: Raman, Raman optical activity, Nuclear magnetic resonance, vibrational averaging, density functional theory

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ATAT@WIEN2k: Calculation of effective cluster interactions within the LAPW method

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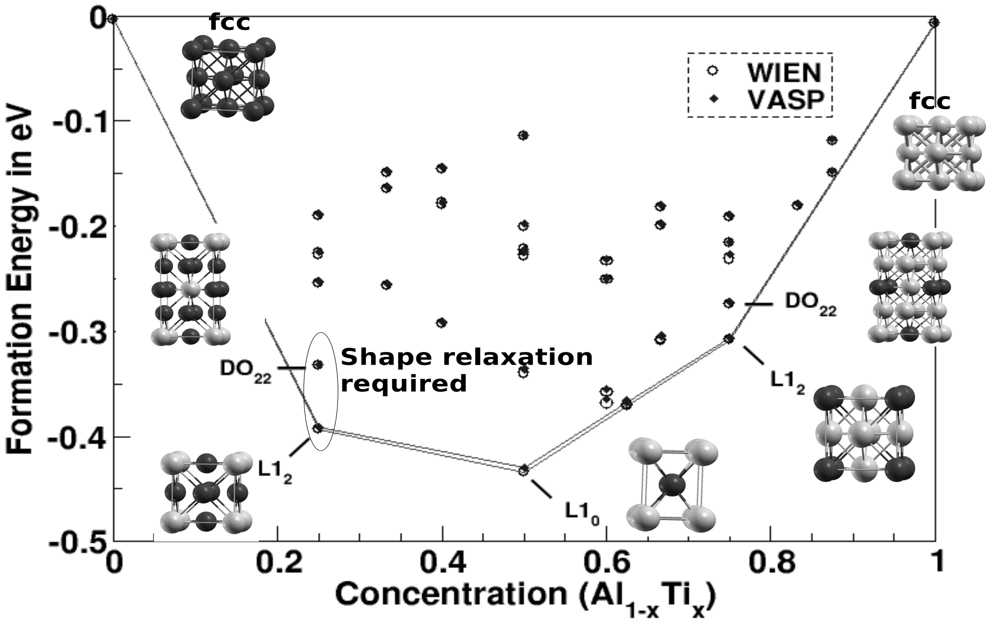
We present an interface between the Alloy Theoretic Automated Toolkit (ATAT) [1] and the program package WIEN2k [2]. ATAT is a free program package that performs the cluster expansion to obtain effective cluster interactions (ECIs) for alloys, through its MIT Ab-initio Phase Stability (MAPS) program. With the ECIs at its disposal, ATAT does Monte Carlo simulations, with an Ising-like hamiltonian constructed from the ECIs, which has the full accuracy of density functional theory (DFT) calculations. In order to obtain the ECI, MAPS requires to be linked with an ab-inito program. We have interfaced ATAT with the linearized augmented plane wave (LAPW) code WIEN2k, which yields highly accurate total energies for any kind of alloy supercell containing the constituent elements/compounds in arbitrary concentrations and geometries . We present the implementation of our interface between ATAT and WIEN2k and compare our results of the fcc Al-Ti alloy with data from literature.



Keywords: Density functional theory, effective cluster interactions, alloys

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Lattice dynamics of Mg_2Si and Mg_2Ge compounds from first-principles calculations.

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In this work, we present first principals studies of vibrational and thermodynamic properties of the Mg_2Si and Mg_2Ge compounds. All the calculations are carried out using the plane wave pseudopotentials method within the density of functional theory (DFT). The equilibrium lattice parameters are obtained by minimizing the energy with respect to volume. The phonon spectra are obtained by using the density functional perturbation theory (DFPT). The Born effective charges are calculated from the splitting of the optical branches which satisfy the acoustic sum rule. The obtained static dielectric constant is higher than the electronic one for both studied materials. By using the calculated phonon frequencies and the density of states the thermodynamic properties such as entropy, specific heat, free energy and internal energy are evaluated. The obtained values of the heat capacity and the entropy compare well with the measured values.

Keywords : Ab initio, DFT, semiconductor, phonons.

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Validation of projector augmented-wave methods for the calculation of NMR properties of molybdenum

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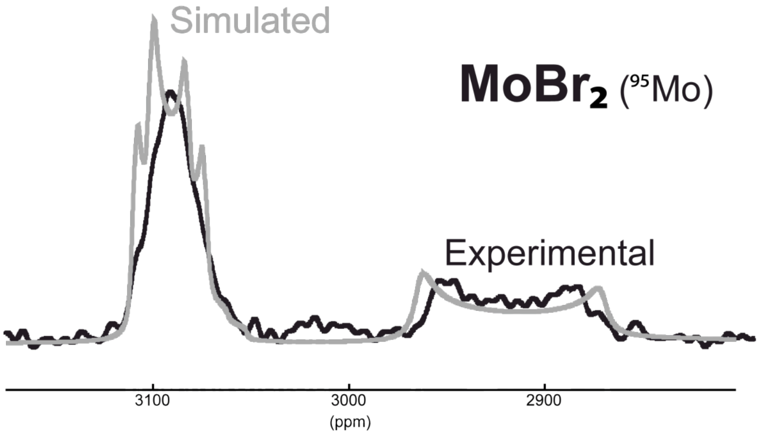
Since the 1980s, the expansion of solid-state NMR has increased significantly owing to the development of new techniques that enable high resolution to be achieved even in the solid state. For inorganic compounds without protons or fluorine atoms, the chemical shift and the quadrupolar interactions are the two dominant interactions responsible for the appearance of the NMR spectra. The corresponding parameters give information about the atomic structure of the compound under investigation. It appears that in many cases, the complexity of the experimental results requires a theoretical analysis for their complete understanding. Until recently, only quadrupolar interaction parameters could be calculated using periodic DFT calculations. Pickard and Mauri presented formalism, named GIPAW for gauge-including projector augmented-wave, for the *ab initio* calculation of all-electron NMR chemical shifts in insulators using pseudopotentials [1].

We present the application of two pseudopotential based methods, projector augmented-wave (PAW) and GIPAW, for the calculation of quadrupolar coupling and chemical shift tensors, respectively, of ^{95}Mo. Validation of these methods is carried out on a series of ternary molybdate compounds as well as a hexacarbonyl complex. The different approximations used as well as the influence of the crystallographic structures considered for the calculations are intensively discussed. Comparison with available experimental results as well as periodic and molecular all-electron *ab initio* calculations are carried out. These *ab initio* methods are used to help in the interpretation of the ^{95}Mo spectra of solid-state compounds containing molybdenum clusters.



Keywords: solid-state NMR, molybdenum, GIPAW

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Broken symmetry calculations of magnetic coupling constants in complexes of [M(PHTFAC)$_2$(NITpPy)] (M=Co, Mn, Cu)

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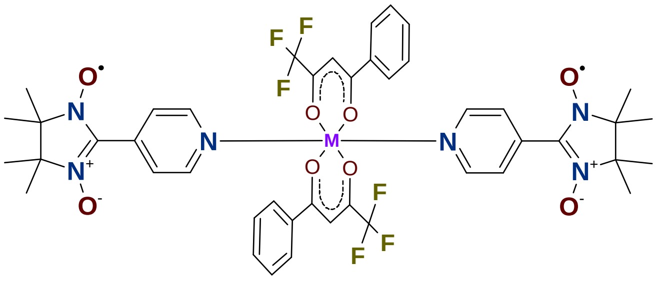
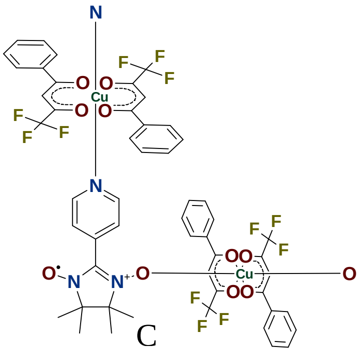
Molecular magnetic compounds have attracted the interest of many chemists and physicists in recent years. Due to the mild conditions of synthesis many of these compounds have been synthesized in recent years, with a variety of architectures. In the present communication we report on B3LYP/D95V/LanL2DZ calculations of magnetic coupling constant, using the broken symmetry approach, for the nitronyl nitroxide radical complexed to the metallo-β-diketonate group[1]. Combination of these blocks through coordination of the radical to the metal complex generates blocks with more than one magnetic center, as seen in Figure 1.

The manganese (A) and cobalt (B) complexes (Figure 1) are structurally similar, with the metal center coordinated in an octahedral environment, two pheniltrifluormethylacetilacetonate (Phtfac) ligands in the *trans* orientation and two nitronyl nitroxide radicals coordinated through the pyridine ring in the axial positions. The adjustment of magnetic measurements showed ferromagnetic interactions with coupling constant J_A^{exp} = 3.0 cm^{-1} and J_B^{exp} = - 4.6 cm^{-1}. The copper complex (C) form a *zigzag* chain with two Cu(pthfac)$_2$ independent sites. In one site the radical is coordinated through the oxygen atom of the nitroxide group while in the other one the coordination is through the pyridine ring. The fit of the magnetic data indicate two constants J_c^{exp} = 29.4 cm^{-1} and $J'_c{}^{exp}$ = - 4.4 cm^{-1}.

The geometries of A and B were fully optimized in the C_i point group. Calculations of the magnetic coupling constant resulted in values of J_A^{calc} = 2.2 cm^{-1} and J_B^{calc} = - 46.0 cm^{-1}. For C, the experimental geometry was used to determine the ground spin state followed by the broken symmetry calculation. Ferromagnetic interactions with coupling constant of 33.2 cm^{-1} were found for complexation via the oxygen atom, while antifferomagnetic interactions with coupling constant of -7.9 cm^{-1} were found for complexation via the pyridine ring.



A (M = Mn) :B (M = Co)



C

Analysis of the magnetic orbitals of the manganese complex reveals that interactions leading to ferromagnetic coupling are stronger than those resulting in antiferromagnetic coupling. For the cobalt complex, although the calculated coupling constant is considerably higher than the experimental value, both experiment and theory predict the same behavior. For the copper complex, calculations allowed determination of the pathway leading to the observed ferromagnetic and antiferromagnetic interactions.

Keywords: DFT calculations, molecular magnetism, coordenations compounds

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Computation of Negative Electron Affinities in DFT : Recent Applications

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For many gas phase molecules, the vertical electron affinity is negative and standard theoretical ways of evaluating this property are troublesome. Previously, we have proposed an unconventional approximation for the electron affinity, based on the energies of the Kohn-Sham frontier orbitals and an approximation for the derivative discontinuity of the energy vs. the number of electrons, i.e. [1,2]

$$A = -\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{LUMO}} - I$$

where $\varepsilon_{\mathrm{HOMO}}$ and $\varepsilon_{\mathrm{LUMO}}$ are the orbital energies obtained with a local functional and I is the ionization energy, computed as the difference of the energies of the cationic and neutral system.

Next, this approximation has been used to control the degree of binding of the electron in this anion is a potential wall approach [3], enabling also the calculation of other properties than the energy of the anion.

In this contribution, we describe our most recent application of our two approaches and we test its ability to describe subtle changes in affinity due to atomic substitution and structural changes

Keywords: Negative electron affinities, derivative-discontinuity, Potential wall

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Orbital Imaging of Conformational Rearrangements and Bond Breakings in Momentum Space

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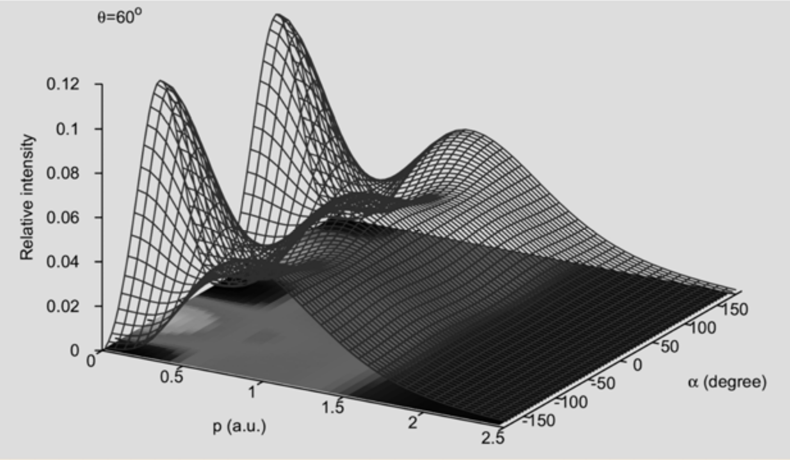
Electron Momentum Spectroscopy (EMS) is a powerful orbital imaging technique, which focuses on (e,2e) electron impact ionization experiments at high kinetic energies. Like with any ionization spectroscopy, EMS experiments are subject to many complications and their interpretation requires extensive theoretical work. This contribution examines in details the influence of nuclear dynamics in the initial ground state and in the final ionized state on the experimentally inferred momentum distributions of ethanol, through a comparison with simulations employing standard (B3LYP) Kohn-Sham orbitals as well as benchmark ADC(3) Dyson orbitals, thermal averaging of the outermost momentum distributions over exceedingly large sets of model structures, and Born Oppenheimer Molecular Dynamical calculations for the radical cation [1,2]. Our results give indications that a strong turn-up of the outermost (e,2e) ionization intensities at low electron momenta is the combined result of (1) the extraordinarily flat nature of the conformational energy map of ethanol, which enables significant departures from energy minima in the ground electronic state, (2) anomeric interactions between an oxygen lone-pair and the central C-C bond, for the minor fraction of conformers exhibiting an hydroxyl (C-C-O-H) torsion angle (α) around 90°, and, last but not least, (3) highly significant stretchings of the central C-C bond due to ionization [~0.5 Å within 40 *fs* when $\alpha(t=0) \sim 90°$], resulting in turn into an enhanced delocalization of the HOMO from the oxygen lone pair onto the methyl group. The turn-up of the outermost (e, 2e) ionization intensities at $p \rightarrow 0$ therefore reflects the charge transfer that preludes an ultra-fast dissociation of the ethanol radical cation ($[CH_3\text{-}CH_2\text{-}OH]^{\cdot+}$) into a methyl radical ($CH_3^{\cdot}$) and a protonated form of formaldehyde ($H_2C{=}O\text{-}H^+$).



Keywords: orbital imaging, anomeric interactions, nuclear dynamics

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Theoretical study of 1,3-dipolar cycloadditions of phenyl azide with different olefins using DFT-based reactivity indexes

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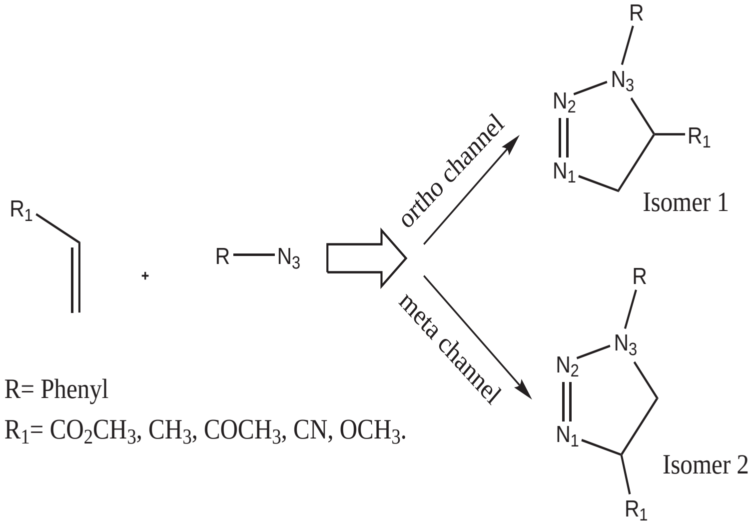
The 1, 3-dipolar cycloadditions of phenyl azide with a variety of olefins have been studied by means of density functional theory (DFT) method. These results derived from the theoretical calculations shown that the concerted mechanism is both kinetically and thermodynamically preferred. The comparison of the calculated results between the 1,3-dipolar cycloadditions of phenyl azide with electron-deficient olefins and electron-rich ones is employed. The calculations have been done in the B3LYP/6-31G* level in gas phase. We led a theoretical study while being based on the following theoretical approaches: the theory of the transition state, the calculation of the activation energy, and the DFT-based reactivity indexes.



R= Phenyl

R_1= CO_2CH_3, CH_3, $COCH_3$, CN, OCH_3.

Keywords: 1,3-dipolar cycloadditions, regioselectivity, DFT calculations, the theory of the orbital molecular, DFT-based reactivity indices.

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Solvent models for calculation of NMR parameters

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Structure of the alanine hydration shell was modeled by Carr-Parinello molecular dynamics (CPMD) [1] and used to explain subtle differences in NMR chemical shifts and indirect spin-spin coupling constants of the neutral (zwitterionic), cationic, and anionic forms of this aminoacid. In comparison with a classical molecular dynamics (MD), the quantum mechanical CPMD approach revealed a more structured solvent and significant differences in the radial and angular distributions of the water molecules around the solute. For snapshot CPMD configurations the NMR parameters were computed by density functional theory (DFT) and averaged. Obtained values were significantly closer to experimental parameters known for ^{15}N, ^{13}C-isotopically labeled alanine than those calculated by conventional implicit dielectric solvent model. The NMR results also clearly indicate a superiority of the CPMD over the MD explicit solvent treatment. Differently positioned waters in the clusters cause an unexpectedly large scattering of the NMR parameters. About 10-20 MD snapshots were needed for a satisfactory convergence. For a more detailed insight we also compare various solvent models including explicit solvent molecules, polarizable continuum models, and a point charge solvent approximation. The NMR chemical shift was found to be much more sensitive to the molecular hydration than the coupling. The results thus indicate a large potential of the NMR spectroscopy and quantum simulations to probe not only the structure of molecules, but also their interaction with the environment.

Keywords: Alanine, Nuclear magnetic resonance, density functional theory, Car-Parinello molecular dynamics

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Scalar-relativistic DFT calculation of structural and electronic properties of mercaptobenzothiazolyl lanthanide complexes with luminescent activity

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Luminescent complexes of rare earth metals attract considerable attention because of their potential applications in the design of organic light-emitting diodes [1]. It is known that luminescent activity in the complexes to a great extent depends on the energy transfer from the ligands to the metal ion, which is realized efficiently when lowest ligand-centered triplet state lies slightly above the resonance energy level of the metal ion [2]. The geometry and electronic structure of thiolate complexes of rare earth metals $Ln(SR)_3(thf)_2$, HSR = 2-mercaptobenzothiazole Ln=La, Ce, Sm, Eu, Tb, Gd, Er, Tm in ground and first excited states was studied using nonempirical density functional PBE approach to focus the problem of theoretical description of their luminescent properties. Only a scalar-relativistic approximation with four-component basis set: Ln [30s29p20d14f6g/9s8p6d3f1g] S [15s11p3d/4s3p1d], C,N,O [10s7p3d/3s2p1d] H [6s,2p/2s1p] [3] allows to describe well the coordination of ligands, see fig. The experimental bond lengths in A from [4] are shown in brackets. The extended basis set: Eu : [10s10p9d7f/5s5p3d4f] S,C,N,O [5s5p2d/3s3p2d] H [5s,1p/3s1p] for SBK pseudopotential lead to strong elongation of Ln-S bond lengths on 0.3 A. It was found that meriodianal arrangement of SR ligands is more favorable than facial one in accordance with experiment.

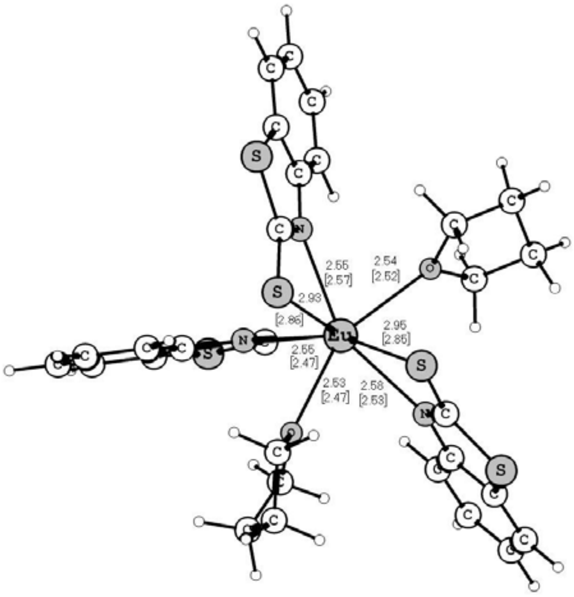

Fig. View of the complex along Eu-S axes

In the first excited studied the spin S=1 of a ligand shell is parallel to the spin S=n/2 of an atomic f^n shell. In the complexes with less than half-filled f-shell (Sm and Eu) there is larger interaction of f-orbitals with π* orbitals of SR-ligands than in the complexes with more than half-filled f-shell (Tb and Tm). However only Eu and Tb complexes possess good luminescence of metal ions. But Eu ion has the lowest energy of interatomic f-f transition, and for Tb complex it was found the smallest distortion of the geometry in the excited state

Keywords: lanthanide complexes, electronic structure, scalar relativistic DFT

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Predicting explosibility properties of chemical substances from a combined DFT-QSPR approach

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The new European regulation of chemicals named REACH (for "Registration, Evaluation and Authorization of Chemicals") turned out in the practical registration phase in December 2008. Under this new regulatory framework, a tremendous number of substances (up to 30000) require a new assessment of hazard properties. However, the complete characterization of toxicological, ecotoxicological and physico-chemical hazards from experimental tests is time-consuming, costly, sometimes not feasible at the R&D stage and potentially risky for the staff. In this context, the development of alternative predictive methods for assessing hazardous properties of chemical substances is promoted in REACH and in the relating new international classification system of substances GHS (Globally Harmonized System for classification and labeling of chemical products).

Quantitative Structure-Activity or Property Relationships (QSAR/QSPR), already extensively used as screening methods in biological and toxicological applications to reduce unnecessary animal testing, are more and more widely developed also to predict physico-chemical properties by academic and industrial scientists.

This contribution focuses on models established to predict accurately the physico-chemical properties of a series of potentially explosive nitroaromatic compounds. An original approach associating the QSPR methodology to quantum chemical calculations has been developed. In a first step, a large set of descriptors (constitutional, topological, geometrical, electronic, quantum chemical) was computed from molecular structures calculated using the Density Functional Theory (DFT). Then, these descriptors were integrated into a data mining analysis (e.g. statistical multilinear regressions) to link them quantitatively to experimental properties characterizing explosive substances, like thermal stability, electric spark or impact sensitivity. Once validated, the obtained models are expected to be finally included into a global tool aiming to assess physico-chemical hazards.

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The derivative of the Lieb definition for the energy functional with respect to the particle number and the spin number

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The nature of the explicit dependence on the particle number N and on the spin number N_s of the Lieb definition for the energy density functional [1,2] is examined both in spin-free and in spin-polarized density functional theory [3]. First, it is pointed out that the nonuniqueness [4,5] of the external magnetic field $B(\underline{r})$ corresponding to a given pair of density $n(\underline{r})$ and spin density $n_s(\underline{r})$ in spin-polarized density functional theory implies, for ground states, the nonexistence of the derivative of the SDFT Lieb functional $F_{N,Ns}[n,n_s]$ with respect to N_s. Giving a suitable generalization of $F_N[n]$ and $F_{N,Ns}[n,n_s]$ for $N \neq \int n(\vec{r})d\vec{r}$ and $N_s \neq \int n_s(\vec{r})d\vec{r}$, it is then shown that their derivatives with respect to N and N_s are equal to the derivatives, with respect to N and N_s, of the total energies $E[N,v]$ and $E[N,N_s,v,B]$ minus the external-field energy components, respectively.

Keywords: Lieb functional, particle-number dependence, spin-number dependence, derivative discontinuity, nonuniqueness of magnetic field

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How relativistic effects control elemental Astatine chemistry

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Astatine (At, Z=85: [Xe]$4f^{14}5d^{10}6s^{2}6p^{5}$) is below iodine and belongs to the halogen group. One of its isotopes, ^{211}At, is a promising candidate as a therapeutic agent in nuclear medicine [1] if one considers the energy of the α particles emitted as well as its physical half-life (7.2h). Since there are no stable isotopes of astatine, the chemistry of astatine remains not very well understood. In most cases, astatine is believed to behave as a halogen but the chemical similarity between astatine and its nearest halogen neighbor, iodine, is not always obvious. It as been reported that astatine presents a metal-like behavior when existing under the oxidation states +I and +III as At^{+} and AtO^{+} species [2]. The number of studies dealing with the complexation properties of the cationic forms of astatine remains limited. This is related to the low availability of astatine (production with accelerators capable of accelerating alpha particles to high energies, investigations derived from radiochemical studies at ultra-trace concentrations, typically between 10^{-12} and 10^{-15} mol L^{-1}). Recently, we investigated experimentally the reaction of complexation of At(I) and At(III) with organic and inorganic ligands [3]. A competition method based on solid/liquid separation or liquid/liquid extraction is proposed to determine the equilibrium constants. The aim of this study is to assess the experimental methodology by the confrontation to theoretical investigations.

Astatine is very heavy element with important relativistic effects. Hence, very specific quantum chemistry methods must be used. The spin-orbit density functional theory (SO-DFT) approach, which uses two-component relativistic effective core potentials (RECPs) including spin-orbit terms, has been used to investigate the spectroscopic properties of At, At_2 and HAt species. In conjunction with our own built up basis sets (double and triple zeta augmented with diffuse and polarization functions), SO-B3LYP and SO-M06 calculations yield results in good agreement with that of the literature.

Aqueous solvation effects must also be taken into account in order to compare measured and computed equilibrium constants of the astatine reactions. Therefore, specific parameters for At have been introduced in standard continuum solvation models (PCM models coupled to UAHF and UAKS cavities). The reaction of At(I) and At(III) with Cl^{-}, Br^{-} and SCN^{-} were studied as a test set using this cost-effective computational methodology. Obtained results compare very well to the experimental derived values. Effects of solvation and spin-orbit coupling on astatine chemistry will be specifically discussed in this poster.

Keywords: relativistic DFT, spin-orbit coupling, solvation effects

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DFT-NJC analysis of stereochemical effects on NMR spin-spin coupling constants

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Spin-spin coupling constants are one of the most used NMR parameter for sterochemical analyses [1-3]. The natural J-coupling (NJC) method [4] allows the analysis of the scalar Fermi contact (FC) contribution (usually the most important) to J_{NM}. The electron delocalization and the hyperconjugative interactions affect the FC term notably[1-3]. The calculated FC contribution J^{FC} can be partitioned into three main parts:

$$J^{FC} = J^{Lewis} + J^{deloc.} + J^{repol.}$$

The effects of conjugative or hyperconjugative type can be analysed using the delocalization part, $J^{deloc.}$ that involves the terms or contributions from donor-acceptor interactions.

In this work the delocalization terms have been studied for many molecules of stereochemical interest. As an example, in the spectra of syn and anti conformers of furan-2-caboxaldehide molecule, it was observed that there is a very large difference in $^2J_{C_2-H_f}$ between both, syn and anti, conformers [2]. These differences can be interpreted (see Figure 1) using the delocalization or hyperconjugation contributions calculated at the DFT-NBO theory.

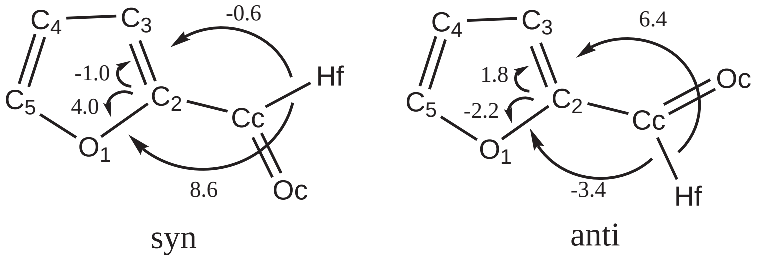

Figure 1: Main delocalization contributions ($\sigma_{C_C-H_f} \rightarrow \sigma^*_{C_2-O_1}$, $C_2(CR) \rightarrow \sigma^*_{C_2-O_1}$, $\sigma_{C_C-H_f} \rightarrow \sigma^*_{C_2-C_3}$ y $C_2(CR) \rightarrow \sigma^*_{C_2-C_3}$), in Hz, for Furan-2-carboxaldehyde molecule.

Keywords: Natural bond orbital, natural J coupling, delocalization contribution.

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Giant magnetic anisotropy energy of Fe^+ ions in $SrCl_2$ and $KTaO_3$ lattices

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Materials with large magnetic anisotropy energy (MAE) are intensely sought due to their technological relevance [1]. In the case of insulating materials containing *3d* ions in axial symmetry and with a spin $S > 1/2$ the MAE is directly related to the zero-field-splitting (ZFS) term $H_{ZFS} = D(S_z^2 - 1/3\ S^2)$ in the *effective* spin Hamiltonian. Common Kramers ions like Fe^{3+}, Cr^{3+} or Mn^{2+} in inorganic lattices give rise to values of $|D|$ which are in the range 0.01-1 cm^{-1}. Despite this fact experimental EPR data carried out on the *less common* Fe^+ ion in $SrCl_2$ [2] and $KTaO_3$ [3,4] strongly suggest that D should be much higher than the Zeeman energy for the Q-band (1 cm^{-1}). This relevant conclusion is supported by the fact that only the $|3/2; -1/2> \rightarrow |3/2; 1/2>$ transition, whose energy is independent on D, is detected in EPR experiments [2-4]. According to these facts we have tried to determine what the actual D values for Fe^+ doped $SrCl_2$ and $KTaO_3$ are. In order to do so, we have first calculated, using DFT [5,6], the large off-center distortion in the <100> direction starting off from the substitutional position as supported by experimental data [2,3]. For obtaining the D value at the equilibrium geometry the *multi-reference density functional theory* has been used [7] together with multi-configurational CASPT2 calculations. As a salient feature *both* methods lead for $SrCl_2$: Fe^+ to a D value practically equal to 50 cm^{-1} which means a MAE *two orders of magnitude* bigger than that found for Fe^{3+}, Cr^{3+} or Mn^{2+} ions in inorganic compounds. This result is comparable or even larger than other recently reported giant MAEs for atoms on surfaces or magnetic clusters [1]. In the case of $KTaO_3$: Fe^+ the calculated value $D=18\ cm^{-1}$ is also huge though smaller than that for $SrCl_2$: Fe^+ as it could be inferred looking at the $g_\perp - g_{||}$ quantity [2,3] which is also reproduced by our calculations. In a second step we have tried to understand what the microscopic origin of this giant MAE is. As the experimental spin-orbit parameter, ξ, of free Fe^+ ion is only equal to 356 cm^{-1} we have verified that the very high D values found for these systems mainly come from the position of the ^4E first excited state lying *only* 600 cm^{-1} above the ground state for $SrCl_2$: Fe^+. The origin of this crucial fact and its link with the strong off centre distortion will be discussed in detail.

Keywords: magnetic anisotropy, pseudo Jahn-Teller, DFT

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Rare earth oxide alloys on Si(111) substrates: Theory and experiment

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Continuous effort is spent over the last years to develop high-k dielectrics suitable for integration into Si technology as exchange for SiO_2 in order to reduce leakage currents. Possible candidates include rare earth oxides (RE), where especially Gd_2O_3 is promising since its lattice parameters match Si very closely. Using alloys of RE oxides allows even more flexibility in tailoring structural and electronic properties.

Here we investigate the growth, interface formation, and electronic structures of the RE oxides on Si(111) by combining *in situ* X-ray diffraction in molecular beam epitaxy, carried out at BESSY, with density functional theory investigations (DFT). The DFT calculations are carried using the abinit computer code [1-3]. The explicit inclusion of all f-electrons allows for a description of different bonding situations of the RE elements. The correlation of the f electrons is treated using the LDA+U approach. Different phases of the rare earth oxides are studied, including the hexagonal and the cubic (bixbyite) RE_2O_3 as well as the cubic fluorite structure REO_2 for the pure RE oxides as well as a number of their alloys, like $LaLuO_3$. Especially the bixbyite structure is computationally demanding, the unit cell contains 40 atoms. Usually, it is approximated by a simple modification of the fluorite structure, see e.g. [4]. The stability of the different bulk phases and structure formations depending on the oxygen chemical potential is discussed with respect to the occupation of the f shell, ranging from La with 0 up to Lu with 14 electrons. Possible interface formations between RE oxides and Si(111) are investigated based on the X-ray diffraction studies. The electronic band structure, band offsets, and dielectric properties are calculated. Special emphasis is given to the $LaLuO_3$ alloy, since it is already known to have valence and conduction band offsets with more than 1 eV to Si for the (001) orientation [5]. $(La_xLu_{1-x})_2O_3$ matches the Si lattice at about $x = 50\%$, with improved electronic properties over Gd_2O_3. We also find differences in the electronic properties between random and digital alloys (stacking of layers) in the (111) direction which can be partially explained by differences in the internal strain distribution.

Keywords: LDA+U, rare earth oxides, high-k dielectrics

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Computational Study of the Jahn-Teller Effect in Cu(II) Chelate Complexes: DFT/MM Approach

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Jahn-Teller (JT) effect is frequently observed in transition metal chemistry, as degenerate ground states for coordination compounds, e.g. Cu(II) complexes, are common [1]. A detailed analysis of the distortion of a several Cu(II) chelate complexes—tris(ethylendiamin)copper(II) ($[Cu(en)_3]^{2+}$), bis(cis,cis- 1,3,5-triamino-ciclohexan)copper(II) ($[Cu(tach)_2]^{2+}$), bis(cis,cis-1,3,5-trihidroxy-ciclohexan) copper(II) ($[Cu(thch)_2]^{2+}$), etc. is presented.

Multimode JT effect [1] in these molecules is treated with a new apraoch using DFT, recently proposed by us [2], based on the analogy between the JT distortion and reaction coordinates [3]. DFT calculations are performed by the means of a multideterminental DFT procedure developed by our group for the study of the JT systems [2, 4]. Conformations and the strain of the chelate rings are analysed with the Consistent Force Field (CFF) Molecular Mechanics program [5].

Approach presented here allows getting direct insight into the coupling of electronic structure and nuclear movements. This is of particular interest in various fields of chemistry, e.g. in coordination, bioinorganic, material chemistry, or in discussing reaction mechanisms.

Keywords: Jahn-Teller Effect, DFT/MM, Cu(II) Chelate Complexes

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DFT study of the normal strains and elastic properties of Muscovite-Paragonite series.

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Crystal structure and elastic stiffness constants of $2M_1$ muscovite-paragonite series have been calculated by means of quantum-mechanical methods based on Density Functional Theory with specially adapted numerical LCAO and norm conserving pseudopotentials [1]. The crystal structure, bond distances and especial geometrical features of muscovite, 50%Na-50%K intermediate, and paragonite agree with the range of experimental values in literature. Normal strains are analysed as a function of average strains of bond and specific geometrical features.

Elastic stiffness constants are calculated with the generalized Hooke law and with the help of finite strain method. Normal strains propagate along crystal structure and bonds according to their bonding. Strain of interlayer space is the larger of the crystal structure. Values of elastic stiffness constants agree with the monoclinic symmetry, the bonding and the range of experimental values of muscovite-paragonite series. Bulk and shear moduli are also calculated, and approximately agree with the known experimental values.

Keywords: Muscovite, Paragonite, Muscovite-paragonite intermediates, crystal structure, elastic stiffness constants.

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Effect of a uniform electric field on the dual fluorescence activity of some amino compounds

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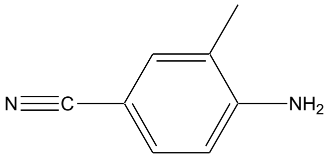
The time-dependent density functional theory has been used to study the effect of an external uniform electric field on the dual fluorescence activity of three compounds, the 3M4AB-CN, the TMAB-CN and the DMABE (Figure below). It is well recognized that the study of a system under an electric field may be useful to model environmental effects.

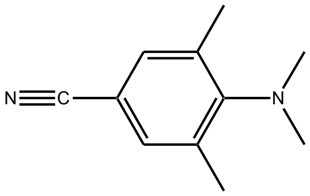
Full geometry optimizations and excitation energies have been obtained with the PBE exchange-correlation functional coupled with TZVP basis set, with extra diffuse functions. To have a good description on diffuse excited states, the asymptotically corrected exchange-correlation potential of van-Leeuwen-Baerends was used. Using a development version of the NWChem code v5.0, which includes a uniform electric field, has performed all calculations.

This work has been divided in two parts. Firstly, we studied the behavior of the excitation energies of the ground state geometries under the application of an external electric field, by using several directions of it. Secondly, we investigated the influence of a uniform electric field on the dual fluorescence phenomenon according to the twisting intermolecular charge-transfer mechanism; obtaining the potential energy surface of the ground states along the twisting angle.

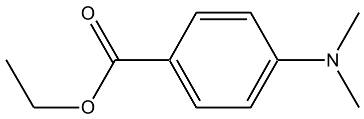
The presence of an electric field modifies significantly the absorption of the studied compounds, in general the increment of the strength field increase the absorption energy. In some cases an absorption band is strongly shifted when electric field is applied.



3M4AB-CN



TMAB-CN



DMABE

Studied systems: 3M4AB-CN (3-methyl-4-(N,N-dimethylamino) benzonitrile); TMAB-CN (3,5-dimethyl-4-(N,N-dimethylamino) benzonitrile); DMABE (p-(dimethylamino) benzoic acid ethyl ester).

Keywords: fluorescence, electric field, TDDFT.

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Prediction of MCD of Rare-Earth $M_{4,5}$-Edge XANES for Rare-Earth Iron Garnets Based on First-Principles Calculation

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Rare-earth iron garnets (RIGs), with the general formula $R_3Fe_5O_{12}$, are one of the most interesting materials for information technology-related applications because of their unique magnetic properties. For the detailed investigation of local electronic structure around magnetic ions, magnetic circular dichroism (MCD) of x-ray absorption near-edge structure (XANES) is quite useful. However, only few of the experimental MCD of rare-earth (RE) $M_{4,5}$ -edge XANES for RIGs have been reported to date [1,2], mainly due to the difficulty in theoretical analysis arising from the coexistance of multiplet effects and relativistic effects. In order to overcome this difficulty, we have recently developed a program to calculate MCD spectra based on our relativistic configuration-interaction (CI) calculation program. [3]

In the present work, we performed systematic prediction of MCD of RE $M_{4,5}$ -edge XANES for RIGs based on the non-empirical relativistic CI calculation program using RO_8^{13-} model cluster with effective Madelung potential produced by point charges. The theoretical MCD spectra for $Er_3Fe_5O_{12}$ and $Tb_3Fe_5O_{12}$ are shown in Fig. 1. The systematic calculation exhibited an interesting tendency where the MCD at M_5-edge changes sign from negative to positive as the atomic number increases. The spin and orbital moments of the RE ions were also estimated using the explicitly obtained many-electron wave functions.

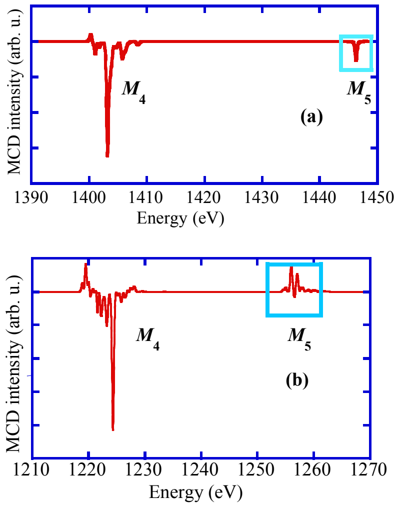

Fig 1. Theoretical MCD spectra of (a) Er $M_{4,5}$-edges for $Er_3Fe_5O_{12}$ and (b) Tb $M_{4,5}$-edges for $Tb_3Fe_5O_{12}$

Keywords: MCD, rare-earth iron garnets, first-principles calculation

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Modeling the N-Methylacetamide Structure and Anharmonic Vibrational Spectra

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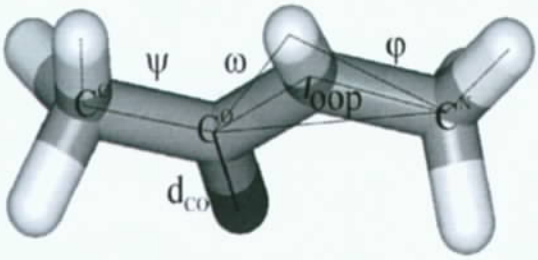
The N-methylacetamide molecule (NMA) is an important model for peptide and protein vibrational spectroscopy containing the main amide chromophore. In the past, some NMA geometry and spectral features could not be entirely explained at the harmonic level or by a single-conformer model. The spectra were also found to be very dependent on molecular environment. We remeasured NMA Raman and infrared spectra in a variety of conditions, and simulated them to separate the fundamental, dimer and harmonic bands.

For geometry, the MPX, and CCST(T) wavefunction methods in vacuum predicted a broad nitrogen out of plane potential well, which DFT failed to reproduce. In polar solvents the potential shape becomes more harmonic and the amide group is more rigid. On the other hand, the increasing solvent polarity enhances other anharmonic phenomena, such as the coupling between the carbonyl stretching (amide I) and lower-frequency amide bending modes, which explains the amide I band splitting or asymmetry often observed experimentally. The CH_3 group rotation modeled by a rigid rotor model [1] explained some features of the NMA spectra in a solid hydrogen matrix. In room temperature the methyl rotation contributes to a non-specific inhomogeneous band broadening only.

The potential energy surface of the CH_3 rotation was also found to be dependent on the solvent. Computed (DFT, MP2) anharmonic Raman and IR spectra well agree with the experiments in different solvents. The anharmonic corrections of harmonic vibrational spectra were based on a fourth-order Taylor expansion of the potential. The anharmonic spectra were found superior to the harmonic ones, both for the DFT (B3LYP) and MP2 calculations. The vibrational spectroscopy supported by the calculations thus sensitively probes the amide structure, flexibility, and interactions with the environment.



Keywords: NMA, DFT, anharmonic, vibrations, Raman spectra, infrared

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Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} Binding Chalcogen-Chalcogen Bridges: a Compared MP2 and DFT Study

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In a recent work [1], we have investigated the interactions between Co^{2+} and cysteine/selenocysteine without finding convincing differences between the two systems whereas some biological distinctions exist among the two chalcogens. These differences may arise from chalcogen-chalcogen bridges present in biological systems. We have investigated the binding of late first row transition metals with chalcogen-chalcogen bridges represented by minimal models (H_2O_2, H_2S_2 and H_2Se_2). The use of such small models allows us to employ a large atomic basis set and compare DFT and MP2 results with CCSD(T) reference data we have performed using the same basis. All methods agree in finding Cu^{2+} complexes the most stable ones and, for each given metal, H_2Se_2 complexes more stable than H_2S_2 ones and these latter more stable than the correspondent H_2O_2 ones. Albeit this qualitative agreement between all the considered methods, quantitatively we found a big difference between MP2 and B3LYP, in structural and energetic properties. In particular, DFT largely overestimates the binding energies, while MP2 slightly underestimates them with respect to CCSD(T) calculations. Note that also other popular functionals (hybrid MPW1PW91, hybrid meta GGA functional M05, meta DFT functional TPSS, GGA functional BLYP and the well known LSDA functional SVWN) overestimate the binding energy, such that it seems to be an intrinsic DFT failure. The main discrepancy was found for Cu^{2+}. The comparative analysis of B3LYP and MP2 wavefunctions explains the differences found between two methods and why the Cu^{2+} complexes show the bigger one.

Finally CCSD(T) calculations, slightly modifying MP2 insights, found that all the three complexes present the same metal binding energy order, and notably $Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+}$.

Keywords: transition metals, chalcogen, various functionals

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In silico assessment of chemical stability for drug substances

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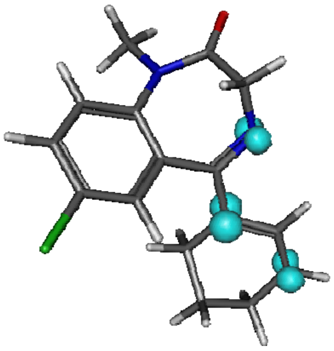
The chemical stability of active pharmaceutical ingredients (API) can be studied by physico-chemical stress tests but the interpretation of the results to get the degradation pathways is often difficult. We present here, how an *in-silico* approach has been combined with a chemical expertise to help controlling the stability of the drug substance and advise the pharmacists for formulation of the drug product in order to prevent chemical degradation. Stability studies have shown that the vast majority of degradation reactions are either hydrolysis or radical oxidation by triplet oxygen of air, also called autoxidation.

Hydrolysis reactions are usually well explained by the nucleophilic function in the Fukui theory. Sometimes, one has to consider an activation of the API by protonation or by a reaction with a Lewis acid. For hydrolysis, a pKa prediction software and a quantum chemistry program coupled with a good visualizer are usually enough. Nevertheless the radical susceptibility function in the Fukui theory shows little relationship with radical autoxidation, but a good correlation with oxidation *via* direct electron-transfer to oxygen.

After a study of the reaction path for autoxidation, initiated by the presence of a radical, the most common pathway is a chain reaction where the slowest step is the abstraction of one hydrogen atom on the API from the radical initiator. This radical reacts instantaneously with triplet oxygen from air to form the peroxide radical. The determination of the most stable hydrogen-abstracted-API radical by quantum chemistry and the observation of its spin density offer a new insight on the autoxidation degradation mechanism.



Spin density after hydrogen abstraction of tetrazepam (myolastan)

Keywords: Drug substance, degradation, hydrolysis, oxidation, degradation

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Magnetic Property of Gold Metallic Clusters

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We present first-principles theoretical calculations of the structural, electronic and magnetic properties of small metallic gold clusters whose size covers from 9 to 16 atoms. The studies make use of a linear combination of atomic Gaussian-type orbitals within the context of Kohn-Sham density functional theory. Appealing to an empirical many-body potential in which the electronic degree of freedom is treated in some average sense, the lowest energy structures of these clusters are first determined using the parallel tempering multicanonical basin hopping plus genetic algorithm [P. J. Hsu and S. K. Lai, J. Chem. Phys. **124**, 044711 (2006)]. These structures are then employed as initial atomic configurations in the density functional theory. A comparison of the structures obtained from these two methods permits an understanding of the role played by electrons in their distribution on atoms in clusters, and hence unravels the unanticipated magnetic property in Au cluster. The relevant issue of the stability of a cluster and the factors that govern the amazing magnetic properties will be reported.

Keywords: magnetic properties, metallic clusters, density functional theory

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Ultrafine copper phthalocyanine complex and its molecular structure in solvents

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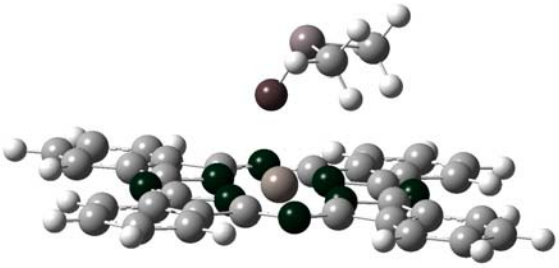
Electrophoretic display (EPD) has attracted a great deal of interests due to its low cost, low weight, good flexibility and low power consumption. Particles applied in EPD are required excellent dispersion and stability in a fluid medium with higher charge, micron size and narrow particle size distribution [1]. Therefore, much research has focused on modification of pigment particles to alter the properties such as surface charge, steric stabilization and interparticle ineractions etc [2]. In this work, ultrafine blue pigment copper phthalocyanine(CuPc) complex particles were prepared by anti-solvent precipitation with *in situ* modification and the stability of CuPc complex in different solvents was first studied using DFT method.

Prepared CuPc-DMSO complex particles were characterized by SEM, FTIR and Zeta potential test. Experimental results showed the prepared particles with average size of 608nm displayed significant improvement in stability and electrophoretic mobility. Sedimentation of the prepared particles in the medium was nearly down to zero within 100h and the electronic response time reduced to 1.14s compared to 45.4s of crude particles.

Besides, geometry and vibrational spectroscopy of CuPc-DMSO complex were investigated at B3LYP / Lanl2dz level for Cu atom and B3LYP / 6-31G for other atoms using Gaussian 03 program. The optimized geometry of the complex in gas phase was shown in following figure. The calculated FT-IR spectrum of the complex was in good accordance with the experimental data. Solvent effects had been taken into account based on the polarizable continuum model (PCM) with CCl_4 and H_2O as solvents. Computed results presented the dipole moments of CuPc-DMSO varied from 5.919D to 7.360 D and the solvent energy increased 14 kJ/mol in going from the $\varepsilon_r = 2.228$ (CCl_4) to $\varepsilon_r = 78.39$ (H_2O), which indicated obvious solvent effects on CuPc complex. Meanwhile, the calculated results appeared that the CuPc complex was more stable in the medium of lower dielectric constant, which should provide some suggestions for our experiments.



Keywords: ultrafine CuPc-DMSO complex, anti-solvent precipitation, DFT, solvent effects

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Atomic layering and related postmelting effects in small liquid metal clusters. A DFT orbital-free molecular dynamics study.

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Using an orbital-free molecular dynamics method[1], where density-functional theory is used to calculate the forces acting on the nuclei, whose motion is treated classically, we have calculate the specific heat of Na_{25}[2]. It shows interesting anomalies above the melting phase-change region: (a) it continuously decreases with increasing temperature, an effect observed also in bulk liquid metals [3]. A resolution of the liquid vibrational modes into radial and tangential components shows that it is the gradual conversion of vibrational modes into diffusion modes which causes the specific heat to decrease. (b) On top of the previous decreasing trend, the specific heat shows a fine structure, with undulations that are induced by temperature-dependence of the radial atomic layering in the liquid cluster. The surface layering provides the cluster with a well-defined average radial structure, which in turn is characterized by certain average energy; so changes in the average radial structure are reflected in the specific heat. The calculations also reveals an interesting correlation between the temperature a which atomic layering disappears, the lost of long-time oscillations of the radial velocity autocorrelation function (VACF), and the substantial increase in the evaporation rate events in the cluster. The presence of atomic layering in the cluster is equivalent to an effective potential energy barrier acting against radial diffusion which is reflect in the backscattering oscillations of the radial VACF. For clusters it is natural that evaporation becomes more noticeable when radial diffusion is less obstructed.

Keywords: DFT, specific heat, postmelting

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Electron and vibrational spectroscopies using DFT, plane waves and pseudopotentials: CASTEP implementation

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Density functional theory can be used successfully to interpret spectroscopic properties of solid state materials. The relevant solutions are usually available in disparate DFT codes, so that it is difficult to use a consistent approach for predicting various spectroscopic features of a given material. This talk reviews the latest CASTEP [1] developments that are aimed to provide a collection of analytical tools within one DFT package. The applications reviewed include core-level EELS [2, 3], solid state NMR [4], optical properties [5, 6], IR and Raman spectroscopy.

The plane-wave pseudopotential method as implemented in CASTEP has been used successfully to study structures, mechanical properties, and phase stability of inorganic materials [1, 7, 8]. Applications of this total energy based approach to the prediction and interpretation of analytical techniques are less well publicized:

- Linear and nonlinear optical spectra [5, 6] can be used to help design new materials or to interpret observed behavior of materials under extreme conditions.
- Vibrational frequencies are calculated using either the linear response formalism or the finite displacement technique [9]. The results help to interpret inelastic X-ray scattering data [10] and in a combination with electric field response provide access to infrared and Raman activities of vibrational modes.
- Solid state NMR predictions have been used to analyze structures of complex molecular crystals [11], inorganic crystals [4], functionalized carbon nanotubes [12], etc.

In summary, CASTEP offers a reliable and validated suite of spectroscopic properties as well as the tools for structural studies of materials.

Keywords: density functional theory, electron energy loss spectroscopy, Raman spectroscopy

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A Combined Charge and Energy Decomposition Scheme for Bond Analysis

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In the present study we have introduced a new scheme for chemical bond analysis by combining the Extended Transition State (ETS) method[1] with the Natural Orbitals for Chemical Valence (NOCV)[2]. The ETS-NOCV[3] charge and energy decomposition scheme based on the Kohn-Sham approach makes it not only possible to decompose the deformation density, Δρ, into the different components (such as σ, π, δ, etc.) of the chemical bond, but it also provides the corresponding energy contributions to the total bond energy. Thus, the ETS-NOCV scheme offers a *compact*, qualitative and quantitative, picture of the chemical bond formation within one common theoretical framework. The applicability of the ETS-NOCV scheme is demonstrated for single (H_3X-XH_3, for X = C, Si, Ge, Sn) and multiple (H_2X=XH_2, H_3CX≡XCH_3, for X = C, Ge) covalent bonds between main group elements, for sextuple and quadruple bonds between metal centers (Cr_2, Mo_2, W_2, $[Cl_4CrCrCl_4]^{4-}$) as well as for double bonds between a metal and a main group element ($(CO)_5Cr$=XH_2, for X = C, Si, Ge, Sn). We include finally two applications involving hydrogen bonding. The first covers the adenine-thymine base pair and the second β-agostic interaction between C-H bonds and metal center in alkyl complex (see Figure below).

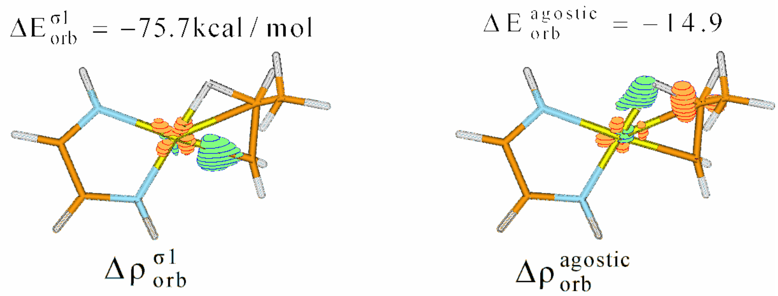

Figure. The contours of relevant deformation density contributions $\Delta\rho^{\sigma 1}_{orb}, \Delta\rho^{agostic}_{orb}$ *describing the bonding between the cationic nickel based fragment and the n-propyl group together with the corresponding energies obtained from ETS-NOCV scheme*[3].

Keywords: energy decomposition scheme, natural orbitals for chemical valence, deformation density, bond orders.

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Understanding the origin of the local $T_d \rightarrow O_h$ phase transition in $BaF_2:Mn^{2+}$ at T~50 K by means of DFT calculations and vibronic coupling theory

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More than 30 years ago a remarkable phenomenon was observed for the *substitutional* Mn^{2+}impurity in BaF_2. While at $T > T_c \approx 50$ K, the EPR spectra of BaF_2: Mn^{2+} reflects a cubic symmetry where the eight F^- ligands of the MnF_8^{6-} complex are fully equivalent, similarly to what is found for Mn^{2+} in CaF_2 and SrF_2, however, below T_c the local symmetry becomes tetrahedral [1], where four ligands are laying at a short distance from Mn^{2+} impurity, R_S, while the rest are at a longer distance, R_L. The existence of this *reversible* phenomenon (called a local phase transition [1]) was confirmed by subsequent ENDOR measurements [2] which also proved that the phenomenon cannot be ascribed to any nearby defect. Despite the *singular behaviour* displayed by Mn^{2+} in BaF_2, not observed for other MF_2 (M = Ca, Sr, Cd) lattices or in any fluoroperovskite, no satisfactory explanation of this surprising phenomenon has been reported yet.

Seeking to clarify this relevant issue, DFT calculations on three Mn^{2+}–doped MF_2 (M = Ba, Ca and Sr) fluorites lattices have been carried out using clusters involving up to 51 atoms. As a salient feature it is found that while the local symmetry is cubic for $CaF_2:Mn^{2+}$ and $SrF_2:Mn^{2+}$, for $BaF_2:Mn^{2+}$ there are two equivalent tetrahedral configurations which are more stable than the cubic one by about 50 cm^{-1}. The calculated $R_S = 2.33$ Å and $R_L = 2.62$ Å values for the T_d geometry are consistent with R_L-$R_s = 0.25$ Å derived from the analysis of the two isotropic superhyperfine constants [3]. A detailed analysis of vibrational states associated with the double well APES sheds light on the origin of the local phase transition [4]. Indeed the maximum of the nuclear density is found to correspond to a T_d symmetry only in the lowest level but to a cubic symmetry for any excited vibrational level. Therefore, as temperature rises, the excited states become populated and the system transits from tetrahedral to cubic. A reasonable quantitative explanation of $T_c = 50$ K is obtained once the coupling of the tetrahedral distortion with a second low frequency (77 cm^{-1}) t_{1u} mode is considered.

The instability in $BaF_2:Mn^{2+}$ is shown to be favoured by a softening of the Mn^{2+}-F^- force constant as a result of a significant increase (8%) of the Mn^{2+}-F^- distance as passing from $CaF_2:Mn^{2+}$ to $BaF_2:Mn^{2+}$. A careful insight into present results by means of vibronic theory [4] reveals the role of t_{1u} charge transfer orbitals for making possible the instability in $BaF_2:Mn^{2+}$.

Keywords: pseudo Jahn-Teller, impurity centres

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Kinetic-Energy/Fisher-Information Indicators of Chemical Bonds

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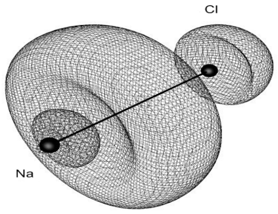
The kinetic energy (contra-gradience) criterion, related to the non-additive Fisher information in the resolution determined by the basis-functions $\chi = \{\chi_i\}$, e.g., the Atomic-Orbitals (AO), is used to localize chemical bonds in molecules. The interference, non-additive (*nadd.*) contribution to the molecular Fisher-information density, $f^{nadd.}[\chi; \boldsymbol{r}] = f^{total}[\chi; \boldsymbol{r}] - f^{add.}[\chi; \boldsymbol{r}]$, where $f^{total}[\chi; \boldsymbol{r}]$ is the *molecular* (overall) distribution and $f^{add.}[\chi; \boldsymbol{r}]$ denotes its AO-additive part, is used to determine the bonding regions in the molecule. These closed basins of the physical space, for which $f^{nadd.} < 0$, thus identify regions of a relatively diminished Fisher information content, compared to this reference AO-additive value. Such volumes represent a locally-decreased gradient content of the system wave-function thus reflecting less “order” (more “uncertainty”) in the molecular distribution of electrons, and hence their delocalization via the system chemical bonds. This suggests the use of the zero–*contra-gradience* surface $f^{nadd.}[\chi; \boldsymbol{r}] = 0$, as sensitive detector of the presence of the chemical bond. The preliminary results from the minimum-basis-set SCF MO/STO-3G calculations are generated for representative diatomics (H_2, N_2, HF, HCl, NaCl) and selected polyatomic systems: diborane, ethylene, acetylene, ethane, butadiene, benzene, and small propellanes. These illustrative examples are shown to convincingly validate the applicability of the contra-gradience probe in exploring the bonding pattern in the molecule from the novel perspective of the Fisher-information/kinetic-energy redistribution.



Keywords: Bond indices, Fisher information, Information theory

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Computational pK_a calculations of mono and diprotic pyridines by quantum methods

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Gas phase deprotonation free energies and aqueous solvation free energies of 10 monoprotic and 6 diprotic pyridines were calculated using CBS-QB3 and HF/CPCM or B3LYP/CPCM methods. The results have been processed considering three thermodynamic cycles for absolute or relative pKa calculations. In these cycles, different experimental values of solvation free energies for proton, water and hydronium were considered [1-3]. Moreover, calculated *ab initio* and DFT values were used when possible. Results show that the inclusion of explicit single water molecule interacting with pyridine nitrogen improves predictions in 1.5 pKa units. Water molecule causes an increase in the solute-solvent surface interaction and allows the continuum method to reproduce correct solvation free energy differences between acids and bases. The correct combination of quantum methodology and thermodynamic cycle leads to very accurate results, with mean absolute errors of 0.3-0.5 pKa units for monoprotic and 0.7-0.9 pKa units for diprotic pyridines.

Calculated p*K*a values and errors for non-hydrated and mono-hydrated pyridine and hydroxypyridines. pK_a values were calculated using CBS-QB3 for gas-phase calculations and CPCM/HF/6-31G*//CPCM/HF/6-31+G* for aqueous solvation free energies.

Substituted pyridines		non-hydrated pyridines		mono-hydrated pyridines	
R-pyridine	exp. pK_a[4]	calc. pK_a	error	calc. pK_a	error
R = H	5.23	2.57	-2.66	4.58	-0.65
R = 2-OH pK_{a1}	0.75	-1.15	-1.90	1.22	0.47
R = 2-OH pK_{a2}	11.65	17.58	5.93	12.27	0.62
R = 3-OH pK_{a1}	4.79	6.32	1.53	5.61	0.82
R = 3-OH pK_{a2}	8.75	6.64	-2.11	7.37	-1.38
R = 4-OH pK_{a1}	3.20	2.23	-0.97	3.73	0.53
R = 4-OH pK_{a2}	11.12	12.29	1.17	10.66	-0.46
Mean absolute error			2.32		0.70
Standard deviation			3.02		0.82

Keywords: theoretical pKa, substituted pyridines

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An alternative to study the anomeric centre absolute configuration of the methyl glycosidic carbohydrates. Theoretical investigation

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This work is a theoretical contribution to study vibrational circular dichroism spectroscopy[1,2] (VCD) of different Monosaccharides: Methyl D-galactopyranoside, Methyl D-xylopyranoside, Methyl L-arabinopyranoside, Methyl D-glucopyranoside, Methyl D-mannopyranoside and Methyl L-fucopyranoside, with R and S absolute configurations of the anomeric carbon at the CH stretching region. This investigation are established in isolated and solvated states using DFT/B3LYP-6-31G* and PCM Methods. Those monosaccharides are constituted of multiple chiral centres, this is why, it is not easy to determine the absolute configuration of those chiral centres, especially the anomeric one. The alternative is to study the CH stretching region. T. Taniguchi and all[3], remark that in this region a reversal of the absolute configuration at a single chiral center could strikingly change the VCD spectral pattern, as was observed for some monosaccharides in the mid-IR region.

Currently most carbohydrate analyses are based on achiral methods such as NMR or Mass Sspectroscopy, and chiral approaches are limited to a few techniques such as optical rotation or ECD[4]. The vibrational circular dichroism (VCD) technique provides enhanced stereo-chemical sensitivity allowing all portions of the molecule to be interrogated. All carbohydrates absorb IR and thus VCD spectroscopy should be capable of extracting detailed stereochemical information on carbohydrates. This stereochemical information's, namely, glycosidic linkages α or β, gives the significant features of carbohydrates and the glycosidation position of the glycosyl acceptor.

Keywords: VCD, PCM.

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Hydrated metal-oxide versus dihydroxide structures of $[MO2H2]^+$ cations (M = Fe, Co, and Ni)

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The formal metal(III) cations $[MO_2H_2]^+$ (M = Fe, Co, and Ni) can be generated by electrospray ionization of aqueous solutions of the corresponding metal(II) nitrates. In contrast to M = Fe, the fragmentations of $[CoO_2H_2]^+$ and $[NiO_2H_2]^+$ imply that the hydrated metal-oxide cations, $(H_2O)MO^+$, are more favourable compared to the dihydroxo isomers $M(OH)_2^+$ than for M = Fe. The reaction pathways have been studied using the density functional theory for two multiplets of $[MO_2H_2]^+$ species (M = Fe–Ni). The energetic profile analysis allows us to explain the fact that $Fe(OH)_2^+$ to be more stable than $(H_2O)FeO^+$, whereas the opposite applies for M = Ni and both isomers are energetically close for M = Co.

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Dual Spin Filter Effect in a Zigzag Graphene Nanoribbon

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By first principle calculations [1,2] based on the non-equilibrium Green function method and the density functional theory within a local density approximation, a dual spin filter effect under finite bias voltages is demonstrated in an antiferromagnetic junction of symmetric zigzag graphene nanoribbon (ZGNR) [3]. Unlike conventional spin filter devices using half metallic materials, the up- and down-spin electrons are unidirectionally filtered in the counter direction of the bias voltage, making the junction a dual spin filter. On the contrary, asymmetric ZGNRs do not exhibit such a spin filter effect. By analyzing Wannier functions [4] and a tight-binding model, we clarify that an interplay between the spin polarized band structure of pi and pi* states near the Fermi level and decoupling of the interband hopping of the two states, arising from the symmetry of the wave functions, plays a crucial role in the effect.

Keywords: Zigzag graphene nanoribbons, spin filter effect, non-equilibrium Green function method, density functional theory

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Cluster calculations of ESR parameters of the positively charged oxygen vacancy in bulk semiconductor tin dioxide SnO_2

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We present density-functional theory (DFT) calculations of the electron spin resonance g- and hyperfine coupling tensors $\mathbf{A}$, in cluster models of positively charged oxygen vacancy V_{O}^{+} in semiconducting tin dioxide SnO_2 [1]. We include consistently all the leading-order contributions to the g-shift as well as to the hyperfine coupling. Convergence of the results with the cluster size, basis set, choice of exchange-correlation functional, choice of the method of the termination as either pseudohydrogen termination [2] or embedding via a finite point charge array reproducing the Madelung potential of the intact lattice [3], are carefully investigated. The results call for a definite reassignment of the experimental g-value [4,5]. We also investigate the energy levels of the impurity states via the Kohn-Sham orbital energies as well as electron affinities and ionization potentials of cluster models of the defect free bulk, positively charged vacancy (V_{O}^{+}) and neutral charged vacancy (V_{O}^{0}) structures. The methodology will be adopted to the study of surface defects relevant for gas-sensing applications.

Keywords: density functional theory, ESR, cluster calculations

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First-principles structural and electronic properties of Ge[110] nanowires

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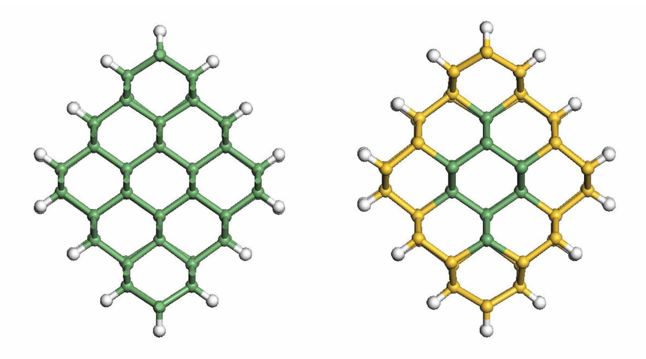
Germanium /Germanium-Silicon core/shell nanowires are expected to play an important role in future electronic devices [1-3]. Using first-principles plane wave calculations within density functional theory in the generalized gradient approximation we investigate the structural and electronic properties of model core/shell Ge/Ge-Si nanowires. In particular, the effect of the amount of surface passivation with H is described. The effect of silicon substitution in the shell of the wires is detailed. The diameters of the nanowires considered are in the range of 4.6 to 18.9 Å and the wires' axis are oriented along the [110] direction. The diameter dependence and the substitutional effects on the binding energy and the band structure are extensively investigated considering the relative contribution of quantum confinement and surface effects.



Keywords: Nanowire, Band structure, Germanium, Silicon

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Geometry and electronic distribution of polyaniline oligomers

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In the past two decades polyaniline (PANI) is among the most extensively investigated polymer systems. Nevertheless, the nature of its most attractive electric, optical, magnetic and mechanical properties is not fully understood yet.

In the recent years the number of theoretical investigations on PANI, employing *ab initio*/DFT quantum chemistry methods grows steadily. PANI properties are sensitive to both bond length alternation and degree of deplanarization. The latter is represented by the torsion angles, which are important characteristics of the polymer chain, influencing its optical spectrum. This structural descriptor is related to the π-delocalization in the system, responsible for charge mobility along the chains. Environment (comprising solvent, monomer excess, oxidizing and protonating agents, neighboring polymer chains) also has impact on PANI geometry. To our knowledge, direct correlation between electron structure and macroscopic features of PANI has not been derived.

The investigated models in the current study are: tetramers of the emeraldine form (EB) and its fully protonated salt (ES); octamers of the neutral EB and the pernigraniline form (PNB). Neutral PNB and EB octamers are optimized with UHF, UB3LYP and UBLYP employing 6-31G* basis set in vacuum and water (PCM) in order to select the most accurate computational protocol. The fully protonated tetramers and all doubly protonated EB octamers (singlets and triplets), modeling the conducting emeraldine salt, were simulated at the UBLYP/6-31G* level in PCM. The results for ES-HCl in PCM are compared with those obtained in vacuum

The optimized tetramers and octamers are analyzed in terms of structural characteristics and electron density distribution. Magnetic characteristics of the singlet and triplet protonated forms are discussed, too.

The results indicate that the doping process with HCl affects appreciably the molecular and electronic structure of the emeraldine base tetramers both in vacuum and in solvent. The geometry parameters are slightly affected by hydration. The results from the natural population analysis indicate that the charge density distribution and the charge transfer are both qualitatively and quantitatively different in PCM.

PCM increases the polarization along the chain in octamers too. Protonation influences the electron density distribution most markedly in the vicinity of the protonated site but propagates along the chain as well. The stability of the spin states is also affected by the position of protonation. The spin density distribution suggests stabilization of the high spin structures by local spin delocalization or spin polarization.

The dualism bipolaron-polaron has been discussed.

Keywords: Polyaniline (PANI), protonation, solvent effect, polarons vs. bipolarons, DFT

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Oral : Local coordination structure and proton-transport properties of Brownmillerite based ceramic materials for fuel cell application

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In view of the ever growing demand of alternative energy concepts hydrogen based solutions seem to be among the most promising ones. Brownmillerite[1] based ceramics have proven to be suitable materials for use as solid state electrolytes in proton ceramic fuel cells (PCFC) due to their high proton conductivity and stability with respect to carbon dioxide [1]. We present a detailed investigation of the underlaying proton conduction mechanisms and their sensibility towards different kinds and quantities of substituents. The studied compounds are based on $Ba_2In_2O_5$ with In being substituted by Ti and Zr, and the Ba by Sr and have strongly disordered structures which can readily be hydrated via the incorporation of H_2O.

The talk will present an overview of the obtained results focusing on the local coordination structure of the different substituents and their impact on proton transport. To this end, we conducted extended structural DFT investigations combining static, vibrational (harmonic approximation) and *ab initio* molecular dynamics approaches. Those give insight into the characteristics of the dehydrated as well as the hydrated material. The results are confronted with experimental findings from X-Ray absorption spectroscopy, IR/Raman spectroscopy, experimental hydration enthalpies and conductivity measurements.

All structural DFT calculations as well as the *ab initio* molecular dynamics were performed with the VASP package using PAW-PBE basis sets.

Concerning the Ti substituent a distinct preference for a tetrahedral coordination of Ti is observed which is rather unusual. Also size and oxidation degree effects for the different substituents will be commented on. Molecular dynamics results are especially illustrative giving direct access to the transport behaviour of protons in different local environments: for example in rather large cells (ca. 150 atoms) their behaviour at realistic operating temperatures (800°C) enables to explain their enhanced conductivity in substituted materials (here 25% Ti) compared to the pure mother compound $Ba_2In_2O_5$.

Keywords: proton conduction, Brownmillerite, *ab initio* molecular dynamics

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[1] Can be viewed as Perovskite structure with a concentration of ordered oxygen vacancies of 1/6.

Potential Energy Surface for H_2O-H_2 dimer

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We have developed a potential energy surfaces, PES, for the H_2O-H_2 dimer based in the concept of the harmonic expansion functional applied to diatom-diatom interactions [1,2] and partitioned as a sum of two contribution, the external one, accounts for the interaction contribution depending on the "dimer-dimer" relative distance *r* and orientation, and the internal one, depending on the oxygen position according to the radial axis that connects the two dimers, as applied to the H_2O_2 $-$Rg [3] and H_2S_2 $-$Rg [4]. The framework of the supermolecular approach was used, as well as the counterpoise-corrected interaction energies [5] in B3LYP/aug-cc-pVQZ level. The energies were calculated in fifteen leading configuration according the orientation of the molecules $(\alpha, \theta_a, \theta_b, \phi)$, where $0 \leq \alpha \leq 2\pi$ measure the oxygen position, $0 \leq \theta_a \leq \pi$ and $0 \leq \theta_b \leq \pi$ are the polar angles of the orientation of the vectors along the H_2 bonds with respect to *r* and $0 \leq \phi \leq \pi$ is the relative torsion angle of the two H_2 axis. For each leading configuration the H_2O and H_2 geometries are kept frozen, 101 energies points are calculated, and the PES for the radial part, $\upsilon_{L_aL_bL}(r)$, are constructed by fitting the energies to a fifth degree generalized Rydberg function. The final PES is given by:

$$V(r;\alpha,\theta_1,\theta_2,\phi) = \sum_i w_i(\alpha) \sum_{L_a,L_b,L} \begin{pmatrix} L_a & L_b & L \\ m & -m & 0 \end{pmatrix} \upsilon_{L_aL_bL}(r) Y_{L_a}^{m}(\theta_a,0) Y_{L_a}^{-m}(\theta_b,\phi) \qquad (1)$$

The isotropic average potential is 0.1336 kcal mol^{-1} and distance 3.5704 Å comparable with the results of Valiron et al. [6] and Phillips et al. [7].

Keywords: Van der Waals dimers, H_2O-H_2

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Conformations, Structure and Vibrational Spectra of Diethyldichlorosilane from Theory and Experiment

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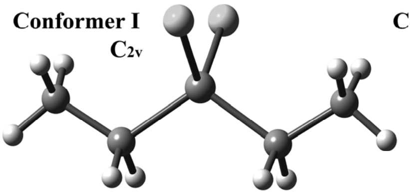
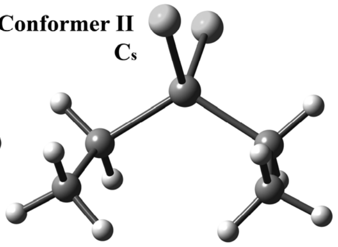
It has been demonstrated that four different molecular conformations represent minima on the PES of the diethyldichlorosilane molecule. Their relative abundances on the gas phase as well as the multiconformer molecular structure of the species have been determined by the combined use of quantum mechanical calculations (B3LYP and MP2 methods with the 6-31G*, cc-pVDZ and cc-pVTZ basis sets) and data from gas-phase electron diffraction (GED) experiments. After the refinement of the theoretical model, the lowest R_G value was obtained for a sample composition of 24% of conformer I (C_{2v}), 22% of conformer II (C_s), 14% of conformer III (C_2) and 40 % of conformer IV (C_1), which is in reasonable agreement with theoretical predictions.

Besides, the IR spectra of the liquid and gas phases and the Raman spectrum of the liquid phase of DEDCS have been recorded and thoroughly analysed on the basis of the SQMFF methodology, taking into account the theoretical results from B3LYP/6-31G* and B3LYP/cc-pVTZ calculations of the vibrational spectra of the four conformers into study. In this way, a complete vibrational assignment of the species have been performed, including the 700 – 300 cm^{-1} spectral region, that can only be explained if more than one conformer is considered, giving spectroscopic evidences of the conformational mixture in the samples.

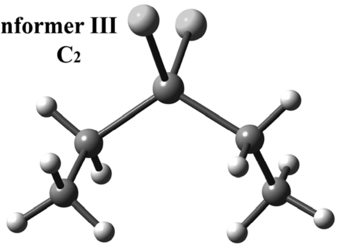
Conformer I
C_{2v}



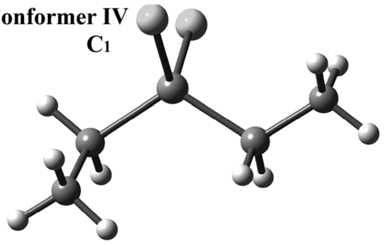
Conformer II
C_s



Conformer III
C_2



Conformer IV
C_1



Keywords: Diethyldichlorosilane, GED, IR, Raman, DFT

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An In-depth DFT Approach to the Design of Hybrid-Spin Magnetic Complexes

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Theoretical and experimental investigations of the exchange interaction between magnetic centers in single-molecule magnets or solid state systems are one of the main research topics in modern molecular science [1]. The spin-hybrid magnets, constructed of stable organic radicals and transition metal ions, have indeed attracted attention as promising building blocks of molecule-based materials [2]. To this end, the understanding of the exchange coupling mechanism between the metal ion and the organic radicals is of key importance.

The magneto-structural correlations in such systems are crucial for the interpretation of magnetic behavior and spin exchange pattern. This geometry dependence required for reliable properties prediction is the reason why the theoretical investigations on metal-radical heterospin systems reported in the literature borrow geometry parameters from X-ray data for known compounds.

This poses the question whether we can go beyond the experimentally-aided theoretical interpretation, or are we helpless without the X-ray information? Regretfully, the prominent structure-properties relationship deters one of the main goals of computational chemistry – the design of unknown materials with expected or predefined properties. That is why our approach aims at rational design dealing with the excessive isomeric variety of organometallic magnetic complexes in order to find the most appropriate candidates with the desired magnetic behavior. The main purpose of this study is to set up and test a theoretical algorithm for accurate description of the molecular geometry of similar spin-hybrid systems and to find and rationalize the relationship between structure and magnetic properties.

The targets of this contribution are based on two metal-organic complexes of bis(hexafluoroacetylacetonato)copper(II) [Cu(hfac)$_2$] ligated with 3- and 4-(*N*-oxyl-*tert*-butylamino)-pyridines [3]. Discussion of the results is based on energy separation of the geometrically optimized spin states, atomic spin densities, and natural orbital analysis. It was shown that qualitatively the results are basis-set-independent. Spin density distribution and orbital analysis allowed rationalization of the stable spin states of the complexes. Based on comparison between the characteristics of the free radical-ligand and the complex with Cu(acac)$_2$, a protocol for molecular design of spin hybrid systems with desired magnetic properties is suggested.

Keywords: molecular magnetism modelling, hybrid-spin systems, DFT

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Defects, surface, and electronic structure of compound semiconductors and amorphous molecular solids

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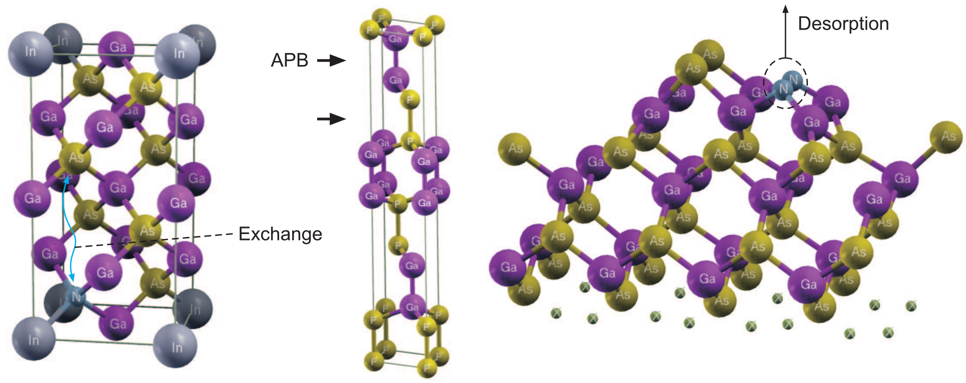
The paper is intended to provide several illustrative examples on application of the density functional theory to further understanding of structural changes in compound semiconductors that involve surface and bulk effects.

In complex semiconductor alloys, the nearest-neighbor bond configuration can affect the width of the band gap. For example, diluted nitride $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{N}_y\mathrm{As}_{1-y}$ alloys evidence openning of the energy gap after annealing at high temperature. Detail analysis shows that the observed increase of the energy gap after annealing is due to nitrogen diffusion from Ga- to In-rich environment driven by a trade-off between strain and chemical energy associated with braking of Ga-N bonds and creation of In-N bonds [1,2].

Epitaxial growth of dilute nitride III-N-V semiconductors that form a material basis for long wavelength optoelectronics entails great difficulties because of the very low solubility of nitrogen. Recent experiments show an evidence of enhancement of the nitrogen content in compressively strained layers grown under non-equilibrium growth conditions. Under such circumstances, incorporation of nitrogen is determined by its desorption from the surface. Results on desorption of N_2 molecule from strained $\beta 2(2\times 4)$ GaAs surface will be presented.

One of the concepts of silicon-integrated photonics requires deposition of III-V compound semiconductors on (100) Si surface. The presence of monolayer steps of Si surface inevitably leads to formation of antiphase boundaries (APBs) in overgrown layers. By optimizing the growth conditions, it became possible to force antiphase boundaries to self annihilate that improves the structure quality drastically. Studying the formation energy of antiphase boundaries in GaAs and GaP provide a feedback to understanding of experimental observations.

Calculation of the electronic structure of a semiconducting amorphous selenium and evaluation of the electron-phonon coupling for the purpose of modeling of the high-field transport is the current work in progress and will be presented as a "late news" results.



Keywords: isoelectronic substitutional impurity, antiphase boundary, surface reconstruction, desorption, electron-phonon coupling

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Theoretical study in B3LYB/6-311++G** level, of the six gluco-piranosyl-myo-inositol regioisomers.

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Glycosyl inositols are sugar-inositol conjugates found in prokaryotic and eukaryotic cells. The inositols are the nine isomeric forms of cyclohexanehexol, a group of small and very stable polar molecules that have versatile properties, four isomers occur in nature, and the other five are unnatural synthetic isomers[1]. The -myo-inositol is the most widely distributed nature isomer, although has the meso configuration, in the combined form it occurs almost always as an optically active derivative.

Recently two positional isomers of glucosyl-myo-inositol with anti-inflammatory activity, are obtained by enzimatical process. NMR and SM analysis was used to characterise these compounds. And, it was formulated as 1, 4-O-α-D glucopyranosyl-myo-inositol is one of the reaction product. The absolute configuration of the myo-inositol ring and the sugar moiety was not determined due OH residues of 4- and 6-position on myo-inositol are completely equivalent. A detailed analysis of the unassigned NMR correlations in the 2D-NMR spectra revealed that the second product was 1, 1-O-α-D-glucopyranosyl-myo-inositol again due to symmetry of the myo-inositol ring, substitution at C-1 or C-3 results in equivalent structures, and the smaller number is assigned. So the absolute configuration of the myo-inositol ring and the sugar moiety was not determined due OH residues so it seemed to be impossible to determine which is the bonding position with glucose by the NMR spectroscopy[2].

Due these result, in order to advance in the knowledge to the ruling factors in the gluco-pyranosil´s behaviour, we performed a theoretical study in B3LYB/6-311++G** level. Here is obtained the structure, the frequencies calculations, and the physicalchemistry and electronic properties, to the six glucopyranosyl-myo-inositol regioisomers by the GAUSSIAN program.

It is clear that the distinction in the molecular behavior, are due to the relative position to the axial hydroxyl group in the molecule rings. The comparison between, the resulting substantial differences in it conformation, and the obtained properties values, allow us to propose an explanation about it molecular behavior and it intermolecular interactions.

Keywords: reactivity, conformation, gluco-inositol-derivatives.

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Structural and electronic properties of layered titanate Ln2Ti2O7 (Ln = La or Nd)

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Perovskite structure of rare earth titanate oxides are of growing interest in the recent year. $Ln_2Ti_2O_7$ belongs to the family of perovskite layer structure compounds which is one of interesting ferroelectrics substances characterized by high Curie temperature (Tc > 1500 °C), high coercive filed and a low dielectric constant [1,2]. In addition, compared with conventional ferroelectric materials, such as lead zirconium titanat or strontium bismuth tantalate, these materials do not contain volatile element which may cause leakage problem due to a possible increase of defect density. Recently, much attention has been focused on the photocatalytic activity in the water splitting with the help of these compounds [3,4]. It has been shown that the photocatalytic activities are highly dependent on the electronic band structure for these materials.

In the present work, we have studied the structural and the electronic properties of the layered titanate photocatalysts by mean of first-principles calculations. These calculations were performed in the framework of density functional theory (DFT), within the generalized gradient approximation (GGA). The total energy calculation and the analysis of the electronic structure are performed within the projector augmented wave (PAW) method as implemented in the Vienna Ab-initio Simulation package (VASP) [5] and the full-potential linearized augmented planewave (FPLAPW) as implemented in the WIEN2K package [6].

It is found that the monoclinic $P2_1$ phase of the $Ln_2Ti_2O_7$ compounds is stable in energy compared to the orthorhombic ones. This phase sustains ferroelectric layers of strongly distorted TiO_6 octahedra. The ferroelectric behavior of this phase persists in the orthorhombic $Cmc2_1$ one whereas the C*mcm* phase becomes paraelectric. We have also predicted the existence of a paraelectric phase, for the $La_2Ti_2O_7$ compound, with the P*2/m* symmetry. Four the electronic structure of these compounds, we have established that the conduction band of $La_2Ti_2O_7$ consisted mainly of Ti *3d* and La *5d*, whereas the valence band consisted mainly of O *2p* and Ti *3d*. The empty La *4f* level was found to be located in the conduction band. The occupied and unoccupied Nd *4f* level in $Nd_2Ti_2O_7$ was shifted to lower energy. The unoccupied Nd *4f* level located between the conduction band and the valence band was found to be detrimental to photocatalytic activity in water splitting because it could act as an electron-trapping site.

Keywords: DFT, PAW, FPLAPW, layered titanate, structural and electronic properties

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Hydrogen Bond Dynamics in Proton Conductors from Ab-initio Molecular Dynamics Simulations and Spectroscopy

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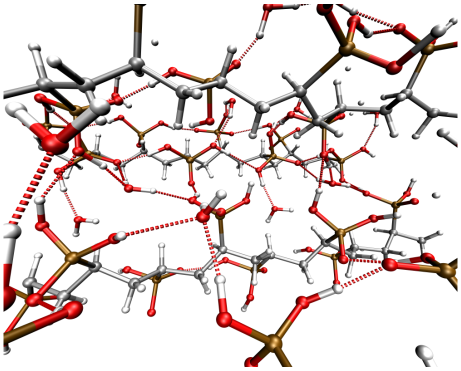
We describe the structure and the molecular dynamics of acidic protons in in polyvinylphosphonic acid by means of ab-initio molecular dynamics simulations of simplified periodic polymers. The comparison with results from solid-state NMR experiments shows that the local structural features of the complex hydrogen bonding network are well reproduced. The statistical distribution of the dihedral CP–OH angle during the molecular dynamics simulation exhibits a specific pattern that leads to an almost complete decay of the NMR signal at a specific temperature. This powerful combination of electronic-structure calculations with experiments provides detailed information about the topology of the hydrogen bonding network in view of the distribution of intra-chain and inter-chain hydrogen bonds.

The central aim is the understanding of the proton transport mechanism in polymer membranes, and to characterize its type as either Grotthus- or vehicle style. To this purpose, it is important to understand the functionality of "crystal water" which is built into the hydrogen bonding network. An additional focus lies on the effect of topological and charge defects in the polymer. Such defects greatly influence the conductivity due to the inhibition of the percolation pathway. Our studies are the first quantitative measure of structural defects in phosphonic acid polymers.



Local fragment of a phosphonic acid-based polymer, a promising candidate for high-temperature PEMFC fuel cell membranes.

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Dynamic Response Property evaluation with Long range Correction

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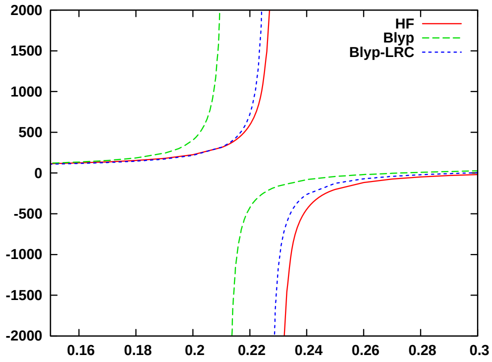
Evaluation of response property is important, yet one of the difficult problems Density Functional Theory (DFT) encountered. That relates to the fundamental problem of Self Interaction Error (SIE) in the approximated DFT methods. The problem arises remarkably in the large conjugated systems which provide enhanced optical properties such as electric polarizability and hyperpolarizabilities. The overestimate of the charge response against external perturbation is the result of incapability to reproduce the correct potential under the applied field which is generated through virtual orbitals in wavefunction theories. Although Kohn Sham (KS) methods brings a corresponding formulation of the response function as in the wavefunction theory, adiabatic approximation (AA) assumed in the approximated methods has grater effect in the DFT than wavefunction theories where the phase is correctly taken into consideration in the Hamiltonian. We have introduced the Long range Correction (LC) replacing the two-body DFT coulomb force by the Hartree Fock force in a range depending manner. This method corrects the overestimate of DFT response of the delocalized electrons in the spatially enhanced dimension. The calculated electric polarizability and hyperpolarizabilities under the static electric field are much more reasonable than the one computed by the pure DFT with popular functionals [1,2]. We here investigate the dynamic response of the many-electron systems using same methodology. The non-linear response such as non-linear susceptibilities is typically observed under the field oscillating with a finite frequency and the capability to describe the dynamic response of the system is required to theories. The polarizability computed by the DFT with LC shows improvement from the value overestimated by pure DFT methods for over a wide range of the applied frequency towards resonance [3]. We will discuss the extension of the algorithm for the evaluation of dynamic hyperpolarizabilities and show some numerical results.



Keywords: response property, long range correction

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Calculation of chemical shift using LF-DFT

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Ligand field- density functional theory (LF-DFT) [1] is a tried and tested method for calculating ligand field parameters in a non-empirical approach and therewith obtain properties of transition-metal complexes. Its power has been showed for the calculations of e.g. zerofield splitting [2], g- and A-tensor [3].
^{59}Co-NMR chemical shift σ calculation using perturbation theory in given framework of LF-DFT is implemented for transition-metal complexes as expansion of LF-DFT scripts.

Keywords: LF-DFT, chemical shift

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Comparative calculation of FeO by ZINDO\1, ab initio and DFT.

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Electronic structure of FeO has been calculated by ZINDO\1, ab initio and DFT. Calculations of FeO have been executed for electronic configurations with multiplicities 1, 3 and 5. The Small 3-21G, Medium 6-31G* and Large 6-31 G** basis sets have been used for ab initio and DFT calculations. The Lee-Yang-Parr correlation potential in combination with the Becke88 exchange potential and the Hartree-Fock exchange potential has been used for DFT calculations. We received the electronic configuration $\ldots(1\delta\uparrow)^1(2\pi\uparrow)^2(3\sigma\uparrow)^1$ in calculations by ZINDO\1, ab initio and DFT using Hartree-Fock exchange potential at bond length $1.8A^0$. The Becke88 exchange potential in combination with the Lee-Yang-Parr correlation potential is no appropriate for short distances. Such combination of potentials is appropriate for long distances in FeO [1]. We received too that bond order increases if the multiplicity increases. Otherwise the bond length decreases if the multiplicity increases. The highest unoccupied level in DFT calculation has significance (-8.36 eV) that is relatives to first ionization potential (8.71eV) in FeO [2]. Analysis of the atomic orbital electron populations shows that there is the promotion of the electronic density from 4s-AO to 4p-AO in iron atom. Such promotion is not corresponding with theory of spin glasses but spin glasses sets in FeO-nanoparticles appear at long interatomic distances in nanoparticles that have sizes 0.3 mkm [3]. For particles that have the sizes 45-74 mkm appear magnetic properties due to of crystal environment [4].

Keywords: electronic structure, ionization potential, atomic orbital electron population

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Stress Tensor of Chemical Bonds

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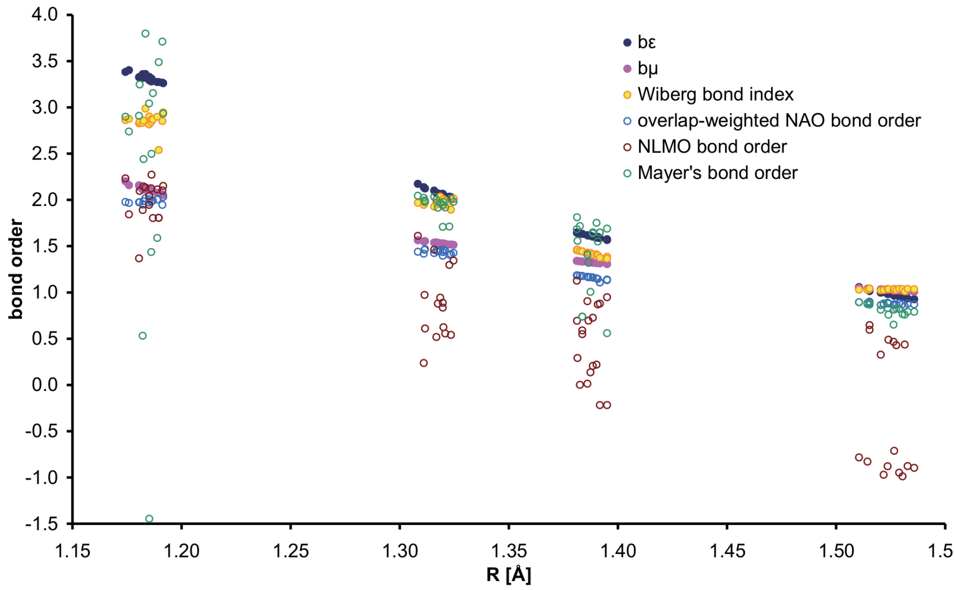
The stress tensors are used widely for description of internal forces of matter. For some time it is also applied in quantum theory in studies of molecular properties in chemical systems. Electronic stress tensors measure effects caused by internal forces acting on electrons in molecules and particularly those between bonded atoms. Utilized here stress tensor originated bond orders expressing bond strengths in terms of these internal forces. The unique concept of energy density and electronic chemical potential based bond orders gives natural evaluation of interaction strength comparing with classical definition, considering delocalized nature of electrons. The relation to electronic energy causes that among others it may be used to predict relative stabilities of geometrical isomers or even conformers. The regional chemical potential is also used to predict chemical reaction coordinate [1,2]. We also elucidate the role of electronic stress tensor in a one-electron molecule using H_2^+ whose exact wavefunctions are known [3].

$$b_\varepsilon = \frac{\varepsilon^S_{\tau AB}(\vec{r}_L)}{\varepsilon^S_{\tau HH}(\vec{r}_L)}, \quad b_\mu = \frac{b_\varepsilon}{(n_{AB}(\vec{r}_L)/n_{HH}(\vec{r}_L))} = \frac{\varepsilon^S_{\tau AB}(\vec{r}_L)}{n_{AB}(\vec{r}_L)} \cdot \left(\frac{\varepsilon^S_{\tau HH}(\vec{r}_L)}{n_{HH}(\vec{r}_L)}\right)^{-1}$$



$$E_{AB} = \int d^3\vec{r}\varepsilon^S_{\tau AB}(\vec{r}), \quad N_{AB} = \int d^3\vec{r} n_{AB}(\vec{r}), \quad \mu_R = \left(\frac{\partial E_R}{\partial N_R}\right) \Leftrightarrow \frac{\varepsilon^S_{\tau AB}(\vec{r})}{n_{AB}(\vec{r})}$$

Keywords: stress tensor, bond order, regional chemical potential

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Investigation of Hydroxamic Acid Tautomers by DFT Method

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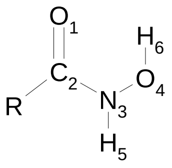
Hydroxamic acids [1] are very important natural compounds. They are among the most well studied compounds due to their significance in biological activity since the first reported by Lossen in 1869 [2].

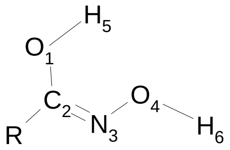
Hydroxamic acids are a class of compounds, which display interesting chemical and biological properties. They are also capable for the inhibition of a wide variety of enzymes [3] and there is no doubt that their inhibitory effect is in correlation with chelation of the metals by the hydroxamate function. Because of their importance, hydroxamic acids have been the subject of some computational investigations including semi empirical and ab initio [4] at different levels of theory that some of those have focused on their acid-base properties [5] and other included their protonated species.

Although the growing interest in the study of hydroxamic acid is observed, but structures of hydroxamic acids are still the subject of many controversies. Because potentials for tautomerism, their transition state energy and properties have been recognized as a particular characteristic of hydroxamic acids and these aspects have not been investigated to their full extent.

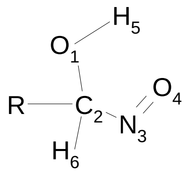
In this research, all of important aspects of some simple hydroxamic acids, their tautomers and transition states in gas phase and solvent were explored using DFT calculations. Three tautomers (a,b,c) were defined for each molecule. As well as, two transition states between these tautomers can exist. In all cases, the order of stability of tautomers is tautomer **a** (keto form, N-hydroxy amide), tautomer **b** (iminol form, α-hydroxy oxime) and tautomer **c** (α-nitroso alcohol), respectively. In addition, T.S$_1$ (between tautomers **a** and **b**) is more stable than T.S$_2$ (between tautomers **b** and **c**). All tautomers and transition states are optimized at the B3LYP/6-311++G** level. Our results confirm the observed experimental data about most stability of tautomer **a**. Also because of great quantity of all barriers, converting of these tautomers to each other is impossible at room temperature.



a (keto-form)



b (oxime-form)



c (nitroso-form)

Additionally, DFT calculations are applied to calculate optimized structure of tautomers and transition states and to estimate the barrier energy and reaction rate constants of the hydrogen exchange between tautomers in presence of 1-3 molecules of water with applying counterpoise method for deleting basis set superposition error (BSSE). The computed activation barrier shows us that the barrier energy of solvent assisted tautomerism is very lower than simple tautomerism and this water-assisted tautomerism is very faster than simple tautomerism, especially with assisting one or two molecules of water.

Keywords: Hydroxamic Acids; Transition State; DFT calculations

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Elastic and vibrational properties of high pressure ice polymorphs

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Determinations of physical properties and phase relations of high pressure ice polymorphs are of fundamental importance for physical, chemical, geophysical and planetary sciences. High-pressure phase diagram of ice clarified by diamond anvil cell experiments showed that hydrogen bonded molecular phases iceVIII and VII transform to an atomic iceX at ~60-80 GPa [1,2]. This pressure induced hydrogen bond symmetrization is also theoretically predicted to occur in hydrous minerals, δ-AlOOH and phase D ($MgSi_2O_6H_2$) at much lower pressures ~ 30 and 40 GPa, respectively [3]. Accompanied with this hydrogen bond symmetrization, significant changes in their compressibilities, vibrational, and elastic properties have been found out. In particular, some of diagonal elastic constant components along the hydrogen bonds of these minerals anomalously increase across the hydrogen bond symmetrization, while shear components show gradual increases. Concerning the vibrational properties, a strong decrease of the OH stretching mode frequencies is observed with increasing pressure until the hydrogen bond symmetrizes. This is followed by a moderate increase of the OH vibrational frequencies in the symmetric hydrogen bond phase. These elastic hardening and vibrational softening/hardening seem characteristics for the hydrogen bond symmetrization. These changes can be expected to be more prominently in ice in which all the water molecules are connected each other only via the hydrogen bonds. Since the pressure dependence of elastic constants of ice VIII, VII and X has not been reported so far, we investigate the elastic and vibrational properties of high-pressure phases of ice VIII and X by means of first principles techniques in order to inspect the effect of hydrogen bond symmetrization on these phases.

Keywords: hydrogen bond, high pressure, elasticity

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Structural Interpretation of J-coupling Constants Calculated in Guanosine and Deoxy-Guanosine

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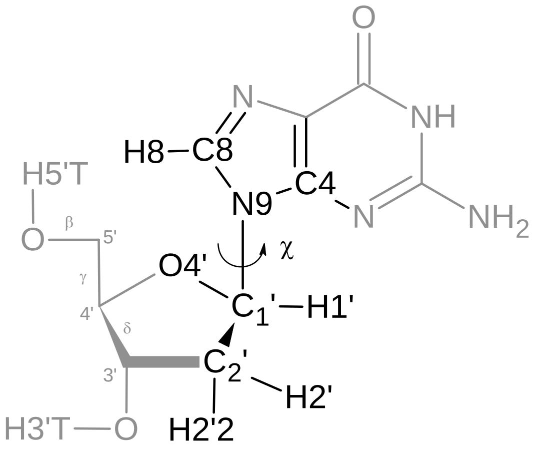
The relationship between the the glycosidic torsion angle χ, the three-bond couplings ^{3}J(C8-H1’) and ^{3}J(C4-H1’), and the four one-bond couplings ^{1}J(C8-H8), ^{1}J(C1’-H1’), ^{1}J(C2’-H2’) and ^{1}J(C2’-H2’2) in deoxyguanosine and the three one-bond couplings ^{1}J(C8-H8), ^{1}J(C1’-H1’) and ^{1}J(C2’-H2’) for guanosine has been analyzed using density functional theory - B3LYP /6-31G**. The influence of the backbone conformation, sugar composition and the sugar pucker, and molecular environment including water solvation has been also considered in modeling the structural dependence of the J-couplings on local structure.

New parameterizations of the Karplus equation was calculated for the ^{3}J(C8-H1’) and ^{3}J(C4-H1’) couplings assigned to the χ torsion angle similar to Munzarová et al.[1] The J-couplings calculated on the geometry grid in the nucleosides were compared with those taking into account the effect of base pairing occurring in the WC/SE RNA base pair family[2] as well as with available experimental data.



Keywords: guanosine, J-coupling, DFT

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Comprehensive Analysis for Co^{2+} Impurity Doped in II-VI Semiconductors Based on First-Principles Calculations

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II-VI semiconductors including Co^{2+} are attractive materials due to their potential applications as phosphors or diluted magnetic semiconductors. Historically, theoretical analysis of TM impurities in ZnS was performed by Watanabe and Kamimura based on the molecular orbital calculations combined with the ligand field theory [1]. However, in order to clarify the correlation between the local structure and the local electronic state of the impurity ion, it is important to compare the spectra of the same ion in different host crystals. Moreover, investigation from different aspects such as core excitation and its magnetic anisotropy is also useful. In the present work, we performed a comprehensive investigation of Co^{2+} in II-VI semiconductors by analyzing both optical absorption and x-ray absorption near-edge structure (XANES) as well as its magnetic circular dichroism (MCD) based on first-principles relativistic configuration-interaction (CI) calculations [2].

Among II-VI semiconductors, ZnO, ZnS, ZnSe, ZnTe, CdS, CdSe and CdTe were selected as host crystals. Since Co^{2+} substitutes for Zn or Cd site, the model clusters consisting of the central Co^{2+} and neighboring four anions with C_{3v} symmetry (for ZnO) or T_d symmetry (for the other crystals) were constructed. They were embedded in the point charges at the external atomic positions to reproduce the effective Madelung potential. The multiplet calculations were performed using the non-empirical relativistic CI calculation program developed in our group. The oscillator strengths of the electric-dipole transitions between the multiplets were calculated directly using the explicitly obtained relativistic many-electron wave functions. For easy comparison with the experimental spectra, the contribution from each transition was broadened by an appropriate Gaussian function.

Figure shows the theoretical absorption spectra of *d-d* transition of Co^{2+} in II-VI semiconductors. There are two peaks corresponding to transitions from ${}^4A_2(F)$ to ${}^4T_1(F)$ and ${}^4T_1(P)$ as expected for tetrahedral sites. The results indicated that the peak energy decreases as the atomic number of anion increases in accordance with the experimental spectra. Although the reported experimental XANES and MCD are limited, the theoretical $L_{2,3}$-edge XANES for Co^{2+} in ZnO and its MCD spectra were also in good agreement with the experimental data. The agreement with the experimental spectra was improved further by considering the effect of ligand holes.

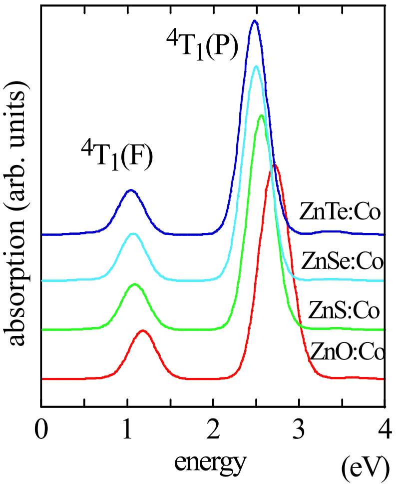

Fig. Theoretical optical absorption spectra of Co^{2+} in II-VI semiconductors

Keywords: II-VI semiconductors, Co^{2+}, XANES, MCD

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Modeling of charge-transfer excited states in rhenium(I) carbonyl bipyridine and phenantroline complexes.

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Femtosecond fluorescence spectroscopy experiments on a series of complexes $[Re(L)(CO)_3(bpy)]^{n+}$ (L = Cl, I, n = 0; L = pyridine, n = 1) identified excited states which participate to the ultra-fast intersystem crossings (~ps time scale) and mainly contribute to the luminescence properties of these molecules[1]. In order to understand the character and dynamics of optically excited states quantum chemical calculations were performed on $[Re(L)(CO)_3(bpy)]^{n+}$ and $[Re(etim)(CO)_3(phen)]^{+}$, which is utilized as light-absorbing chromophore incorporated in protein structure. DFT calculations employed the hybrid functionals either B3LYP or Perdew, Burke, Ernzerhof exchange and correlation functional (PBE0). The solvent was described by the polarizable conductor calculation model (CPCM) (G03) or conductor like screening model (COSMO) (Turbomole). Low-lying singlet and triplet excitation energies at the ground-state geometries were calculated by time-dependent DFT (TD-DFT) and compared with CASSCF/MS-CASPT2 results (MOLCAS 7.2, MOLPRO). Calculated excitation energies and oscillator strenghts were used for interpretation of experimental UV-vis spectra.

Optimized excited-state geometry was calculated for the lowest singlet and triplet states of each complex by TD-DFT using Turbomole. The lowest triplets were optimized also by the unrestricted Kohn-Sham approach (UKS). Calculations of vibrational frequencies were performed at optimized geometries. Calculated shifts of CO stretching frequencies well reproduce experimentaly measure FFTIR spectra, it was shown that the inclusion of the solvent effect improves the agreement between calculated and measured ν(CO) splitting.

The knowledge of spin-orbit couplings between low-lying singlet and triplet states is necessary for the interpretation of inter system crossing (ISC). Spin orbit (SO) coupling elements between low-lying singlet and triplet states were either estimated from experimental atomic spin-orbit parameters and TD DFT results or calculated by several quantum chemical approaches: TD DFT (ADF), MRCI with the use of spin-orbit pseudopotentials by MOLPRO program and SO-RASSI of MOLCAS 7.2 package based on CASSCF/MS-CASPT2. This work compares DFT calculated results with ones obtainded by wave functions based ab initio methods.

Acknowledgements*:* Support from Academy of Sciences of the Czech Republic (KAN 100400702) and the COST D35 action (grant OC 139) is gratefully appreciated.

Keywords: Re diimine complexes, DFT, inter system crossing

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Thermodynamic and DFT Studies on the Thermoelectric Effects of Semiconducting Materials

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Thermoelectric effects of semiconducting materials are studied by the thermodynamic method incorporating with density function method for a system in the presence of an electric field. The present new method incorporating the Clausis-Mossotti equation with thermodynamics is demonstrated to be a very useful for simulating the dielectric constant and the Seebeck coefficient for semiconducting materials [1].

The polarizability in the Clausis-Mossotti equation in general includes three parts; electric polariability, atomic polariability and orientation polariability. The dominant contribution for semiconducting materials comes from electric polariability. The APT and Mulliken charges computed by DFT method are utilized to simulate dipole moment at a given electric field, and then derivatives of dipole moments with respect to electric field lead to the electronic polarizability. Finally, the dielectric constant is evaluated from Clausis-Mossotti equation.

The Seebeck coefficient that is key factor to determine thermoelectric conversion efficiency of the materials is calculated from the thermodynamic method with use of the chemical potential. The Helmholtz free energies are computed first by DFT method at various temperatures, and then the Seebeck coefficient can be evaluated from partial derivative of Helmhotz free energy with respect to temperature. However, This Seebeck coefficient must be divided by the dielectric constant in the present method in order to be considered as the Seebeck coefficient for a solid-state material.

Three semiconductor thermoelectric materials, Mg2Si, FeSi2 and SiGe, are chosen for simulation with four kinds of DFT functionals, B3LYP, BLYP, M05 and M05-2X. Table 1 and Table 2 show simulated results in comparison with experimental measurements for dielectric constants and Seebeck coefficients, respectively. The present method shows good agreement with experimental measurements, and surprisingly it works even better then conventional energy band structure theory for calculating the Seebeck coefficient.

Table 1: dielectric constants.

dielectric constant	Mg2Si	FeSi2	SiGe
present calculation	11.86	27.806	13.571
experiment result	13.3	27.6	13.95

Table 2: Seebeck coefficients (μ V/K)

Seebeck coefficient	Mg2Si	FeSi2	SiGe
present calculation	284 / 334	118.8/ 140.4	196.3/ 220.9
experiment result	180 / 280	190 / 170	345 / 325

Keywords: Dielectric constant, Seebeck coefficient, polarizability, and thermoelectric effects

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Density Functional Theory in the Analysis of Jahn-Teller and Related Effects

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The Jahn-Teller (JT) effect is the subject of extensive research, both experimental and theoretical. The JT theorem states that a molecule with a degenerate electronic ground state spontaneously distorts along non-totally symmetric vibrational coordinates. This removes the degeneracy and lowers the energy. The theory underlying the JT effect is based on a perturbation expression of the potential energy surface near the point of electronic degeneracy [1]. The coefficients in the expression of potential energy have a physical meaning. A method based on the multideterminental DFT, for the study of the JT systems developed in our group [2], can be applied for the calculation of the these parameters and rationalizing the microscopic origin of the problem. The JT parameters obtainned using DFT are in excellent agreement with experiment.

JT effect is controlled by the molecular symmetry. Group theory allows identifying the symmetry of the JT distortion, which is for simple molecules usually determined by one single normal coordinate that satisfies the symmetry requirements. In complex molecules, the JT distortion is a superposition of many different normal coordinates. In the JT semantics this is called the multimode problem. The treatment of this problem using DFT recently proposed by us [3] will be presented. It is based on the analogy between the JT distortion and reaction coordinates [4]. This aspect was often neglected so far. Within the harmonic approximation the JT distortion can be analysed as the linear combination of all totally symmetric normal modes in the low symmetry minimum energy conformation. Contribution of the normal modes to the distortion, their energy contribution to the JT stabilisation energy, the forces at high symmetry cusp and detailed distortion path can be estimated quantitatively. This approach allows to get very detailed picture on the interaction between the deformation of the electron distribution and the displacements of the nuclei. This is of great significance in various fields, not only in the larger JT systems, but also in the systems like spin crossover compounds, mixed valence compounds, photochemical reactions etc.

Examples of our work include studies of small organic radicals, e.g. cyclopentadienyl radical and benzene positive and negative ions, JT active coordination compounds, e.g. VCl_4, Cu(II) chelate complexes, JT active metallocenes, e.g. cobaltocene and manganocene, ligand driven light induced Fe(II) spin crossover complexes, etc. Emphasise is given to the analysis of a sophisticated counterplay between the electronic distortion due to the JT effect, mainly localized on the central metal ion, and the distortion of the ligand conformation in metal complexes.

Keywords: Density Functional Theory, Jahn-Teller Effect, Multimode Problem

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Enhanced Li intercalation into TiO_2-B Nanowires. A computer modelling study

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Current search for new battery materials to enhance energy and power density is concentrated on nanomaterials, with their superior properties brought to live by interplay between the structure and the effects of nanosize [1]. The most promising new anode material available today is a nanowired form of TiO_2-B, where this interplay results in desirable properties of high capacity, good reversibility [2,3], and exceptionally fast Li-insertion [4]. In this material, effects of the nanoscale play an important role, leading to significant improvement over intercalation properties of polycrystalline TiO_2-B. Currently, the mechanisms underlying Li-insertion in TiO_2-B are not understood and the origin of the enhanced properties is still unclear. With the aid of density functional simulations, we built a comprehensive description of Li-intercalation into TiO_2-B to shed light on the mechanisms governing intercalation on the nanoscale.

We demonstrate that "standard" computational protocol adopted and successfully used to study intercalation properties of various titanate materials [5] fails to predict intercalation behaviour of TiO_2-B consistent with the experimental observations. Using a "modified" protocol for the bulk and the surface to account for complexity of the energy landscape, we monitor the evolution of location, geometry and stability of insertion sites with the Li-concentration as well as the evolution of diffusion pathways and barriers. We demonstrate that exceptionally fast Li-insertion observed for this material results from its capacitor-like behaviour at $[Li]/[Ti] \leq 0.5$, and elucidate the roles played by the surface, bulk, and the nanosize. We show that at $[Li]/[Ti] > 0.5$ Li-intercalation is limited by Li self-diffusion, which restricts the insertion capacity. Though on the nanoscale Li-diffusion is enhanced, the full theoretical capacity predicted here for TiO_2-B is still not reached in electrochemical experiments.

Using the example of TiO_2-B, we highlight fundamental mechanisms governing intercalation on the nanoscale, and demonstrate that dynamics of Li-insertion may not be directly related to transport properties of equilibrated nanosamples.

Keywords: Li-batteries, intercalation materials, TiO_2-B

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Correlation among Order−Disorder, Electronic Levels, and Photoluminescence in $SrTiO_3$: Sm Nanostructure

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There is much interest in the areas of science and technology in transition metal oxides with an ABO_3 perovskite structure, owing to their wide variety of unique electronic, magnetic and optical properties. Among the photofunctional materials, much attention has been paid to metal oxides with the band gap energy corresponding to near ultraviolet or visible light, e.g. perovskite-type compounds, because of a broad spectrum of potential applications [1].

Within this class of perovskite compounds, $SrTiO_3$ (ST), in its crystalline form, displays a semiconductor behavior and when pure ST is excited by radiation above its energy band gap, which usually ranges from 3.2 to 3.4 eV, a broad greenish luminescent band appears whose intensity decreases rapidly when the temperature is above 50 K [2]. There are in the literature different approaches to explain the radiative decay taking place in perovskite-like structures. But, it is well established that impurities, surface states, and defects play an important role in the photoluminescence (PL) properties of perovskite-type oxides [3].

From the experimental side of this work, $SrTiO_3$ and $SrSm_{0.01}Ti_{0.99}O_3$ (ST_Sm) nanostructured powders were prepared by the polymeric precursor method (PPM). Order and disorder has been investigated by means of X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) images, Electron Paramagnetic Resonance (EPR) and photoluminescence (PL) emission experimental techniques.

From the theoretical side, first principles quantum mechanical techniques, based on density functional theory at B3LYP level, have been used in sense to give a theoretical approach to the experimental PL results. It was simulated three disorder-type in the crystalline (ordered) cubic 1x 1 x 2 supercell, as fallow: in the network former (Ti), in the network modifier (Sr) and in the network former-modifier (Ti/Sr).

The experimental results, in the disordered powders, indicated that defects in the lattice are linked to inherent defects formed by complex clusters. First principle calculations indicate that generate localized states, in the band gap reduce the gap energies. As the structural order increases, the gap energy increases. These observations confirmed the fact that PL is directly associated with the localized states existing in the band gap and that the degree of order-disorder changes these localized states.

The complex clusters already existing in the ground state facilitate the emission process leading to PL, i.e, the radiative recombination. In our model, the Wild Band Model, the most important events occur before excitation, that is, before the photon arrival. The deep and shallow complex clusters generate localized states in the band gap and inhomogeneous charge distribution in the cell, thus allowing the trapping of electrons. The localized levels are energetically distributed, so that various energies are able to excite the trapped electrons.

Keywords: $SrTiO_3$:Sm, DFT calculations, photoluminescence

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Vibrational Spectra and Molecular Structure of N-Substituted-6-Acylbenzothiazolon Derivatives. A Combined DFT, Ab initio HF and Experimental Study.*

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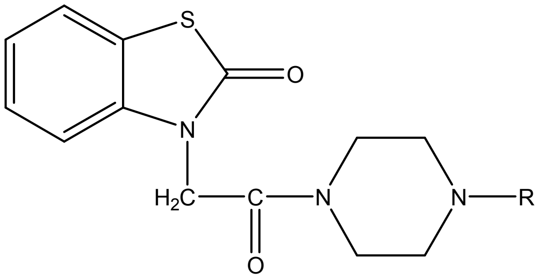
ABSTRACT

The molecular structure, vibrational frequencies and the corresponding vibrational assignments of two novel drug precursor 6-acylbenzothiazolon derivatives in the ground state were calculated by using *ab initio* HF and DFT/B3LYP methods with 6-31G(d,p) basis set. The molecular structure was interpreted depending on theoretically obtained results. The solid-state FT-IR spectrum was measured and compared with calculated values. Regarding vibrational frequencies, we found that DFT/B3LYP method performed better for the frequencies compared to HF method.



R= Methyl, Ethyl

Figure. The shemes of studied molecules

Keywords: 6-Acylbenzothiazolon, Drug precursor, FT-IR, DFT, HF

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POSTER PRESENTATIONS

Topic 2.

Density Matrices, current functionals and density functionals

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Fully nonlocal proposals for the Exchange Energy Density Functional

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We present several fully nonlocal exchange energy density functionals that reproduce the linear response function of the free electron gas. These fully nonlocal functionals are constructed following the ideas previously used for nonlocal kinetic energy density functionals (KEDFs), from the original ideas for XC by Gunnarsson, M. Jonson and B.I. Lundqvist: [1] and for the KEDFs by Chacón-Alvarellos-Tarazona [2], to those of García-González et al. [3], Wang-Govind-Carter [4] and finally García-Aldea-Alvarellos [5].

For the KEDF, the exact linear response function of the free electron gas is analytically known. For the case of the exchange energy the response function is not known, but several approximated formulas has been proposed. In this work we have used the response function proposed by Utsumi and Ichimaru [5], even we must remark that the ansatz we propose here can be used to reproduce any other response function with the same scaling properties.

We have developed two families of new nonlocal functionals for the exchange energy. The first family is constructed with the mathematical structure of the LDA approximation – i. e. the Dirac functional for the exchange. The second family has the structure of the gradient correction in the second order gradient expansion approximation. All the functionals are constructed is such a way that they can be used in localized systems and in extended systems. As an important property, all these functionals, when using a constant reference electron density and making the evaluation in the momentum space, can achieve a quasilinear scaling with the system size.

Keywords: Exchange Energy Density Functional, Free Electron Gas, Linear Response Function, Linear Scaling

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Direct mapping between exchange potentials of Hartree-Fock and Kohn-Sham schemes

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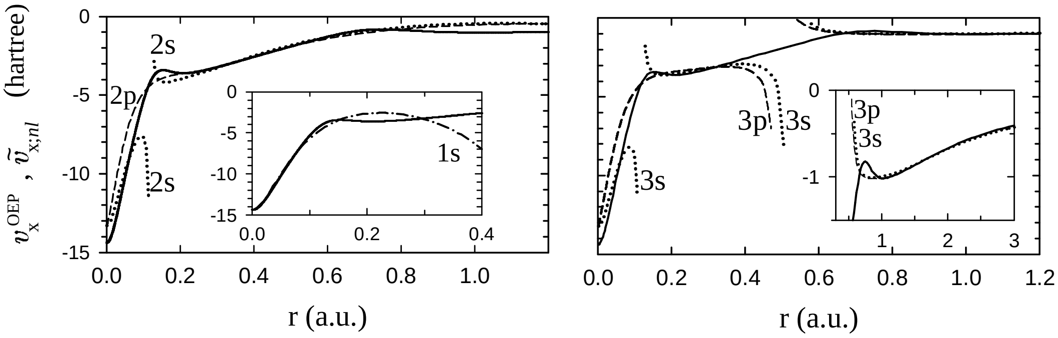
The present study [1] reveals that the outstanding proximity of the Kohn-Sham (KS) and Hartree-Fock (HF) orbitals [2,3] results from the properties of the HF *orbital-specific* exchange potentials

$$v^{\mathrm{HF}}_{\mathrm{x}a\sigma}(\mathbf{r}) \equiv \left[\hat{v}^{\mathrm{F}}_{\mathrm{x}\sigma}\phi^{\mathrm{HF}}_{a\sigma}(\mathbf{r})\right] / \phi^{\mathrm{HF}}_{a\sigma}(\mathbf{r}) \tag{1}$$

obtained with the non-local Fock exchange operator $\hat{v}^{\mathrm{F}}_{\mathrm{x}\sigma}$ acting on the HF orbitals $\phi^{\mathrm{HF}}_{a\sigma}$. It is found that, in closed-l-subshell spin-compensated atoms, all potentials $v^{\mathrm{HF}}_{\mathrm{x}a\sigma}(\mathbf{r}) = v^{\mathrm{HF}}_{\mathrm{x}nl}(r)$ calculated for orbitals $\phi^{\mathrm{HF}}_{a\sigma} = \phi^{\mathrm{HF}}_{nlm}$ that belong to a given atomic shell S_n, almost coincide with each other within the region of this shell after they are shifted by suitably chosen orbital-dependent constants $D_{nl;nl}$. Each shifted orbital-specific potential $\tilde{v}^{\mathrm{HF}}_{\mathrm{x}nl}(r) = v^{\mathrm{HF}}_{\mathrm{x}nl}(r) + D_{nl;nl}$, where $D_{nl;nl} = \langle\phi_{nlm}|v^{\mathrm{OEP}}_{\mathrm{x}} - \hat{v}^{\mathrm{F}}_{\mathrm{x}}|\phi_{nlm}\rangle$, represents, with high accuracy within the corresponding atomic shell S_n, the exact local exchange potential $v^{\mathrm{OEP}}_{\mathrm{x}}(r)$ (defined in the OEP approach). This high accuracy is obtained for $D_{nl;nl}$ calculated with both the KS orbitals ϕ_{nlm} and the HF ones. An even closer representation of $v^{\mathrm{OEP}}_{\mathrm{x}}(r)$ is given by the shell-specific exchange potential $v^{(n)}_{\mathrm{x}}(r)$ defined as the average of various potentials $\tilde{v}^{\mathrm{HF}}_{\mathrm{x}nl}(r)$ from the same shell. Simultaneously, it becomes clear why, in atoms, the exact exchange potential $v^{\mathrm{OEP}}_{\mathrm{x}}(r)$ has the characteristic structure of a piecewise-like function where each part spans over the region of an atomic shell and it has distinctively different slope $dv_{\mathrm{x}}(r)/dr$ in consecutive shells [4]. It has to be stressed that the obtained representation of $v^{\mathrm{OEP}}_{\mathrm{x}}(r)$ with orbital- or shell-specific exchange potentials is a distinct feature that is not directly related to the well-known step-like shell structure of the response part of the exchange potential. The revealed properties of the HF exchange potentials $v^{\mathrm{HF}}_{\mathrm{x}nl}(r)$ explain not only the proximity of the KS and HF orbitals but also the high quality of the Krieger-Li-Iafrate and localized HF (or, equivalently, common-energy-denominator) approximations to the exchange potential.



Keywords: exact exchange potential, Hartree-Fock method, orbital-dependent functionals

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Activation enthalpies of pericyclic reactions: when generalized-gradient approximations (GGA) works better than hybrid functionals.

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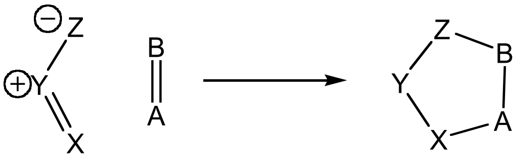
We have assessed the performances of three recently proposed functionals, RC [1], TCA [2], and *Rev*TCA [3] by calculating the activation enthalpies for ten pericyclic reactions and eighteen 1,3-dipolar cycloadditions. We have found that the local functional (RC) gives results only marginally better than the LDA ones, while the two GGA functionals, TCA and *Rev*TCA, both strongly improve the results with respect to PBE.

The performances of TCA and *Rev*TCA are not far from those of B3LYP and become even better for 1,3-dipolar cycloadditions when a large basis set is used. This is especially interesting, considering that TCA and *Rev*TCA don't contain fitted parameters, while B3LYP was optimized for systems containing light atoms such as those considered in the present work. This result does suggest that functionals belonging to the GGA class are not intrinsically less accurate than more elaborate and more time-consuming approaches.



Keywords: DFT, exchange-correlation functionals, pericyclic reactions

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Understanding polyoxometalates through charge density : a DFT study

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With a large spectrum of applications, polyoxometalates form a class of inorganic compounds whose properties depend mainly on their size, mass and charge but also their ability to transfer electrons and protons [1,2]. Previous structural studies on hexa and heptapolyanions, represented on Figure 1, have shown that density-functional methods lead to results in good agreement to experimental data [3,4], especially when using functionals based on the Vosko-Wilk-Nusair (VWN) form of the Local Density Approximation [5] compared to the Generalized Gradient Approximation. Relativistic effects have been also considered through the zeroth-order regular approximation (ZORA) [6], including either only scalar effects or spin-orbit coupling as well. Interactions with an aqueous environment have been modelled by the COSMO approach [7]. Using the same computational strategy, reliable spectroscopic properties such as Infra Red and Raman spectral traces can also be calculated and assignments of vibrational modes performed. It has been shown that $[M_7O_{24}]^{6-}$ spectra obtained using pseudo-gas phase calculations reproduce the experimental data most satisfactorily, particularly when the aminopyridinium counterion is considered [8].

Influence of the solvent improves slightly metal-terminal oxygen bonds but in $[W_7O_{24}]^{6-}$ some tungsten-oxygen bonds which involve pseudo-terminal oxygen atoms are found to be very sensitive to the interactions with water and can shorten considerably. To clarify this result, we have focussed on atomic charges and charge density of different polyanions showing also that Hirshfeld charges were not well adapted to polyoxoanions.

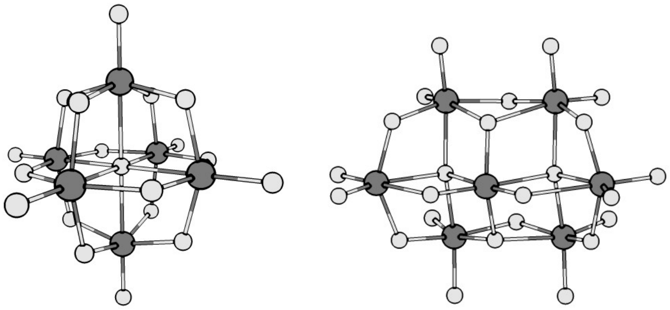

Figure 1: Structure for the polyanions $[M_6O_{19}]^{2-}$ and $[M_7O_{24}]^{6-}$. Metal and oxygen atoms are represented in dark and light grey, respectively.

Keywords: polyoxometalates (POMs), IR and Raman spectroscopy, Hirshfeld charges, charge density

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Ground State and Metastable States of Uranium Dioxide: a DFT+U Investigation

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Numerous experimental and modelling investigations have been performed on uranium dioxide because of its technological value as the standard nuclear fuel for pressurized water reactors. Its accurate description, however, remains challenging. Within the Density Functional Theory (DFT) formalism, the treatment of the strong correlations between the *5f* electrons of uranium requires a particular care. Several approximations of the DFT were used during the last decade in order to improve the treatment of electronic correlations, such as hybrid functionals, the self-interaction correction or the DFT+U formalism. The DFT+U approximation in particular has been widely used to investigate the structural and electronic properties of the uranium dioxide bulk, as well as the stability and behaviour of the point defects created during in-pile irradiation [1-6]. Numerous discrepancies, however, are observed between these various studies, especially on the formation energies of point defects. In addition, despite the conflicting results, none of the authors from references 1 to 5 mentioned any convergence problem to the ground state. It has been shown lately [7,8] that finding the system ground state in the DFT+U formalism is difficult because of the existence of numerous energy minima (metastable states). In order to get an accurate description of uranium dioxide, one must therefore monitor the occupation matrices of the uranium *5f* orbitals to make sure that the ground state has been reached, as has been done on cerium [9] and plutonium oxides [10].

We present here the results of our study of the ground state and metastable states of UO_2 using the DFT+U approximation and the GGA-PBE functional. To determine the ground state of UO_2, we have performed a systematic study of numerous different electronic states and compared the energies of the minima obtained. We have then computed the properties of UO_2 for the ground state determined and compared them with experimental data, as well as the previous modelling results.

Keywords: Uranium dioxide, DFT+U, ground state, occupation matrices

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’Mindless’ DFT Benchmarking

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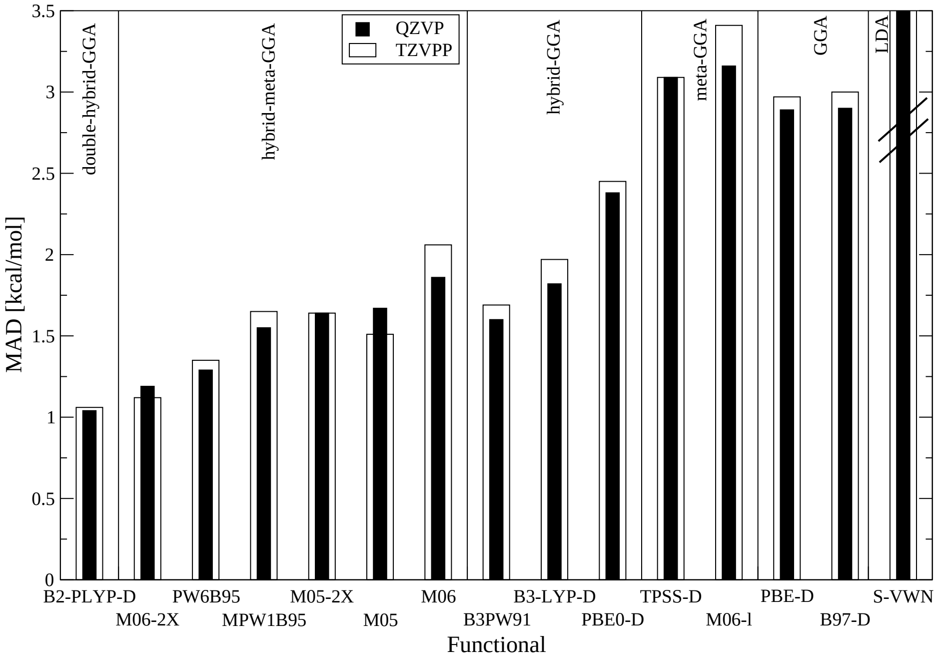
It has recently been shown that so called ’Mindless Benchmarking’ is a useful new approach for the generation of thermodynamical benchmark sets [1]. The original ansatz was based on test sets of randomly generated ’artificial molecules’ (AMs) that rely on systematic constrains rather than uncontrolled chemical biases. In order to calculate chemically meaningful relative energies, the AMs were decomposed into hydrides and diatomics. For these reactions, CCSD(T)/complete basis set reference energies were calculated, which were used to benchmark a variety of density functionals.

We present further development of this ansatz, including an improved method to generate AMs which was used to compose sets with larger AMs of up to 16 atoms. Electronically more complicated systems were also accounted for by introducing cationic AMs. In addition to this, we developed two new methods to generate relative energies: the decomposition of the AMs into hydrides only and the ’isomerisation’ of the AMs, where the atoms of a given AM are rearranged in a random manner.

CCSD(T)/CBS(2,3) reference data were generated to benchmark various density functionals. The effect of the size of the AMs, decomposition method and charge was analysed.

We found that the above mentioned extensions to the original ansatz support the previous results [1] and Perdews metaphor of ’Jacobs Ladder’ [2] for the ordering of density functionals.



Keywords: thermochemistry, density functional benchmarking

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Insulating Ground States of Transition-Metal Monoxides from Exact Exchange

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The exact exchange of density functional theory is used to calculate the electronic structure of the antiferromagnetic (type II) phases of the transition-metal monoxides MnO, FeO, CoO and NiO at $T = 0$. In contrast to the local density (LDA) and generalized gradient approximation, the exact exchange (combined with LDA correlation) correctly yields insulating ground states for all four compounds. The values for the band gaps and magnetic moments obtained with this parameter-free *first principles* method are in good agreement with the experimental data. While correlation plays a major role for the electronic structure, these results demonstrate that the mere opening of a gap in FeO and CoO is already obtained on the level of density functional theory, if the exact, multiplicative exchange potential is combined with a full potential method. State-dependent potentials are not required for obtaining a gap.

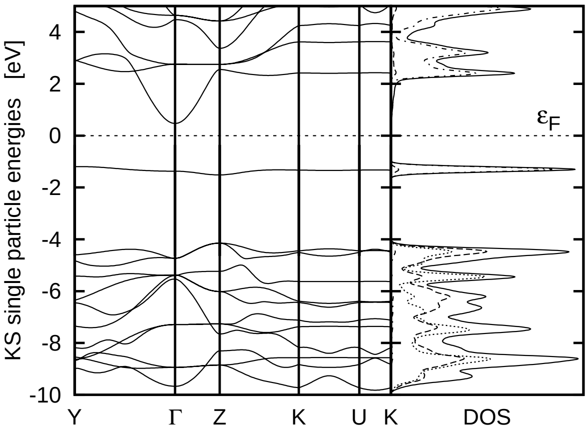

Figure 1: Band structure of FeO (AF II phase) obtained by plane-wave pseudopotential calculation with the exact exchange in combination with LDA correlation, using the full optimized potential method for the evaluation of the exchange potential [1]. Also shown are the total (solid line) and partial densities of states: O$2p$ – dotted line; Fe$3d$ from sites with majority ↑ – dashed line; Fe$3d$ from sites with majority ↓ – dash-dotted line.

Keywords: exact exchange, optimized potential method, Mott insulators

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New exchange-correlation functionals employing an exact exchange Kohn-Sham method

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At present numerically stable optimized effective potential (OEP) methods are accessible for plane waves [1] as well as Gaussian basis sets [2]. This enables the implementation of new exchange-correlation functionals where the exchange part of the exchange-correlation energy and potential are treated exactly within a Kohn-Sham (KS) method. To use these functionals the method of *Heßelmann et al.* [1] was efficiently implemented in the quantum chemistry program package TURBOMOLE [3]. Restricted and unrestricted calculations for molecules are possible. The implementation makes also use of the symmetry of the system which means that the OEP equation is constructed from and solved for symmetrized molecular orbitals and symmetrized auxiliary basis functions for the finite symmetry point groups.

The convergence behaviour of the OEP method was studied by calculating the exchange potential in two different ways. The first one solves the OEP equation and uses this solution in the same iteration step to calculate the exchange potential while the second solves the OEP equation and uses the solution in the following iteration step to calculate the exchange potential which avoids half of the calculations of the integrals needed for exchange energy. Special basis sets for OEP methods are presented.

Keywords: Optimized effective potential, exchange-correlation functional, convergence behaviour

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How far can one go with empirical fitting procedures for density functionals?

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Density functionals (DFs) usually depend on a varying number of parameters. These are either determined by fulfilling physical boundary conditions or by fitting them empirically to accurate reference data. A variety of exchange and correlation functionals was proposed in the past and with common quantum chemical codes it is quite easy to arbitrarily combine these with each other. When doing this, though, the question arises whether the parameters of a certain exchange functional are optimal when combining them with a specific correlation functional. For example one may ask, whether the B-LYP functional would yield better results if the parameters were optimized according to this specific combination of Becke88 exchange with Lee-Yang-Parr correlation.

Furthermore, it is sometimes observed that e.g. for thermodynamics the TPSS meta-GGA functional yields similar results as the PBE functional. This happens, though, at a higher computational cost due to the inclusion of the kinetic energy density. Do physical boundary conditions lead to restrictions that inhibit an even better performance of a certain DF, like TPSS? Would lifting these restrictions improve the performance of TPSS relatively to PBE? Finally, how far can one go with the empirical fitting procedure for DFs in general?

In this systematic study we try to answer these questions. Based on a well balanced fit set, the functional parameters of the popular B-LYP, mPW-LYP, PBE and TPSS methods are fully reoptimized. This reoptimization is carried out with an empirical dispersion correction (DFT-D [1]) to take into account dispersion effects and to withdraw possible long-range effects from the semi-local functional parts. Afterwards, a thorough benchmark study (validation sets) is carried out to investigate the performance of the optimized functionals (denoted by the prefix 'o'). The results indicate that reoptimizing the functional parameters has a strong influence on energetics and just a minor one on geometries. The reparameterized versions oB-LYP and oPW-LYP now yield almost identical results, which is not the case for B-LYP and mPW-LYP. The results of the reparameterized methods are generally better than for the original ones for the validation sets. The optimized oPBE version shows a very heterogeneous behavior, meaning that in some cases the method performs better than the original PBE and in some cases the results become worse (e.g. the quality of geometries slightly worsens). oTPSS shows a comparable behavior. Although an overall improvement compared to TPSS is observed, its performance relatively to oPBE is still like that of the original methods. Therefore it is deduced, that the reason why TPSS energetics are often similar to those of PBE does not stem from physical constraints.

In cases where energetics of large systems, that can only be treated on the (meta-)GGA levels, are important, the reparameterized DFs appear as a good alternative to the original methods.

Keywords: density functionals, benchmark study, computational chemistry

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Density functional theory for strong-interacting electrons

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We present an alternative to the Kohn-Sham formulation of density functional theory for the ground-state properties of strongly interacting electronic systems. The idea is to start from the limit of zero kinetic energy [1,2] and systematically expand the universal energy functional of the density in powers of a “coupling constant” that controls the magnitude of the kinetic energy. The problem of minimizing the energy is reduced to the solution of a strictly correlated electron problem in the presence of an effective potential, which plays in our theory the same role that the Kohn-Sham potential plays in the traditional formulation. We obtain the leading term in the expansion of the energy functional and discuss several schemes for approximating the remaining terms. Preliminary applications to quantum dots in the medium and strongly-correlated regime are presented, and the use of our results to improve state-of-the-art Kohn-Sham density functional theory is discussed.

Keywords: density functional theory, strong correlations, low-dimensional systems

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Insight into the Performance of (recently proposed) GGA functionals

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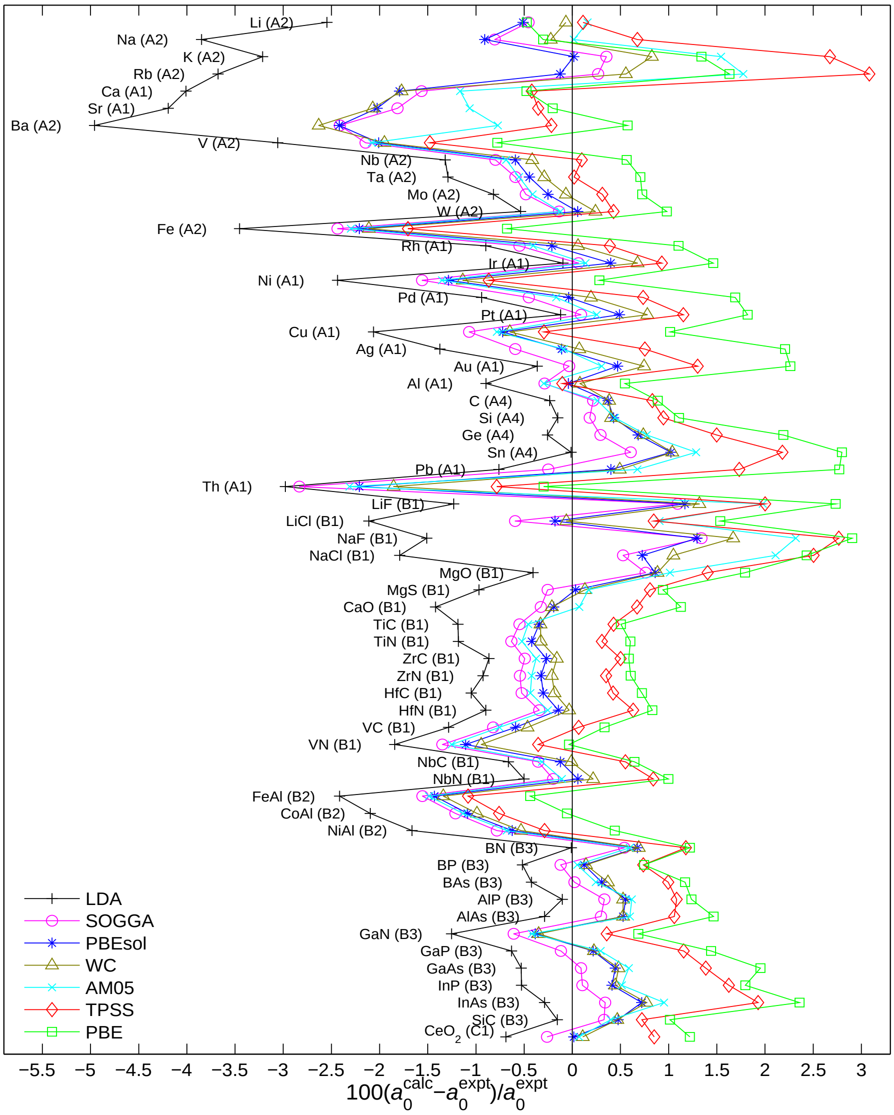
The generalized gradient approximation is still the most used exchange-correlation functional for the calculations of the geometry and electronic structure of solids. Very recently new GGA functionals have been proposed which should improve upon PBE in particular for the equilibrium volume of solids. We have calculated the equilibrium lattice constant for a large test set of 60 solids with the Wien2k code and show general trends about the performance of those functionals [1]. Furthermore we analyse the spatial distribution of the electron density, the reduced density gradient, and the E_{xc} contributions for a few selected compounds to gain insight into the performance of GGA functionals.



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Quantum Chemistry and DFT

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The purpose of this contribution is to make a connection between Density Functional Theory (DFT) and Quantum Chemistry (QC). To start we assume that the exchange-correlation functional of DFT, $E_{xc}[\rho]$, can be written as $E_x[\rho] + E_c[\rho]$.

For the ground states of atoms we argue that Kohn-Sham calculations with an optimum exchange functional E_x should reproduce Hartree-Fock (HF) energies, and that the dynamic correlation functional E_c should provide the atomic correlation energies.

For the hydrogen molecule ground state we consider whether KS calculations with an optimum E_x should reproduce the energies of the Heitler- London wavefunction, constructed with optimised atomic orbitals (often called the Spin-Coupled Valence Bond wavefunction). E_c should then give the additional correlation energy such that $E_x + E_c$ gives the Full Configuration Interaction energies. Potential energy curves for these two components are shown.

We then examine the performance of well-known exchange and correlation functionals. Within these criteria, currently used E_x do not contain sufficient left-right correlation, whilst currently used E_c contain an excess of dynamic correlation, at the molecular equilibrium and distorted situations.

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Improved description of correlation energies using the random phase approximation

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Density functional theory (DFT) applying the local density or generalized gradient approximation (LDA, GGA) leads to errors in the bond length of the order of 1 % and atomization energies are not reproduced with chemical accuracy. Furthermore, the (semi-)local LDA and GGA do not properly account for long-range van der Waals interactions, and consequently miss important contributions to the binding energies of rare gas and molecular crystals.

The adiabatic connection fluctuation-dissipation theorem (ACFDT), which provides, in principle an exact expression for the correlation energy, has received increased interest in the recent years (e.g., [1]-[3]). Within this framework, the exchange-correlation energy is expressed as a functional of the linear response function of the system. In the present work, we evaluate lattice constants and atomization energies of molecules and extended systems within the ACFDT framework applying the random phase approximation (RPA) for the evaluation of the linear response function.

The RPA energy includes the exact exchange energy and a compatible correlation energy that also accounts for long-range van der Waals interactions. We found that the rare-gas solids Ne, Ar, and Kr are well described within the RPA and the correct long-range $1/V^2$ volume dependence of the correlation energy is reproduced [3]. For insulators and metals, covalent and ionic bonded systems, RPA lattice constants are in very good agreement with experiment and deviate on average by only 0.25 % from experiment. Atomization energies, however, are throughout too small ($\approx$ 0.2 eV/atom) and the mean error remains close to the one obtained using the PBE-GGA. As heats of formation are nevertheless much better described than applying the PBE functional, the RPA atomization energies seem to be better balanced. This is also observed when comparing RPA results for diamond and graphite to the PBE ones. The RPA not only predicts the equilibrium geometries of both structures very accurately, also the energy difference between these two structures gets close to the experimental values.

Welcome to Lyon!

Keywords: correlation energy, exact exchange, van der Waals interaction

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Local hybrid density functional approximations using gaussian-type local mixing functions

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It has been prooven to be a successful approach in Kohn-Sham density functional theory to mix some amount of exactly computed exchange with some density functional type exchange into the exchange correlation functional. [1] No constant amount was found to describe all properites well: More exact exchange is desireable for barrier heights and less exact exchange is favorable for thermochemistry. Additionally, the optimum amount of exact exchange varies also with the employed density functional approximation: LDAs usually need more exact exchange than GGAs which need more than meta-GGAs. A possible solution to this problem is the incorporation of a position dependent fraction $f(\mathbf{r})$ rather than a constant fraction of exactly computed exchange into the XC functional at each point in space:

$$E_{\mathrm{XC}}^{\mathrm{Lh}} = \int f(\mathbf{r}) \cdot e_{\mathrm{X}}^{\mathrm{exact}}(\mathbf{r}) \ d^3\mathbf{r} + \int [1 - f(\mathbf{r})] \cdot e_{\mathrm{X}}^{\mathrm{DFA}}(\mathbf{r}) \ d^3\mathbf{r} + E_{\mathrm{C}}^{\mathrm{DFA}}$$

The very first implementation of a local hybrid was finished in 2003 [2] which used the self-correlation function τ_{W}/τ as local mixing function $f(\mathbf{r})$. This ansatz showed promising barriers and the qualitative correct dissociation of two center three electron systems but unfortunally disappointing thermochemistry. Further works [3-6] showed that scaled variants and other local hybrid functionals can compete with global hybrid functionals also in thermochemical test sets.

This work starts from the ansatz to place gaussian type functions where we believe exact exchange is favorable (at the nuclei and between two atoms in stretched bond situations). The difficulty of this ansatz in the endeavor to construct non-empirical local hybrid functionals which outperform global hybrids in common thermochemistry and barrier height test sets is to find suitable ingredients as coefficients and exponents of the gaussian functions. Another path is to construct semi-empirical local hybrids by fitting the parameters to a good performance in these test sets.

One competitive non-empirical local hybrid density functional approximation will be shown together with parametrized approaches. The most successful version can be considered as a perturbation to the global hybrid PBEh.

Keywords: DFT, exchange functional, local hybrid

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Vorticity expansion approximation for the exchange-correlation energy functional of the current-density functional theory

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The current-density functional theory (CDFT)[1,2] and its relativistic version, relativistic current- and spin-density functional theory (RCSDFT)[3,4], are useful methods for describing the ground-state properties of magnetic materials where the orbital current-density is induced. In order to perform actual calculations within the CDFT or RCSDFT, the exchange-correlation energy functional must be devised in practicable forms. We have recently proposed the vorticity expansion approximation (VEA) for the exchange-correlation energy functional by requiring it to satisfy exact relations (sum rules) that have been derived from scaling properties of the exchange-correlation energy functional[5-8]. Due to the well-behaved forms, the VEA formula can well reproduce the exchange and correlation energies of the homogeneous electron liquid under a uniform magnetic field[7].

For the purpose of evaluating the validity of the VEA formula, we have derived Levy's asymptotic bounds for the exchange-correlation energy functional of the CDFT and confirmed that the VEA formula satisfies the bounds[9]. We also showed that the VEA formula satisfies other sum rules which are not used in constructing the VEA formula, and are derived from uniform and nonuniform coordinate scalings[10].

In this presentation, in order to further evaluate the VEA, we derive some asymptotic conditions and bounds by using the coordinate scaling of electrons and adiabatic connection. It is found that the VEA formula exactly satisfies these conditions, though the local density approximation (LDA) formula of the CDFT does not.

In conjunction with previous results, we can confirm that almost all of sum rules (totally more than 50 sum rules) are fulfilled by the VEA, while less than half of them are by the LDA formula. Thus, the validity of the VEA formula is confirmed successfully from the viewpoint of sum rules.

In addition, in order to calculate electronic structures on the basis of the CDFT, we present the exchange-correlation potentials that are derived from the VEA formula. We apply them to open-shell atoms and ions where the spontaneous orbital current-density exists. We will discuss the effects of the spontaneous orbital current-density on the electronic structure.

Keywords: current-density functional theory, vorticity expansion approximation, exchange-correlation energy functional

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Computational scheme for calculating the pair density

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The pair density (PD) functional theory has gotten a lot of attention recently, because it provides a possible way to go beyond the density functional theory. After the PD functional theory was proposed by Ziesche[1], a lot of works have been done so far[2-7]. However, almost all such works have been purely formal, and practical schemes for calculating the ground-state PD have been hardly reported so far. The lack of practical schemes in the PD functional theory is mainly due to the N-representability problem of the PD[2-9]. Namely, if we employ the variational principle with respect to the PD, the search region of PDs is restricted within the set of N-representable PDs. Unfortunately, the necessary and sufficient conditions for N-representable PDs have not yet been obtained in a practical form although many attempts have been done so as to obtain them[2-9].

Recently, we have proposed a practical scheme for calculating the ground-state PD[10] by utilizing the extended constrained-search theory[11]. In this scheme, the search region of PDs is restricted in the set of PDs that are constructed from the single Slater determinants (SSDs). Namely, the best solution is searched within the set of restricted but definitely N-representable PDs. It can be characterized as the initial theory of the PD functional theory, because this scheme just corresponds to the Hartree-Fock approximation of the wave function theory and because this scheme provides a practical approach to calculate the ground-state PD[10]. Very recently, we have performed actual calculations on the basis of this initial scheme, and illustrated that about 20% of the correlation energy is reproduced by this scheme[10].

Similarly to the Hartree-Fock approximation that gives a good starting point for more accurate wave function theory, various kinds of approaches to calculate the ground-state PD may be possible on the basis of the initial scheme. As the first step toward developing more accurate PD functional theory, we attempt to extend the search region of the ground-state PD in two ways, i.e., (a) by using the correlated wave function such as the Jastrow wave function[12], and (b) by means of the solutions of the initial scheme as basis functions of the variational method. Due to the extension of the search region, we expect that the schemes may cover more correlation effects than the initial scheme. In this talk, we will mention the above strategies and present the calculation results for the neutral atomic systems.

Keywords: pair density, pair density functional theory, correlation energy

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The Kohn–Sham Potential in Restricted and Unrestricted Spin-DFT

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We revisit the problem of describing open-shell systems within density-functional theory. As a first step, we consider an exact Kohn–Sham formalism (i.e., without introducing approximate exchange–correlation functionals) [1]. There are two different approaches for such a description: In a spin-restricted treatment, only the total electron density of the system is used, and the Kohn–Sham reference system is chosen as a system of noninteracting electrons that has the same total electron density as the interacting system. The wavefunction of this reference system is given by a spin-restricted Slater determinant and as such is an eigenfunction of the total spin operator $\hat{S}^2$, but its spin density does not agree with the spin density of the interacting system. In a spin-unrestricted treatment, both the total electron density and the spin density of the system are considered, and the Kohn–Sham reference system is chosen as a system of noninteracting electrons that has the same total electron density *and spin density* as the interacting system. The wavefunction of this reference system is given by a spin-unrestricted Slater determinant and it is in general not an eigenfunction of $\hat{S}^2$. However, its spin density does agree with the spin density of the interacting system.

Both treatments offer perfectly valid descriptions of open-shell systems. However, since they differ in the definition of the Kohn–Sham reference system, they imply different definitions of the Kohn–Sham potential, of the noninteracting kinetic-energy, and of the exchange-correlation energy. These differences are worked out and are illustrated for simple model systems by considering accurate Kohn–Sham potentials that are reconstructed from electron densities (and spin densities) obtained from high-quality *ab initio* calculations.

Keywords: Spin-DFT, Kohn-Sham potential

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’Mindless’ DFT Benchmarking

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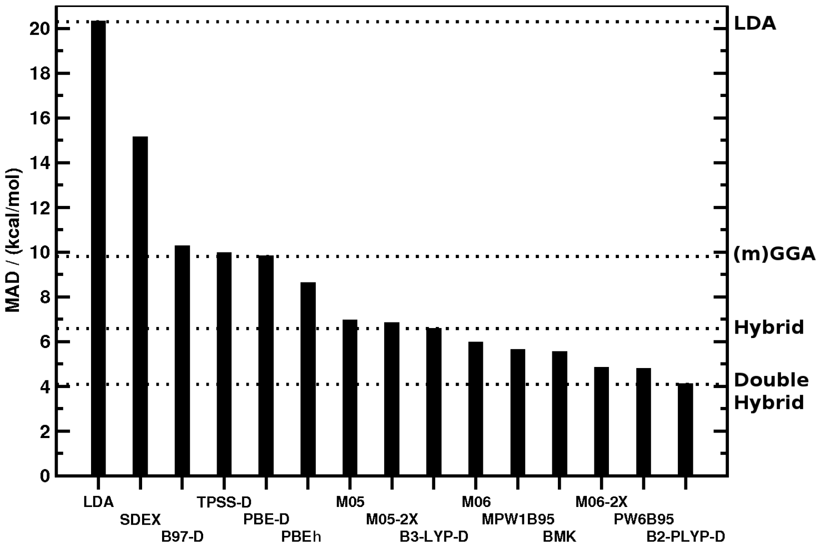
A diversity oriented approach for the generation of thermochemical benchmark sets is presented. Test sets consisting of randomly generated ’artificial molecules’ (AMs) are proposed that rely on systematic constraints rather than uncontrolled chemical biases. In this way, the narrow structural space of chemical intuition is opened up and electronically difficult cases can be produced in an unforeseeable manner. For the calculation of chemically meaningful relative energies, AMs are systematically decomposed into small molecules (hydrides and diatomics). Two different example test sets containing eight-atomic, single-reference, main group AMs with chemically very diverse and unusual structures are generated. Highly accurate all electron, estimated CCSD(T)/complete basis set reference energies are also provided. They are used to benchmark the density functionals S-VWN, BP86, B-LYP, B97-D, PBE, TPSS, PBEh, BH-LYP, B3-PW91, B3-LYP, B2-PLYP, B2GP-PLYP, BMK, MPW1B95, M05, M05-2X, PW6B95, M06, M06-L and M06-2X. In selected cases an empirical dispersion correction (DFT-D) has been applied. Due to the composition of the sets it is expected that a good performance indicates ’robustness’ in many different chemical applications. The results of a statistical analysis of the errors for the entire set with 165 entries (average reaction energy of 117 kcal/mol, dubbed as the MB08-165 set) perfectly fit to the ’Jacob’s ladder’ metaphor for the ordering of density functionals according to their theoretical complexity. The mean-absolute-deviation (MAD) decreases very strongly from LDA (20 kcal/mol) to GGAs (MAD of about 10 kcal/mol) but then less pronounced to hybrid-GGAs (MAD of about 6-8 kcal/mol). The best performance (MAD of 4.1-4.2 kcal/mol) is found for the (fifth-rung) double-hybrid functionals B2-PLYP-D and B2GP-PLYP-D, followed by the M06-2X meta-hybrid (MAD of 4.8 kcal/mol). The significance of the proposed approach for thermodynamic benchmarking is discussed and related to the observed performance ranking also regarding wave function based methods.



Keywords: thermodynamic benchmarking, artificial molecules, double hybrid density functionals

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Iterative diagonalization for orbital optimization in Natural Orbital Functional Theory

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Natural Orbital Functional Theory (NOFT)[1] constitutes a promising formalism for the description of electronic systems in terms of the natural orbitals and their occupation numbers. Usually, the solution is established with an embedded loop algorithm: in the inner loop we look for optimal occupation numbers for a given set of orbitals, whereas in the outer loop we optimize the natural orbitals under the orthonormality constraints for fixed occupation numbers. Nowadays, the orbital optimization is the bottleneck of this algorithm. Calculations based on diagonalization techniques have confirmed its practical value since the resulting orbitals are automatically orthogonal, hence effective single-particle equations are desirable for finding the optimal orbitals.

In this presentation, a new procedure which yields the natural orbitals by iterative diagonalization of a Hermitian matrix **F** is introduced[2]. The off-diagonal elements of the latter are determined explicitly from the hermiticity of the matrix of the Lagrange multipliers. An expression for diagonal elements is absent so a generalized Fockian is undefined in the conventional sense, nevertheless, they may be determined from an aufbau principle. Thus, the diagonal elements are obtained iteratively considering as starting values those coming from a single diagonalization of the matrix of the Lagrange multipliers calculated with the Hartree-Fock orbitals after the occupation numbers have been optimized. The method has been tested on the G2/97 set of molecules for the PNOF[3-5]. The PNOF approach arises from a reconstruction of the two-particle reduced density matrix by means of the cumulant expansion, and an explicit antisymmetric construction of the cumulant in terms of two symmetric matrices.

To help the convergence, we have implemented a variable scaling factor which avoids large values of the off-diagonal elements of **F**. The elapsed times of the computations required by the proposed procedure are compared with a full sequential quadratic programming optimization, so that the efficiency of the method presented here is demonstrated.

Keywords: Reduced Density Matrix Theory, Natural Orbital Optimization, Iterative Diagonalization Method, G2/97

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A mixed Thomas-Fermi and Weizsäcker Orbital-Free Functional

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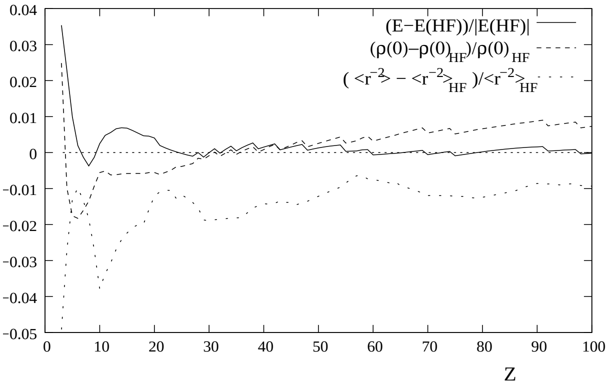
Orbital-free density functional methods, which accomplish with the initial spirit of DFT, are considered as a convenient approach for large coulomb systems for reducing the computational cost of solving the Kohn-Sham equations [1].

In this work we introduce a density functional based on the Thomas-Fermi and Weiszäcker ones by means of a division of space in two regions: $\mathcal{R}_1$ contains all the points near the nuclei where $|\vec{r}-\vec{R}_i| \leq R_i^0$ ($\vec{R}_i$ is the position of nucleus i and R_i^0 a radius for the near-nuclear region, which scales as Z^{-1}), and $\mathcal{R}_2$ corresponds to the rest of space. In the former region, as the potential is dominated by the nuclear attraction $-Z/|\vec{r}-\vec{R}_i|$, the kinetic energy functional is taken as the Weizsäcker term, which reproduces exactly the kinetic energy of the strongestly bound orbital, and in the latter, where the potential can be considered as slowly varying, we use the Thomas-Fermi functional for the kinetic energy, because in this region the wavefunctions can be approximated by local plane waves.

Therefore our model is based upon the following kinetic energy functional (atomic units used):

$$T_M[\rho] = \frac{1}{8}\int_{\mathcal{R}_1}\left[\frac{|\vec{\nabla}\rho|^2}{\rho} - 2\Delta\rho\right] d\vec{r} + \frac{3}{10}\left(3\pi^2\right)^{2/3}\int_{\mathcal{R}_2}\rho^{5/3} d\vec{r} \tag{1}$$

A benchmark application is performed for spherical atoms without electron correlation and a comparison to Hartree-Fock results. The density and energy obtained with this approach are equal to those obtained from a modified Thomas-Fermi-Dirac approach studied in previous work [2]. Among the merits of this approach, are worth to mention that (i) total energies and radial expectation values are given with a few percent from HF values for atoms, cations and stable anions; (ii) the density at the nucleus $\rho(0)$ is described more accurately than with the Thomas-Fermi-Dirac-Weizsäcker-Hodges (forth order) model; (iii) the Kato's cusp-condition for the density is exactly hold, and (iv) the proper scaling of average properties with both Z and N for atoms and ions is obtained. The comparison of some quantities to HF results is illustrated in the figure below.



Procedures for applying this model to problems without spherical symmetry, e.g. to molecules and electron-atom elastic scattering will be discussed.

Keywords: orbital-free, density functionals, atomic properties.

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Lower Bounds on the Exchange-Correlation Energy in Reduced Dimensions

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In 1979 Lieb [1] planted a landmark in quantum many-body physics by proving the existence of a lower bound on the indirect part of the Coulomb interaction. For the purpose of quantitative calculations, on the other hand, existence of a bound is not enough - it is wished it to be as tight as possible. A tighter versions of Lieb's bound was later derived by Lieb and Oxford [2]. This version, known as the Lieb-Oxford (LO) bound, is routinely used as key constraint in the construction of many modern density functionals [3,4], which in turn are used in calculations of the electronic structure of atoms, molecules, nanoscale systems, and solids.

On the other side, and in connection with recent advances in low-dimensional physics it is important to ask whether LO-like bounds exist and can be formulated also in reduced dimensions, in particular since the study of low-dimensional systems today forms a significant part of condensed matter and material physics.

The bound can be expressed in terms of the *indirect part* of the interaction energy; for a D-dimensional system, it may be written as

$$W_{xc}[\Psi] \equiv \left\langle \Psi | \hat{V}_{ee} | \Psi \right\rangle - U[n] \geq - C_D \int d^D r \, n^{\alpha}(\mathbf{r}) \ ,$$

where the electron-electron (e-e) interaction operator is Coulombic, i.e., $\hat{V}_{ee} = \sum_{i>j} |\mathbf{r}_i - \mathbf{r}_j|^{-1}$. Its expectation value is calculated over any normalized many-body wave-function $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$. $n(\mathbf{r})$ is the corresponding density, and $U[n]$ is the classical Hartree energy. We note, however, that the existence of a bound of this form has been rigorously proven for only 3D and 2D, and that the tighest possible form (i.e., the smallest possible value of $C_D > 0$) is unknown in all dimensions [5].

In this talk I will (i) show that the exponents of n are consequences of *universal* scaling properties of the e-e interaction; (ii) present the exponent α of a possible one-dimensional bound; (iii) provide the tightest estimate to date of the numerical prefactor C_D $(D = 3, 2)$, which amounts to a dramatic improvement for $D = 2$, and the first proposal for C_1; (iv) discuss unexpected parameter independence and universality of the bound with respect to the model chosen for interactions in 1D; and (v) show results for the 1D and 2D bounds againts analytical and near-exact numerical data for various low-dimensional systems, which displays an interesting *dimensionaly crossover* in the low-density limit [6].

Keywords: Lieb-Oxford bound, exchange-correlation energy, reduced dimensions

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Compact analytic representation of the correlation energy of uniform electron gas

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A new expression of the correlation energy density of the uniform electron gas is derived based on the adiabatic connection method. It covers with a single form the transition between high-density and low-density regions in the range $0.1 \leq r_s \leq 30$, parsing the entir spin-polarization range $0 \leq \xi \leq 1$. We argue that the universality implied by the short-wavelength hypothesis goes both ways, and a model that works well for finite systems may be adapted to describe the uniform electron gas as well.

Some real space features of the underlying electron pair correlation function are illustrated and compared to available benchmarks.

Keywords: correlation energy, uniform electorn gas

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Exchange and correlation in two-dimensional systems: Derivation of accurate and practical functionals

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Practical success of density-functional theory depends on finding good approximations for exchange and correlation. So far, most density functionals have been developed in three dimensions (3D) with a view to studying the properties of atoms, molecules, and solids. Such efforts for two-dimensional (2D) systems have been relatively scarce despite the rapidly increasing theoretical, experimental, and technological interest in 2D structures such as semiconductor layers and surfaces, quantum-Hall systems, graphene, and various types of quantum dots.

Here we present our very recent advances in the development of non-empirical 2D density functionals for both exchange and correlation [1-5]. For finite, inhomogeneous 2D systems, all these functionals lead to considerably more accurate results than the commonly used 2D local spin-density approximation (LSDA).

For the exchange, adapting the strategy of Becke and Roussel [6] to 2D, and thus modeling the cylindrical average of the exchange hole, we derive both implicit and explicit 2D density functionals for the exchange energy [1]. Both functionals lead to accurate results when compared with exact reference data for the uniform 2D electron gas (2DEG) and few-electron quantum dots, respectively. Further generalization of the functional to ring topology leads to accurate description of the electronic exchange in quantum rings, even in the quasi-one-dimensional limit, where the (2D) LSDA is explicitly shown to fail [2]. Parallel to this approach, we have also derived a more standard generalized gradient approximation for the 2D exchange, which reduces the error of the LSDA by a factor of four [3] (see also poster of J. G. Vilhena).

For the correlation, which is of extraordinary importance in low-dimensional systems, we have developed two functionals [4, 5]. The first one [4] is based on modeling of the correlation-hole functions satisfying a set of exact properties [7]. Excellent performance is obtained in comparison with numerically accurate quantum Monte Carlo data for quantum dots in magnetic fields, as well as for the 2DEG. Our second correlation functional [5] originates from an extension of the Colle-Salvetti approach [8] to 2D, supplemented by a Gaussian approximation for the pair density. The resulting *local* approximation for the correlation energy broadly outperforms the LSDA, and it is very straightforward to implement.

Keywords: two dimensions, exchange, correlation, quantum dot, quantum ring

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A Density Matrix Functional with correct correlation description

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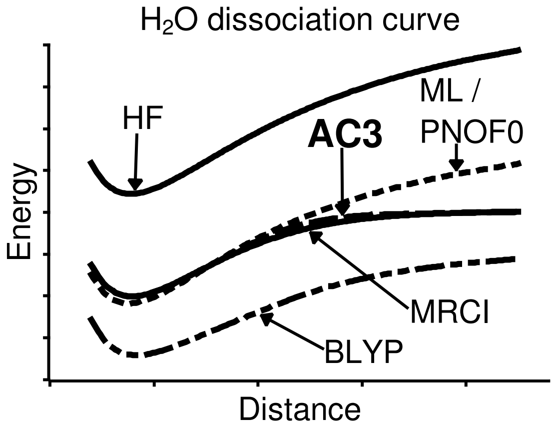
While Density Functional Theory (DFT) is successfully applied to many problems in Quantum Chemistry it fails to describe bond breaking processes correctly. The reason is a lack of static correlation. We present a Density Matrix Functional (DMF) that captures dynamical **and** static correlation. This is demonstrated for the dissociation curve of the ten-electron hydrides [1].

In Density Matrix Functional Theory (DMFT) all orbitals are fractionally occupied. The contribution of a pair of orbitals to the exchange correlation energy is regulated by a function of the occupation numbers. We show that two natural choices suffice to obtain excellent results [2]. The well-known exchange-type contribution and a square root dependence is used. The latter is taken from the exact functional in the two-electron case [3].
For the correct description of the dissociation curve it is necessary to identify the bonding and anti bonding orbitals. This is done with a switching function. It smoothly switches between the weakly correlated case at equilibrium and the strongly correlated case at the dissociation limit.

Our functional (AC3) performs excellently on the dissociation curves of the ten-electron hydrides. The average absolute error at equilibrium distance is 3.3%. The maximum error along the dissociation curve is ca. 9 kcal/mol. The maximum is typically found at intermediate bond distances.
AC3 outperforms all competing functionals, HF, BLYP and other DMF like ML [4] and PNOF0 [5] in the dissociation region. All competitors yield a qualitatively wrong dissociation curve, severely underestimating the stability at the dissociation limit. In contrast, AC3 dissociates to the correct limit.



Keywords: DMFT, strong correlation, dissociation curve

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New DFT correlation functionals:
Developments and tests

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The predictive ability of DFT calculations rests on the accuracy of the analytical approximations used for the exchange-correlation functionals. We have recently developed new correlations functionals (named TCA and *Rev*TCA) [1,2] at the gradient corrected level that have revealed competitive with some of the most common (and more time-consuming) KS/HF hybrid functionals. They are built on the Ragot-Cortona [3] functional, using known exact conditions and without fitting procedure. This is achieved by an average gradient analysis. Besides, *Rev*TCA enables an exact treatment of the hydrogenoid atoms. After recalling the basic equations of these approximations, we will present some results for a wide variety of physico-chemical properties (atomization energies, geometries, hydrogen-bonded complexes, organometallic complexes) to illustrate the performances of these new functionals.

Keywords: DFT, exchange-correlation functionals, theoretical developments

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Numerical Evaluation of Two-electron Four-Center Integrals for Pseudo-Atomic Orbitals

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A new computational method has been developed for the evaluation of electron repulsion integrals (ERIs), based on the mathematical formulae derived by Talman [1]. Since all the computations including the Fourier-Bessel transform of the basis functions are performed numerically, this method can calculate the ERIs even for non-analytic wave functions. Using the method, we have succeeded to calculate ERIs for the strictly localized pseudoatomic orbital (PAO) wave functions which are used as the basis functions in the order-N density functional calculation program OpenMX[4,5]. The finite truncation of the PAO functions significantly reduces the number of overlapping functions, so that the computation overhead for, for example, the numerical Fourier-Bessel transform is negligible.

Keywords: exact exchange, hybrid functional method

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Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential

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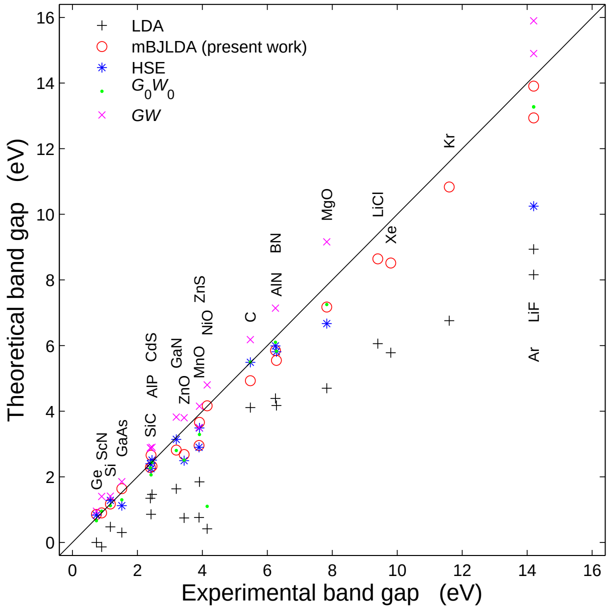
Recently, Becke and Johnson [1] proposed a semilocal exchange potential which reproduces very well the shape of the exact exchange potential constructed from the optimized effective potential. We showed that this semilocal potential improves (albeit moderately) over the LDA and PBE potentials for the band gap of solids [2]. In order to have further improvement in the results for band gaps, we modified the Becke-Johnson potential (mBJLDA). This new potential leads to agreement with experiment (see figure below) which is very good for all types of solids we considered (e.g., wide band gap insulators, *sp* semiconductors, and strongly correlated $3d$ transition-metal oxides) and is of the same order as the agreement obtained with the hybrid functionals (e.g., HSE) or the GW methods. This semilocal exchange potential, which recovers the LDA for a constant electron density, mimics very well the behavior of orbital-dependent potentials and leads to calculations which are barely more expensive than LDA calculations. Therefore, it can be applied to very large systems in an efficient way.



Keywords: exchange-correlation potential, band gaps, solids

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Stockholder partitioning of the density matrix over atoms and bonds

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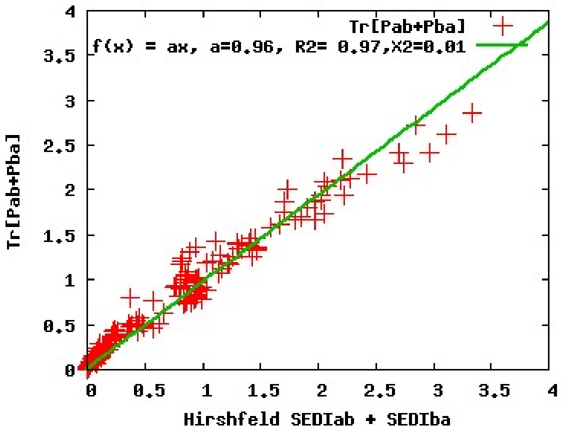
The treatment of molecules as a set of bonded atoms, fundamental to chemistry, has not yet an unbiased solid physical basis in ab initio quantum chemistry. The efforts to create that basis, are grouped in the concept of Atoms in Molecules (AIM). An AIM is a method that tries to define [1] atoms (and bonds) as quantum mechanical objects within the ab initio molecule. There is no unique AIM definition. However, AIM's can be useful as a very efficient framework for interactions between molecular fragments and as a tool to quantify the effects of a molecular environment with all its similarities and transferabilities that build up chemistry.

Up to now many AIM methods focus on the simplest quantum mechanical objects, the molecular electron densities, to define molecular atoms. The introduction of chemical bonds actually requires at least the concept of orbitals, and therefore the partitioning of molecular density matrices over atoms and bonds.

We formulate a method [2] based on similarity principles to partition the molecular (1th order) density matrix over the the atoms and bonds. We use existing iterative Hirshfeld atomic weights [3] in our implementation, to make the partitioning of the molecular density matrix consistent with the iterative Hirshfeld partitioning of the density.

The method is explored using a diverse set of 50 small molecules. Atomic and bond matrices are analyzed, the bonding process is evaluated theoretically and the number of electrons in the bond matrices is compared to the SEDI (Shared Electron Distribution Index)[4] number of shared electrons.

The partial number of electrons in the bond is found to correlate well with the SEDI index.



Keywords: Atoms In Molecules, density matrix, partitioning

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Theoretical Studies on Infrared Spectra and Molecular Structure of N-Substituted-6-Acylbenzothiazolon Derivatives.*

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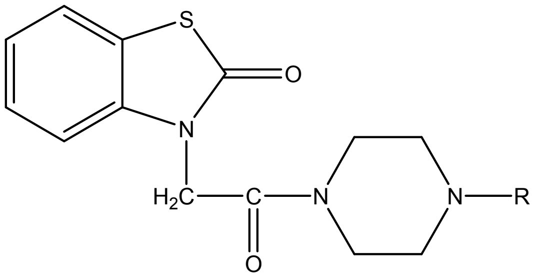
ABSTRACT

In this study, molecular structure, vibrational frequencies and infrared intensities of two 6-acylbenzothiazolon derivatives, which are thought as new drug precursor, in the ground state were calculated by using *ab initio* HF and DFT/B3LYP methods with 6-31G(d,p) basis set. The molecular structure was interpreted depending on theoretically obtained results. The FT-IR spectra have been measured in the solid-state and compared with calculated values.



R= i-propyl, butyl

Figure. The shemes of studied molecules

Keywords: 6-Acylbenzothiazolon, Drug precursor, FT-IR, DFT, HF

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* This work has been supported financially by Scientific and Technical Research Council of Turkey via Project number of 108T192.

POSTER PRESENTATIONS

Topic 3.

Linear scaling methods

MRChem implementation of the direct SCF approach for Density Functional Theory

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We present our implementation of a Direct SCF solver for the Kohn-Sham equations of DFT using multiwavelets. By making use of a method originally proposed by Kalos[1] the K-S equations are rewritten in an integral form and solved iteratively for each occupied orbital: the trial functions are minimized in analogy to a preconditioned steepest descent algorithm. By this approach the lengthy full computation and subsequent diagonalization of the Fock operator is then avoided.

Multiwavelets are employed for their attractive properties such as vanishing moments, disjoint support, arbitrary and predefined accuracy, adaptivity of the representation. Moreover the usage of a multiwavelet basis makes it easy to adaptively apply operators in an integral form by using the so-called Non-Standard (NS) form of the corresponding Green's function kernel. Lately this approach has been pursued by Harrison and coworkers[2]. We will here show our implementation with emphasis on its distinctive features, such as the complete calculation of all components (64) of operators in the NS form and a fully adaptive algorithm.

Keywords: Multiwavelets, Integral equations, Adaptivity, Predefined Accuracy, Direct solver

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Parallelization of the MRChem multiwavelet DFT program

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We present a parallelization scheme for a multiwavelet DFT program, as implemented in the MRChem program. The MRChem program implements a fully numerical, multiresolution DFT method for molecular calculations, using multiwavelets as basis functions. Multiwavelets are refinable functions with attractive mathematical properties, like error control and selective refinement. The DFT equations are solved using an integral operator formalism, by iteratively applying a Green's function to a set of trial orbitals. The integral operator is represented in the so called non-standard (NS) form. In the NS form the integral operator becomes banded, sparse and blocked, which inherently makes the method scale linearly with problem size. In the present work we present algorithms implementation for the following operations: Projection of an analytical function onto a wavelet manifold, traversing and refining function trees and the construction and application of an integral operator in the NS form. We also present timings and computational scaling data for solving the Poisson and DFT equations.

New Algorithms for Efficient Conventional and Nondynamical DFT Calculations

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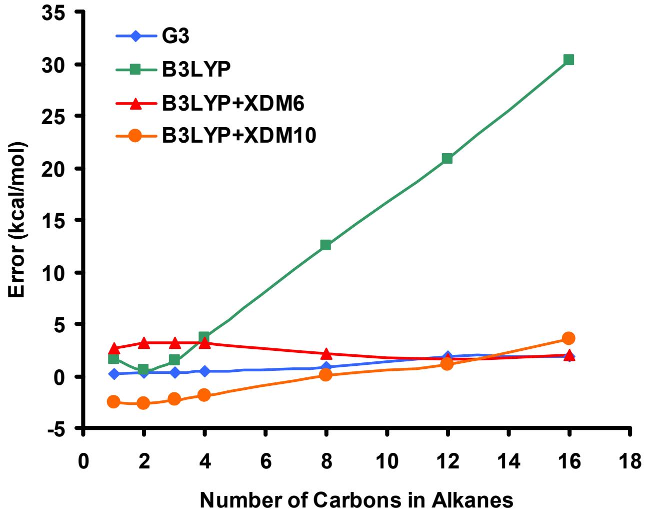
We report recent progress of the research team at Q-Chem Inc. on the development and implementation of new DFT algorithms and functionals. First, we will present a new method for the numerical integration of the exchange-correlation (XC) term that speeds up the calculation by 4-7 times without loss of accuracy. The new method, called multiresolution exchange-correlation (mrXC), takes advantage of the variation in resolution among the Gaussian basis functions, and shifts the calculation associated with low-resolution (smooth) basis function pairs to an even-spaced cubic grid [1, 2]. More recently, we have devised algorithms for the implementations of the self-consistent DFT calculation with Becke's post-Hartree-Fock nondynamical correlation model [3] and Becke and Johnson's exchange-hole dipole moment (XDM) model for dispersion [4]. Various aspects of the algorithms, including the efficient and accurate calculation of the exact exchange potential, will be discussed. The performance of these two models will be illustrated through chemical problems that have challenged mainstream DFT.



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P304

Elongation Cutoff Technique at Kohn-Sham Level of Theory

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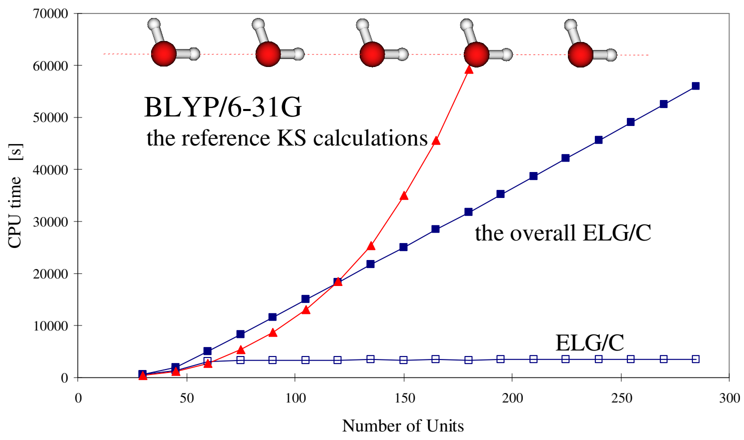
The elongation (ELG) method [1] uses the concept of locality and works in a regionally localized molecular orbital (RLMO) basis set. In this method the system is partitioned into several fragments. The way of fragmentation of molecular system is analogous to the experimental polymerization/copolymerization reaction mechanism; a polymer chain is extended by adding a monomer unit stepwise to a starting oligomer while keeping the variational degrees of freedom fixed. The ELG cutoff (ELG/C) technique [2] takes the full advantage of sparsity of Kohn-Sham (KS) matrix in RLMO basis.

In this presentation, a linear-scaling implementation of ELG/C that speeds up KS self-consistent field calculations is shown. The ELG/C KS scheme is based on local exchange-correlation space approximation. Such approximation improves efficiency of the method without introducing additional numerical error. The ELG/C KS method is tested on several illustrative examples. A comparison of ELG/C timings for model systems with the reference KS calculations is given. The analysis includes the overall CPU (central processing unit) time and its most time consuming steps. The obtained results indicate that the ECT is a very efficient sparse matrix algebra scheme.



Keywords: linear scaling methods, fragmentation techniques, elongation cutoff method

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Auxiliary Density Perturbation Theory

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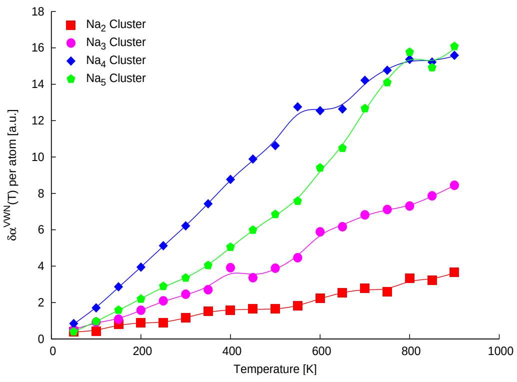
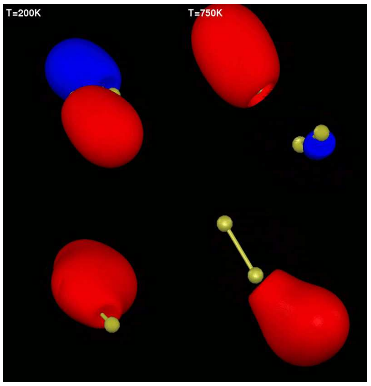
A new approach, named auxiliary density perturbation theory, for the calculation of second energy derivatives is presented. It is based on auxiliary density functional theory [1] in which the Coulomb and exchange-correlation potentials are expressed by auxiliary function densities. Different to conventional coupled perturbed Kohn-Sham equations the perturbed density matrix is obtained non-iteratively by solving an inhomogeneous equation system with the dimension of the auxiliary function set used to expand the auxiliary function density. We present working equations for auxiliary density perturbation theory [2] and their efficient implementation in the density functional theory program deMon2k [3]. The extension to time-dependent perturbation is shown, too. The theory is validated by static and dynamic polarizability calculations and by the calculation of nuclear magnetic shielding tensors in the GIAO approximation. It is applied for the calculation of temperature dependent polarizabilities of simple metal clusters [4].





Keywords: Perturbation Theory, Auxiliary Density, Linear Scaling

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POSTER PRESENTATIONS

Topic 4.

Van der Waals interactions

Theoretical Study of the van der Waals phosphorus trihalide Dimers P_2X_6 (X= F, Cl, Br, I)

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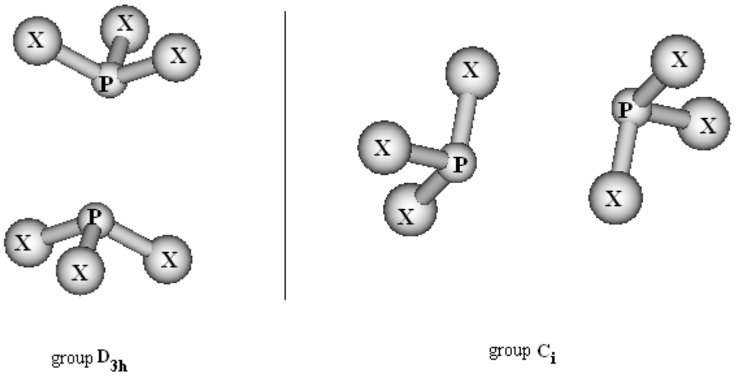
Theoretical studies of interactions between two phosphorus halides monomers of PX3 (X= F, Cl, Br and I) have been performed at DFT and ab initio (MP_2 and CCSD(T)) levels implemented respectively in ADF and Gaussian 03 series of programs. Dimers P_2X_6 at the symmetry D_{3h} and C_i isomers are considered in this work (see Figure below).



Phophorus halides Dimers P_2X_6(X=F, Cl, Br, I)

All isomers identified have been found to be true local minima on their respective ground potential energy surfaces (PES). Geometrical parameters, Infrared spectroscopy spectra, dipole moment of the optimized structures for the monomers and dimers phosphorus halides are calculated and discussed on the base of halides electronegativities. Only a few experimental data of these species are available. Our results are in good agrement with the experimental and theoretical studies[1,2].

Van der waals interaction energies are quantified for P_2X_6 (D_{3h} and C_i), Therefore, the dimerisation of phosphorus trihalides decreases in the order $PI_3 < PBr_3 < PF3 < PCl_3$. Results show a favored interaction in the case of C_i symmetry which is explained by the phosphor donor lone pair into vacant halide d orbitals

Keywords: Phosphorus halide dimers structure, Van der Waals interaction, Vibrational spectroscopy.

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Fractional charges, fractional spins and van der Waals interactions: An electron density perspective

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Three key problems in DFT are fractional charges, fractional spins [1] and van der Waals interactions [2]. Rather than considering these from the usual viewpoint of the energy, we consider them from an electron density perspective. Results are presented for H_2^+ and H_2.

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Application of dispersion-corrected density functional theory to benchmark sets of intermolecular interactions

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The extension of density functional theory to account for van der Waals (dispersion) interactions is a longstanding problem and topic of active research, due to the importance of van der Waals forces in biomolecules and intermolecular interactions, and the failure of conventional GGA and hybrid functionals to describe dispersion interactions. We have previously shown that the Becke-Johnson dispersion model [1] can be combined with standard GGA functionals (PW86 [2] for exchange and PBE [3] for correlation) to yield excellent binding energy curves for rare-gas diatomics [4]. Here we present the application of the GGA+dispersion method to extended benchmark sets for intermolecular interactions, including hydrogen bonding, electrostatic interactions, small van der Waals complexes and biomolecular systems.

Keywords: van der Waals interactions, Becke-Johnson dispersion model, benchmark sets

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Accurate interaction energies at DFT level by means of an efficient dispersion correction

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Since Density Function Theory has been introduced into the world of computational chemistry, countless studies on “large” systems have been performed that have otherwise would have been impossible. However, the use of DFT can become problematic when systems are examined where dispersion interactions are important, such as often is the case in biologically active systems. Therefore, the adjustment of DFT methods for a correct descriptions of dispersion interaction is nowdays a topic of an active research.

In this work an approach is presented for correcting interaction energies obtained at the DFT level by means of dispersion energies, calculated from dispersion coefficients.[1,2] The approach combines the expressions of Becke and Johnson [3] for dispersion coefficients with the Hirshfeld approach for partitioning of molecular polarizability tensors into atomic contributions [4]. Due to the availability of atomic polarizability tensors, the method is extended to incorporate anisotropic contributions, which prove to be important for complexes of lower symmetry. The method is validated for a set of eighteen complexes, for which interaction energies were obtained with the B3LYP, PBE and TPSS functionals combined with the aug-cc-pVTZ basis set and compared with the values obtained at CCSD(T) level extrapolated to a complete basis set limit. It is shown that very good quality interaction energies can be obtained by the proposed method for each of the examined functionals, the overall performance of the TPSS functional being the best, which with a slope of 1.00 in the linear regression equation and a constant term of only 0.1 kcal/mol allows to obtain accurate interaction energies without any need of a damping function for complexes close to their exact equilibrium geometry.

Keywords: Interaction Energies, Dispersion, Hirshfeld

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Importance of Dispersion Interactions For Supramolecular Inclusion and Cage Compounds

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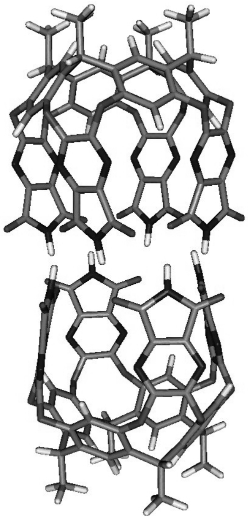
Results for two supramolecular systems are presented. The first is a complex in form of a capsule (B97-D/TZVP optimized structure shown on the right side), which is capable of self-assembly and valuable as a microenvironment for chemical processes [1]. To overcome the shortcomings of standard functionals in KS-DFT regarding the important van der Waals (dispersion) forces, an empirical R^{-6} type dispersion correction has been applied (DFT-D) [2]. The formation energy of the capsule, the deformation energy and the binding energy of several enclosed guests (alkanes from methane to tetradecane, p-xylene, benzene) is investigated. The computed binding energy for $C_{14}H_{30}$ is -51.7 kcal/mol (B97-D/TZVP) with a dispersion contribution of 106.9 kcal/mol, so that the complex becomes unbound at the uncorrected level. The quality of the optimized structures could be demonstrated by a comparison of computed and experimental NMR chemical shifts.



The second compound is the well known fullerene C_{60}, which has been suggested as a model for hydrogen storage [3]. This poster presents a thorough investigation of hydrogen molecule complexation inside a C_{60} cage with accurate quantum chemical methods such as DFT-D (e. g. the double-hybrid B2-PLYP-D[4]), (SCS-)MP2 and MP2.5[5], also including one-particle complete basis set extrapolation. It is found that only one H_2 molecule exergonically fits into the cage while the second one becomes just unbound within the error limits of the best computations.

Keywords: supramolecular systems, London dispersion interaction, fullerene

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Interaction of Hydrogen Chains:
RSH-ACFDT Analysis

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The interaction between two distant neutral atoms in the asymptotic regime is well described by the R^{-6} London dispersion. When considering extended subsystems, conventionally one follows the idea of pairwise additivity of R^{-6} contributions between microscopic elements of the subsystems. This standard hypothesis has been recently re-examined by Dobson et al. [1], by calculating correlation energies in the random phase approximation (RPA), and it has been shown to give wrong qualitative results for several systems and various geometries. These studies bring important insights of experimental interest e.g. in the buddle structures of single-wall carbon nanotubes, for the stacking effects in low-dimensional systems, such as graphite and C_{60}, etc.

By now, it is widely accepted that a fully non-local description of the long-range correlation energy (E_C) is primordial to obtain qualitatively correct results for dispersion interactions. Range-separated hybrid (RSH) adiabatic-connection fluctuation-dissipation theory (ACFDT) [2] approach combines non-local explicit exchange and correlation with a density functional theory (DFT) description of short-range electron interaction effects and it has been shown to resolve several drawbacks of standard, full-range random phase approximation (RPA). Here, we investigate the interaction of hydrogen chains by different variants of the RSH-ACFDT approach in comparison with results obtained by standard quantum chemical correlation methods.

Quasi-metallic and insulating prototype systems will be considered as H-chains constructed from equal or alternating arranged H atoms. Cross-sections of the potential energy surface $E_C(L,D)$ with respect to the chain length (L) and chain separation distance (D) will be investigated both for quasi-metallic and insulating cases in two different configurations, i.e. two chains in parallel and in pointing geometries [3]. The validity of the power law resulting from the conventional pairwise summation of R^{-6} contributions will be compared to the RSH-ACFDT predictions. The predictions of $E_C(L,D)$ for the quasi-metallic and insulating hydrogen chains in the pointing configuration will be compared with that for the model within hydrodynamical picture in [3].

Keywords: Adiabatic-Connection Fluctuation-Dissipation Density-Functional Theory (ACFDT), Range-separated Hybrid (RSH), Random Phase Approximation (RPA)

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Intermolecular hydrogen bonding and DFT: when does it work?

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The nature of the hydrogen bonding has been discussed and a classification of hydrogen-bonded compounds has been suggested for the case of the furan-HX (X = F, Cl, and Br) complexes.

It was shown why MP2, a well-adapted approach to the hydrogen-bonded systems, can not provide good results for these difficult cases [1].

On the ground of a systematic study, we point out the necessary and sufficient conditions for a method being able to provide acceptable results. We will see that for such a challenging compounds, only CCSD(T) method using a large basis set Aug-cc-pVTZ can provide results close to the experimental ones. We emphasis on the structural and vibrational properties. A good theoretical treatment of the vibrational frequencies constitute always a very difficult task for all the computational chemistry, particularly when we include the anharmonic effects.

We will analyze the position of various functionals (GGA and meta-GGA, purs and hybrid functionals) to study the intermolecular hydrogen bonding, and we will give a number of simple rules to indicate when the DFT method works and when it does not work.

Keywords: Hydrogen-Bonding, Dispersion, DFT

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DFT and Molecular Dynamics Investigations of π-π Interactions in Zipper Assemblies

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Supramolecular assemblies of *p*-oligophenyl/2,6-dialkoxynaphthalenediimide diads are proposed to give access to the unique zipper architecture [1] with long lived photoinduced charge separation and an efficient photocurrent generation. In the present contribution we report quantum chemical investigations of substituted naphthalenediimides (NDI) and their π-π dimeric complexes as the essential building blocks for this unique architecture.

Chloro, bromo, methoxy, and methylamine substituted NDIs were computed to evaluate the effect upon the naphthalene core by the increasingly electron donating substituents. Even though our main focus was on the 2,6-NDI core substituted substrates, a limited evaluation of regioisomers was also undertaken. Quadrupole moments, electrostatic potentials and other computed electronic properties suggest that among the series of substituted NDIs, the 2,6-dimethoxy-NDI is a good candidate to form the π-stacks with high conductivity [2].

The capacity to form the π-stacks from the substituted NDI monomers is evaluated by in-depth modeling of π-π dimer complexes. They are optimized with several DFT methods and namely the Truhlar's M06-class functionals [3], which was reported to give good results for π-π interactions. Comparison of results obtained with several DFT and *ab initio* methods will be discussed.

For the 2,6-dimethoxy-NDI the computed properties of the dimeric complexes indicate particularly strong π-π interaction, which is reflected in the short interplanar distances (d = 3.37 Å, see Figure) and fairly strong binding interaction energy. The QM results for NDI monomers, and π-π complexes were also correlated with molecular dynamic simulations of the supramolecular zipper assemblies.

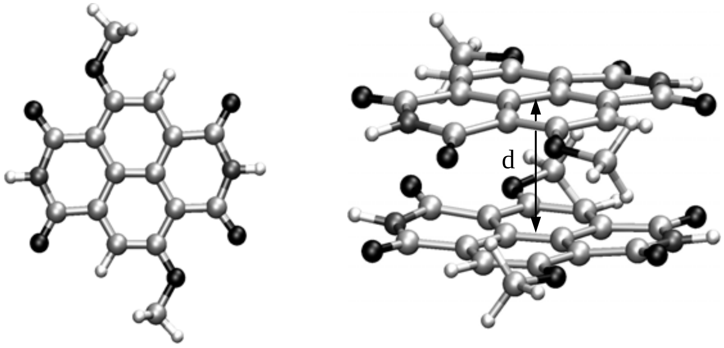

Figure: 2,6-dimethoxy-NDI : monomer (left) and π-π complex (right)

Keywords: π-π interactions, supramolecular assemblies, MD simulations, M06-class functionals

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Application of DFT/CC method for the description of H_2O and H_2 physisorption on graphitic surfaces

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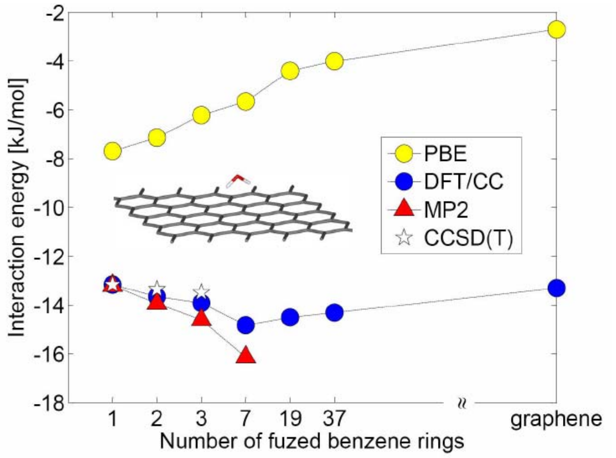
The accurate calculations of interaction energies of water and molecular hydrogen with various graphitic materials, including graphite, graphene, or carbon nanotubes (CNT) is of great interest due to both technological (e.g., hydrogen storage) and biological (e.g., water interaction with biomolecules) relevance. At the same time such calculations represent a major challenge for the computational chemistry. The reliable calculations on these systems require a periodic model and a method that can accurately describe weak non-covalent interactions. Standard GGA functionals (that are routinely used within the framework of periodic model) cannot be used since they do not account properly for non-covalent interactions. A recently developed DFT/CC method[1] represents one of the possible extensions of standard DFT aimed for an accurate description of weakly bound molecular systems.

A DFT/CC method is based on the pair-wise representability of the DFT error ($\Delta E_{DFT/CC}$, defined as the difference between DFT and CCSD(T)/CBS interaction energies) in terms of the inter-atomic distances. $\Delta E_{DFT/CC}$ is evaluated on a suitable reference set ($H_2O \ldots C_6H_6$ and $H_2 \ldots C_6H_6$ for water and H_2 complexes on graphitic materials, respectively) by means of Reciprocal Power Reproducing Kernel Hilbert Space Interpolation, and then it is used for correcting the interaction energies obtained at the DFT level for larger systems. A very good accuracy has been reported recently for gas phase and solid phase systems.[2, 3]



The most stable adsorption complex of water on graphite is the circumflex structure (both OH's directed towards the surface) above the center of the 6-member carbon ring that has $\Delta H^o(0\ K) = -11$ kJ/mol. Figure shows how the water interaction depends on the size of the PAH at the DFT/CC, PBE, MP2 and CCSD(T) levels; a good agreement between DFT/CC and CCSD(T) is apparent.

The calculated interaction energy of H_2 with graphene (5.4 kJ/mol) is in very good agreement with experimental value (5.0 kJ/mol). The potential energy surface for $H_2 \ldots$graphite obtained at the DFT/CC level was evaluated and used for the calculations of vibrational eigenvalues and compared with experimental data. Calculated interaction energies for H_2 inside and outside single-wall CNT are 7.2 and 4.9 kJ/mol, respectively.

Keywords: weak inter-molecular interactions, graphite, CNT

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New density functional theory method for calculations of intermolecular interaction energies

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Despite the rapid development and a plethora of existing density functionals some important phenomena still remain beyond capabilities of common formulations of DFT. Density functionals are notorious for failing to describe correctly intermolecular interactions especially for systems with significant dispersion contribution. The main reason is that the known local and semilocal exchange-correlation functionals are modeling only the short-range interactions. This failure has recently ignited a development of DFT-based methods that would properly take into account weak interactions.

One approach was to add to the DFT interaction energies the dispersion energies computed from simple empirical functions [1]. Another approach was to optimize some parameters in DFT exchange-correlation functionals to reproduce interaction energies for a number of dimers. In particular, the M05-2X functional of Zhao et al. [2] obtained in this way has become very popular. The main problem of the former approach is that a simple addition of dispersion energies to DFT interaction energies does not result in reasonable interaction energies and therefore various nonphysical damping and switching functions have to be introduced to get a usable approach. The main problem of the latter approach is that it appears not possible to optimize the parameters in such a way that the interaction energies are reproduced for the complete range of intermolecular separations. In particular, for all systems with a significant dispersion contribution, the long-range behavior of interaction energies is completely wrong. Another method that offers a solution to the problem of describing intermolecular interaction energies by means of density functionals called SAPT(DFT) is based on symmetry adapted perturbation theory [3]. SAPT(DFT) provides interaction energies of dimers with excellent accuracy. Although employing density fitting in SAPT(DFT) has enlarged its scope of applicability larger systems it is still far less computationally effective than DFT methods.

The method we propose combines the advantages of all aforementioned methods but avoids their deficiencies. The method results from a careful analysis of the sources of failure of the density functionals in reproducing intermolecular interaction energies and identifying the importance of different components of such interactions provided by SAPT. Its development involved designing a new density functional. The method combines the attractive efficiency of DFT with a high accuracy of SAPT(DFT). It does not have to rely on any systematic cancellations of errors and the performed tests shows it provides accurate interaction potentials in the whole range of intermolecular separations for systems of diverse electronic structures also with a significant contribution of the dispersion interactions.

Welcome to Lyon!

Keywords: intermolecular interactions, density functionals, sapt

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Role of van-der-Waals interactions in the collective behavior of solvated electrons

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Substantial experimental and theoretical efforts have focused on properties of solvated electrons in a variety of liquid and glassy systems, because solvated electrons are the most fundamental chemical reagents. Although the phenomenon of electron solvation has been known for at least one and a half centuries, explanations of the collective properties of solvated electrons have remained controversial. Numerous theoretical efforts based of the density functional methods have provided a proper description of solvated electrons only at ultra low concentrations of these quasiparticles. But the most of them can not be applied at increased concentrations, since they ignore completely van-der-Waals interactions between solvated electrons. However simple estimates based on experimental data on the absorption spectrum indicate the static polarizability of the electrons to be about of 10^3 a.u. and increases at least by two orders the similar values for usual molecules. What is why van-der-Waals forces caused by the huge polarizability play a significant role in the collective behavior of solvated electrons.

Using a theory of polarizable fluids, we extend a density functional treatment of an excess electron to the many-electron case corresponding to finite metal concentrations in metal–ammonia solutions (MAS). We evaluate dielectric, optical, and thermodynamical properties of MAS at low metal concentrations.1) Our calculations correlate well with the experimental data on the concentration and temperature dependencies of the dielectric constant and the optical absorption spectrum. The properties are found to be mainly determined by the van-der-Waals interactions between localized solvated electrons, which result in the two main effects: the dispersion attractions between the electrons and a sharp increase in the static dielectric constant of the solution. The first effect creates a classical phase separation for the light alkali metal solutes (Li, Na, K) below a critical temperature. The second effect leads to a dielectric instability, i.e., polarization catastrophe, which is the onset of metallization. The locus of the calculated critical concentrations is in a good agreement with the experimental phase diagram of Na-NH3 solutions. The proposed mechanism of the metal–nonmetal transition is quite general and may occur in systems involving self-trapped quantum quasiparticles. The proposed scenario may provide a new insight into the metal–insulator transitions and open a road for considering the possibility of new exotic electronic phases.

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Van der Waals Interactions by the Pauli Blockade Method within DFT Framework

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It is well known that the first four rungs of DFT fail to include the non-local long-range dispersion interaction necessary to describe Van der Waals complexes. To alleviate the problem, the idea of Hartee-Fock plus dispersion has been successfully adopted by replacing the HF interaction energy by the energy calculated by DFT [1, 2]. Since such an energy does in fact include obscure and not controlled short-range dispersion terms, to avoid double counting properly damped effective dispersion has been used.

We propose a different approach: a formalism to calculate the DFT interaction energy that *a priori* and rigorously excludes the dispersion contribution. The DFT interaction energy may be subsequently supplemented with the accurate dispersion contribution e.g. from the SAPT(DFT) calculations or other DFT long-range methods. To this end, the extension of the self-consistent field Pauli blockade method (PB-HF) [3] using Kohn-Sham description of interacting monomers is presented. The goal of the method, termed Pauli blockade DFT (PB-DFT), is to calculate the interaction energy between Van der Waals systems A and B including electrostatic, induction and exchange-repulsion terms and excluding the dispersion. The monomers interact through coulombic and exchange potentials only, which leads to the neglect of intermonomer correlation. This is achieved via iterative solutions of the Eqs. (1):

$$\begin{cases} \left(\hat{\hat{f}}_{\mathrm{A}}^{n} + \hat{v}_{\mathrm{B}}^{\mathrm{elst},n} + \hat{v}_{\mathrm{B}}^{\mathrm{exch},n} + \eta \hat{\hat{R}}_{\mathrm{B}}^{n}\right) a_i^{n+1} = \epsilon_{\mathrm{A},i}^{n+1} a_i^{n+1} \\ \left(\hat{\hat{f}}_{\mathrm{B}}^{n} + \hat{v}_{\mathrm{A}}^{\mathrm{elst},n} + \hat{v}_{\mathrm{A}}^{\mathrm{exch},n} + \eta \hat{\hat{R}}_{\mathrm{A}}^{n}\right) b_k^{n+1} = \epsilon_{\mathrm{B},k}^{n+1} b_k^{n+1} \end{cases}, \qquad (1)$$

where $\hat{\hat{f}}^{n}$, $\hat{v}^{\mathrm{elst},n}$ and $\hat{v}^{\mathrm{exch},n}$ denote Kohn-Sham, electrostatic and exchange potential operators, respectively, and n is the iteration number. The penalty function, $\hat{\hat{R}}_{\mathrm{A}}^{n} = \sum_{i \in \mathrm{A}} |\tilde{a}_i^n\rangle \langle \tilde{a}_i^n|$, together with Löwdin orthogonalization of orbitals after each iteration, $\{a_i^{n+1}, b_k^{n+1}\} \rightarrow \left\{\tilde{a}_i^{n+1}, \tilde{b}_k^{n+1}\right\}$, ensure that the Pauli exclusion principle is not violated in the course of iterations. The advantage of the iteration procedure is that the resulting contributions are not affected by higher-order terms that are notorious in the perturbative approach and are usually collected under the delta Hartree-Fock term (δ_{HF}).

The procedure bears conceptual resemblance to the bivariational approach of Wesołowski and Cortona [4, 5], differing in that here we on purpose do not aim at calculating the full DFT interaction but only a well defined fragment — the SCF analog. The resulting PB-DFT interaction energies are compared with the interaction energies from other DFT + dispersion methods and with exact values for a variety of systems. The results prove very satisfactory and indicate that the PB-DFT method is a reliable tool in the field of intermolecular interactions.

Keywords: Van der Waals interactions, dispersion, double-counting.

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Correlation Hole in Two-Electron Systems: Van der Waals Interaction and Temperature Effects

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Description of electronic correlations often depends on the chosen formalism and approach. Therefore, such formalism independent concepts as density matrices are useful in bridging the gap between different views. Also, the (exchange–)correlation hole is a useful concept in describing the correlation phenomena in a transparent way.

In this study we restrict ourselves to two-electron systems, He atom and H_2 molecule, to evaluate the correlation-only features without involving exchange. We use the path-integral Quantum Monte Carlo (PIMC) [1] approach that offers us a transparent way to include and analyze the electronic correlations without any restrictions from basis sets or forms of the many-body wavefunction. However, QMC becomes computationally challenging already with small systems. With PIMC we evaluate the finite-temperature mixed state density matrices directly by sampling the NVT ensemble.

We show the correlation hole features evolution in He atom as a function of distance from nucleus and evolution of the hole as a function of bond length in H_2 molecule, following the scheme of Baerends and Gritsenko [2]. We find agreement in terms of well-defined exchange and correlation concepts. The van der Waals interaction at long "bond lengths" is analyzed in a transparent way from the imaginary time dynamics of the particles. We also consider high-temperature effects on the above correlation holes, where contributions from excited states are analyzed.

Finally, we analyze the correlations in the dipositronium molecule Ps_2 the same way as in case of H_2 molecule. In Ps_2, many of the above discussed features appear more pronounced [3]. Positronium atom Ps is a hydrogen atom like pair of a positron and an electron, and correspondingly, dipositronium is a four-particle molecule formed by two positronium atoms. Ps_2 molecules were recently observed experimentally [4], for the first time.

Keywords: Correlation hole, van der Waals interaction, Quantum Monte Carlo

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Dispersion coefficients based on the local response approximation

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Non empirical determination of the inter-atomic dispersion coefficients is introduced based on the local response approximation due to Dobson and Dinte (DD). [1] In this approximation, the real-space density response function is locally expressed in terms of the total electron density ρ,

$$\chi_{\mathrm{local}}(\mathbf{r}, \mathbf{r}', \omega) = \nabla_{\mathbf{r}} \cdot \nabla'_{\mathbf{r}} \left[\frac{\rho(\mathbf{r})\delta^3(\mathbf{r}-\mathbf{r}')}{\omega^2 - \omega_P^2[\rho(\mathbf{r})]} \right], \tag{1}$$

where $\omega_P = \sqrt{4\pi\rho}$ is the local plasma frequency.

Based on the local response and the Zaremba-Kohn expression of the exact second-order dispersion energy, [2] DD derived doubly-local density functional for the dispersion energy between nonoverlapping fragments. [1]

$$E_{\mathrm{disp}} = -\frac{3}{16\pi^{3/2}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}^6} \frac{\sqrt{\rho(\mathbf{r}_1)}\sqrt{\rho(\mathbf{r}_2)}}{\sqrt{\rho(\mathbf{r}_1)} + \sqrt{\rho(\mathbf{r}_2)}} \tag{2}$$

The same functional was also derived prior to DD by Andersson, Langreth, and Lundqvist (ALL), from the different physical context. [3]

Combining the ALL functional with the long-range corrected (LC) density functional, [4] Kamiya *et al.* [5] and Sato *et al.* [6] have sucessfuly described various inter-molecular interactions. However, the computational cost of the ALL functional is high because of the numerical double integral. The presence of singular $1/r_{12}^6$ term is also problematic.

In the present study, we propose to use the local response (LR) in calculating multipole-expanded dispersion (D) coefficients. The LRD coefficients are then combined with the LC-DFT through the damped atomwise expression.

$$E = E_{\mathrm{LC-DFT}} + \sum_{n\geq 6} \sum_{A>B} C_n^{AB}/R_{AB}^n \cdot f_{\mathrm{damp}}^{(n)}(R_{AB}) \tag{3}$$

We discuss the new method in terms of its accuracy and efficiency based on several numerical results.

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Universal Inter- and Intramolecular Empirical Correction Formula for Generalized Gradient Approximation Density Functional Theory

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Density functional computations of alkane reaction energies suffer from systematic errors which accumulate with increasing system size.[1] Remarkably, Perdew's "Jacobs-ladder" is reversed for these reactions: SVWN5 clearly outperforms PBE and even larger errors are obtained with TPSS. An efficient way to correct the errors is to add an empirical atom pair wise interaction-correction, inspired by the Lennard-Jones potential (R^{-6} dependence).[2] The presented results show that higher order correction terms (R^{-8} and R^{-10} dependent) together with the universal damping function of Tang and Toennis[3] reduces these errors more efficiently with even less empiricism. For general applicability, the TT-damping function is augmented by a second damping function in order to have negligible corrections at covalent distances. The scope of this correction (dD10) is simultaneously expanded to intermolecular interactions. We test several combinations of first-principle functionals along with the new correction (PBE-dD10, PBEsol-dD10 and RGE2-dD10) and find that PBE-dD10 gives the most reliable results, closely followed by RGE2-dD10. The results outperform or match B2PLYP-D and M06-2X, two of the newer functionals with increased accuracy for weak interactions.

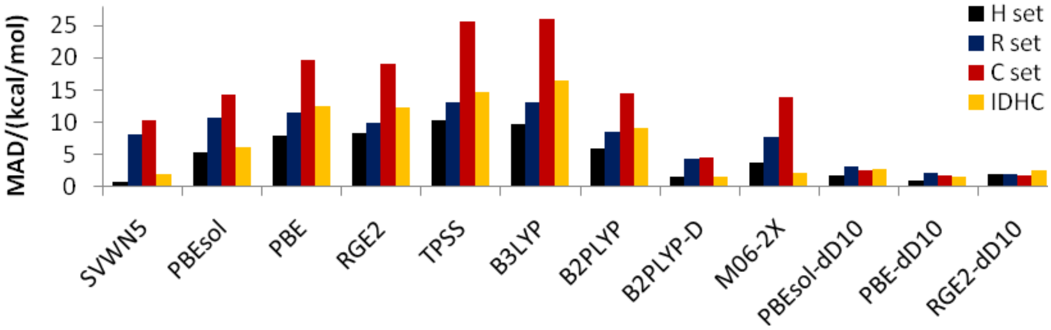

Figure 1 Mean absolute deviations over hydrocarbon chains (H set), rings (R set), cages (C set) and the diverse set for intramolelecular dispersion interactions (IDHC).

Keywords: density functional theory, empirical correction, generalized gradient approximation

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Oral model of Abstracts for DFT09
Accurate molecular van-der-Waals interactions from ground-state electron density

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We present a parameter-free method for an accurate determination of long-range van der Waals (vdW) interactions from mean-field electronic structure calculations. Our method relies on the summation of interatomic C_6 coefficients, derived from the Hirshfeld partitioning of the electron density of a molecule or solid and accurate reference data for the free atoms. The mean absolute error in the C_6 coefficients is 5.5% when compared to accurate experimental values for 1225 intermolecular pairs, irrespective of the employed exchange-correlation functional. We show that the effective atomic C_6 coefficients depend strongly on the bonding environment of an atom in a molecule. Finally, we analyze the vdW radii and the damping function in the C_6R^{-6} correction method for density functional theory calculations.

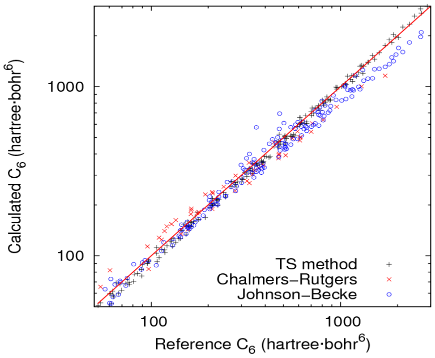

Figure 1: Comparison of our method to other first-principles methods for van-der-Waals C_6 coefficients.

Keywords: Van der Waals interactions, Hirshfeld partitioning, atoms-in-molecules

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Chemistry and Physics, DFT09, Lyon, France.

Van der Waals Interactions from Range-Separated Density Functional Theory

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Range-separated hybrid (RSH) density functional theory has been used successfully in calculating weak Van der Waals interactions [1,2,3]. In those calculations, the electron-electron interactions were separated into a short range part which is described by density functionals and a long range part by a common correlated *ab initio* approach, such as MP2, CCSD(T), or random phase approximation (RPA). In this poster, we present a comparative study for the rare gas dimers and other molecular systems by the RSH+MP2/CCSD(T)/RPA schemes, as well as by the pure MP2 and CCSD(T) methods. The dependencies of the calculated interactions on the short range functionals and on the size of basis sets are also examined. All the calculations are done with a development version of the MOLPRO code [4].

Keywords: Range-separated hybrid functional, Rare gas dimer, Van der Waals interaction

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POSTER PRESENTATIONS

Topic 5.

Time-dependent DFT

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

The Substituent Effect and Spectral Properties of Aluminum Tris (quinolin-8-olate) Derivatives : by the DFT and TD-DFT Calculation

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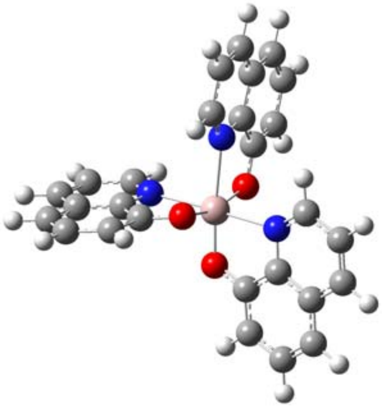
The HOMO, LUMO, E_g (the energy gap between HOMO and LUMO), maximum absorption wavelength (λ_{abs}^{max}), and the relative oscillating strength (*f*) of the Alq3 and its derivatives in the ground state were calculated by using the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) methods, based on the optimized structure by DFT/ B3LYP/6-31G* calculation. All calculated results are in good agreement with the experimental data. The electron donating substituents in the phenoxide site of the *mer*-Alq3 increase the π-delocalization compared with the substituent to the phenoxide side of the quinolinolate ligand. It increases the HOMO energy and caused the λ_{abs}^{max} to be red-shifted related to that of *mer*-Alq3-Ph. The electron withdrawing substituents in the pyridine site of the *mer*-Alq3 increase the π-delocalization in the pyridine site to the quinolinolate ligand also. This calculated results showed that the calculated LUMO energy and the λ_{abs}^{max} are enhanced significantly compared with other *mer*-Alq3 derivatives.



Keywords: HOMO, LUMO, TD-DFT.

The cooperative effect of the hydrogen-bonded chains in the environment of a $\pi \rightarrow \pi^*$ chromophore

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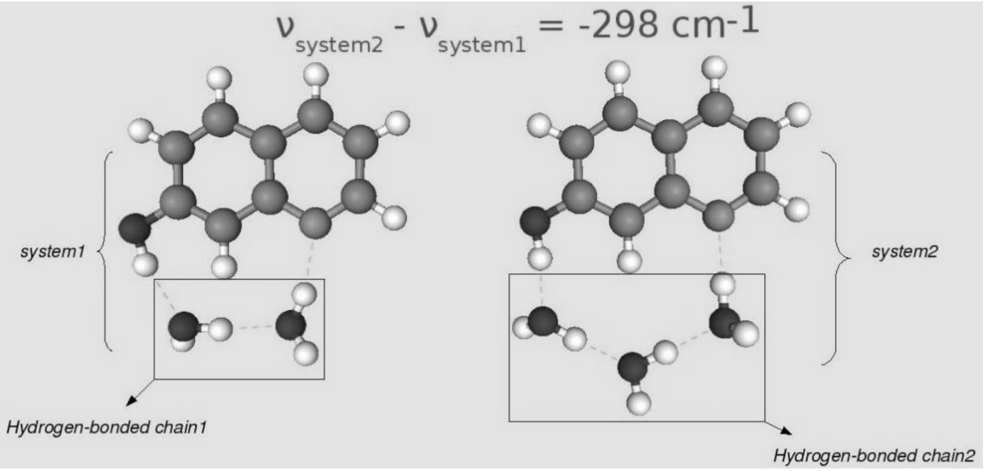
Laser resonant two-photon ionization UV spectra provide clear evidence that the effect of increasing the length of the hydrogen-bonded chain consisting of such molecules as NH_3, H_2O, or CH_3OH bound to the chromophore on the $\pi \rightarrow \pi^*$ excitations of 7-hydroxyquinoline (cis-7HQ) is strongly cooperative [1]. A theoretical analysis of the experimental data usinge the orbital-free embedding formalism [2] is provided to identify the origin of this cooperativity for four chains.

It is concluded, that the electronic coupling between the molecules at the ends of the chain, which are hydrogen bonded to cis-7HQ, rather than changes of the geometry lies at the origin of this cooperativity.



Keywords: electronic excitations, orbital free embedding, Linear-Response Time-Dependent DFT

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Theoretical and experimental study of the vertical excitation energies of ionic and tautomeric forms of pyridoxamine analogues

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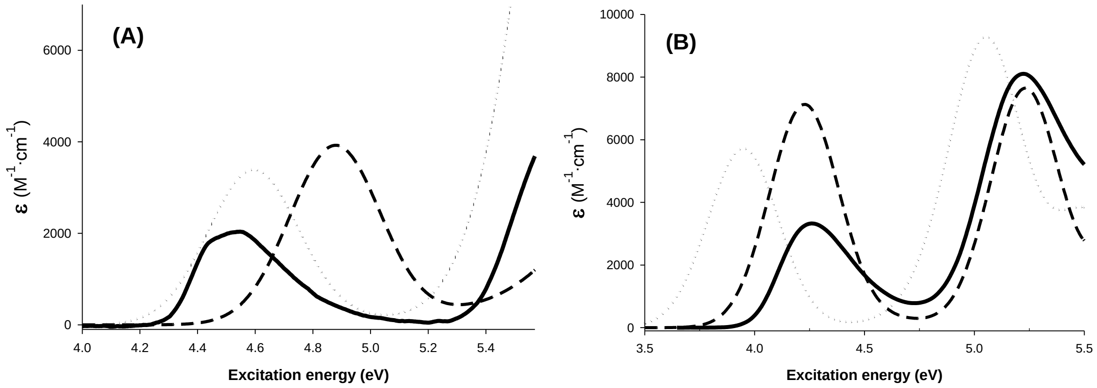
One of the most important B_6 vitamers is pyridoxamine, which is involved in the enzymatic transamination of aminoacids [1] and deemed a potent inhibitor of protein glycation [2]. Despite its significance, little quantitative information about its tautomeric equilibria and the electronic properties of its minor tautomers is still available. The energy of its first π–π^* transition has been determined from changes with the polarity of the medium [3] and photo-induced processes [4].

Spectral deconvolution has proved especially useful for examining molecular systems consisting of inseparable compounds such as tautomers and ionic species in equilibrium but it can be complemented with theoretical calculations.

In this work, we determined the electronic excitation energies of the different molecular species of two pyridoxamine analogues: 4-aminomethylpyridine (4-PAM) and 2-hydroxybenzylamine (2-BNZ). These electronic excitation energies for each molecular species were calculated with the PCM–TD-DFT method on the optimized lowest-energy structures in their ground electronic state. The theoretical results thus obtained were highly consistent with the experimental electronic excitation energies as determined from the deconvoluted UV/Vis spectrum for each ionic form, which facilitated their use as starting parameters for spectral deconvolution. The HCTH functional was found to accurately reproduce electronic excitations in the cationic species and neutral tautomers, and the B3LYP functional to provide accurate predictions of the transitions for the anionic species and zwitterionic tautomers.



Experimental (——) and theoretical [PCM-TD-HCTH/aug-cc-PVDZ (······) and PCM-TD-B3LYP/aug-cc-PVDZ (— — —)] UV/Vis spectrum of H_2B^+ (left) and B^- (right) forms of 2-BNZ.

Keywords: TD-DFT, pyridoxamine, deconvolution UV/Vis

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Hybrid time-dependent MCSCF-DFT linear response based on range separation

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Nowadays, linear response Time-Dependent Density-Functional Theory (TD-DFT) is widely used within the adiabatic approximation for describing excited states properties, because it normally produces useful results at a relatively cheap computational cost, and thus enables the investigation of large molecular systems. However, even though current standard approximate functionals in many cases provide a satisfactory description of the short-range dynamic correlation (Coulomb hole) [1], long-range static correlation effects (strong multiconfigurational character of the wave function) are not treated adequately. In addition, standard linear response TD-DFT usually fails in describing doubly-excited states and Rydberg states. On the other hand, static correlation effects can be described by the linear response Time-Dependent Multi-Configurational Self-Consistent Field (TD-MCSCF) approach but the description of the dynamic correlation requires then a long configuration expansion of the wave function as well as large basis sets, thus preventing large scale calculations. It is therefore of interest to develop a hybrid TD-MCSCF-DFT linear response model which combines the best of both TD-MCSCF and TD-DFT linear response approaches with respect to accuracy and computational cost. This can be achieved rigorously by separating the regular two-electron Coulomb interaction into long-range and short-range parts, as initially proposed by Savin [1]. In this approach, referred to as TD-MCSCF-short-range-DFT (TD-MCSCF-srDFT), the long-range interaction is treated within the MCSCF model and the short-range interaction in DFT (like in the static MCSCF-srDFT model [2]). We will first introduce the linear response TD-MCSCF-srDFT equations using the quasi-energy formalism [3,4] (Floquet theory), present their implementation in a development version of the `DALTON` program package [5], and finally give preliminary results.

Keywords: response theory, multiconfigurational DFT, range separation.

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A Systematic study of TDDFT performance in the detemination of excited state geometry and properties

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Ab initio methods in quantum chemistry allow to calculate many different properties of molecular systems in their ground state. Instead, calculations of emission phenomena, such as fluorescence and phosphorescence, are still a challenge, as they require an accurate determination of excited state structures, which are very difficult to obtain. Our aim is to present a sistematic study on optimization of excited state structures and the following fluorescence, using a large number of chromophores of different type (coumarins, antraquinones, acroleine, azobenzene, dimetilaniline, push pull chromophores) . To this scope we analyze the performance of different DFT exchange-correlation functionals. In fact, till today, there are many sistematic studies concerning the TDDFT performance in reproducing excitation energies and absorption spectra, but not in optimization geometry of ground and excited states and correlated properties (dipole moments and transition dipole moments or emission wavelenghts).

Previous studies on the UV-vis absorption spectra have shown that the local density approximation (LDA) tends to strongly underestimate valence excitation energies of most organic molecules, whereas better performances are obtained with the generalized gradient approximations (GGAs) or with meta-GGA approaches. The most accurate values are usually predicted by hybrid functionals, which explicitly include a fraction of HF exchange. Three different families of hybrid functionals can be defined. The first is composed by global hybrids (GHs), in which the percentage of HF exchange is constant at each point in space. To the second family belong the local hybrids (LHs), characterized by a mixing of HF exchange that depends on the spatial electronic coordinate. Finally, range-separated hybrids (RSHs) use a growing fraction of exact exchange as the interelectronic distance increases, giving a long-range correction (LC) to the original DFT scheme. We will mainly focus on the most widespread GHs and LC, with different percentage of HF exchange, such as B3LYP[1] , PBE0[2] , BHandHLYP[1], B3P86[3], BMK[4], CAM-B3LYP[5] and many others. We will also couple these studies with the effect of the basis set, and therefore compare these methods with high correlated, such as CAS, SAC-CI and CC methods or experimental results, where avaible.

Keywords: TDDFT, excited state geometries and properties

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13th Intern. Conf. on the Applic. of Density Functional Theory in
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Core-level spectroscopy using time-dependent DFT methods: Application to NEXAFS spectra of metalloporphyrins

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This contribution deals with the computation of core-level spectra using density-functional methods, in particular time-dependent density functional methods. Core-level spectroscopies such as the NEXAFS method are important experimental tools in surface science, although the interpretation of such spectra is not always straightforward without support from theory. The reliable computation of such spectra, however, is not as simple as for UV/Vis spectra using density-functional methods.

It is known since quite some time that core excitation energies computed with TDDFT and conventional (GGA type) functionals are usually off the experimental excitation energies by several eV. At first sight this failure might come as a surprise because the same functionals tend to perform well for UV/Vis spectra. It is now well understood that this problem is due to the poor match of core orbital energies with true core ionization energies in combination with the failure of LDA or GGA exchange-correlation kernels to account for relaxation effects. In this contribution we show that an adiabatic exact-exchange kernel derived from a local exact-exchange potential, as recently implemented by Hesselmann and Görling, can provide relaxation shifts to the exact-exchange orbitals which are large enough to obtain qualitatively correct core excitation energies within a proper TDDFT framework.

Another, more pragmatic yet simple way is to "correct" the orbital energies by using standard hybrid functionals which include nonlocal Hartree-Fock exchange. We show that the well-known BHandHLYP functional proves useful for the interpretation of NEXAFS spectra. By applying a simple selection scheme we show that NEXAFS spectra can be computed at the same effort as usual valence excitation spectra.

Keywords: time-dependent DFT, spectroscopy, NEXAFS, transition metal complexes

Double-excitations in Time-Dependent Density-Functional Theory for molecular systems

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Time-Dependent Density Functional Theory (TDDFT) has shown impressive results for the simulation of spectroscopic properties of molecules and solids. After its formulation for molecules in the so-called Casida equations [1], numerous applications have appeared simulating successfully optical spectra, circular diachroism, and NMR shifts. However, the fact that Casida's formulation only includes single-excitations, offers wrong qualitative results in situations that are largely influenced by double- and higher-excitations [2,3]. Those situations are very common in photochemistry, including photoinduced bond-breakings and the photochemistry of open-shell systems and biradicals. The need for a theory that can handle these situations and is affordable for large molecular systems is obvious.

The problem of double-excitations in TDDFT has not been formally understood until recently. Maitra *et al.* showed that a frequency-dependent exchange-correlation kernel permits the construction of a suceptibility with poles at the double-excitations transition energies [4]. Casida generalized the idea by using a Green's function approach [5]. In the context of solid-state physics, by making use of a GW self-energy and the Bethe-Salpeter equation, frequency-dependent exchange-correlation kernels have been constructed [6,7]. For molecules, the procedure has been based on the time-dependent analogues of the OEP equations. Especially interesting is the frequency-dependent exact exchange-only kernel of Görling [8].

In this poster, we present the equations for constructing a OEP-based frequency-dependent exchange-correlation kernel from perturbative Green's function approaches. The Superoperator Polarization Propagator Approach (SOPPA) [9] and the Algebraic Diagramatic Construction [10]. The two methods have been shown to take into account the interaction between the ground-state, single- and double-excitations in a balanced way. We present the SOPPA and ADC formalism within the KS framework that can be implemented to account for double-excitations in TDDFT.

Acknowledgements: MHR acknowledges funding from the French Ministry of Education.

Keywords: Time-Dependent Density Functional Theory, Double-Excitations, Polarization Propagator, Green's functions approach, frequency-dependent exchange-correlation kernel

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Charge-transfer excitation energies with TDDFT-EXX method

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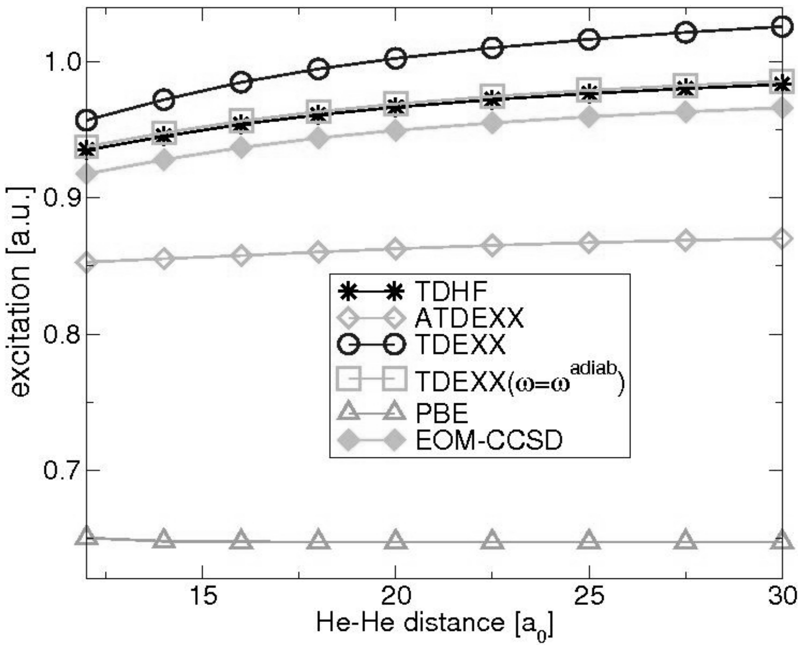
A new time-dependent density functional theory (TDDFT) method with exact-exchange kernel is proposed. In comparison with the present orbital-dependent TDDFT methods the presented approach does not require a numerical unstable inversion of Kohn-Sham response function. The proposed method in combination with frequency-dependent exact-exchange kernel provides the qualitatively correct long-range behavior of charge-transfer (CT) excitation energies. The results of the CT excitation energies for the systems of HeH^+ [1] and He_2 are presented. In the latter case the results of calculations performed with frequency-dependent TDDFT kernel revealed the good agreement with TDHF approach, providing the proper long-range asymptotic of the CT excitation energies. In the case of the simple two-electron system of HeH^+ it was shown that the KS eigen value difference is essential for the behavior of the excitation energies and importance of exchange-correlation potential in the KS calculations can be crucial.



Keywords: TDDFT, exchange, kernel

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An investigation of the electronic excitation spectra of photoenolizable quinoline derivatives

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A correct description of the absorption spectra of 3-benzoyl-2-benzyl-1-methyl-1H-quinolin-4-one (QC1), 3-benzoyl-1,2-dibenzyl-1H-1,8 naphtyridin-4-one (QC18A) and 3-benzoyl-1-benzyl-2-methyl-1H-1,8-naphtyridin-4-one (QC18B) is a prerequisite for a meaningful investigation of the photochromism and photoenolizability of these compounds [1]. In this study, we thus advocate a general strategy to investigate electronic excitation spectra of medium-sized molecules.

In order to identify a reliable exchange-correlation functional with time dependent density functional theory (TDDFT), the above mentioned molecules have been stripped to their essential part (QC0), which is small enough for their excited states to be computed employing approximate coupled cluster-based methods (RI-CC2) and the second order algebraic diagrammatic construction scheme (ADC(2)). This is important for comparison since TDDFT is known to have difficulties with states exhibiting double excitation or charge-transfer (CT) character. For locally excited states energetically well below the ionization potential (e.g. $\pi\pi^*$ or $n\pi^*$ transitions), on the contrary, TDDFT provides high-quality results. Additionally, we suggest three different functionals with a varying amount of Hartree-Fock exchange, e.g. 0% (BLYP), 20% (B3LYP) and 50% (BHLYP), to be used to evaluate the extent of charge-transfer failure and thus the expected quality of the TDDFT results.

Following this procedure for the study of the excited state spectra of QC1, QC18A and QC18B [2], the B3LYP functional has been chosen. Electron attachment and detachment densities have been considered and the lowest singlet and triplet excited states are investigated. Eventually, a suggestion for the photoenolization mechanism of the studied quinoline systems is made based on the results for the model QC0.

Keywords: photochromism, absorption, time dependent density functional theory

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Design of new ZnO based DSSC using a DFT and TD-DFT methods: a combined molecular and periodic approach

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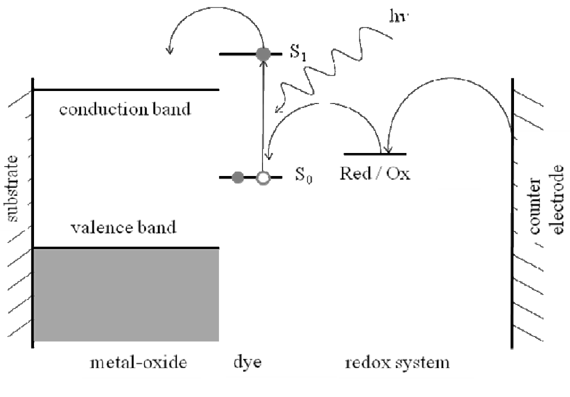
The last century saw developments of many ways for converting solar energy to electricity. The most well-known method is based on the electron-hole formation in an n-p junction of silicium. More recently (1999 [1]), Grätzel and coll. proposed a new concept of solar cells, called dye sensitized solar cells (DSSC) which presently yield an overall efficiency of 11.2%. DSSC are made of a dye (ex. a Ru complex or a fully organic dye such as eosin), adsorbed on a surface of a wide bandgap semidonfuctor (ex. TiO_2 or ZnO), in contact with an electrolyte (ex. I_3^-/I^-) and closed by a counter electrode (ex. Pt). At the excited state, because of light absorption, the dye can inject an electron in the conduction band of the metal-oxide. The electrons are collected at the back of this photo-electrode. The resulting oxidized dye is reduced by a reducing agent present in the electrolyte (ex: I^-), this latter being regenerated at the counter electrode.

Zinc oxide appears to be a good support for the dye adsorption because of its large band gap (3.3-3.4 eV) and its good electronic conductivity. Moreover, it can be directly electrodeposited with a high cristallinity and a high specific area [2]. The highest overall conversion efficiency (5.6 %) using ZnO based DSSC was obtained by Yoshida et al, with a metal free indoline dye, the so-called D149 [3].

Theoretical investigations have been performed on such ZnO based systems in order to optimize the conversion efficiency. A molecular approach (DFT and TD-DFT) was used to study the properties of the isolated dye [4] and a periodic approach was performed to investigate the interaction between the adsorbed molecules and the metal-oxide surface [5] with the aim of better understanding the leading interactions ruling these solar cells macroscopic behavior.



Schematic representation of DSSC working principle

Keywords: DSSC, TD-DFT, ZnO

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Solvation Effects on the Optical Properties of Crystal Violet

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We present a joint experimental and theoretical study of the photoabsorption and photodissociation behavior of crystal violet (CV), that is, the tris[p-(dimethylamino)phenyl]methyl cation (see Fig. 1, Left) [1]. The photodissociation spectra of isolated and microsolvated crystal violet have been measured. A single band is observed for the bare cation (see Fig. 1, Right). This is in good agreement with the calculated vibronic absorption spectrum based on time-dependent density functional theory (TDDFT) calculations. The interaction of crystal violet with a single water molecule shifts and broadens the photodissociation spectrum, so that it approaches the spectrum obtained in solution. Theoretical calculations of the structure of the complex suggest that the shift in the absorption spectrum originates from a water molecule bonding with the central carbon atom of crystal violet. Beyond a crystal violet complexed with a single molecule, crystal violet among liquid water was also simulated using a QM/MM approach, where the crystal violet is studied using TDDFT and the water molecules are represented with point charges. The splitting of the absorption band observed within such a theoretical model agrees with the experimental observations.

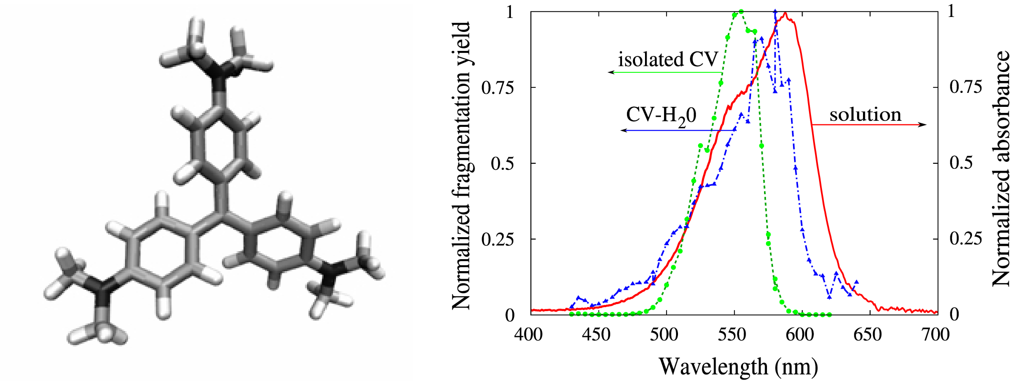

Figure 1: **Left**: Octopolar propellor shape of the crystal violet (carbon in grey, nitrogen in black and hydrogen in white). **Right**: Experimental UV absorption spectra of crystal violet in aqueous solution (red solid line), compared to the photoinduced fragmentation yield of the molecule in the gas phase, either isolated (green dashed line with dots) or complexed with a single water molecule(blue dashed line with triangles).

Keywords: Microsolvation, Photodissociation, Time-Dependent Density Functional Theory, Octopolar molecule, Crystal violet

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Behaviour of Conical Intersections within Noncollinear Spin-Flip Time-Dependent Density-Functional Theory: Oxirane as Test Case

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The ground and excited states of a molecule with N internal degress of freedom are often described by N-dimensional potential energy (hyper)surfaces (PESs) in an $(N+1)$-dimensional hyperspace. Rather than simply crossing to form an $(N-1)$-dimensional hyperline, configuration interaction arguments indicate that two PESs should cross in an $(N-2)$-dimensional hyperpoint, known as a conical intersection (CX). Such intersections play an important role in understanding certain spectroscopic features and are now also believed to play a role for photochemical reactions similar to that played by transition states in thermal reactions. Thus theoretical investigation of CXs is important for shedding light on the aforementionned phenomena. These typically use multireference methods. However CXs should, in principle, also be accessible through single-reference time-dependent density-functional theory (TDDFT) calculations provided the exchange-correlation (xc) functional is sufficiently exact. The ability of TDDFT with practical approximate xc functionals to describe CXs has been questionned by Levine *et al*. [**?**] While their argument is basically correct, an *approximate* CX was readily found in TDDFT investigations of oxirane photochemistry.[**?**]The absence of an *exact* CX in conventional TDDFT calculations is nevertheless disturbing and variants which should produce an *exact* CX are worth investigating. One such approach is the noncollinear spin-flip TDDFT (SF-TDDFT) proposed by Wang and Ziegler. [**?**] Calculations were carried out for oxirane in the neighborhood of an important CX obtained from complete active space self-consistent field (CASSCF) calculations using SF-TDDFT as implemented in the DEMON2K program [**?**] and were compared against the CASSCF, as well as the previous configuration interaction singles (CIS) and TDDFT, surfaces. A true CX does indeed seem to be present in SF-TDDFT, albeit shifted from the CASSCF CX. Implementation of analytic gradients for excited-state surfaces as well as CX search routines will be necessary for a more detailed investigation.

Keywords: conical intersection, potential energy surface, SF-TDLDA/TDA, analytic gradient

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Analytical Energy Gradient of Coulomb-attenuated Time-Dependent Density Functional Methods for Excited State

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We present an implementation and validation of the analytical energy gradient of time-dependent density functional theory (TDDFT) using coulomb attenuated (CA) functionals[1] for excited state energies, dipole moments, geometries, and vibrational frequencies. The CA-TDDFT gradient is based on previous long-range corrected (LC) TDDFT of Chiba et al.[2] and the Z-vector formalism of Furche and Ahrichs.[3] Geometry optimzation using CA-TDDFT was carried out for molecules (substituted stilbenes and coumarins) having intramolecular charge transfer (CT) excited states and for a series of small molecules (CO, HCN, CH_2O, CH_2S, CCl_2, C_2H_2, *trans*-$(CHO)_2$). We assess the results of the CA functionals, the long-range corrected LC-BLYP functional, and the B3LYP hybrid functional, by comparing to accurate experimental data. The results highlight the applicabilty of different functionals for excited state properties.

Keywords: TDDFT, gradient, long-range corrected functional, coulomb attenuated functional, quadratic response

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Environmental effects on the UV spectra of H-BQPTH$_2$-Ph$^+$: A TD-DFT study

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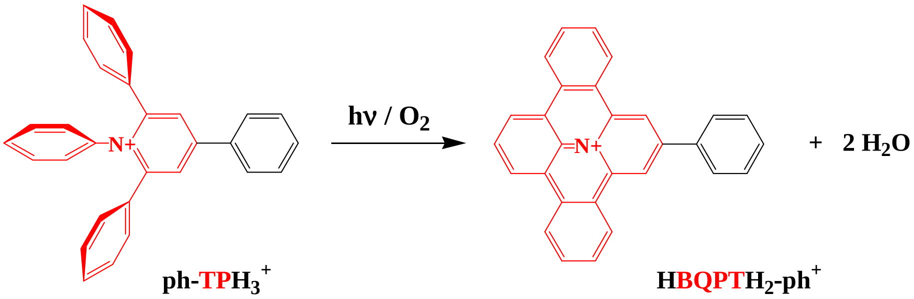
With the aim of designing new Photochemical Molecular Devices (PMDs), able to display a target photochemical behavior, a series of systems containing transition metal ions (Os(II) and Ru(II)) have been recently studied [1]. Basically, the topology adopted for these novel PMDs derives from that of acceptor dyads (**P–A**) devised to produce charge separated states (CS) upon light excitation in the framework of researches devoted to artificial photosynthesis.
These supermolecules are comprising the following functional elements:

- **P**: the photosensitizer unit, here a Ru(II) or Os(II) complex;
- **A**: an electron(s)-accepting unit which traps the electron promoted from ***P**.

In this case, we have developed the use of monocationic triarylpiridinium group (ph-TPH$_3^+$) as acceptor component (**A**). We are now interested in the *fused* derivatives of these polyaryl-pyridiniums (HBQPTH$_2$-ph$^+$) which have studied by the means of the Density Functional Theory and the Time-Dependent DFT. The computed data are compared with the available experimental results.



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Elaboration of a theoretical procedure for the colour prediction of carbonyl dyes

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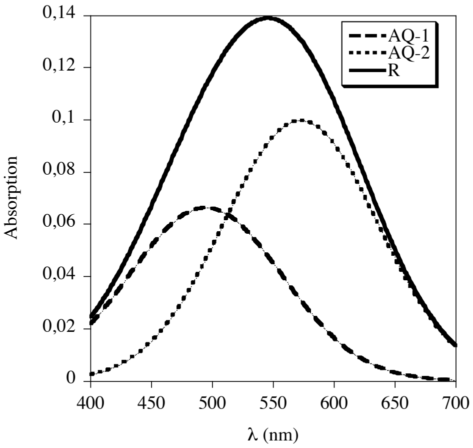
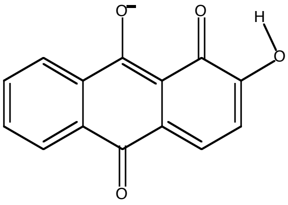
We have elaborated a theoretical procedure that allows a fast evaluation of the colour of carbonyl derivated dyes. Quantum chemistry approaches and, in particular, the density functional and the time dependent density functional theories [1] have been used in order to take into account both the solvation and the pH effects on the position of the absorption band of maximal intensity in the UV/VIS region of the electromagnetic spectrum. More precisely we here present the results obtained for the anthraquinone derivatives, and it turns out that : (i) B3LYP [2] and PBE0 [3] are the more reliable hybrids for the transition energy calculations, (ii) the basis set required in order to reach converged values of excitation energies are significantly extended, (iii) the solvent effects are huge and consequently have to be taken into account, (iv) a statistical treatment of our results via a simple or multi-linear regression allows to improve the accuracy of the procedure [4-6]. Finally, we have extended our procedure to the investigation of the impact of tautomers on the absorption spectra of neutral and anionic alizarin and quinizarin dyes, for which our approach is able to predict an excitation energy with an accuracy of 0.08 eV [7].





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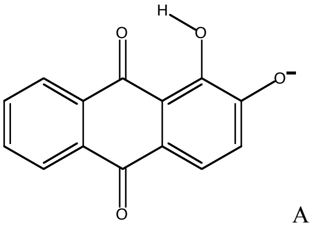

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Keywords: TDDFT, colour, carbonyl dyes

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Dynamical hierarchical methods for the irradiation of clusters and molecules in contact with an environment

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We present a hierarchical approach for the description of the dynamics of clusters or molecules in contact with an environment. Typical applications of this formalism concern the deposit of metal clusters on inert surfaces, the response of an embedded cluster to a intense short laser pulse or the irradiation by ions of molecules of biological interest.

We treat the cluster/molecule by means of explicit time dependent Density Functional Theory (DFT) for the electrons, classical molecular dynamics for the cluster's ions and we use a classical treatment of matrix/environment constituents (including an account of dynamical polarizabilities of the constituents of the environment). Such an approach bears some similarities with standard QM/MM (Quantum Mechanics/Molecular Mechanics) methods of quantum chemistry used in the context of biological systems, but now with an explicit time dependent account of the polarizabilities of the constituents of the environment, which is a crucial aspect in truly dynamical scenarios.

We apply this modelling to gentle situations (soft deposition) and to more violent scenarios (hindered Coulomb explosion of embedded clusters) following both electronic, ionic (cluster) and atomic degrees of freedom explicitely. We also consider the case of the irradiation of small organic molecules as uracyl to a bypassing ion.

The deposition cases show the influence of net charges in the capability of the cluster to strongly attach to the surface. We discuss the possibility to observe, as a dynamical process, the sticking or the inclusion of single Na in Ar substrate. Effects of Na charge, initial kinetic energy given to the Na and size of the Ar substrate are explored. We show that neutral Na sticks or is reflected on the Ar surface, while Na^+ always penetrates the Ar substrate.

The case of short and intense laser excitation of embedded clusters allows to explore various (possibly violent) dynamical scenarios. We discuss microscopic mechanisms of laser induced dynamics, taking as test case $Na_8@Ar_{434}$. We analyze both electronic, ionic (cluster ions) and atomic (matrix atoms, matrix polarizability) dynamics and show how the matrix accommodates the, initially electronic, excitation of the embedded metal cluster which acts under such conditions as a chromophore. We discuss the results in relation to recent experiments dedicated to shaping of embedded metal clusters.

Both situations (gentle deposition, violent irradiation) show the crucial importance of a proper inclusion of electronic degrees of freedom in this demanding domain of embedded/deposited clusters. To the best of our knowledge, such a modelling including a non adiabatic treatment of electrons is the first theoretical attempt to account for such intrincate scenarios.

The extension of the above desscribed formalism to the case of irradiated organic molecules reveals intriguing difficulties on the time dependent treatment of the self interaction corrections to be included in the DFT approach. This is compulsory to attain acceptable ionization potentials and thus develop a proper access to low energy irradiation phenomena. We propose a method to overcome such difficulties. Examples of applications are presented on small model molecules.

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A Computational Study of the Absorption Spectra of Formazans

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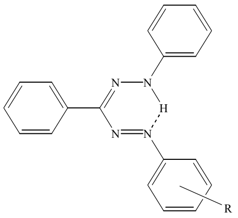
In general, formazans are focus of much interest in organic and medicinal chemistry because of their biochemical usefulness. Some related molecules which penetrate various plant and animal tissues react with enzymes to form formazans. And these molecules produce a colored stain. This effect was investigated by considering that formazans might be important in view of their use in the determination of activity of tumor cell [1,2], and the evalution of the cytotoxicity of several compounds [3].

The molecular and electronic structure of formazans has attracted considerable experimental interest [4-6]. As a predictive tool for structure properties, molecular modelization techniques allow a solution for the interpretation of experimental data. For the calculation of electronic structures of large molecules, the most widely used method is density functional theory (DFT). In recent years, time-dependent density functional theory (TD-DFT) [7],which is the extended form of DFT to excited states, has become the method used for theoretically evaluating excited state geometries and energies.A limited numbers of DFT and TD-DFT investigations have been carried out on formazans[8,9].

The present work aims describing the synthesis, comparing the results of computational study and experimental UV-visible spectroscopic properties on a series of formazans CH_3, Br, and Cl as substituent.



R: $-CH_3$, -Br, -Cl

By using PBE1PBE functional with the 6-311G(2d,2p) basis set, the agreement between experiment and theory is excellent for formazans.

Keywords: Formazans, spectroscopy, DFT, TD_DFT

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Quantum Chemical Studies on the Structures of Some Heterocyclic Azo Disperse Dyes

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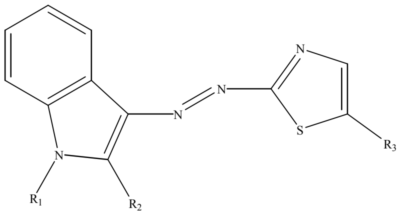
It has been known for many years that azo compounds are the most widely used dyes in various fields such as the dyeing of textile fiber, the coloring of different materials, biological-medical studies and advanced applications in organic synthesis [1]. The prediction of molecular and spectroscopic properties of dye molecules is an important part in the designing process. One of the most widely used methods to calculate ground-state geometries in computational chemistry is the DFT [2]. The extension of DFT to excited states is known as TD-DFT method and has been used to describe optical and spectroscopic properties of the medium size and large molecules [3].

In the present work, we have attempted to determine and evaluate the optimized structural parameters, the λ_{max} in UV-vis spectra of the following hetarylazoindole dyes using DFT and TD-DFT methods, and possible correlations were searched between experimental and computational data.



I

1. $R_1 = H, R_2 = Ph, R_3 = H$
2. $R_1 = H, R_2 = Ph, R_3 = CH_3$
3. $R_1 = H, R_2 = Ph, R_3 = NO_2$

4. $R_1 = CH_3, R_2 = Ph, R_3 = H$
5. $R_1 = CH_3, R_2 = Ph, R_3 = CH_3$
6. $R_1 = CH_3, R_2 = Ph, R_3 = NO_2$

II

7. $R_1 = H, R_2 = CH_3, R_3 = H$
8. $R_1 = H, R_2 = R_3 = CH_3$
9. $R_1 = H, R_2 = CH_3, R_3 = NO_2$

10. $R_1 = CH_3, R_2 = CH_3, R_3 = H$
11. $R_1 = CH_3, R_2 = R_3 = CH_3$
12. $R_1 = CH_3, R_2 = CH_3, R_3 = NO_2$

The agreement between the calculated and experimental maximum absorption wavelengths is excellent. In addition, it can be suggested that TD-DFT method is a valuable method in the prediction of the excitation states for this type of compounds.

Keywords: Heterocyclic azo disperse dye; DFT; TD_DFT; UV-vis

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DFT Excited States: Predicting Failures and Improving Accuracy

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For GGA and hybrid functionals, we have demonstrated [1] a broad correlation between TDDFT excitation energy error and the degree of spatial overlap between the occupied and virtual orbitals involved in the excitation. We used this to propose a diagnostic test for identifying problematic charge-transfer (CT) excitations: when the overlap drops below a prescribed threshold, the excitations become unreliable. We have also demonstrated that the correlation is essentially eliminated using Coulomb-attenuated functionals, yielding significantly improved CT excitations.

In the present work, we apply these ideas to a series of triazene chromophores [2] and extend them to the study of excited state potential energy surfaces.

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Physical signatures of discontinuities of the time-dependent exchange-correlation potential

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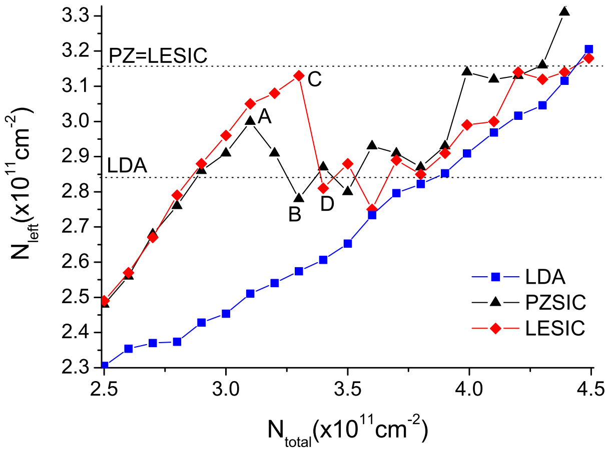
The effect of two different self-interaction corrections (PZSIC [1] and LESIC [2]) is investigated for doped semiconductor quantum wells. The exact exchange-correlation potential in time-dependent density-functional theory is known to develop steps and discontinuities upon change of the particle number in spatially confined regions or isolated subsystems [3, 4]. Here we demonstrate that the self-interaction corrected adiabatic local-density approximation for the exchange-correlation potential has this property, using the example of electron loss of a model semiconductor quantum well system in the effective-mass approximation. We then study the influence of the exchange-correlation potential discontinuity in a real-time simulation of a dissociation process of an asymmetric double quantum well system, and show that it dramatically affects the population of the resulting isolated single quantum wells. This indicates the importance of a proper account of the discontinuities in time-dependent density-functional theory descriptions of ionization, dissociation or charge transfer processes [5].



Keywords: time-dependent density-functional theory, exchange-correlation potential discontinuity, self-interaction correction

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POSTER PRESENTATIONS

Topic 6.

Catalysis, reactivity and surface properties

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Exploring 1,2-Hydrogen Shift in Silicon Nanoparticles with G3//B3LYP: Application of Transition State Group Additivity

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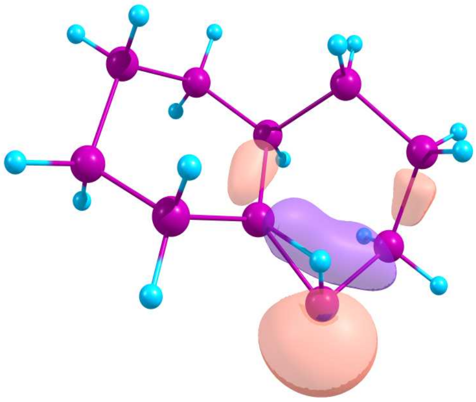
Chemical vapor deposition is an important method by which semiconductors are formed industrially. Pyrolysis of the feed gas, typically SiH_4 or Si_2H_6, at low pressures is the standard protocol for the formation of polycrystalline silicon. Polymerization of silicon hydrides in the gas phase causes deposits on the growing semiconductor surface forming point defects. Optimizing reactor design and process conditions plays a key role in the control of nanoparticle formation. A clear understanding of the routes to polymerization will also allow for the control of technologies where nanoparticles are intentionally formed. These technologies create tailored nanoparticles for optoelectronic and biophotonic applications in which the size and crystallinity of the particles play integral roles.

One reaction family that is important in silane pyrolysis is silylene-silene isomerization, or 1,2-hydrogen shift. Accurate rate constants for 35 silylene-silene isomerizations have been calculated using G3//B3LYP [1] with geometries and frequencies from B3LYP/6-31G(d). This family was explored with hydrides containing up to 10 silicon atoms, and the reactions exhibit a double barrier, which has been confirmed experimentally [2]. The first barrier includes the formation of a hydrogen-bridged intermediate species from a divalent silylene with low activation energy. The second barrier (see image) converts this stable intermediate into the π-bonded silene.



Benson's group additivity model was applied to predict the pre-exponential factor A and activation energy E_a for the 1,2-hydrogen shift in silicon hydrides. The transition state group additivity (TSGA) model, previously applied to the pyrolysis of hydrocarbons [3], predicts rate constants with superior accuracy compared to the Evans-Polanyi structure/reactivity relationship for E_a and A, which is the approach that is currently used in the development of detailed kinetic models of silane pyrolysis. The TSGA method possesses several advantages that should interest kineticists seeking parameters for the 1,2-hydrogen shift in silicon hydrides. This method requires a number of parameters similar to that of the Evans-Polanyi structure/reactivity relationship, but (1) allows one to gain insight into the conformational changes in the reactive center during reaction, (2) can be implemented into an automated network generation model, and (3) circumvents the need to calculate accurate enthalpies of reaction as required for the Evans-Polanyi structure/reactivity relationship. The structure of the reactants for a given reaction family is all that is required to allow accurate kinetic parameter estimation.

Keywords: kinetics, silicon hydrides, hydrogen shift, group additivity

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Origins of the Enantioselectivity in Cinchona Alkaloid Catalyzed [1,3]-Sigmatropic Rearrangements

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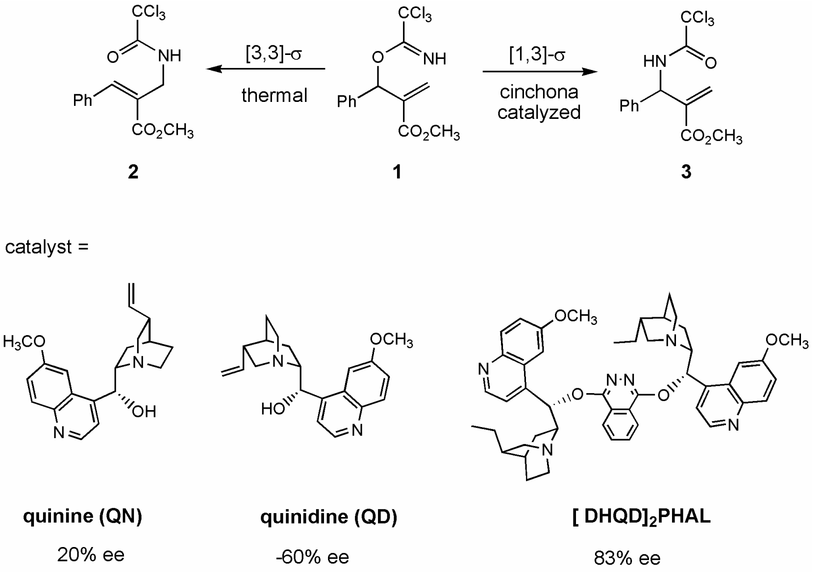
Cinchona alkaloids have found extensive use in organic chemistry as organocatalysts in asymmetric synthesis. They hold the advantage of being natural products possessing a binding site that can selectively catalyze many organic transformations leading to products of biological interest.[1-2] Despite the large number of reports on the use of cinchona alkaloids as organocatalysts, the origins of the enantioselective catalytic activity of most of the cinchona alkaloid derivatives remain unexplored. In this study, Density Functional Theory is used to investigate the [1,3]- and [3,3]-sigmatropic rearrangements of *O*-allylic trichloroacetimidates to trichloroacetamides in the presence of cinchona alkaloids. The [1,3]-sigmatropic rearrangement is catalyzed via an S_N2' mechanism and is favored by 6.0 kcal/mol free energy difference as compared to the alternative [3,3]-sigmatropic rearrangement. The presence of H-bonding between the catalyst and the substrate determine the stereochemistry of the reaction.



2 1 3

quinine (QN) 20% ee

quinidine (QD) -60% ee

[DHQD]$_2$PHAL 83% ee

Keywords: chinchona alkaloid, stereoselectivity, [1,3]-sigmatropic rearrangement

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A DFT study and structural characterization of a novel aryl ether trimer

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Abstract : in this work, we study the reaction between 4-tert-Butyl-methoxybenzene **1** and 2,2'-dimethoxy-5,5'-di-tert-butylbiphenyl **2** (Fig1). Based on various calculation methods such as SCF/6-31G* and DFT/B3LYP with the 6-31G*standard basis set, we discuss from a thermodynamic point view the possibility and the stereoselectivity of these reactions. In order to determine the reliability calculation methods in treatment of this system type, we optimized the geometry of 1-methoxy-bis-2,3-(2'-methoxy-5'-tert-butylphenyl)-4-tert-butylbenzene **3a**. Keeping in mind the stereochemistry of molecule **3a**, we compared our theoretical results with X-ray experimental data [1]. Results show that the DFT/B3LYP with basis set 6-31G* is more reliable with this system type.

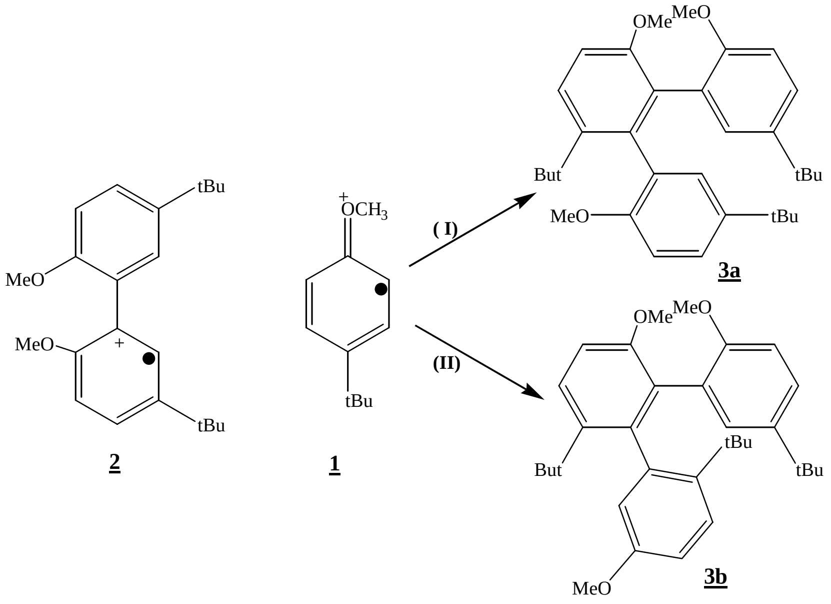

Fig1

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Dinuclear Dicyclopentadienyl Titanium Complexes

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The design of ligands to generate bimetallic systems has been developed with the aim of finding reactivity patterns different from those observed for similar monometallic complexes[1]: cooperative effects between the metal atoms in group 4 dinuclear complexes have been shown to induce new and important modifications in polymerization behavior compared to mononuclear systems.[2] Reaction of compound $[(\mathrm{TiCl_2})_2(\mu\text{-}\{(\eta^5\text{-}\mathrm{C_5Me_4SiMeO})_2(\mu\text{-}\mathrm{O})\})]$ with 2 eq of TlCp at 80ºC afforded $[(\mathrm{TiClCp})_2(\mu\text{-}\{(\eta^5\text{-}\mathrm{C_5Me_4SiMeO})_2(\mu\text{-}\mathrm{O})\})]$ (**2as**) as the unique reaction product out of three possible products**,** where a and s are referred to the different position the Cp ligands can take with respect to the Si-O-Si bridge (*anti* or *syn*). Alkylation of isomer **2as** with LiMe gave a mixture of the three possible isomers $[(\mathrm{TiMeCp})_2(\mu\text{-}\{(\eta^5\text{-}\mathrm{C_5Me_4SiMeO})_2(\mu\text{-}\mathrm{O})\})]$ (**3as**, **3ss**, **3aa**) the proportion of which was dependent on the temperature conditions. Isomer **2as** reacted with Lewis acids $\mathrm{E(C_6F_5)_3}$ (E = B, Al) and with $\mathrm{Li[B(C_6F_5)_4]}$ to give the chloro bridged dititanium compounds $[(\mathrm{TiCp})_2(\mu\text{-}\{(\eta^5\text{-}\mathrm{C_5Me_4SiMeO})_2(\mu\text{-}\mathrm{O})\})(\mu\text{-}\mathrm{Cl})][\mathrm{Q}]$ (Q = $\mathrm{ClB(C_6F_5)_3}$, $\mathbf{4^+}$**-B**; $\mathrm{ClAl(C_6F_5)_3}$, $\mathbf{4^+}$**Al**; Q = $\mathrm{B(C_6F_5)_4}$, $\mathbf{4^+}$**-C**) as the unique reaction products. DFT studies were carried out to determine the stability of isomers **2** and **3**, to determine which chlorine atom in compound **2as** was more easily eliminated and also to clarify the transformation of isomer **2as** into the mixture of isomers **3as**, **3ss** and **3aa** during the alkylation reaction.

Keywords: catalysis, dititanium compounds, DFT methods

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A DFT study of the Temperature dependence of the N_2O reaction on $[Fe(\mu\text{-}O)(\mu\text{-}OH)Fe]^+$ in ZSM-5 zeolite

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Fe-ZSM-5 has shown to be a very efficient catalyst not only in the oxidation reaction of alkenes and aromatics using N_2O as oxidant but also in N_2O decomposition reaction. According to several authors, it has been concluded that the common denominator of these two reactions operating on Fe-ZSM-5 is the formation of highly active oxygen atoms called "α-oxygen" or O_{ad}.

$$\mathbf{N_2O == N_2 + O_{ad}}$$

Although extensive experimental and theoretical studies performed over the past few years, there are still controversies concerning the nature of the active sites in particular concerning the nuclearity, the valence state of active iron sites operating under reaction conditions as well as on the rate limiting step[1]. In the present study we report the calculations of the rate constants for the whole catalytic N_2O decomposition on $ZSM\text{-}5^{-}[Fe(\mu\text{-}O)(\mu\text{-}OH)Fe]^+$ binuclear active site through 8 elementary steps, using a DFT approach and a large cluster model [2]. We will show that the catalytic cycle involves a change in the electronic spin state intermediate. Comparison between HS state and antiferromagnetic state of the iron core will be presented. The valence state of the iron species will be discussed for all the reaction steps. The temperature dependence of the reaction mechanism has been considered also. The investigation of the rate constants evidences a switch of one elementary reaction rate at 720 K. This switch corresponds to the dissociation of the second N_2O molecule which becomes the slowest step with temperature increases. We will show how the present DFT study suggests that atomic oxygen species saturating binuclear iron active sites are the most abundant surface intermediates and that O_2 formation is the rate limiting step of the overall catalytic cycle. The temperature dependence of the rate constants explains the experimental transient response curves of N_2O decomposition obtained at various temperatures [3].

Acknowledgements

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Keywords: α-oxygen , N_2O, Fe-ZSM-5, DFT, broken-symmetry, antiferromagnetic, kinetics

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Bias-Exchange Metadynamics for the Study of Organic Reactions

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We show how the combination of Bias Exchange Metadynamics with Car-Parrinello molecular dynamics (CPMD) leads to vast improvements in the study of even the most elementary chemical reactions. Bias Exchange Metadynamics is a recently introduced methodology that allows the fast parallel reconstruction of the free energy of a system in a virtually unlimited number of variables. The value of the method was demonstrated then for the folding of a Triptophane cage miniprotein on the classical potential energy surface. We present new density functional results for the seemingly simple gas phase $CH_3CH_2F + F^- \rightarrow CH_2{=}CH_2 + F^- + HF$ elimination reaction (E2) that were beyond the scope of other methods, and demonstrate a significant speed-up in the computations compared to earlier metadynamics studies.

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Interaction of bromine molecule with carbon nanotube

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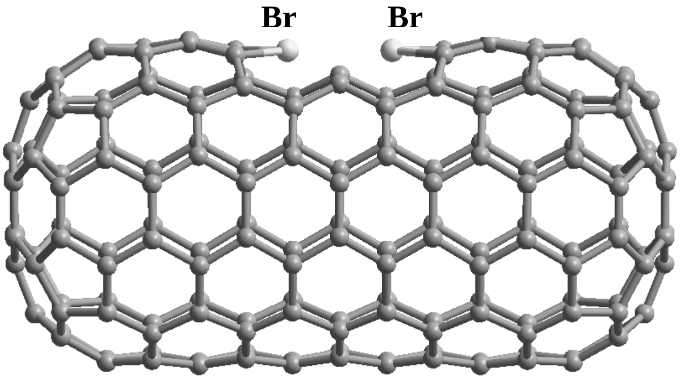
A set of spectroscopic experiments (Raman, x-ray photoelectron, near-edge x-ray absorption fine structure) detected a change in the electronic structure of carbon nanotubes (CNT) after few days holding of sample in bromine vapors. Here we present results of examination of interaction of CNT with bromine molecule within density functional theory (DFT). The calculations have been carried out using a hybrid MPW1K method where the exchange term is a sum of 25% Hartree-Fock exchange interaction and 75% local Slater functional with gradient correction Perdew-Wang 1991 modified by Adamo and Barone and the correlation term is presented by local and non-local Perdew-Wang 1991 GGA II functional. This method was shown to give 1% error in the length of bromine molecule with using of minimal STO-3G basis set. The carbon nanotube was modeled by a fragment of armchair (6,6) tube having 5 hexagons in the length and closed by hemi-spheres at the ends.

Optimization of geometry of a Br2-CNT system found three local energy minima and position of bromine atoms over meta-connected carbon atoms of a hexagon provides the lowest energy of the system. The Br-C distance was calculated to be equal 3.2 Å that indicates the physical sorption of bromine molecule on the surface of ideal CNT. However, approaching of bromine molecule to an atomic vacancy led to spontaneous broken of Br-Br bond and attachment of bromine atoms to the carbon ones constituted the boundary of vacancy. The binding energies of carbon 1s-electrons calculated for C-Br covalent bonds were found in good correspondence with the experimental values.



Keywords: carbon nanotube, bromine, binding energy

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Stability of formate species on β-Ga_2O_3: a combined DFT and IR investigation

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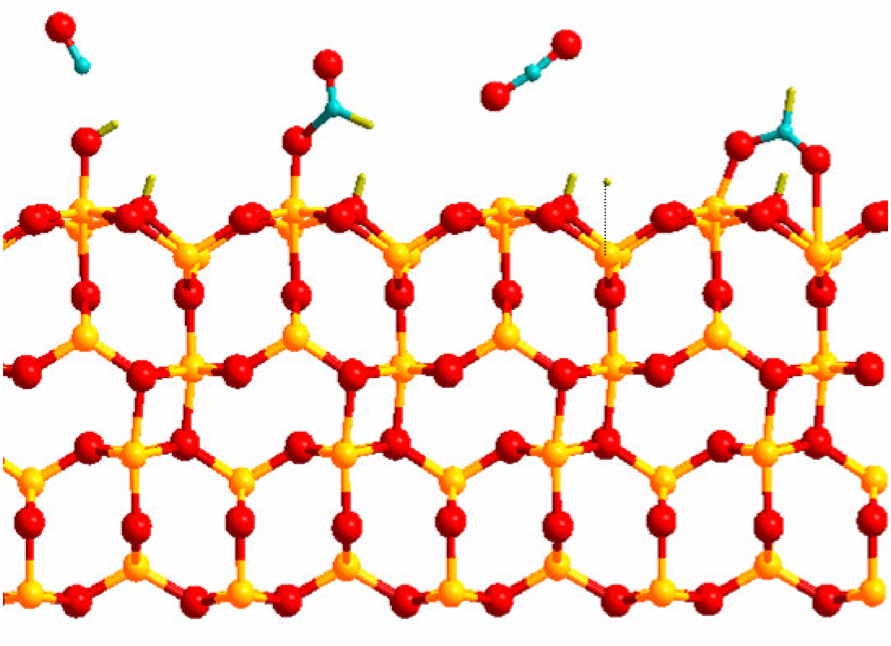
Gallia (gallium oxide) has proved to enhance the performance of metal catalysts in a variety of catalytic reactions involving methanol, CO and H_2. The presence of formate species as key intermediates in some of these reactions has been reported, although their role is still a matter of debate. In this work, a combined theoretical and experimental approach has been carried out in order to characterize the formation of such formate species over the gallium oxide surface. Infrared spectroscopy experiments of CO adsorption over H_2 (or D_2) pretreated β-Ga_2O_3 revealed the formation of several formate species. The β -Ga_2O_3 (1 0 0) surface was modelled by means of periodic DFT calculations with the VASP program (PBE functional, 400 eV cutoff). The stability of said species and their vibrational mode assignments are discussed together with the formate interconversion barriers. A possible mechanism is proposed based on the experimental and theoretical results: first CO inserts into surface (monocoordinate) hydroxyl groups leading to monocoordinate formate; this species might evolve to the thermodynamically most stable dicoordinate formate, or might transfer hydrogen to the surface oxidizing to CO_2 creating an oxygen vacancy and a hydride group. The barrier for the first step, CO insertion, is calculated to be significantly higher than that of the monocoordinate formate conversion steps. Monocoordinate formates are thus short-lived intermediates playing a key role in the CO oxidation reaction, while bidentate formates are mainly spectators [1].



Keywords: formate, CO, hydroxyl, hydride, Ga_2O_3

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Gas binding to gold and palladium nanoclusters in the context of catalytic oxidation and reduction reactions

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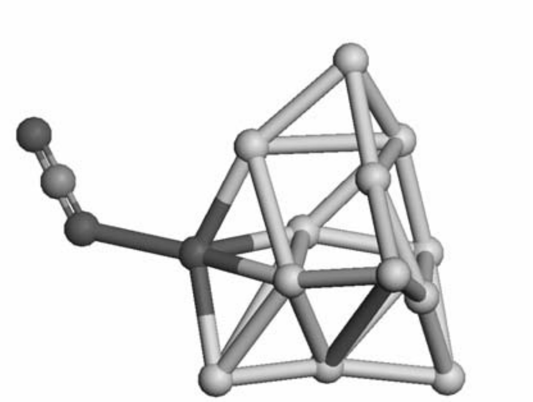
In recent years there has been an explosion of interest in using metal nanoclusters of 5 to 50 atoms to catalyse reactions of different gas species. One such reaction is the oxidation of hydrocarbons catalysed by gold nanoclusters[1]. Density functional theory has been demonstrated to be an effective tool in elucidating the mechanism of this reaction[2]. This study is focused on the question whether pure gold or gold mixed metal nanoclusters may be catalytically active for reduction reactions of CO_2. Given the ever-increasing amounts of CO_2 generated by industry catalysts of this sort may be useful in effectively utilising and managing this carbon source.

To test their catalytic activity the ability of Au_{13}, $Au_{12}Pd$ and $Au_{11}Pd_2$ nanoclusters to bind species typically found in the oxidation and reduction of small hydrocarbons has been investigated[3]. This has been done by means of atom centred DFT calculations. Binding energies of CO_2, H_2, CO, O_2, CH_4, H_2O, $^{\cdot}O$, $^{\cdot}H$, $^{\cdot}CHO$, $^{\cdot}CO2H$ and $^{\cdot}OH$ have been calculated. For pure gold nanoclusters CO_2, H_2 and CH_4 were found to not bind, O_2 and H_2O bound weakly with binding energies less than 15 kcal mol^{-1}, with the rest binding strongly with binding energies in the range 26-68 kcal mol^{-1}. Binding additional gas molecules did not greatly reduce the binding energy.

Adding palladium to the clusters created binding sites for all of the test gases. An example of CO_2 binding to a palladium atom is shown in the following figure. Reaction energies and state barriers were also calcuated for some typical gas splitting reactions. These show that palladium lowers the enthalpy of reaction as well as the transition state barrier for reacting CO_2, making the mixed-metal nanocluster a more effective catalyst.



Keywords: Nanocluster, reduction, catalysis

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First atomistic model of amorphous silica-alumina surfaces: Pseudo-Bridging Silanols as versatile Brønsted acid sites

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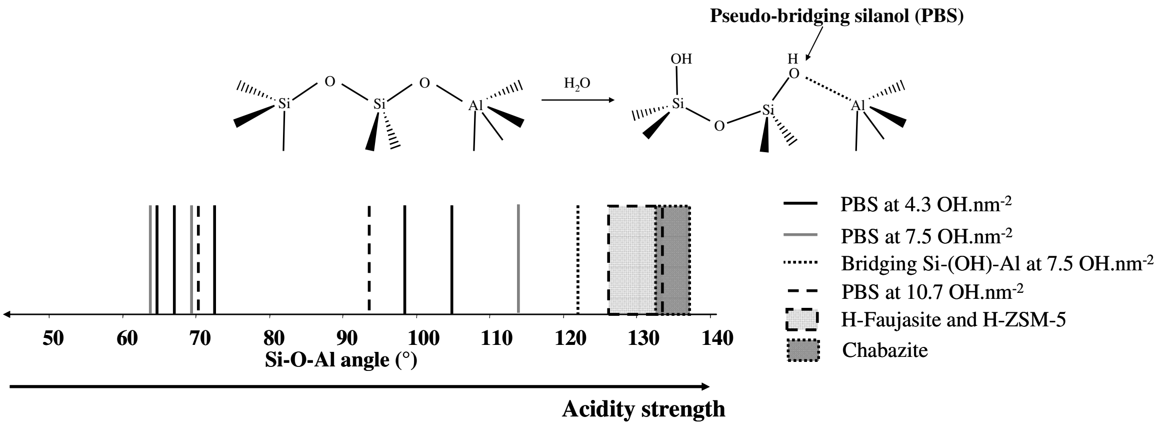
Unravelling the structure and acidity of amorphous silica-alumina (ASA) is a main challenge in catalysis. The existence of zeolite-like bridging OH groups is strongly debated. Herein we propose the first ASA surface model, by simulating the amorphization process upon contacting silica derivates with the γ-Al_2O_3 surface, which reveals original Lewis and Brønsted acid sites.[1]

Periodic Density Functional Theory (DFT, GGA-PW91) geometry optimization are performed with the VASP 4.6. code. The size of the systems modeled is typically around 500 atoms, to account for amorphization within a periodic cell. Exchange of OH groups of γ-Al_2O_3 (100) with $Si(OH)_4$ is simulated to reproduce the surface structure of ASA samples obtained from organosilane deposition on alumina followed by hydrolysis. Without any thermal treatment, our calculations demonstrate that silica aggregates are formed, in weak contact with γ-Al_2O_3, only by few anchoring points. Stabilization and phase transition is provided upon further thermal treatment, modeled by a simulated annealing sequence as follows: (i) DFT geometry optimization with VASP, (ii) Force-field NVT molecular dynamics at 1023 K with the GULP program (Catlow potentials), (iii) DFT quenching of stable states from (ii). An ASA phase is formed, revealing some original Lewis acid sites thanks to extraction of Al atoms from the alumina surface to the ASA phase.

Hydroxylation of the ASA surface is studied as a function of the temperature and the water pressure. Original Brønsted acid sites are then revealed and called Pseudo-Bridging Silanols (PBS, see Figure). A small amount of bridging Si-OH-Al groups is also found. The calculations of O-H stretching frequencies (VASP and ANHARM module) and ^{1}H, ^{27}Al and ^{29}Si NMR shielding constants (CASTEP NMR, GGA-PBE) allow the validation of the surface model. The intrinsic Bronsted acidity of the Si-OH-Al groups is shown to depend on the Si-O··Al angle (see Figure), which explains the numerous acidity strengths recorded experimentally.



Keywords: silica-alumina, acidity, PBS

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Influence of aza substitution on racemization barriers and acidobasic properties of helicenes

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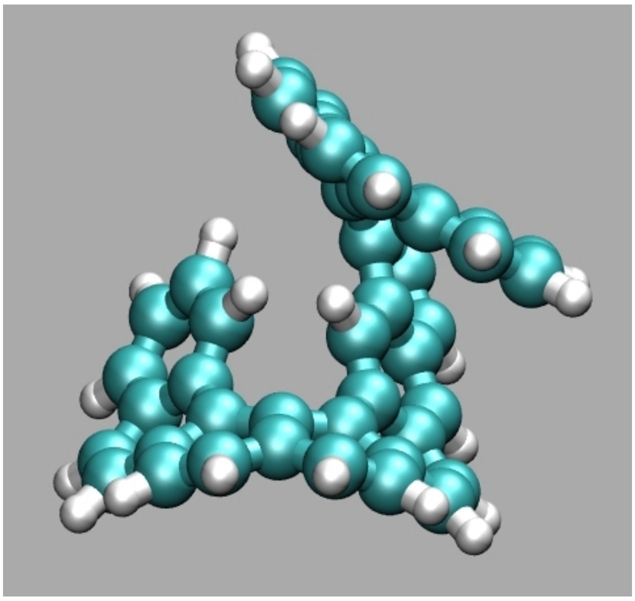
Transition state structures of [5], [6] and [11] helicenes, 1-aza and 2-aza-[6] helicenes were determined by DFT calculations, corresponding racemization barriers were evaluated and compared to experimental results. Results are in quantitative agreement with experimental data, where available. DFT calculations and linear regression were also used to estimate pK_a values of 1-aza and 2-aza [6]helicenes.



Keywords: helicene, pKa, DFT, racemization barrier

The double bond behavior within the C=C congeners of 14th group elements

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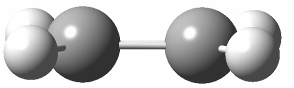
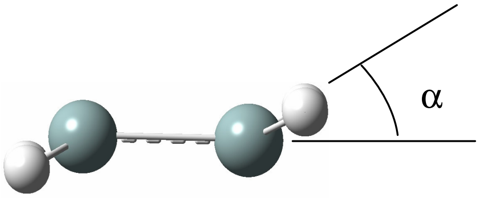
The chemistry of group 14 elements is the most developed thanks to the widely abundant carbon atom in the organic fields to its structural behaviour. Many properties of the C atom are not encountered in heavier atoms compound of the 14 group elements but there are others that occur as one descend deeply into this column. The double bond X=X (X elements of 14th group) is a fascinate example illustrating such a reproducibility. However if this bond provide a planar environment in organic compounds, the corresponding ones of Si, Ge, Se and Pb atoms exhibit a trans-bent structure. This is well known many years ago but the phenomena behind this behavior deserve a meticulous analysis.

We present in this communication the factors responsible of the non planarity of the ethylene congeners: disylene, digeremene, distanene, and diplumbene[1-3]. We will show that these factors will give rise to a zigzagging structure in conjugated and aromatic high sized molecules.

This study is undertaken at B3LYP/6-311+G(3df,2p) levels of theory. All the examined systems are computed without geometrical restrictions and the final optimized geometries are characterized by vibrational calculations.

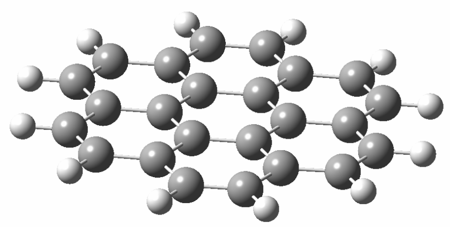


Ethylene; D_{2h}

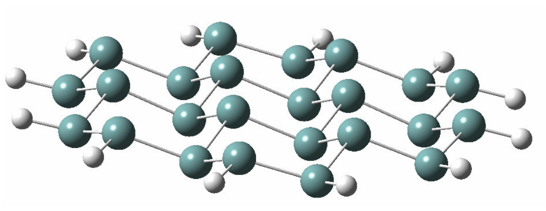


X_2H_4; C_{2h}

X	C	Si	Ge	Sn	Pb
α	0	35	53	63	71°



Coronene



$Ge_{24}H_{12}$

Keywords: ethylene congeners, hyperconjugation

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A comparative DFT study of adsorption and diffusion of Carbon on pure Ni and Ni3Pd alloy.

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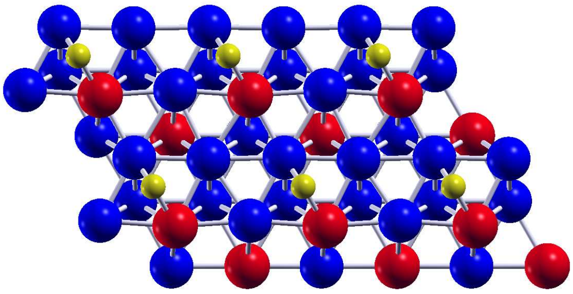
The work is the quantic simulation part of the ANR PNANO ECLAT project, in collaboration with IRCE Lyon, CEA Liten Grenoble and St. Gobain Research Aubervilliers, in the direction of a new LCD screen technology based on carbon nanotubes (CNT) emission.

The diffusion of a carbon atom in the bulk and on the surface of a Ni_3Pd alloy has been studied by means of DFT methods. This kind of diffusion processes seems to be the crucial step in the CNT catalyzed growth. The state of the art for the CNT growth is a process catalyzed by pure nickel or pure iron particles, but this doesn't exclude the possibility to deal with new materials which in principle allow to better control the growing mechanism. Furthermore, the possibility to find a new precursor for the catalytic process, which works at lower temperatures and which can be integrated in devices such as CNT lightening based LCD screens, is technologically challenging because it would permit to introduce in the process low melting point glasses, 2-3 times cheaper than the the borosilicate glasses already in use. On this context, our target is to properly model such a precursor, trying to understand the mechanisms involved in the diffusion and growth of CNT on metal particles. Starting from pure nickel to have a standard reference, we then began to study a promising system: NiPd alloy in the composition Ni 25% Pd 75%.

We performed DFT calculations in the Generalized Gradient Approximation (GGA) using the Perdew-Wang (PW91) functional as implemented in the VASP code. We investigated all the possible adsorption sites on both (111) and (100) surfaces, in the subsurfaces and in the bulk and we calculated all the energy barriers for the relative diffusion processes using the Nudge Elastic Band (NEB) algorithm as implemented in the VASP code. In the following figure is represented the transition state for the (111) surface diffusion : blue spheres nickel atoms, red spheres palladium atoms, yellow spheres carbon atoms.



The first results are quite promising. The carbon atom tends to avoid the palladium atoms and wants to maximize its coordination with nickel atoms. This is true for the surfaces, for the subsurface and for the bulk. The palladium effect can explain also the different behaviour of the carbon on the alloy with respect to pure nickel diffusion. In fact, if for the latter the surface diffusion seems to be easier, the opposite is true for the alloy, where the vertical penetration of the carbon towards the subsurface is energetically favored. Therefore, the palladium atoms lying on the surface act as a perturbation against the free carbon diffusion on the surface. As a result, the carbon atom is « trapped » between the first and the second layer, since both the vertical processes toward the bulk and the surface are more expensive than the subsurface diffusion. This effect could be important in the mechanisms which lead to the CNT growth, since it provides different channels which allow, for instance, a better selectivity (i.e. nanotube growth vs. fiber growth) compared to the pure nickel processes, where the surface diffusion seems to be easier as the vertical motion turns out to be more difficult.

A Computational Study on the Kinetics and the Mechanism of Urethane Formation

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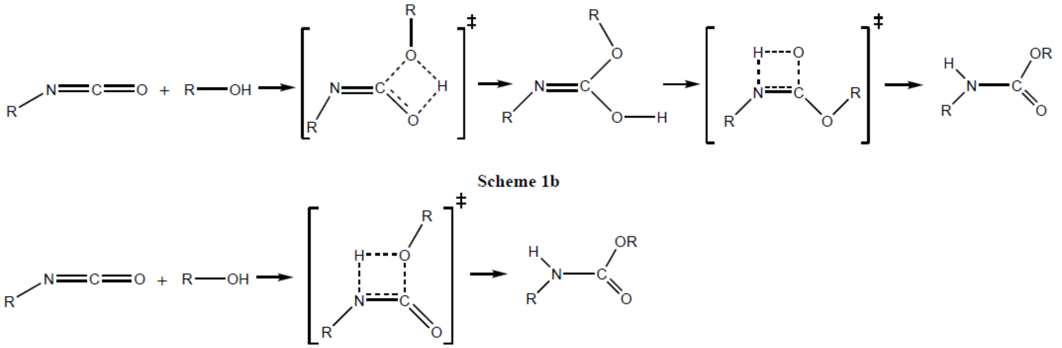
Polyurethanes (PU) are used as coatings, adhesives, reaction injection molding plastics, fibers, foams, rubbers, thermoplastic elastomers, and composites. The reaction of alcohols with isocyanates giving carbamates and its application to polyfunctional alcohols and isocyanates forms the basis of the polyurethane formation. The investigation of the mechanism and catalysis of these reactions is important for the production of tailor-made polyuretanes for the specific purposes of the industry.

In literature, two possible pathways proposed for the alcoholysis of isocyanates, either in a stepwise fashion, with an addition of the alcohol across the C=O bond to yield an enol intermediate, followed by a 1,3-H-shift giving the urethane product (Scheme 1a), or in a concerted fashion, in which the alcohol addition is carried out across the N=C bond and immediately results in the product (Scheme 1b) [1].


Scheme 1a

Scheme 1b

Scheme 1.Schematic representation of alcoholysis reaction of an isocyanate with an alcohol via **a.** stepwise path **b.** concerted path

In this study, the reactions of several diisocyanates with n-butanol and 1,2 ethyleneglycol is investigated by means of computational chemistry tools. The diisocyanate molecules used in this study are shown in Figure 1. The DFT method employing the B3LYP functionalize with the 6-31+G** basis set has been used. The obtained results enabled us to shed a light on the effect of structural differences both on the mechanism and the kinetics of the reactions. The calculated results were also compared with experimental ones[2].

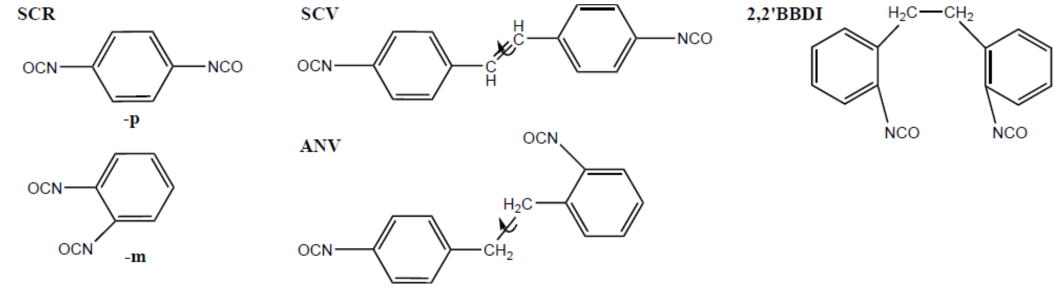


Figure 1. The diisocyanate molecules used. a.)SCR, b.)SCV, c.)ANV, d)2,2' BBDI.

Keywords: SCR, SCV, ANV, 2,2'BBDI, DFT.

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Theoretical study of the peroxidation mechanism of diethyl ether

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A great number of organic compounds spontaneously decompose, by a free-radical reaction of the carbon chain with molecular oxygen, in a self-propagating process of auto-oxidation which may generate a large variety of peroxide molecules. Many laboratory accidents can be ascribed to the presence of such peroxides in chemicals stored, often under poor conditions, for over-long periods. Ethers are typical solvents showing such a behavior.

However, few works are focused on the study of their reaction of oxidation. Dimethyl ether (DME) is the most investigated ether experimentally [1, 2] and theoretically [3], since it has a relevant role in the domain of biofuel for its good ignition properties. Some experimental works also exist on the other ethers often used as additives in fuel and biofuel: diethyl ether [4, 5], diisopropyl ether [4] or methyl tert-butyl ether [6].

This work, carried out within the INERIS research project named RIPER (for "study of RIsk linked to the PERoxidation of chemical products"), proposes the theoretical study, at the DFT level of theory, of all the possible decomposition reaction paths of diethyl ether. Furthermore, this study will lead to develop a detailed chemical kinetic model of the auto-oxidation process of DEE and to better understand its accidental risks.

Keywords: DFT, peroxidation, diethyl ether

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DFT study of methylpropanoate reactivity on NiMoS catalyst.

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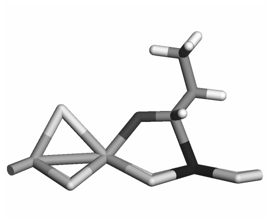
The increase of interest for alternative solutions to fossil fuels leads to the study of bio-oils. Renewable sources of energy allows reduction of Greenhouse gas emission compared to fossil fuels, nevertheless they also present several disadvantages (high viscosity, immiscibility to standard fuels or poor heating value ...), due to their high content in oxygenated compounds. Hence reducing oxygen content is required to make bio-oils valuable. This can be performed through hydrodeoxygenation (HDO) reactions.

In this context, oxygenated compounds derived from methylpropanoate are studied. Periodic DFT calculations are performed with VASP code[1,2], combined with the climbing image – Nudged Elastic Band (CI-NEB) method[3] for the study of reactivity.

In a first part, the adsorption of methylpropanoate and of the main derived oxygenated compounds (propanoic acid, propanal and propanol) is considered on the nickel promoted catalyst (NiMoS). Other reaction products like H_2O, CO and CO_2 are also studied. All these compounds have a similar behavior with an interaction between O and Mo. Only the propanal presents a specific adsorption. In fact, the proximity of Molybdenum and Nickel atoms allows the chemisorption of propanal in a di-sigma mode, represented in the small insert, with both C-Ni and O-Mo bonds.



Following this adsorption overview, the reactivity has been considered. According to experimental results on promoted catalysts[4-6], removal of oxygen atoms can occur according to two different pathways on promoted catalysts: hydrodeoxygenation (HDO) itself which leads to the corresponding hydrocarbons and water via an alcohol intermediate and decarbonylation or decarboxylation producing C_{n-1} hydrocarbons and CO or CO_2. According to the reaction scheme proposed by Senol *et al.*[6], HDO occurs from propanol, after hydrogenation of propanal. Hence propanal hydrogenation is first considered and occurs very easily thanks to the bidentate adsorption mode. Elimination of oxygen is then studied through different pathways. Finally the competitive route of decarbonylation will be presented on NiMoS.

Keywords: hydrodeoxygenation, decarbonylation, NiMoS

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The role of Coulomb explosions in Sr^{2+} + Urea reactions in the gas-phase

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The gas-phase reactions between urea and Sr^{2+} have been investigated by means of electrospray mass spectrometry techniques and density functional theory (DFT) calculations with the aim of exploring the topology of the $[Sr(urea)]^{2+}$ potential energy surface (PES). The MS/MS spectra of $[Sr(urea)]^{2+}$ complex show that the ion decomposes by losing NH_3 and HNCO, although additional intense peaks are also observed at *m/z* 43.9,103.9 and 129.8. G96LYP DFT calculations, using a modified LanL2DZ basis set [1] for Sr, allowed us to rationalize these observations through an examination of the structures and bonding characteristics of the various stationary points on the $[Sr(urea)]^{2+}$ potential energy surface (PES). Suitable mechanisms for the loss of NH_3 and HNCO have been proposed. In addition, our calculations suggest that the *m/z* 43.9, 103.9 and 129.8 peaks correspond to the H_2NCO^+, $SrNH_2^+$, and $[Sr,N,C,O]^+$ product ions, respectively, which are produced in Coulomb explosion processes. Analogous peaks were found in the MS/MS spectra of $[Ca(urea)]^{2+}$ reactions[2]. However, for the $[Sr(urea)]^{2+}$ system additional peaks are observed at *m/z* 59.9 and 87.8, which correspond to Sr^+ and $urea^+$ which are formed in new Coulomb explosion processes. Urea behaves as an oxygen base with respect to Sr^{2+}, the calculated binding energy being 360 kJ mol^{-1}.

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Glycine adsorption at the Anatase (101) surface

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The bioactivity of TiO_2 depends on the phase of the oxide and on the surface exposed. In this work we have investigated the interaction of the aminoacid Glycine (as simple model of biomolecules) with the (101) anatase surface. Periodic density functional calculations (DFT) have been employed. Regular surfaces and nanosheets of oxide have been considered.

2D-3D transition for cationic and anionic Gold clusters. A kinetic energy density functional study.

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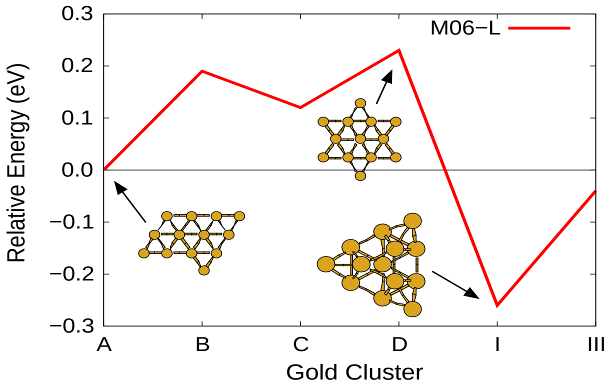
We present a Density Functional Theory study on the energetics of isolated Au_n^+ (with n=5-10) and Au_n^- (with n=8-13) gold clusters. We compare our results to both theoretical and experimental values from the past literature, finding the use of Meta-Generalized Gradient Approximation functionals, in particular the M06-L functional, of importance in order to match experiment. The M06-L values suggest a cross over between 2D and 3D structure for n=8 and n=13 for cationic and anionic clusters, respectively. We suggest that the MGGAs stronger tendency towards 3D structures lies their smaller gradient enhancement. Moreover we show how MGGAs, contrary to GGAs with smaller gradient enhancements, do not overestimate the bond energies by combining the information contained in the reduced gradient and kinetic energy.



Keywords: Gold clusters, MGGA functionals, 2D-3D transition

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Structure identification of H clusters on graphite

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We here report on the magnetism and stability of H dimers on a graphene sheet. The dimers investigated here are found to be in ferromagnetic, antiferromagnetic, or nonmagnetic states. Results obtained from DFT calculations on the H dimer adsorption are analyzed with the help of spin-density maps. We thereby show that the dimer stability results from the magnetic properties of the pair of H atoms on graphene. The enhanced stability of dimers adsorbed in *ortho* and *para* positions is particularly emphasized and is a consequence of the formation of a π bond. This provides a rationalization of the H dimer stabilities and magnetic properties [1].

L. Hornekaert et al [2] observed H clusters on graphite whose structure is not resolved by Scanning Tunneling Microscopy. The comprehensive view we here produce help us in identifying these clusters as hydrogen hexamer. We produced simulated STM images at different bias voltage that match perfectly well with experimental ones. The enhanced stability of H hexamers is also understood.

Keywords: graphite, STM, adsorption

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Support effects in supported metal oxides studied with chemical reactivity indices.

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Supported vanadium oxides constitute an important group of catalysts within the family of supported metal oxides [1]. Consisting of a vanadium oxide phase dispersed on the surface of another oxide these catalysts are used in a multitude of oxidation reactions like the selective oxidation of alkenes and alkanes. Originally this support oxide was intended to improve the mechanical strength of the catalyst. Yet, there is unquestionable evidence that the support choice has an important influence on the reactivity of the catalyst, as turnover frequencies change by different orders of magnitude for different oxides:

$$3{,}9.10^{-3} \text{ for } VO_X/SiO_2 < 3{,}6.10^{-2} \text{ for } VO_X/Al_2O_3 < 2{,}0 \text{ for } VO_X/TiO_2 \sim 3{,}0 \text{ for } VO_X/ZrO_2$$

This effect, often named support effect is still not completely understood [2] since current explanations rest on the electronegativity differences between the supports. Therefore chemical reactivity indices are applied on these systems [3].

A structural model for an isolated vanadium oxide supported on SiO_2, Al_2O_3, TiO_2 and ZrO_2 is developed, grounded on previous computational studies [4], and validated trough comparison with experimental findings.

For a more profound understanding of the global oxidation process each of its three major parts were subjected to an extensive analysis with the appropriate descriptors, being CHELPG charges [5] for adsorption and desorption parts and the local softness, a quantity emerging from conceptual DFT [6-7], for the remaining actual oxidation. By this way, it was possible to obtain a mechanism in line with current insights [8].

Through comparison of the reactivities of the different supports it became possible to search for the support effect. Results suggested that support influence mainly plays in the adsorption part, an idea that was further rationalized with the concept of bond-ionicity which strongly correlates with the experimental TOF. This approach proved that chemical reactivity indices can give additional insight into the support effect and we anticipate that their use can be extended to other supported metal oxides.

Keywords: conceptual DFT, CHELPG charges, catalysis, supported metal oxides.

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A DFT study of the Diels-Alder reaction of butadiene and acrylaldehyde catalyzed by an ionic liquid

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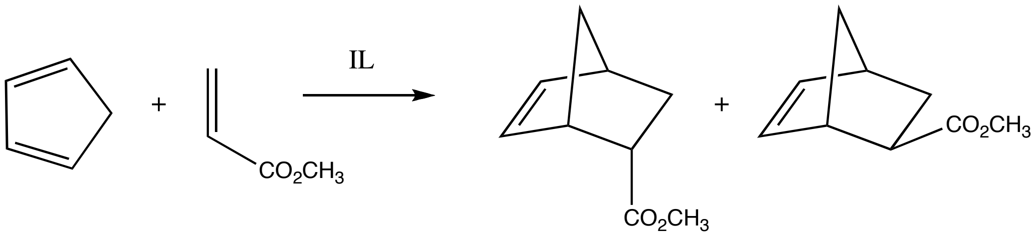
Ionic liquids continue to attract considerable interest in the chemistry research community as non-volatile solvents for organic reactions. Some reactions have been observed to give unusual kinetics or selectivities when carried out in ionic liquids and this includes a high endo-selectivity in the Diels-Alder reaction of cyclopentadiene and methyl acrylate (see figure). For this reaction, Aggarwal *et al*. have attributed this selectivity to a hydrogen bond formed between the cation of the ionic liquid and the methyl acrilate.[1]



Our purpose is to study that reaction from a theoretical point of view to try to explain the origin of the above commented selectivity. Owing to the size of the system, it is computationally very expensive to carry out an accurate post Hartree-Fock study. So, the use of a DFT methodology will be advisable. In order to find a suitable method, in this contribution we present a preliminary work in which a comparison between the results from several functionals (B3LYP, B3PW91, PBE1PBE) are compared with those obtained with post HF methods (Moller-Plesset, Coupled Cluster). To perform this comparison a simplified model of the system was chosen; to our knowledge, no theoretical study of Diels-Alder reaction of butadiene and acrylaldehyde, catalyzed by ILs, has been carried out. The selected ionic liquid was [bmin][BF4] in which the butyl group was substituted for a methyl group to save computation time.

Keywords: ionic liquids, DFT methods, Diels-Alder reaction

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Structure investigation of the surface of complex metallic alloys: combined experimental STM studies with ab initio STM simulations

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Complex metallic alloys (CMA) are defined as intermetallics presenting a crystalline structure based on a giant unit cell containing up to several hundreds of atoms. Quasicrystals can be regarded as the ultimate case with a unit cell of infinite dimension. The structure of CMAs is best described by a network of highly symmetric clusters of a few tens of atoms, usually with icosahedral or decagonal shape. The exotic atomic structure of this new class of materials is responsible to a host of unusual properties - at least when judged against their chemical composition. Useful properties of CMAs are surface properties, such as low friction, oxidation resistance and low adhesion [1].

The detailed knowledge of the surface structure is a necessary step for further studies of surface properties at a fundamental level. Scanning Tunneling Microscopy (STM) is a powerful experimental tool, since it can describe surfaces with atomic resolution. However, STM does not image the atomic structure of the surface but rather the electron density distribution in a certain energy interval below or above the Fermi level and at a certain distance above the surface, depending on the tip-sample distance and the voltage applied between them. A combined experimental approach with ab initio electronic structure calculation is therefore essential.

In this work, we show how ab initio STM simulations can help to determine the structure of the complex (100) surface of the $Al_{13}Co_4$ crystal. Atomically flat terraces separated by a step height equal to half of the unit cell parameter ($\frac{a}{2}$) exhibit two possible surface terminations depending on the annealing time and temperature selected. Both surface layers have been related to incomplete planes present within the bulk structural model. The close match between simulated and calculated STM images validates the proposed surface model [2].

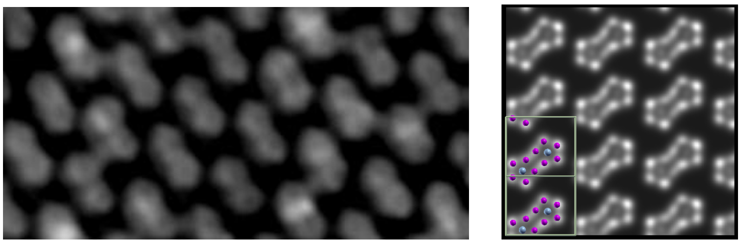

Figure 1: Experimental (left) and calculated (right) STM images of the (100) surface of $Al_{13}Co_4$.

Keywords: Complex metallic alloys, ab initio STM simulations,

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Chemistry of peroxynitrite and its derivatives.

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There are evidences in litterature that oxidative stress, which seems to be one of the causes of many diseases (cancer or Parkinson's disease for instance) [1] [2], could be related to the presence of peroxynitrite in implicated cells. Indeed, it is well-known that a good specific marker for peroxynitrite presence is the nitration of tyrosine residues, which has been observed numerous times. Moreover, it has been found that peroxynitrite is synthesized by a cell, whenever it endures an exterior attack [3].

In order to gain some insights on the biological activity of peroxynitrite, we have studied, at an ab-intio DFT level, its formation, oxidation, and decomposition.

Our calculations on peroxynitrite formation from superoxide radical and nitrogen monoxide suggest a mechanism involving two spin states, with a crossing between singlet and triplet energy surfaces, typically treated in the framework of two-state reactivity[4].

Finally, since the carbon dioxide-peroxynitrite adduct, due to the relatively high concentration of CO_2 in intracellular and interstitial fluids (10-30 mM), is considered as one of the active forms of peroxynitrite we analyzed also its mechanism of formation. In particular, we focused on the possible formation of a radical pair from the CO_2-adduct, similar to the one proposed by Estevez et. al., $[NO_2°,HO°]$[5]. This radical-pair formation might account for the CO_2-adduct decomposition kinetics, hence for its reactivity.

Keywords: peroxynitrite, DFT, oxidative stress

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A DFT Study of Methanol Oxidation to Formaldehyde on a Vanadium Oxide Cluster: an example of two state reactivity mechanism

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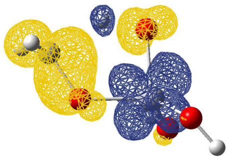
Abstract

The oxidation of methanol to formaldehyde on a tetrahedral vanadium oxide cluster model V=O(OH)$_3$ has been studied by density functional theory at the B3LYP/6-311G(2d,p) level. Two reaction paths leading to formaldehyde as product were explored. In the first path, a proton transfer from acidic proton of methanol to V=O group takes place leading a methoxy-intermediate followed by a hydrogen transfer from methoxy-intermediate to OH group yielding formaldehyde and water elimination [1]. The second path involves the adsorption of methanol followed by a proton transfer to OH group releasing a water molecule; the methoxy intermediate then evolves through different pathways to generate formaldehyde. The transition states associated to hydrogen transfer are biradicaloid and they need to be treated by the broken-symmetry approach. Moreover, a typical Two State Reactivity (TSR) mechanism [2] is found along the pathways associated to the hydrogen transfer since two potential energy surfaces are involved (singlet and triplet). Minimal Energy Crossing Points (MECP) were characterized to describe the minimum energy reaction pathway.



Keywords: Methanol, TSR, Broken-Symmetry

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The periodic DFT investigation of the effect of the Al content on the properties of the acid zeolite H-FER

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The acid zeolites constitute a very important class of shape-selective acidic catalysts used in wide variety of industrial applications. Their acidic properties are due to presence of the Brønsted acid (BA) groups, Si-O(H)-Al, where a hydroxyl bridges Si and Al atoms of the zeolite framework.

The present theoretical study adopting the periodic DFT approach (employing projector augmented-wave method) aimed to investigate the properties of the particular acid zeolite, the protonic ferrierite (H-FER), with respect to variable content of aluminum in the sample (Si/Al ratios 71:1, 35:1 and 8:1). The H-FER samples with different Si/Al ratios were characterized in terms of the structure, location and relative stabilities of the BA groups which were further described with respect to the OH stretching frequencies of their hydroxyl groups.

Two types of BA groups having the different OH stretching frequency were identified: (a) OH groups pointing to a void space in the zeolite channel system, show the highest O–H stretching frequency (≈3610 cm^{-1}), (b) OH groups involved in the intra-zeolite H-bonding showing smaller OH stretching frequency. The relative population (based on the relative stabilities of particular BA groups) of the BA groups involved in the intra-zeolite H-bond (type (b)) was found to depend on the Si/Al ratio.

The change of the relative stabilities of the BA groups with the Si/Al ratio can result in the population of different BA groups. Several effects driving the change in the relative stabilities were singled out: (a) The electrostatic repulsion between a pair of protons in close proximity. (b) Increased stability of BA group involving SiO_4 tetrahedron characterized by Si(*n*Al) descriptor with $n \geq 2$. (c) Stabilization due to the formation of intra-zeolite H-bond. (d) An unspecific effect connected with the structural strain due to the presence of additional framework AlO_4 tetrahedra.

Regarding the OH stretching frequency ν_{OH} of the BA groups in H-FER samples of various Si/Al ratios, it was shown that the frequency depends primarily on (a) the H-jump and H-bond formation, (b) the change of the Si-O(H)-Al angle, a good ν_{OH}/Si-O(H)-Al correlation is reported; ν_{OH} increases with decreasing value of the Si-O(H)-Al angle, (c) a small unspecific effect, and (d) the Si(*n*A1) descriptor, that shifts frequencies higher for increasing *n*. However, the effects (b) and (d) are strongly coupled: the effect of the Si(*n*Al) expresses dominantly via the change of the Si-O(H)-Al angle that, in turn, results in the change of ν_{OH}. Thus the effect of the Si(*n*Al) should be rather viewed as a secondary effect.

Keywords: projector augmented-wave method, acid zeolite, ferrierite, Si/Al ratio

On the Use of Reactivity Indices Derived from Conceptual DFT to Rationalize Reactivity Differences between DNA Bases

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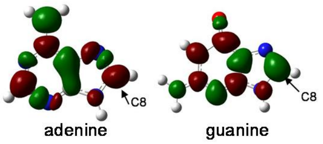
DNA bases can undergo damages under physiological conditions or consequently to an exposition to a genotoxic agent. Generally, it can be noticed that all bases do not show the same sensibility towards the formation of one kind of lesion. To some extent, the evaluation of reactivity indices derived from conceptual DFT can provide elements of rationalization.

Example 1. Under physiological conditions, cytosine can be deaminated by hydrolysis. It is known that 5-methylcytosine deaminates fivefold faster than cytosine. As for cytosine derivatives with a saturated C5-C6 bond, they deaminate even easier. It seems that it is directly related to the local electrophilic power of carbon C4 of the base involved in the reaction. This was checked by evaluation of condensed reactivity indices such as: ω^+_{C4}, $\Delta\omega_{C4}$, s^+_{C4} and $\frac{\Delta f_{C4}}{\eta^2}$ (Fig. 1.a). [1]

Example 2. When DNA is exposed to an ionizing radiation, hydroxyle radicals are produced which are susceptible to capture an hydrogen atom from the methyl group of a thymine. As a consequence, an electrophilic radical is produced, able to attack carbon C8 of an adjacent puric base. It is observed that an intrastrand cross-link is formed more efficiently between thymine and guanine than between thymine and adenine. The evaluation of the dual descriptor $\Delta f(\vec{r})$ [2] for both puric bases shows that carbon C8 of guanine, contrary to the adenine one, is more nucleophilic than electrophilic and thus more susceptible to undergo an electrophilic attack (Fig. 1.b). [3]

	ω^+_{C4}	$\Delta\omega_{C4}$	s^+_{C4}	$\frac{\Delta f_{C4}}{\eta^2}$
Cytosine	0,34	0,32	0,49	0,81
5-Methylcytosine	0,39	0,34	0,58	0,95
5,6-dihydrocytosine	0,59	0,58	0,85	1,34

(a)



(b)

Figure 1: (a) Values of different C4-condensed reactivity indices for cytosine, 5-methylcytosine and 5,6-dihydrocytosine - (b) $\Delta f(\vec{r})$ for adenine and guanine. The red areas correspond to positive values of $\Delta f(\vec{r})$, and the green ones to negative values.

Keywords: DNA damage, B3LYP, conceptual DFT, dual descriptor, local electrophilicity

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P628

A DFT study of the decomposition of ethyl and ethyl 3-phenyl glycidate

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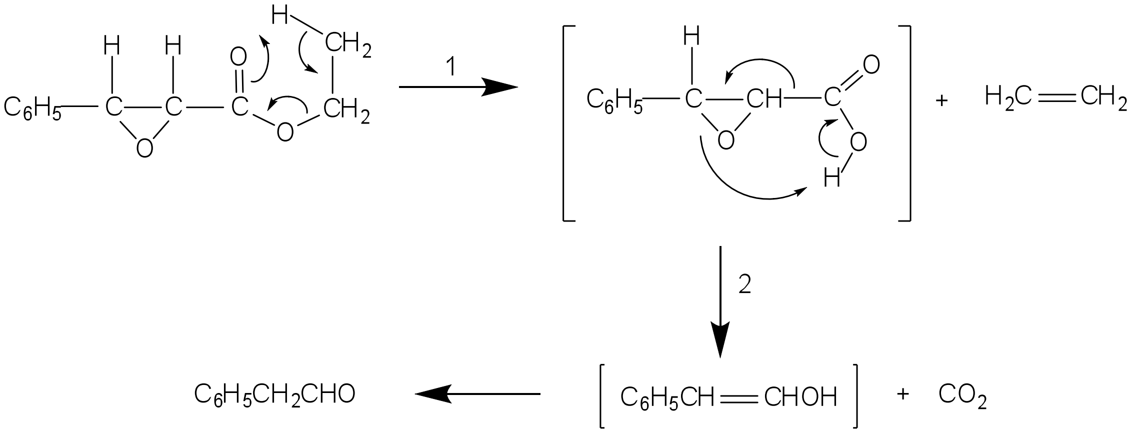
In experimental investigations, this type of glycidic esters are converted to aldehydes and ketones.[1] A proposed mechanism indicates that the ethyl side of the ester is eliminated as ethylene through a concerted six-membered cyclic transition state, and the unstable intermediate glycidic acid rapidly decarboxylates to give the corresponding aldehyde.[2]

DFT calculations are carried out in order to probe this proposed mechanism. Geometries of the different reactants, products and intermediates are optimized using the B3LYP functional and 6-31+G* and 6-31++G** basis sets. The vibrational frequencies were calculated at the same level. The results will be compared with MP2 and experimental results.



Keywords: elimination, DFT methods, ethyl glicidate

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Unraveling the Mysteries of CO_2 Disproportionation by Binuclear Ni-NHC Complexes. A Theoretical Approach.

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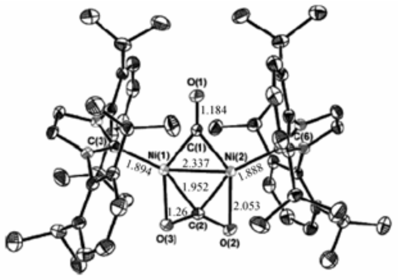
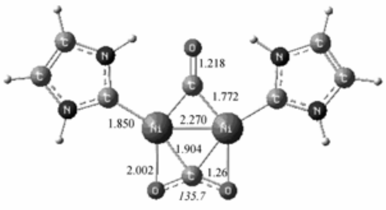
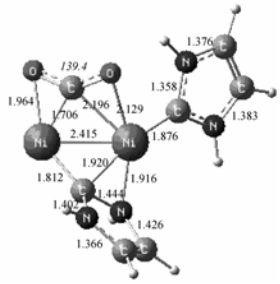
The mechanism of CO_2 disproportionation into CO and "CO_3" by the binuclear nickel complex $[(NHC)Ni]_2$, a reaction which has recently been achieved in the laboratory[1], is thoroughly investigated with the help of quantum chemical methods based on Density Functional Theory. The results show that the mechanism consists of two main steps, namely an initial decomposition of CO_2 into CO and O, followed by an electrophilic attack of a second CO_2 molecule to the oxo-ligand produced, the former step being the rate-limiting step of the process, having an activation barrier of 32.3 kcal/mol.

The theoretical calculations also indicate that formation of a Ni–(NHC)–Ni bridge precedes the CO_2 decomposition. This bridging of the NHC molecule discloses a so far unknown feature of NHCs' reactivity, that is their ability to bind to two metal centers in a μ-η^1,η^2- fashion, a coordination mode that has never been observed in X-ray structures of coordination compounds nor has ever been postulated in chemical texts.







Furthermore, the experimentally observed by Sadighi et al.[1] peculiar μ-η^2,η^2- bridging mode of the CO_2 ligand in the final disproportionation product $[(NHC)Ni]_2(\mu\text{-}CO)(\mu\text{-}\eta^2,\eta^2\text{-}CO_2)$ is investigated and analyzed in terms of orbital interactions. Also, the molecular orbitals responsible for the two different types of NHC coordination are discussed.

Inter alia, the aromaticity of the NHC molecule either ligated or bridged is investigated in these complexes, resulting in different properties depending on the coordination mode and the planarity of the NHC's ring. Finally, attempts to explore the net catalytic ability of the Ni–Ni "core" towards CO_2 decomposition revealed that the metal skeleton exhibits virtually the same reactivity with that of the parent $[(NHC)Ni]_2$ complex.

Keywords: CO_2 disproportionation, reaction mechanism, CO_2 bonding, NHC aromaticity

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A MECHANISTIC STUDY ON [3+2] CYCLOADDITION AND CYCLOPROPANATION REACTIONS OF 1,3-DIOXEPINE DERIVATIVES IN THE PRESENCE OF COPPER(I) CATALYST

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In the reactions of diazo compounds with olefins, metal-carbenes are obtained as intermediates in the presence of transition metal catalysts. Depending on the nature of the olefin species, metal-carbenes can result numerous paramount organic reactions such as cyclopropanation, cycloaddition and stevens re-arragement[1]. In this study, a series of carbene transformation reactions reported by Talinli et al. [1] has been modeled at the B3LYP/6-31G(d) level of theory. In the experiments, dimethyldiazomalonate (DMDM) was chosen as diazo molecule and copper(II) acetylacetonate Cu(acac)$_2$ as catalyst. The reaction of DMDM with 4,5-dihydro-2-methyl-1,3-dioxepine (**M1**) in the presence of Cu(I) as a catalyst, furofuran product was obtained (Figure 1a). When the 4,7-dihydro-2-methyl-1,3-dioxepine (**M2**) was used as olefin under the same reaction conditions, a mixture of cyclopropanation and Stevens Rearrangement products with a ratio 74:26 was obtained (Figure 1b). The computational results discussed herein allowed us to understand the dynamics of catalytic [3+2] cycloaddition reaction. The experimental product distribution for the reaction of DMDM with 4,5-dihydro-2-methyl-1,3-dioxepine and 4,7-dihydro-2-methyl-1,3-dioxepine in the presence of Cu(I) catalyst has been reproduced and explained by means of computational tools. Calculated results enabled us to explain reactivity behaviors based on differences in free energy barriers and NBO analysis.

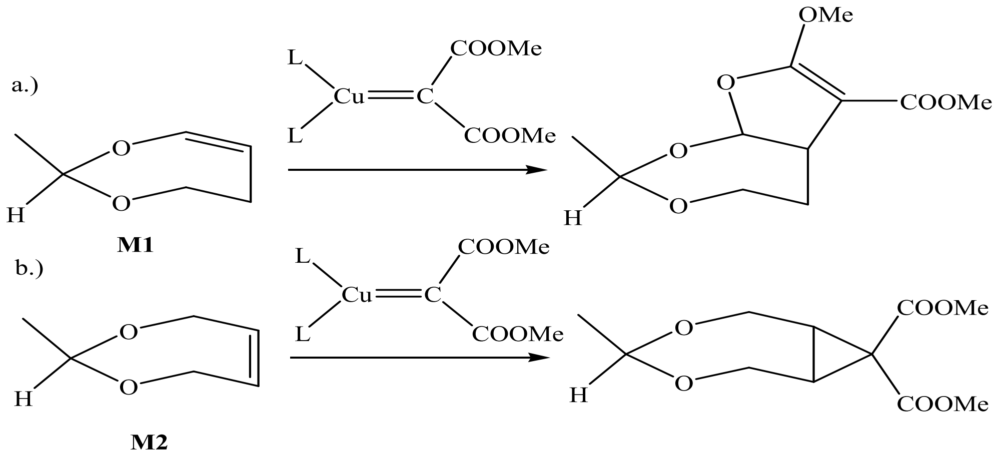

Figure 1. Schematic representation of copper-catalyzed a) [3+2] Cycloaddition reaction of 4,5-dihydro-2-methyl-1,3-dioxepine (**M1**) b.) Cyclopropanation reaction of 4,7-dihydro-2-methyl-1,3-dioxepine (**M2**).

Welcome to Lyon!

Keywords: [3+2] Cycloaddition, cyclopropanation, metal-carbenes.

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DFT approach of polymer ageing mechanisms: Study of some chemical reactions at the interface Silica/polyethylene.

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The polymers age more or less rapidly during their industrial exploitation. The understanding of the nature and origin of the degradation of polymers formula is of great interest to select the materials and then to optimize the devices. In particular, the degradation under irradiation is of major concern for the nuclear industry. The various factors known to have a non negligible influence on the ageing are: the rate of O_2 diffusion, the temperature, the nature and quantity of charges and the chemical nature of the polymer. The main purpose of this study is to determine the chemical reactions occurring at the interface charge/polymer. The goal is to characterise the mechanisms of the polymer deterioration at the atomic level. The formulas of interest are constituted of a simple polymer – the polyethylene – and of amorphous silica – for the charge.

Based on DFT calculations and under the light of very precise experimental work [1], different possible ways of the polyethylene deterioration at the interface with silica have been investigated. The structural and spectroscopic properties of reactive species and products as well as the adsorption mechanisms at various steps of the ageing have been evaluated.

Many surface sites have been experimentally characterized on silica surface. The most relevant ones are modeled individually using periodic surfaces of β-cristobalite and edingtonite phases. After having carefully checked the relative stabilities of these different surfaces, the effect of local environment (H-bonding, presence of water molecule) and the formation of radicals created under irradiation have been studied.

The polyethylene is modeled by a linear alkane chain. The influence of the length of the alkane chain on its geometrical and energetical properties has been ensured. The formation of radicals and defects in the perfect polyethylene chain is studied both under aerobic and anaerobic atmosphere.

Finally, the interaction between polymers and amorphous silica sites (both pure and degraded) is processed. The study has been especially focused on the influence of these interactions on the stability of silica sites and on the formation of defects on both silica and polymers. For comparison with experience, infrared and raman vibrational frequencies, as well as RMN shifts of silica sites are computed, with or without interaction with the polymer.

Keywords: DFT, silica, polyethylene, interface, infrared spectroscopy, degradation, interaction between inorganic and organic compounds.

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Study of the Spontaneous Deamination of Cytosine by Computational and Conceptual DFT

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Under physiological conditions, cytosine - a DNA base, spontaneously deaminates into uracil [1]. This work is aimed at characterizing the mechanism of formation of this highly mutagenic lesion.

By means of computational DFT studies, a reaction mechanism in agreement with available experimental data at neutral pH is proposed [2]. It involves an assisted nucleophilic addition as the rate-determining step (Fig. 1.a), through a 6-centres concerted mechanism (Fig. 1.b). The reaction force analysis (Fig. 1.c) indicates that the step follows a very asynchronous mechanism [3]. Moreover, contrary to the potential energy profile, it allows an easy identification of the relative orientation between cytosine and two water molecules which corresponds to the reactive complex [4].

Using conceptual DFT tools, information is provided to rationalize reactivity differences observed between cytosine and modified structures such as N3-protonated-, C5-methylated- and C5-C6-saturated-cytosine. All those modifications tend to increase the local electrophilic power of carbon C4. This was checked by evaluation of condensed reactivity indices such as: ω^+_{C4}, $\Delta\omega_{C4}$, s^+_{C4} and $\frac{\Delta f_{C4}}{\eta^2}$ [4].

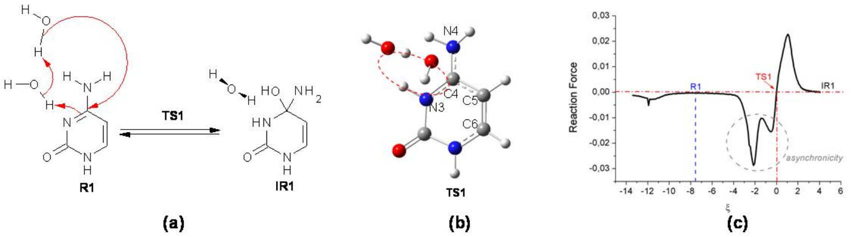

Figure 1: Scheme of the rate-determining step of the proposed mechanism for the spontaneous deamination of cytosine at neutral pH (a), geometry of the transition state (b) and corresponding reaction force profile (c).

Keywords: DNA damage, B3LYP, conceptual DFT, reaction force, local electrophilicity

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Oxygenation of the phenylhalocarbenes.
Are spin allowed or spin forbidden reactions?

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The oxygenation of phenylhalocarbenes has been investigated through the use of density functional theory and ab initio approaches. This reaction is predicted to be spin-allowed when the phenylhalocarbene is substituted with electron-withdrawing groups at the para position of the aromatic ring, due to the practical degeneracy of the singlet and triplet carbene states. Conversely, for the unsubstituted compounds the reaction mechanism involves a spin-forbidden process, with a rather large spin-orbit coupling between the singlet and triplet potential energy surfaces. These results permit to offer a rationale explanation of the variations observed in the experimental rate constants.

Keywords: Halocarbene Reactivity, Spin-polarized DFT, Oxygenation.

P634

ELF quantification of the donating properties of electron-rich carbon ligands

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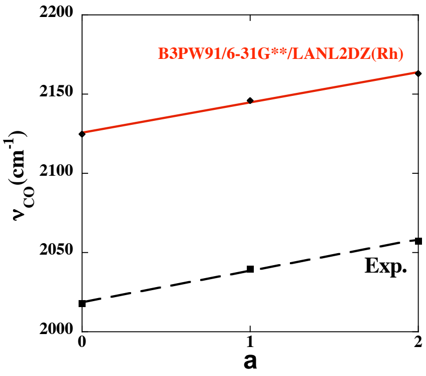
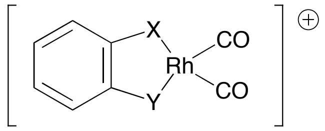
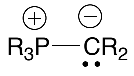
On the basis of experimental and DFT calculated infrared CO stretching frequencies in isostructural dicarbonylrhodium complexes, phosphonium ylides have been shown recently to be stronger donating C-ligands than their N-heterocyclic-diaminocarbenes counterparts [1].

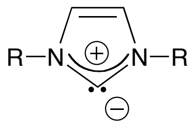


$[\eta^2\text{-}(o\text{-}C_6H_4(NHC)_{\mathbf{a}}(Ylide)_{\mathbf{2\text{-}a}})Rh(CO)_2]^+$



X,Y = NHC, phosphonium ylide

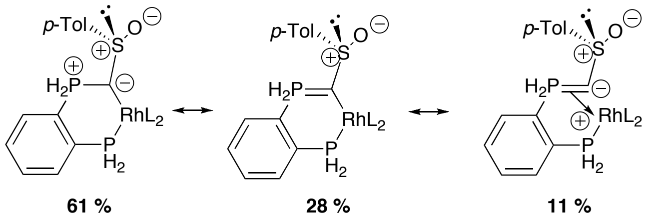




Phosphonium ylide diaminocarbenes NHC

However, the latter approach allows to estimate the global metal-ligand electron transfer only. To distinguish between the various effects, i.e. the donation and back-donation effects in the framework of the Dewar-Chatt-Duncanson model, a new method combining electron localization function (ELF) analysis and fragment orbital analysis has been disclosed [2]. It is here applied to compare the electronic ligand properties of phosphonium ylides, diaminocarbenes and hybrid ylide-diaminocarbenes involved in various Pd or Rh complexes.

The yldiide ligand resulting from deprotonation of a cationic rhodium complex of chelating semi-stabilized phosphino-phosphonium sulfinyl-ylide ligand, is expected to be even more strongly donating than phosphonium ylides. The calculated structure of both the free and coordinated yldiide were investigated by ELF analysis. The rhodium-yldiide bond may be described by three main Lewis structures. The major one involves σ-bonding with an anionic carbon atom while the minor one is related to π-bonding [3].



Keywords: ELF analysis, donor-acceptor properties, electron rich C-ligands, ylides

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Theoretical identification of the interactions between the zeolite framework and the hydrocarbon pool in methanol-to-olefin conversion

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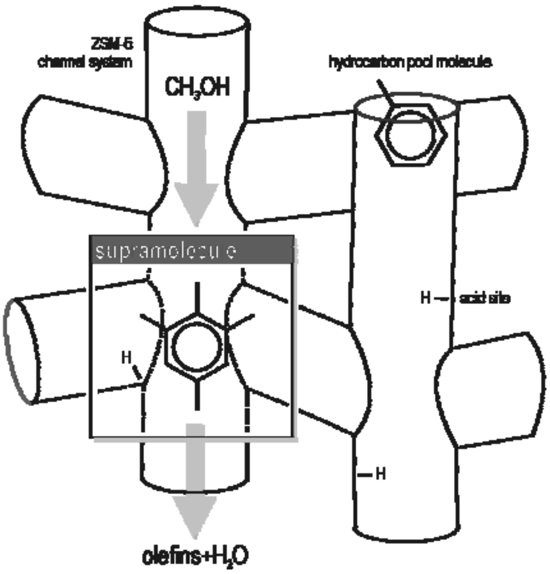
The rapidly increasing demand of oil-based chemicals calls for the development of new technologies based on other natural sources. Among these emerging alternatives, the methanol-to-olefin process (MTO) in acidic zeolites is one of the most promising. However, unraveling the reaction mechanism of such an extremely complex catalytic process like MTO conversion has been a challenging task from both experimental and theoretical viewpoint. For over 30 years the actual mechanism has been one of the most discussed topics in heterogeneous catalysis.[1] Instead of plainly following *direct* routes,[2-3] the MTO process has experimentally been found to proceed through a *hydrocarbon pool* mechanism, in which organic reaction centers act as homogeneous co-catalysts inside the heterogeneous acid catalyst, adding a whole new level of complexity to this issue.[4-5] Therefore, a more detailed understanding of the elementary reaction steps can be obtained with the complementary assistance of theoretical modeling.



In this work, a complete supramolecular complex of both the zeolite framework and the co-catalytic hydrocarbon pool species is modeled through state-of-the-art quantum chemical techniques [6-7]. This approach provides a more detailed understanding of the crucial interactions between the zeolite framework and its contents, which form the driving forces for successful methanol-to-olefin conversion. Various levels of theory will be used for this description, containing both standard DFT functionals and Grimme functionals that include corrections for dispersion [8].

Keywords: zeolites – methanol-to-olefins – B3LYP-D

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Morphology of Pt_{13} particle on $CeO_2(111)$ surface

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Abstract

Oxide supported precious metals play an important role in many heterogeneous catalytic reactions. Understanding of the interactions between the support materials and the metal particles is of fundamental importance for the development of efficient catalytic systems for a wide variety of applications. In the present paper, we attempt to address some of the fundamental aspects of these interactions by examining the adsorption of Pt_{13} clusters on the $CeO_2(111)$ surface using density functional theory. The results provide useful physical insights into the adsorption morphologies and adsorption forces that lead to the anchoring of the metals.

For Pt_{13} cluster geometry, in addition to previous available symmetrical ones, we found some other possible competitive structures with two approaches. For the first approach, we got a cluster just by choosing arbitrarily a pyramid and optimizing it the on the $CeO_2(111)$ surface. For the second one, our MD simulation allowing symmetry breaking starting from the least stable symmetrical structures gives some energetically competent unsymmetrical clusters. Among all of the available structures, we cannot find any relationship between the relative stability of the Pt_{13} clusters and other structural properties such as first NN bond length and coordination number. However, in general, the more open the structure tend to be more sable than the compact high symmetrical ones. And there is a good correlation between the first NN bond length and coordination number.

For the adsorption geometry, it is believed that one cannot construct the most energetically favored structure just by depositing the most stable Pt_{13} cluster on the $CeO_2(111)$ surface. After adsorption, first NN bond length of the Pt_{13} cluster tend to become larger than that in the gas phase because the charge transfers from the cluster to the interface and makes the Pt-Pt interaction weakened. The transferred charge mainly forms the Pt-O bonds, but there still is some charge redistributed near the interface not forming any bonds which also contributes the interaction between the cluster and surface. And most of clusters are distorted relative to the gas phases. For the support, the O atoms participating in the bonding with the cluster are pushed upward while the Ce atoms nearby move slightly downward and some charge is found to transfer from the surface O atoms to the Ce atoms. The adsorption energy or relative stability has an rough linear relationship with the interaction energy. As for the transferred charge and deformation energies of cluster and surface, they have no close correlation with the relative stability.

Synthesis and modeling of scorpionate type ligands

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Scorpionate compounds are formed through a specific type of coordination where tridentate ligands bind to a metal in a *fac* manner. The characteristic name refers to the shape of the ligand. In general, the ligand chelates to a metal with two donor sites in a manner analogous to the pincers of a scorpion, while the third donor site comes over the plane formed by the metal and the other two donor atoms, and binds to the metal.

This research focuses on the design of mixed donor (N, O, P, S) scorpionate ligands and involves the synthesis of the mixed donor backbones as well as the molecular modeling of the scorpionate tail which is expected to "sting'' the metal. Nixantphos, first developed by van Leeuwen and co-workers [1], was chosen as a backbone for the preparation of four scorpionate ligands. Thereafter, nixantphos and the O-donor scorpionate ligands were complexed to the iridium precursor. The X-ray crystal structures for the backbone [2], precursor ligand [3] and nixantphos complexed to iridium [4] were obtained. All density functional and geometry optimization calculations were carried out using the Gaussian03 suite of programmes. For iridium the LANL2DZ basis set was employed. The figure below is an example of the scorpionate ligands synthesized where the backbone contains the O and N heteroatoms, the two diphenylphosphine soft donors (pincers), and the tail.

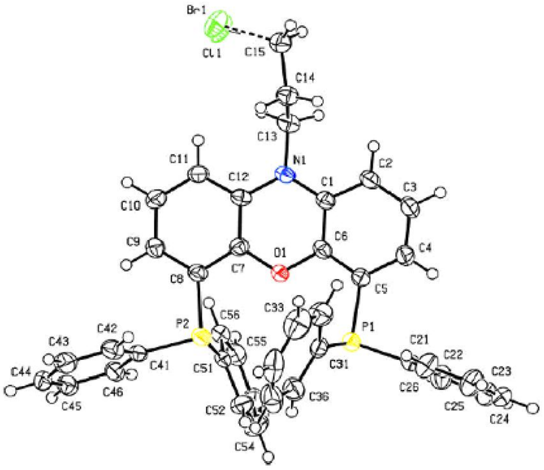

Figure 1. Molecular structure of nixantphos functionalised precursor.

Keywords: scorpionate ligands, iridium, nixantphos

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Can Stable Molecular Compounds of Thorium (V) and Protactinium (VI) Exist?

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Pires de Matos and colleagues have recently shown that the PaO^{2+}ion can be oxidized in the gas phase by N_2O to give PaO_2^{2+}, which formally contains Pa(VI). [1] While this species appears to be stable in the gas phase, its formation from PaO_2^+ requires about 16.6 eV, [1] so it seems unlikely that it will have any importance in synthetic chemistry. However, the ionization of ThO_2 requires "only" 8.7 eV, [2] and the existence of Th(V) compounds therefore cannot be dismissed so lightly.

It has been know for some time that DFT is highly reliable for the prediction of vibrational frequencies of actinide compounds, even when these are open-shell. [3] We believe that DFT is also capable of yielding thermochemical data for gas-phase actinide molecules with useful accuracy and reliability, even when these are open-shell in nature. We have investigated the energetics of gas-phase reactions such as

R1 $ThO_2 + 0.5\ F_2 \rightarrow ThO_2F$

R2 $ThOF_2 + 0.5\ F_2 \rightarrow ThOF_3$

R3 $PaO_2F + 0.5\ F_2 \rightarrow PaO_2F_2$

All three reactions are highly exothermic: R1, ΔE = -308 or –282 kJ/mol (B3LYP or CCSD(T)); R2, ΔE = -273; R3, ΔE = -229 kJ/mol (B3LYP in both cases). The products are therefore capable of existence as molecular species and their stoichiometry seems to imply that they contain "hypervalent" Th(V) or Pa(VI), respectively.

The nature of these compounds will be discussed, in the light of the question posed in the title.

We also present a DFT investigation of the thermochemistry of AnX and AnX_2 neutral molecules and cations (An = Th, Pa; X = H, C, N, O and F), the first instalment of a systematic database of actinide bond energies. Where comparison with experiment can be made, DFT is indeed consistently reliable.

Keywords: actinide chemistry, actinide thermochemistry.

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Selective Hydrogenolysis of Glycerol : Experimental and Theoretical Aspects

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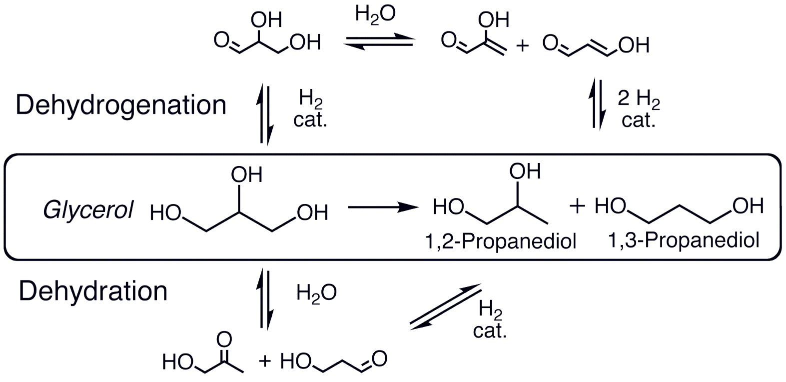
Glycerol is a renewable resource, obtained as a co-product of the transesterification of vegetables oils to produce biodiesel. Its conversion to 1,2-propanediol (1,2-PDO) and 1,3- propanediol (1,3-PDO) in the presence of heterogeneous catalysts has been particularly investigated.[1-4] The selective production of 1,3-PDO has appeared to be much more challenging than the one of 1,2-PDO. Indeed, it hasn't been achieved yet.

To the best of our knowledge, no theoretical study on this topic has ever been published. Moreover, the mechanisms which take place at the surface are still relatively misunderstood. However, coupling DFT calculations with experimental results could be very powerful to explain the metal influence on the selectivity.

Considering previous DFT investigations done in our laboratory, some interesting pieces of information have been pointed out for the dehydration of glycerol on Ni (111), Rh (111) and Pd(111)[5]. We are currently pursuing this work by studying the mechanism of the dehydrogenation of glycerol on Rh (111) and Ir (111) with VASP code (PW91 functional).[6] We are particularly interested in the comparison of the different pathways of dehydrogenation on these metals.



Keywords: chemical reactivity, heterogeneous catalysis, VASP

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Ab Initio Molecular Dynamics Study of the Hydration of Li^+, Na^+ and K^+ Montmorillonite.

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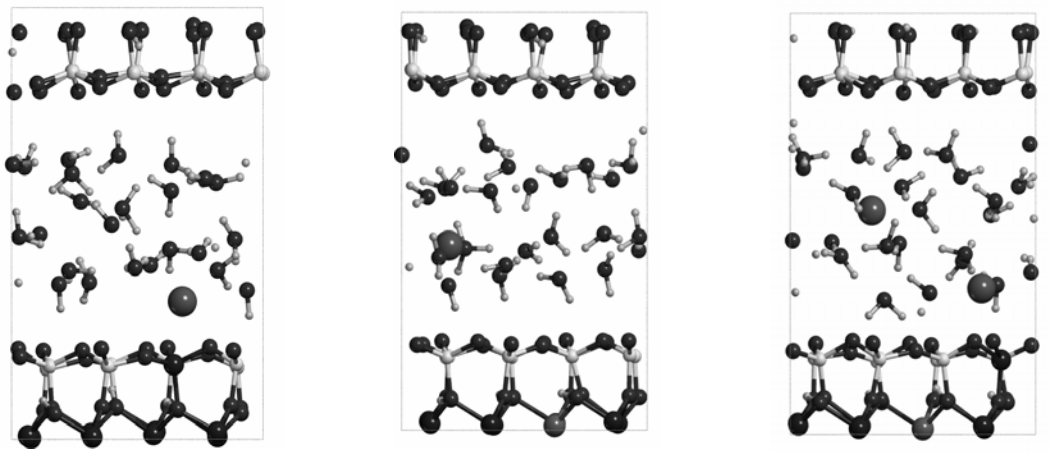
The present work reports ab-initio molecular dynamics simulations, based on Density Functional Theory using the PBE functional, for Li^+- Na^+- and K^+-montmorillonites, and considering three types of isomorphic substitutions in the montmorillonite layer: tetrahedral (Tsub), octahedral (Osub) and both (OTsub). These nine simulations allow us to evaluate the effect of each type of substitution on the inner- outer-sphere complex formation of the alkali cations.

We first observed that water shows a liquid structure, slightly over-structured which is presumably due to the PBE functional. In each of the three kinds of substituted montmorillonites, K^+ remains bound to the surface, confirming its role as swelling inhibitor. In contrast, Li^+ tends to hydrate and coordinate to 4 water molecules in all cases, except for OTsub, for which one of the two Li^+ cations initially bound to the substituted tetrahedral site remains adsorbed on the surface. Finally, Na^+ presents an intermediate behavior, binding to the surface in Tsub montmorillonite but being hydrated in Osub. These simulations point out the effect of the local substitutions toward the cation coordination (inner and outer-sphere) and therefore the importance of performing first principles calculations.



Snapshots of the Na^+-montmorillonite Cell. From left to right: Tetrahedral substitution, Octahedral substitution and Octahedral & Tetrahedral substitutions.

Keywords: Ab-initio Molecular Dynamics, Clay Swelling.

Catalytic Activity of Nucleophiles in the Stepwise Hydrolysis and Condensation Reactions of TMOS: a DFT Study.

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Sol-gel technique is a versatile and efficient method widely used in industry for the preparation, at low temperatures, of oxidic materials with tailored properties, being tetramethoxysilane ($Si(OMe)_4$, known as TMOS) one of the most used alkoxy precursors in the sol-gel processes of organosilicon compounds.[1]

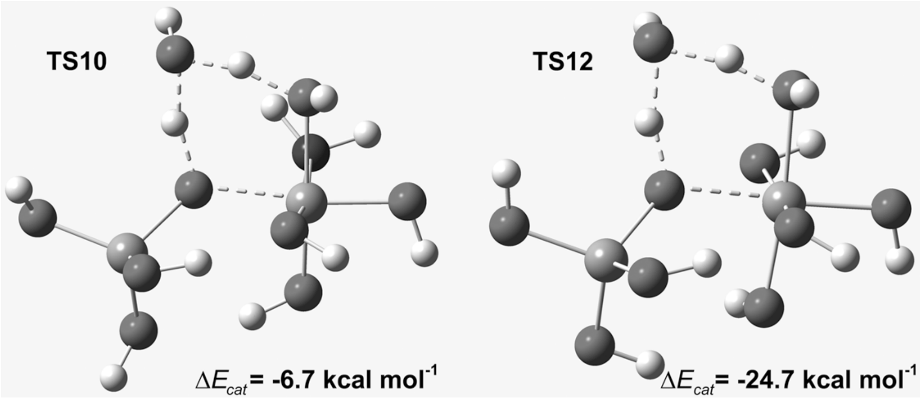
The addition of a base or an acid as catalyst is a common procedure to accelerate the hydrolysis and condensation reactions taking part in these processes. Nevertheless, while the mechanism of acid catalysis has been extensively studied, not as much information is available concerning the nucleophilic catalysis.

In this work, the previously proposed model of catalytic activity of both strong and weak nucleophiles in TMOS hydrolysis reaction [2] has been expanded on the successive stages of hydrolysis, i.e. the stepwise hydrolysis of $(MeO)_{4-x}(OH)_xSi$ ($x = 1$-3) molecules and the subsequent condensation reaction of the totally hydrolysed species, $Si(OH)_4$.

For this task, the structures of the transition states of the abovementioned uncatalyzed processes and the same catalysed with one molecule of ammonia or with one hydroxyl anion (modelling weak and strong nucleophiles, respectively) were optimised, including one and two hydrolysing water molecules in the models. The estimate of the reaction barrier heights using the B3LYP method with the Dunning's type cc-pVDZ and aug-cc-pVDZ (in the case of charged systems) allowed us to predict the catalytic activity of bases.

As a result of our work we can conclude that, in general, the catalytic activity of bases decreases with the number of hydrolysed groups, vanishing in the case of ammonia at x=2 and remaining in the case of the hydroxyl anion up to x=3.

Furthermore, we have noticed that the catalytic effect of ammonia has similar values for both classes of reactions, i.e., hydrolysis and condensation, while the effect of the hydroxyl anion on condensation reactions 3-4 times exceeds that of the ammonia molecule.



Keywords: Sol-gel processes, Tetramethoxysilane, Reaction mechanism, Nucleophilic catalysis

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The Baeyer-Villiger Reaction: Ionic or Neutral?

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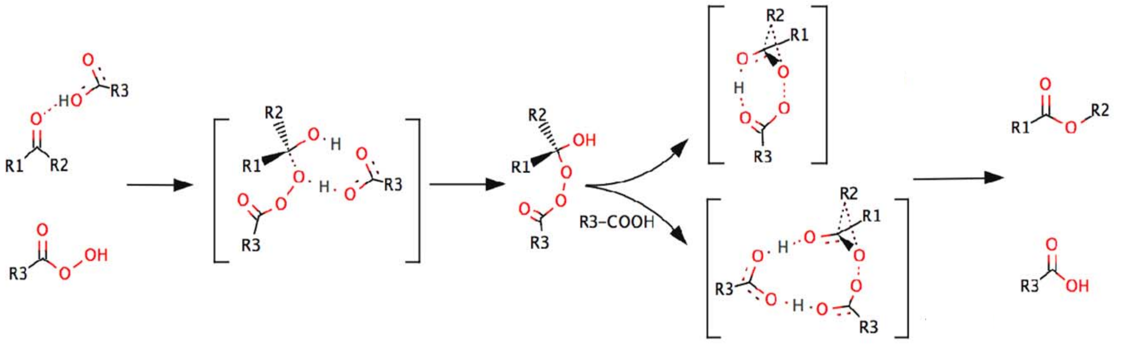
The Baeyer-Villiger (BV) rearrangement, which involves the oxidation of a ketone to an ester or lactone, is a powerful and frequently employed synthetic tool. The basic mechanism consists of two steps: the carbonyl addition of a peracid to a ketone to form a Criegee intermediate, followed by the migration of the alkyl or aryl group of the ketone moiety to the nearest peracid oxygen in the intermediate. Even though this reaction with organic acids and peracids normally takes place in non-polar solvents, a variety of ionic mechanisms are reported in standard organic chemistry texts. In clear contradiction with this type of mechanism are the experiments of Hawthorne and Emmons (*J. Am. Chem. Soc.*, **80**, 6398 (1958)) that show an increase in the rate constant of several BV reactions when the polarity of the solvent is decreased.

Our calculations, using the B3LYP and MPWB1K functionals, indicate that the least energetic reaction pathway in non-polar solvents is non-ionic and fully concerted, as shown in the Figure [1-3]. Even though both functionals describe well the reaction mechanism, the experimental kinetic results are accurately reproduced (with errors below 1 kcal/mol) with the MPWB1K functional [3]. We then focus on the reaction of propanone with performic acid, in the presence of formic acid as catalyst, to study solvent effects on this mechanism. Furthermore, different possible reaction pathways, ionic and non-ionic, that could take place in water are compared to get a better picture of how solvent polarity affects the kinetics of the BV reaction. Our calculations indicate that the experimental findings of Hawthorne and Emmons should still apply in more polar solvent mixtures. Our study questions the general assumption that organic reaction mechanisms in solution always involve ions [4].



Keywords: Baeyer-Villiger reaction, mechanism, solvent effects

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Adsorption of atoms and small molecules on α–Cr_2O_3(0001) surfaces

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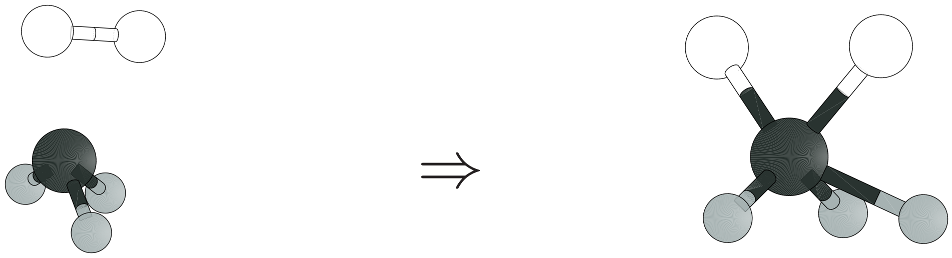
We have investigated adsorption of H, Cl, and S, as well as H_2, Cl_2, HCl, and H_2S, on the chromyl (Cr=O), oxygen (O), and chromium (Cr) terminated α–Cr_2O_3(0001) surfaces with density functional theory. We find that atomic H, Cl, and S chemisorb directly to the oxygen and chromium atoms on the different surfaces. On the Cr=O terminated surface, adsorption is strongest to the oxygen atom, as expected. On the Cr terminated surface, adsorption is stronger to chromium than to oxygen. On the O terminated surface, adsorption of chlorine to chromium is accompanied by significant surface relaxation. The molecules investigated all chemisorb dissociatively. Several adsorption sites have been considered, for all the molecules on the Cr=O, O, and Cr terminated surfaces. The corresponding energy barriers for dissociation are calculated using the nudged elastic band method. Some of the most notable results from these calculations are the formations of : a $CrCl_2$ complex on the Cr terminated surface (see figure below; left: initial complex with Cl_2 above Cr; right: final geometry with $CrCl_2$ complex; only a single CrO_3 unit is shown), and H_2O complex on the O- and Cr=O terminated surfaces.



Keywords: adsorption, dissociation, reaction path

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DFT Study of Hydroxyl Adsorption on Cluster Models of Rh(111) and Rh(100)

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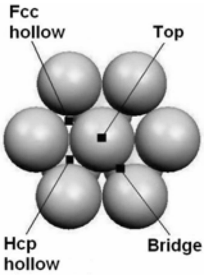
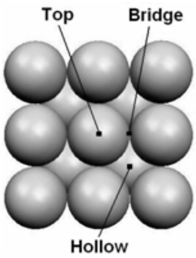
The formation of adsorbed hydroxyl species on metal surfaces plays an important role as this species is an intermediate in many oxidation reactions catalyzed by metals. We have studied the adsorption of OH species on the Rh(111) and Rh(100) surfaces using the PBE0 functional[1]. Cluster models composed of two layers of metal atoms, have been used for each of the crystallographic orientations: Rh_{10}(7+3) and Rh_{18}(12+6) for Rh(111), and Rh_{13}(9+4) and Rh_{25}(16+9) for Rh(100). Rhodium atoms were described by the LANL2DZ pseudopotential, while the 6-31+G(d) basis was used for the O and H. Adsorption energies of OH were calculated by optimization of the adsorbate geometry at the top, bridge and hollow sites. Comparison of adsorption energy values obtained in tests with the 6-311++G(d,p) basis and the Rh_{10} cluster were below 4 kJ mol^{-1}.

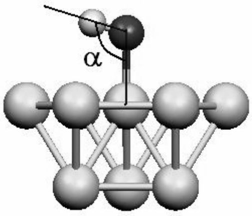
On Rh(111), the top site was found the least stable one with adsorption energy near 200 kJ mol^{-1}, while the most stable sites were the bridge site and fcc hollow with values near 230 kJ mol^{-1}. The surface-O-H angles were 107º(top), 122º(bridge), 171º(fcc) and 176º(hcp). The calculated harmonic O-H frequency ranged from 3763 cm^{-1} (top site) to 3821 cm^{-1} (fcc and hcp sites). In order to evaluate the extent of BSSE error the calculations with the Rh_{10} cluster were repeated using the Counterpoise method of Boys and Bernardi. Slightly smaller adsorption energies were obtained, decreased by around 8 - 12 kJ mol^{-1}. Consideration of the differences of zero point energy between adsorbed and gas phase OH imply an additional decrease of the adsorption energy of 10-12 kJ mol^{-1} on all sites of the Rh_{10} cluster.

On Rh(100), adsorbed OH was most stable at the hollow site (240 kJ mol^{-1}), while no significant difference was found for adsorption at top and bridge sites (214 and 208 kJ mol^{-1}, respectively) (all adsorption energies corresponding to the Rh_{25} cluster).

The effect of applying an external electric field of 0.01 a.u. on the adsorption energy of OH was evaluated. On Rh_{10}(111), when the field causes negative charge in the metal, there is a destabilization of all adsorption sites (from 6 to 23 kJ mol^{-1}), the less affected being adsorption at the top site. When the field is applied as to cause positive charge density on the metal, a slight stabilization of adsorbed OH, around 8 kJ mol^{-1}, is observed for the four adsorption sites. On Rh_{13}(100), when the metal is negative, adsorption on the top and bridge sites is stabilized by 15 and 22 kJ mol^{-1}, while on the hollow site the change is not significant (2 kJ mol^{-1}). Conversely, when the field causes positive charging of the metal, there is a slight stabilization of the OH adsorbed on the hollow site, while the energy on the top and bridge sites remain unaffected.







Keywords: PBE0 functional; OH adsorption; Rhodium

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Theoretical Study of Pt alloys for Oxygen Reduction Reaction in PEM Fuel Cells

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The adsorption of oxygen on metal surfaces is a common chemical reaction that can lead to various structures, these include surface oxide films, oxygen penetration in the subsurface region and bulk oxides, at certain partial pressures and temperatures[1]. The focus of this research is oxygen adsorption and the subsequent oxygen reduction reaction (ORR) on Pt and Pt-Ni alloy. A reaction that is specifically relevant in the proton electron membrane (PEM) fuel cell applications.

PEM fuel cells are believed to be kinetically limited for the ORR due to a loss of surface area at the cathode[2]. One explanation for this phenomenon is the “so called place exchange mechanism” which leads to a thin surface oxide being formed. In an attempt to understand and verify this hypothesis, we are modelling pure Pt and also Pt/Ni alloys in order to determine the relative propensity for oxide film formation and ultimately how adsorbate coverages control the ORR kinetics.

VASP, a plane-wave DFT code has been used to model various facets of the catalyst particles, in particular the ((111), (100) and (110) surfaces. In addition, a range of oxygen coverages at high symmetry sites and oxide thin films have also been modelled as intermediates in the place exchange mechanism. The potential energies generated from these calculations have been augmented by statistical thermodynamics of a classical ideal gas. These allow the influence of temperature and pressure to be included under realistic fuel cell operating conditions[3].

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Fully Relativistic 4*c*-DFT Study of Adsorption of the Heaviest Elements and their Homologs on Gold Surface

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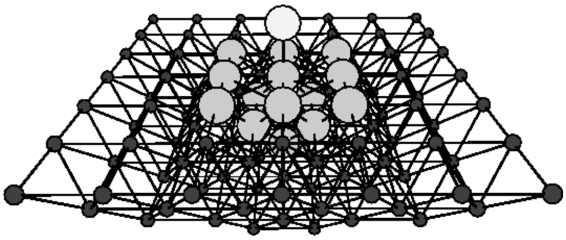
Element 112 and heavier ones produced in man-made nuclear reactions are very unstable and decay in few seconds or milliseconds. Their identification and placement in the Periodic Table can be accomplished through experimental chemical studies using fast separation techniques: by assessing the behaviour of the heaviest elements in comparison with that of the lighter homologs in the chemical groups a unique position in the Periodic Table can be established. One of the techniques is the gas-phase chromatography whereby the elements are deposited on gold surface of detectors in the chromatography column. The measured quantity is the adsorption temperature, T_{ads}, from which the adsorption enthalpy, ΔH_{ads}, is deduced.

Theoretical predictions are indispensable for these sophisticated and expensive experiments with single atoms. Developed in our groups the spin-polarized four-component DFT method [1] is a good instrument to accurately calculate adsorption energies and other properties of the heaviest elements where relativistic effects are most important.

In this work, we predict ΔH_{ads} and T_{ads} of elements 112 and 114 and their lighter homologs Hg and Pb on gold (100) and (111) surfaces. With that aim in view, extensive calculations of ad-atom - gold cluster systems of various size from diatomics to clusters of more than hundred atoms were performed. Also, embedded cluster calculations (see the figure) [2] were performed for medium-size inner clusters and outer clusters of 156 atoms. Convergence was reached with the cluster size and adsorption position (on-top, bridge, two types of hollow).



In the presentation, we will discuss the convergence process and accuracy of the results at various stages of the calculations. We will also discuss chemical properties of elements 112 and 114 which are expected to be very unusual due to the very strong relativistic effects on their outer electron shells. We conclude that element 114 will be stronger adsorbed on gold surface than element 112, which should then be verified experimentally. Our predictions for element 112 [3,4] indicating that it should interact with gold as a d-element, and not as an inert gas, as was expected earlier, were confirmed by the recent experiments [5].

Keywords: 4*c*-DFT, adsorption, heaviest elements, relativistic effects

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DFT Study of the Mechanism of the Dimethyl Carbonate formation from CO_2 with $Me_2Sn(OMe)_2$

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Conversion of carbon dioxide to industrially useful compounds has been a challenge for synthetic chemists and has recently attracted much interest in view of "Green Chemistry". One of the most attractive synthetic goals starting from CO_2 is dimethyl carbonate (DMC).

DMC is classified as a non-toxic and environmentally innocuous chemical. Its primary use is an intermediate for polycarbonate resins and is now considered as an option for fuel additives.

In this research Density Functional Theory (DFT) calculations were performed on the $(CH_3)_2Sn(OCH_3)_2/CO_2/CH_3OH$ system using the ADF 2007 code . The PBE gradient-corrected exchange-correlation functional and the TZP (Triple Zeta plus Polarisation) basis was retained for all the calculations. All the structures were characterized by vibrational analysis in the harmonic approximation.

The energy barriers for direct exothermic monocarbonation reaction of $Me_2Sn(OMe)_2$(**1**) and for the mechanism via a transition state deformed structure were calculated equal to: 29.9 kJ/mol and 56 kJ/mol, respectively. The following dicarbonation is more difficult with a highest energy barrier amounting 43.4kJ/mol. The mechanisms of monocarbonation and dicarbonation of the dimer $[Me_2Sn(OMe)_2]_2$ were studied and lead to significantly lower barrier energies amounting 21.7 kJ/mol, 22.3 kJ/mol, respectively.

As far as dimerization and CO_2 insertion energies are concerned, two routes were examined:
1- Dimerization followed by CO_2 insertion,
2- Monocarbonation of the monomer followed by dimerization.
The first route is more favourable than the second one. The diagrams of Gibbs free energies of the two routes at 25°C and 150°C are quite similar to diagrams of E_0. This indicates that the importance of entropy contribution to Gibbs free energy is rather limited.

Two reactions have been studied for DMC production:
1-The mechanism of the reaction $2Me_2Sn(OMe)_2 + CO_2 \rightarrow$ distannoxane (or ½ distannoxane-dimer) + DMC
via an intramolecular reaction of deformed *monocarbonate* of (**1**) with a large energy barrier.
2- The intramolecular reactions for deformed *dicarbonate* of (**1**) following two paths: both energy barriers are smaller than the energy barrier of the intramolecular reaction of deformed monocarbonate of (**1**).

Also, solvent effect was studied with methanol and toluene

Keywords: carbon dioxide, DFT calculations, monocarbonation, dicarbonation, dimethyl carbonate

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The effect of the supporting cerium oxide on the activity of vanadia catalysts

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The success of CeO_2 in catalytic applications is linked to the unique combination of an elevated oxygen transport capacity coupled with the ability to shift easily between reduced and oxidized states, Ce^{3+} and Ce^{4+}. The strong influence of the oxide support on the reactivity is well-known, yet not understood [1,2].

The limited number of theoretical investigations of ceria-based systems is due to the great difficulty of (standard) DFT-GGA approaches in describing localized f-electron systems [3]. DFT+U and hybrid approaches are both suitable, with the former being computationally less costly [4]. Our recent work includes calculations aimed to understand the localization properties of the $4f$ electrons in reduced ceria-based systems and to investigate the ability of state-of-the-art quantum-mechanical methods to provide an accurate description of the electronic structure of the systems.

Here, we report theoretical models of $VO_n/CeO_2(111)$ ($n = 1 - 4$) with the focus on monomeric species. The calculations are based on DFT+U with the PAW functional as implemented in the VASP simulation package. We discuss the stability of the VO_n species as function of the external conditions such as oxygen partial pressure, vanadia loading and temperature. We combine this analysis with a detailed characterization of the structural, electronic and vibrational properties of these model catalysts. To compare the catalytic activity of the different systems in oxidation reactions we calculate the energy of O defect formation which relate to the reaction energy and the energy of hydrogenation which relates to the energy barrier of the rate-determining step.

From the $VO_n/CeO_2(111)$ phase diagrams under relevant conditions we conclude that ceria stabilizes the 5+ oxidation state of vanadium in mixed oxides (Fig. 1). Reduction of VO_n/CeO_2 by O defect formation is particularly easy (compare with the $CeO_2(111)$ support itself, 1.87 eV/atom [4]). The high catalytic activity of vanadia supported on ceria has its origin in the formation of Ce^{3+} ions instead of V^{3+} or V^{4+}.

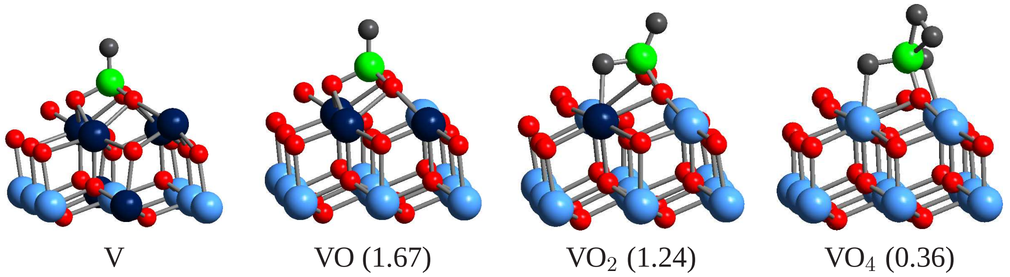

Figure 1: VO_n/CeO_2 stable systems in UHV conditions. Ce^{3+} are dark blue. Oxygen defect formation energies w.r.t. 1/2 O_2 (eV/atom). The 0.36 value corresponds to the $VO_4 \rightarrow VO_2 + O_2$ reaction.

Keywords: cerium oxide, vanadia, f electrons

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Non-Classical Bonding Nature and Novel Fluxional Behavior of Tungsten Dihydride Silyl Complex

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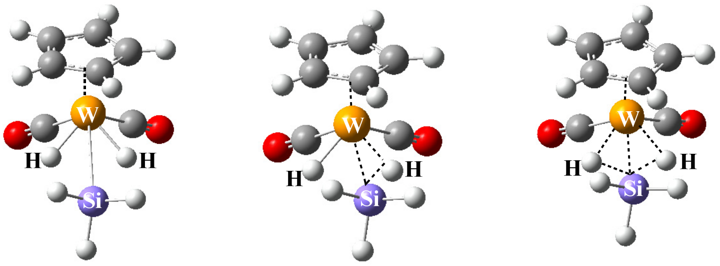
Transition metal complex containing silicon species is attractive research subject in theoretical/computational chemistry because of their non-classical bonding natures and electronic structures. Our recent theoretical studies on such complexes demonstrate their novel bonding natures and electronic structures, which are remarkably different from their carbon analogues [1-3]. A recently reported tungsten dihydride silyl complex is one of those interesting trasition metal complexes including silicon species. Actually, its bonding nature varries among the classical dihydride silyl form (**I**), non-classical η^2-silane form (**II**), and non-classical η^3-silicate form (**III**) depending on the strength of the Si-H inter-ligand interaction (Scheme 1). Here, we wish to present a theoretical study of bonding nature, electronic structure, and fluxional behavior of $Cp(CO)_2W(H)_2[SiH(OMe)\{C(SiH_3)_3\}]$ **1** (Scheme 2) with the DFT method.



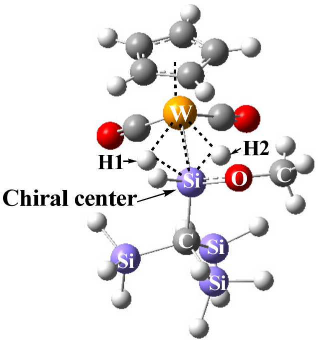
W(IV)
W, Si: Classical
I

W(II)
W: Classical
Si: Non-classical
II

W(II)
W, Si: Non-classical
III

Scheme 1

NBO population and LCMO analysis indicate that the W center takes a d^4 electron-configuration (+II oxidation state) in **1**. This means **1** consists of a silicate-like $(H)_2[SiH(OMe)\{C(SiH_3)_3\}]$ moiety including two non-classical Si---H bonding interactions and a non-classical eight-coordinated W center bearing a W-Si and two W-H bonds. New type of fluxional behavior of **1** was observed, as follows: (1) Position change of $[SiH(OMe)\{C(SiH_3)_3\}]$ occurs with a very small activation barrier (3.0 kcal/mol) through a new silicate-like transition state. (2) Position exchange of two hydrides occurs with a moderate activation barrier (7.5 kcal/mol) through a new W(IV)-like transition state. Because of this fluxional behavior, two hydride ligands become equivalent in NMR time scale despite of the presence of a chiral silicon center.



1
W, Si: Non-classical
H1 and H2 are equivalent
Scheme 2

Keywords: tungsten, dihydride silyl, silicate, non-classical

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Towards a molecular level understanding of activation and hydrogenation of CO_2 on Ni(110) surface using Density Functional Theory

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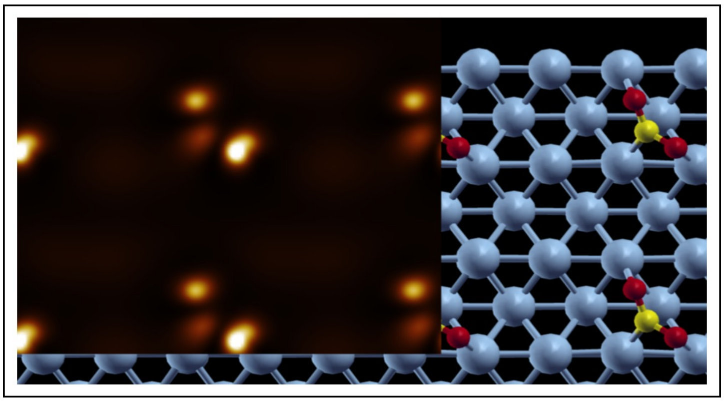
The peculiarity of the interaction of CO_2 with Ni(110) with respect to other metallic surfaces has been recently pointed out by combined theoretical and experimental studies [1].

A deeper investigation based on Density Functional Theory including the analysis of the electron localization function and simulations of scanning tunneling microscopy images is presented here. The role of steps, of undercoordinated surface sites and other defects are also exploited. Preliminar results for adsorption on a NiCu alloy are also discussed, giving insights about the peculiar differences of CO_2 interaction with Ni and Cu surface atoms.

Starting from the formate (HCOO) produced on pure Ni(110) surface from CO_2 by co-adsorbed molecular hydrogen [2], we present here also the results obtained for the following hydrogenation process and reaction paths, simulating the reaction with atomic hydrogen. We analyse the possible formation of formyl (HCO) throughout the reaction HCOO+H --> HCOOH --> HCO+OH, calculating adsorption energies, core-level-shifts, vibrational frequencies of the possible intermediate compounds as well as transition states and reaction barriers.



This work is in collaboration with: Vesselli E., Rosei R., Comelli G. Baraldi A. (Dip. Physics Trieste);De Rogatis L., Savio L., Vattuone L., Rocca M., Fornasiero P. (Dip. Physics Genova)

Keywords: carbon dioxide, Nickel, Etherogeneous catalysis

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Benzene adsorption on Mo_2C: a theoretical and experimental study

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Transition metal carbides constitute an important and interesting class of materials. They present physical and mechanical properties of ceramics, not those of metals, in spite of being conductors. As catalysts, they have proved to be active in hydrogenation, isomerization, HDS, HDN etc. Particularly in what concerns Mo_2C, it has been shown in a previous work [1] that molybdenum carbide supported in Y-zeolite has presented high initial activity in benzene hydrogenation, although it suffers rapid deactivation, and after 2 h of reaction, the conversion was nearly zero. In the present work, we will show that the same behavior is true for pure Mo_2C. Results suggest that benzene initially reacts with adsorbed hydrogen. This hydrogen is adsorbed during carburization process. As long as the adsorbed hydrogen is consumed, benzene molecules adsorb strongly on surface. In order to corroborate this reasoning, we are performing DFT calculation of the interaction of benzene and hydrogen with $Mo_2C(001)$ surface.

Calculations were done using periodic boundary conditions, plane wave basis set and ultrasoft pseudopotential. The exchange and correlation functional of Perdew, Burke and Ernzerhof [2] was used. Occupation was treated by the cold smearing technique of Marzari et al. [3]. All calculations were done with Quantum espresso suite of programs [4]. Bulk Mo_2C calculations were done in an orthorhombic 12-atoms unit cell in a 3x3x3 Monkhost-Pack sampling. The calculated cell constants are a=4.73Å, b=6.06Å, c=5,25Å, which show excellent agreement with experimental values a=4.729Å, b=6.028Å, c=5,197Å [5].

For surface calculations, a slab model was used. A super-cell was constructed by propagation of the original cell 3 times in x and 2 times in y directions, and a vacuum layer of 17 Å was set in z direction. Calculated benzene adsorption energy is -152 Kcal mol^{-1}, which reveals a strong interaction of benzene and Mo_2C surface. Furthermore, the surface significantly relaxes in the presence of benzene molecule. This strong interaction of benzene with surface can be directly related to the deactivation process, since the surface sites can become inaccessible to hydrogen molecules. Work is in progress concerning the interaction of hydrogen with surface in the presence or in the absence of benzene molecules.

Keywords: molybdenum carbide, benzene, adsorption

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Bravais lattice diversity of III-V semiconductors: A comparative study of GaSb(001) and GaAs(001) surface reconstructions

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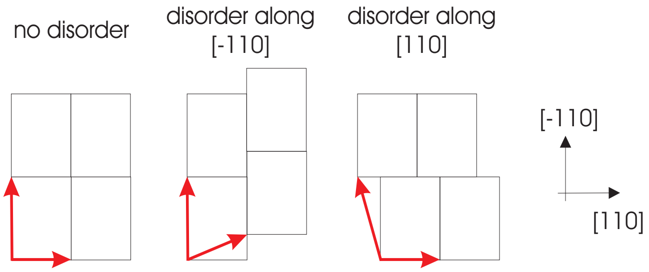
Despite recent progress in understanding surface reconstructions on III-V semiconductor surfaces there is only a limited understanding of surface defects. We explain the experimental discrepancy between symmetries resolved by scanning tunneling microscopy and diffraction techniques (RHEED, X-ray) on a number of different surfaces, like the GaSb(001) and GaAs(001) surfaces, by the formation of one-dimensional disorder boundaries. *Ab initio* calculation within DFT theory are carried out [1, 2] to calculate formation energies for different reconstructions. Difficulties with large number of atoms, which are required in the defect related studies, are overcome by the Bravais lattice type variation. Particularly, a one-dimensional disorder boundary on a surface with a rectangular unit cell is represented by a unit cell with oblique translation vectors. This reduces computational costs significantly. Special care is taken with respect to the k-point set convergence in the plane wave basis.

Specifically, lattice distortion of the (4×3) reconstruction family of GaSb(001) [3] is compared to the GaAs(001) $\beta2(2\times4)$ and c(4×4) reconstructions. Very low defect energies are found for specific (4×3) reconstructions with shifts along $[\bar{1}10]$. A similar behavior is found for the GaAs(001) $\beta2(2\times4)$ reconstruction. On other reconstructions the calculated defect energies are very high, like for the GaAs(001) c(4×4). Low energies would allow for the existence of phase shifted reconstruction regions on short distances which explains, for instance, the thermodynamic stability of the GaSb(001) (4×3) reconstructions, predicted by DFT and observed by STM, and that in diffraction experiments one finds only (1×3) or c(2×6) patterns [4].



Keywords: Surface structure analysis, GaSb, GaAs

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CPMD study of the uranyl interaction with the (001) Face of Gibbsite

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In order to better understand mechanisms involved in the retention of the uranyl ion, UO_2^{2+}, on mineral surfaces, some more specific information concerning the sorption of this radiotoxic element is required. Furthermore, it is of great interest to study sorption on the gibbsite phase, because of the abundance of such aluminium hydroxide in soils. Thus our main goal has been to study the sorption of the aquo uranium (VI) complex onto the most abundant face of gibbsite, the (001) one.

In a first part we studied the interaction of the uranyl ion with the gibbsite (001) face by means of Static Density Functional Theory calculations in vacuum condition using the VASP code[1]. We first calculated the cell crystallographic parameters which are in good agreement with experimental data. In view of studying the uranyl ion adsorption, the second step was to investigate the surface atomic arrangement onto the active gibbsite basal plane. Calculations display very small relaxation of the surface atomic positions relative to the bulk atomic ones. This is basically due to the fact that gibbsite sheets are linked together by weak hydrogen bonds. As it is known experimentally that uranyl ions interact with gibbsite with an inner-sphere mechanism forming bidentate complexes, three different potential adsorption sites were identified. The corresponding surface complexes were optimized and results showed that gibbsite can minimize the diffusion of this radiotoxic compound. However, in this first part just one water monolayer, on top of the gibbsite surface, has been used to model the solvent. Thus, to introduce a better description of the solvent and to take into account temperature in the simulations, we then performed CPMD[3] calculations of the uranyl at the water-gibbsite interface. In a first step we investigated the uranyl ion in the solvent in order to characterise solvation spheres. Then, the interaction of the water molecules with the gibbsite (001) face were simulated and compared to previous static DFT calculations (for the first water monolayer) as well as to experimental results. Finally, the uranyl adsorption process has been simulated.

This study shows that results from static DFT and CPMD calculations are powerful tools, associated with experimental data, to get more insight into the retention process on mineral surfaces.

Keywords: uranyl, gibbsite, adsorption, DFT, CPMD.

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Interaction of atoms with graphitic-like surfaces for astrophysical applications

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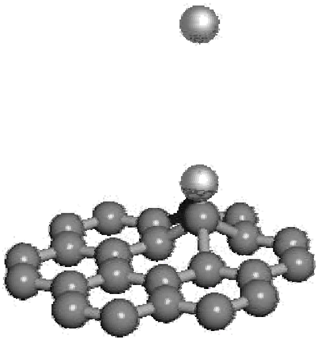
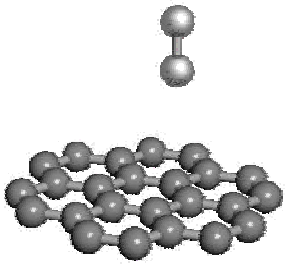
In the interstellar medium, dust grains play a key role in mediating formation of molecular species. With the purpose of quantitative interpretations of the reactive processes, it is of a strong interest to study the interaction of atoms present in the interstellar clouds with grain surfaces. A particular interest in this context is devoted to adsorption of hydrogen atom, which is the most abundant atomic species in interstellar clouds, with the surface of grains of carbonaceous type.

Theoretical studies have been performed in our group by means of DFT/GGA calculations (molecular and periodic) to treat the interaction of hydrogen atoms, and also of a few other atoms, with graphitic-like surfaces (graphene and model of graphene as represented by PAH molecules). Previous studies of our group have considered adsorption properties of hydrogen dimers as depending on adsorption sites and spin coupling [1,2]. The presentation at the conference will focus more on other atom interactions with graphitic-like surfaces such as oxygen [3] and carbon [4], combined with the presence of H atom. The role of defects, such as adatom or vacancy, has also been studied. The properties of these systems, energy and geometry including relaxation of surrounding carbon atoms, are very important in the dynamics of molecular formation, for the reaction probability and for the energy sharing between the nascent molecules (in internal and kinetic energies) and its accommodation to the surface [5, 6].





Keywords: adsorption, molecule formation, graphitic surface

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Grafting of Polyoxometalate on Silica Surfaces

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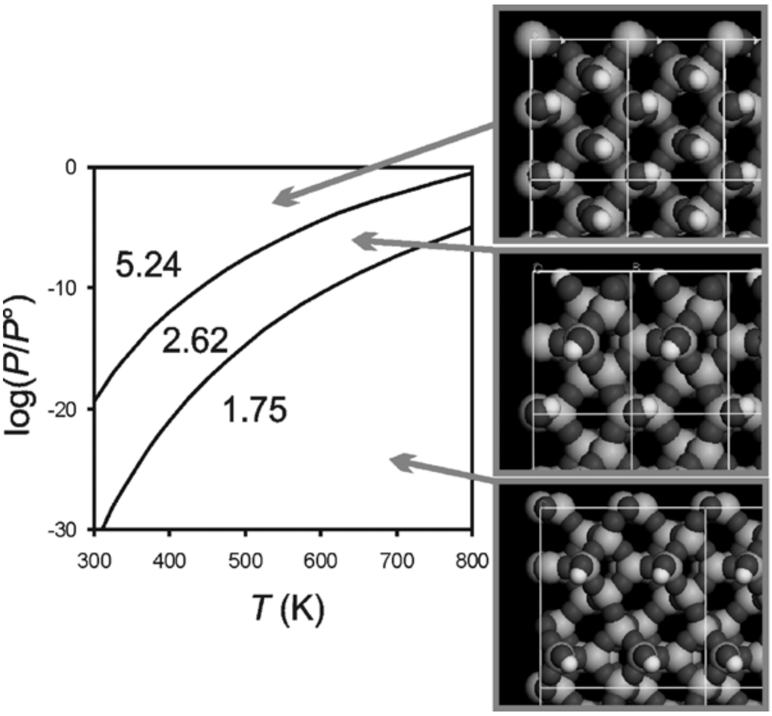
Polyoxometalates (POMs) show versatile and highly tunable properties, which make them interesting catalysts in acid-base and oxidation reactions. Further, their grafting onto surfaces allows the improvement of reaction yields because of the increase of available active sites per surface unit and lowers the waste producing due to separation procedures of liquid phases. The surface has an impact on the property of POM and hence on its activity: very little is known about the rules governing this interplay and of the nature of the bonding between POMs and surface.



In the present communication, the DFT analysis of the grafting of the Keggin complex $H_3PMo_{12}O_{40}$ onto 001-, 101-, and 111-cristobalites (CRIS) surfaces is considered using the VASP code. $H_3PMo_{12}O_{40}$ is a strong acid, which can become covalently bonded to the surface through reaction with the surface hydroxyls of SiO_2 and water elimination. This reaction, as well as the deshydroxylation of SiO_2 surfaces, is endothermic but turns out favorable at high temperature and low water partial pressure. Full stability diagrams of the different systems are given.

Keywords: POM, silica surface, grafting, deshydroxylation, DFT.

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Active Sites for CO, NO and N_2 Dissociation on Ruthenium

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The dissociation of CO, NO and N_2 on transition metal surfaces has been shown to be the reactions that require low barrier in the technologically most important catalytic reactions viz. Fischer-Tropsch (FT), nitric oxide reduction and ammonia synthesis, respectively.[1-3] Several theoretical and experimental studies have been carried on various transition metal surfaces to identify the active sites for the low barrier dissociation of these diatomic species.[1-6] In an experimental and theoretical study Dahl et al showed that the active sites on Ru steps reduce the N_2 dissociation barrier by 145 kJ/mol.[6] They also proposed that minimum of five atoms are required for the N_2 dissociation. We have recently shown that the minimum number of atoms required for CO and N_2 dissociation on the Ru(1121) surface are six and five respectively.[7,8]

In the present work we discuss the active sites for the dissociation of CO, NO and N_2 on the open Ru (1121) surface. We employ periodic density functional approach as implemented in the VASP package to investigate these reactions.[9] Our results show that the dissociation barrier of CO is 65 kJ/mol which is lower than that on the step surface.[7] The crucial factor for such a low dissociation was the structure sensitivity of the active site responsible for the stable product state in the transition and final states. Our study reveals that the B5 sites present on Ru(1121) surface are also highly active for N_2 and NO dissociation. Furthermore, we extend our study to show that these sites are also present and are active for the diatomic molecular dissociation on Ru nanoparticles.

Our main conclusions from this work are as follows, (1) the dissociation of CO, NO and N_2 are structure sensitive reactions and depend on the local electronic and geometric properties of the active sites, (2) the active sites can be only found on the low coordinated planes such as steps, open surfaces as well as nanoparticles and not on flat surfaces and (3) the activation barrier depends on the electronic as well as geometric configuration of the diatomic molecules in the initial, transition and final states during the reaction.

Keywords: active sites, catalysis, periodic DFT

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DFT and High Resolution ^{27}Al MAS NMR Investigation of Aluminum Siting in Frameworks of Silicon Rich Zeolites

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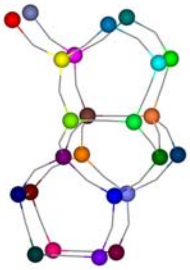
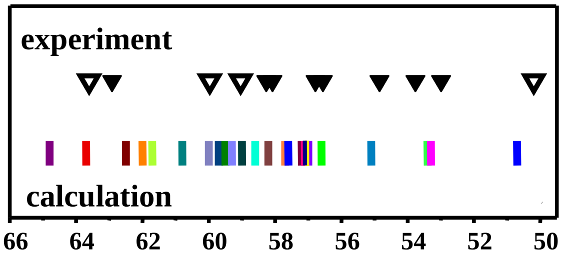
One of the most important properties of silicon rich zeolites is the presence of Al atoms in the zeolite framework and their siting in distinguishable framework T (T = Si, Al) sites. Since the protons, single metal ions and metal-oxo complexes, representing the active sites in catalytic and adsorption processes are bound to AlO_4^- tetrahedra, the crystallographic positions of Al and the local aluminum distribution govern the location of the active sites and their properties. Therefore the knowledge of the Al siting is of crucial importance for both experimental and theoretical studies of catalysts based on silicon rich zeolites.

The siting of Al atoms in distinguishable framework T sites of silicon rich zeolites of the MFI, [1, 2] FER, CHA, and TON [3] structures was investigated employing ^{27}Al 3Q NMR spectroscopy and DFT(BLYP/TZVP)/MM(polarizable force field) calculations. It was found that the siting of Al atoms is neither random nor controlled by the thermodynamics of Al atoms in the distinguishable framework T sites. The calculations employing our newly developed bare charged framework model [1, 2] of a fully hydrated silicon rich zeolite allowed assigning observed ^{27}Al NMR resonances to the corresponding distinguishable framework T sites for the studied structures. In addition, particular attention was paid to the presence of Al-O-(Si-O)$_{1,2}$-Al. Our calculations revealed that the ^{27}Al NMR isotropic chemical shift of Al in Al-O-(Si-O)$_{1,2}$-Al in MFI can be significantly affected (up to 4 ppm) by the presence of the other Al. [4] Thus the existence of Al-O-(Si-O)$_{1,2}$-Al sequences in zeolites can result in a change of properties of AlO_4^- tetrahedra.

T sites of ZSM-5



^{27}Al shifts (ppm) of ZSM-5, Ref. [1, 2]



Keywords: DFT, QM/MM, zeolite, ^{27}Al MAS NMR, BLYP

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Density Functional Theory Analysis of Aluminum Nanostructures for Hydrogen Storage

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Nowadays the engineering problems are focused on the area of nano-sized systems. The study and design of structures in engineering utilizes stress analysis under certain conditions. However it is more complicated for systems of nano-size than for e.g. civil engineering or mechanical engineering. The arising differences between macro and nano-engineering are born from quantum effects, which play significant role in systems of molecular level, thus it has to be taken into account in analysis. The studies of consequences of the electromagnetic forces between electric charges and currents within molecules provide new prospective on interactions between atoms and molecules. The local reactivity of electronic charge might be evaluated using electronic stress tensor [1,2] defined within Regional Density Functional Theory (RDFT) method [3]. The calculated stress based fields show the ultimate strength of the nano-material at different regions (parts, like chemical bonds, chemical groups, and active centers) the structure is composed of. The method has been successfully applied to study of electronic structure and bond phenomena in molecules [4]. Particularly prospective applications of this method are theoretical studies of hydrogen storage materials (HSM) for reversible hydrogen adsorption. The key systems of this research are built by metal nano-clusters showing superior reactivity of its surface comparing to crystalline walls, as shown by numerous results. It is important to mention that metallic and semiconducting clusters, the nanoparticles displaying properties of nano-surfaces, might be produced among others by evaporation in laser beams or by electric impulses as well as in solution. We have found the aluminum clusters in the center of our interest, next to platinum and palladium (metals known as industrial catalysts of hydrogen chemistry), because of its potentially excellent properties for HSM, like low weight and high capacity. Moreover, besides the insights into the engineering of hydrogen storage materials, the research brings valuable information on very poorly known (comparing to boranes) aluminum hydride chemistry. We present the results of electronic stress tensor and regional DFT analysis of small Al-clusters hydrides for the application in hydrogen storage technology. The electronic structure of Al-clusters has been characterized by mapping of local energy density, electronic chemical potential and stress tensor density in the molecular volume. Additionally bond order parameters based on energy density and chemical potential were calculated to evaluate interactions between atoms.

Keywords: hydrogen storage, electronic stress tensor, energy density, Regional DFT

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Hydrothermal synthesis of $VOPO_4.2(H_2O)$: modelisation of the initial reaction mechanisms

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Nowadays, vanadophosphates are still the subject of numerous experimental studies due to the variety of chemical and physical properties exhibited (low dimensional magnetism, catalysis, ionic transport,…). They are also characterized by a rich structural chemistry, that comes from the accessibility to three of the vanadium oxidation states (III-V), the different vanadium coordination polyhedra available (tetrahedra, square pyramids, distorted and regular octahedra) and the diversity of coordination modes with phosphorus tetrahedra. [1-2]

Hydrothermal synthesis has shown to be a particularly fruitful approach allowing to obtain several structurally unprecedented vanadophosphates compounds. However, due to the intrinsic black box nature of the reactor, *in situ* analyses are difficult to perform. Therefore both the chemical species and the mechanisms involved in the nucleation and growth of vanadophosphates remain largely unknown.

Herein, we present results of an investigation by means of both static and ab initio molecular dynamic calculations of the reaction mechanisms of H_3PO_4 with H_3VO_4, the latter having previously demonstrated to be the most stable species under emulated hydrothermal synthesis conditions [3]. Such processes are expected to occur during the formation of the uncharged layers, having the internal connection scheme $[(H_2O)VOO_{4/2}][PO_{4/2}]$, of the prototypical V(V) compound: $VOPO_4.2(H_2O)$ (Fig 1).

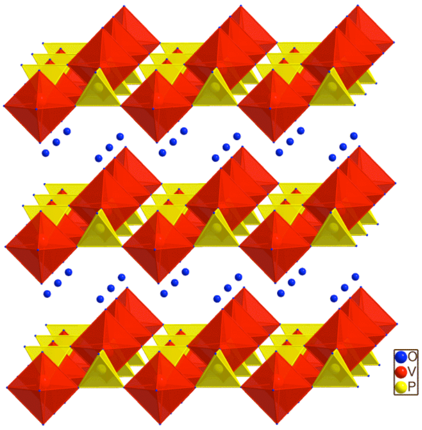

Figure 1 : Crystallographic structure of $VOPO_4.2(H_2O)$. Vanadium coordination octahedra are shown in black and phosphorus coordination tetrahedra in grey. The small black spheres correspond to the oxygens of the interstitial water molecules.

Keywords: vanadophosphates, reaction mechanisms, hydrothermal synthesis

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Characterization of Group 5 Transition Metal Zeolite Framework Sites

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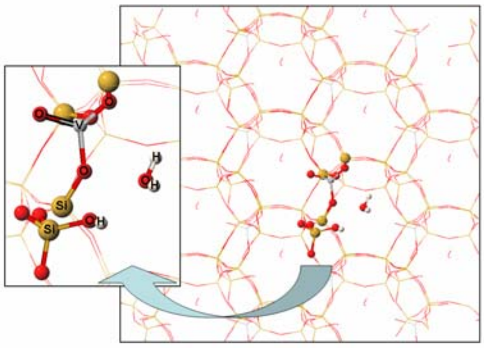
Ab initio periodic DFT calculations on the structural and energy properties of different model vanadium framework sites in vanadium-substituted zeolites containing sodalite cavities are presented and related to experimental FTIR measurements on V containing SiBEA zeolite. The vanadium framework sites are characterized by their calculated geometrical parameters, vibrational frequencies and deprotonation energies. Vanadium(V) is stabilized in the zeolite framework in two different tetrahedral sites: one in the form of a very stable vanadyl group and the other possessing an hydroxyl group. Tetrahedral Vanadium(IV) sites, although much less favorable, are also present with an acidic hydroxyl group. Hydration of vanadium-substituted zeolites is an athermic process. Water does not affect the coordination of vanadium and remains in the center of the cavity. These results are fully consistent with experimental data and allow to identify the molecular structure of vanadium sites in a zeolite framework [1].

The acid/base properties of group 5 zeolitic structures are discussed using the molecular electrostatic potential [2] and Fukui functions [3]. The results point out that that vanadium doped zeolites are less appropriate for electrophilic reactions, yielding minor basic character when they are compared with Nb or Ta doped zeolites. Concerning the topology of the site, an electrophilic attack is predicted to be more appropriate on T=O (T = V, Nb, or Ta) moiety for all three group 5 elements studied. Ta=O site is more reactive and thus less stable, while the high stability of the V=O group is confirmed. For a T-OH site, the basicity of the bridging oxygens and in a lesser extend the Next Near Neighbor bridging oxygens is predicted. The analysis of the results based on the molecular electrostatic potential predicts that Ta zeolites are more suited for reactions with hard electrophiles such as H^+, BF3, etc. In other words, the Ta-OH group is a basic site and is expected to be important in acid-base catalysis. The results are confronted with protonation energies.



Keywords: Zeolites, Vanadium, Niobium, Tantalum, Fukui Function, Periodic DFT

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Unimolecular Reactivity of Uracil-Ca^{2+} Complexes in the Gas Phase: Experimental and Theoretical Study

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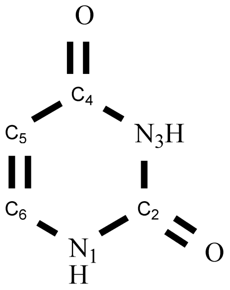
The gas phase reactions between Ca^{2+} and uracil have been investigated by combining mass spectrometry and density functional theory (DFT) calculations carried out at the B3LYP/6-311++G (3df,2p) // B3LYP/6-31+G(d,p) level. We have considered the most stable tautomers of Uracil-Ca^{2+} complexes, which have been studied previously [1]. Positive-ion electrospray spectra show that the reaction of uracil with calcium (II) gives rise to singly charged species. The most intense peak (m/z 56.96) corresponds to $CaOH^+$, which is formed in Coulomb explosion processes. However, the MS/MS experiments show additional peaks, which corresponds to neutral loss, HNCO and H_2O. A systematic study of the spectra obtained with different labelled species, namely, uracil-2-^{13}C, uracil-3-^{15}N, uracil-2-^{13}C-3-^{15}N, concludes unambiguously that the loss of HNCO involves exclusively atoms C2 and N3. Suitable mechanisms for these fragmentation processes are proposed through a DFT theoretical survey of the corresponding potential energy surface.



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A DFT Study on the Mechanism of Ruthenium Catalyzed Azide-Alkyne Cycloaddition Reaction

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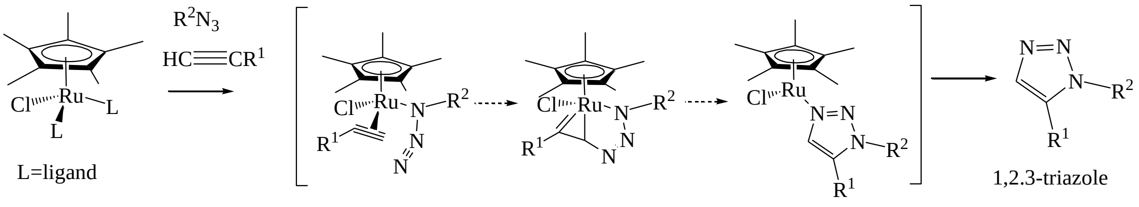
[1,2,3]-Triazoles are important five-membered nitrogen heterocycles since they are biologically active agents and involved in a wide range of industrial applications. The formerly most widely used method of their synthesis was via thermal 1,3-dipolar Huisgen cycloaddition of azides with alkynes. However, with this method some disadvantages, such as high temperature requirement, poor regioselectivity and low yield of product are present, which have been overcome by the 'click' chemistry reported independently by the Sharpless[1] and Meldal[2] groups. Their method of Cu(I)-catalyzed cycloaddition reaction allowed dramatical improvement of regioselectivity to produce the 1,4-regioisomer exclusively, increased the reaction rate up to 10^7 times and eliminated the need for elevated temperatures. Recently, usage of Ru(II) complexes as catalyst enabled the use of both terminal and internal alkynes (unlike the case in Cu(I)) and provided synthetic route to fully substituted 1,2,3-triazoles[3]. In the work of Boren et al, either 1,5 or 1,4-products are obtained depending on the Ru (II) catalyst. It is reported that pentamethylcyclopentadienyl ruthenium chloride [Cp*RuCl] complexes could yield 1,5-disubstituted triazoles while in the absence of Cp* ligand only 1,4-regioisomer forms. In our study, the reaction of Ru catalyzed cyloaddition of alkynes with azides is modeled thoroughly by making use of DFT theory. The mechanism of a series of Ru(II) complexes in azide-alkyne cycloadditions have been investigated and the effect of ligand and the substrate on the reaction mechanism have been elucidated by considering the experimentally worked systems in order to understand the dynamics of the mechanism for synthesizing desired compounds.



Keywords: ruthenium, azide-alkyne cycloaddition, click chemistry

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Adsorption of NO and NO_2 in copper and cobalt exchanged CHA and SAPO-34: Discerning the reactivity of cations

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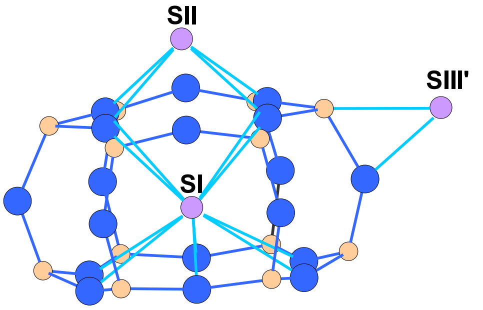
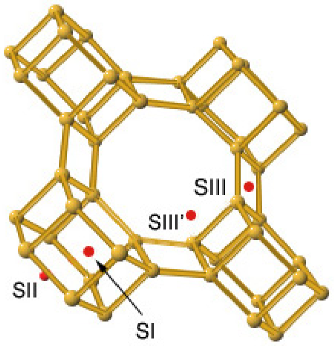
The adsorption of NO and NO_2 at transition metal cations is an important step of the deNOx process, therefore it is a subject of theoretical and experimental studies. Extraframework cations in zeolites and zeolite-related materials form adsorption complexes with different stability, depending on the type of the cation, the cation position, and the composition of the nearest structural building units. Spectroscopic methods (IR, Raman) provide relevant information on the type of bonding in the adsorption complexes, but they are limited in discerning the reactivity of the different cation sites: the frequency shifts are in most cases rather small.

Though the adsorption properties and reactivity of cations in zeolites depend on the nearest cation environment, for accurate theoretical studies it is necessary to take a sufficiently large part of the structure explicitly into account [1]. In the present study we have selected zeolite chabazite and SAPO-34, both with CHA topology and a small unit cell, consisting of 36 atoms. The D6R (double six-ring) is a stable secondary building unit in a number of zeolite structures; for CHA it also corresponds to the unit cell. We apply the cluster method to study cation sites in the vicinity of the D6R [2] with the B3LYP density finctional. Cation sites in the large cage are examined by the ONIOM method, where B3LYP is used for the model system and the semiempirical PM6 method is applied to the real system of size 6T/48T (T=tetrahedral atom: Si, Al in CHA; Si, Al, P in SAPO-34). The extraframework cations are Co(II), Cu(II), Cu(I) and they are located at sites SI, SII, SIII and SIII'.





While NO forms stable adsorption complexes by linking to the cation via the nitrogen atom, NO_2 forms a number of configurations with comparable binding energies. Co(II) cations have preference to site SI in both chabazite and SAPO-34. In SAPO-34 they are able to act as adsorption centers by shifting to the SII site [3]. The cation sites SIII and SIII' which are exposed to the large cage, are of lowest stability, but of highest reactivity. Divalent cations occupy these sites only in chabazite with favorably ordered negative framework charges. Cu(I) cations at the SIII' sites have the highest adsorption capacity towards NO and NO_2.

Keywords: NO adsorption, SAPO-34, B3LYP/PM6 method

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Ion Pair Structure as a Key to Understanding Enormous Substituent Effects on pK a of the CH vertex of $CB_{11}H_{12}^-$ in DMSO

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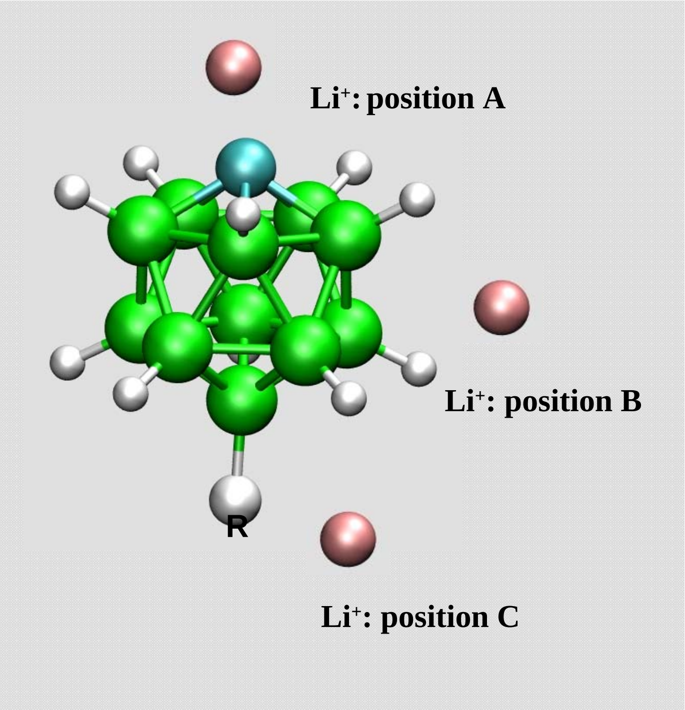
Ab initio calculations and molecular dynamics simulations were used to interpret the enormous influence that substituents in the antipodal position 12 have on the pK_a $CB_{11}H_{12}^-$ value of the CH vertex of in DMSO. It is proposed that the unusual behavior is due to a combination of electronic effects transmitted through the carborane cage with structural changes in ion pair.



Keywords: carboranes, pKa, DFT

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Interaction of Atoms and Small Molecules on Metal Surfaces and Nanoparticles

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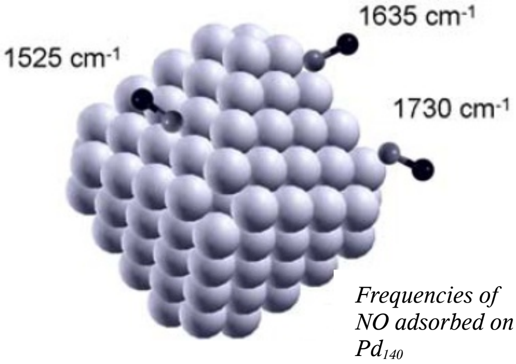
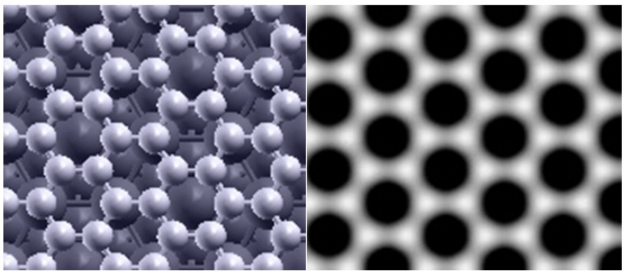
Supported nanoparticles expose special edge and corner sites giving rise to novel adsorption and reaction properties. Experimental identification can make posible to monitor the site occupation during adsorption/reaction. However, this needs the theoretical microscopic description and guidance. In this study we present a combined strategy to study activity and reactivity of atoms and molecules on supported metal nanoparticles. On one hand single-crystal (111) surfaces are considered as models of inner parts of the (111) facets of metal nanoparticles. On the other hand, cuboctahedral clusters of ~ 80 atoms provide size-independent results for adsorption energies, frequencies and other local properties while size-averaged properties tend to bulk limit.[1-3] In this sense, they are the complement to study activity/reactivity at edge/corner sites.

We present results for two different systems where this strategy was succesfully applied: *i*) the study of adsorption of NO molecules on Pd catalysts. The computed results provided characteristic computed vibrational frequencies that are directly connected with experimental IRAS signals, and explained theevolution of signals with coverage.[4] *ii*) the carbon deposition on Pt nanoparticles, where the transition of low-coverage carbidic phases to high coverage graphitic phases is investigated, showing also the effect of nanoparticles in carbon aggregation.[5]



Frequencies of NO adsorbed on Pd_{140}



Graphene on Pt(111) and STM image

Keywords: Supported Metal Nanoparticles, Nitrogen oxide, Carbon

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Fluxional Behaviour of Molybdenum-η^3-allyl-carbonyl complexes: A computational study

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Many transition metal organometallic complexes exhibit fluxionality or stereochemical nonrigidity.[1] Since the pioneering work of Faller *et al.*[2] on the dynamic behavior of pseudooctahedral molybdenum and tungsten complexes up to now, most of the fluxional processes observed in the complexes [MX(η^3-R)(CO)$_2$(L-L)] where M is Mo or W, L-L is a bidentate ligand, X is a monodentate ligand, and R is an alkenyl group have been interpreted in terms of the well-known nondissociative trigonal twist (or turnstile) mechanism, which involves rotation of the face formed by the X and L-L ligands with respect to the face formed by the allyl ligand and two carbonyl groups (see Scheme 1a). Recently, other new reaction mechanisms have also been invoked to explain the dynamic behavior found for the complexes [Mo(η^3-C$_3$H$_5$)Br(CO)$_2$(PPy$_n$Ph$_{3-n}$-*P*,*N*)] (Py= 2-pyridyl; n=2, 3) and [Mo(η^3-C$_3$H$_5$)Br(CO)$_2$(OPPy$_m$Ph$_{3-m}$-*O*,*N*)] (m=2,3).[3] To the best of our knowledge, no detailed theoretical studies have been devoted to understand these kind of rearrangements.

As a first step to get a deeper knowledge of the fluxional processes involved in the complexes [Mo(η^3-R)(CO)$_2$(L-L)X], we undertook a theoretical investigation on the dynamic behavior of [Mo(η^3-C$_3$H$_5$)(CO)$_2$(P-P)Cl], paying special attention to the level of theory used by comparing our theoretical results with the experimental data available.

Keywords: fluxional, dynamic behavior, trigonal twist mechanism, density functional calculations

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Poster Abstracts for DFT09

DFT Study for Loss of Hydrogen Molecule from Acetonitrile Induced by Silver ions in Gas phase

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In the gas phase, it is generally admitted that the interactions of transition metal ions with a variety of ligands such as amines, alcohols, cyano and carbonyl functional groups are electrostatic in nature. These relatively weak interactions are known to preserve the geometry of the ligands in the complex.[1-5] However, recent studies by Drewello *et al*[5] using high resolution Electro Spray Ionization Mass Spectrometry, show that the reaction of a silver ion with neutral acetonitrile molecules leads to silver-acetonitrile complexes with a loss of H_2 molecules (see equation below). This loss indicates a new type of interaction between the Ag^+ and the acetonitrile that is stronger than the electrostatic ones and may play an important role in heterogeneous catalysis and organometallic reactions. For example, the reaction between silver ions and neutral acetonitrile molecules plays a major role in peptide sequence analysis. However it is difficult to predict the exact silver-acetonitrile complex structure and the mechanism behind the hydrogen loss using available experimental methods. Therefore, we have undertaken high-level computational and theoretical studies using Density Functional Theory. We present preliminary results on the structures, binding enthalpies, free energies, entropies and mechanism for H_2 loss for the reaction between one silver ion and two acetonitrile molecules.

$$Ag + 2CH_3CN \xrightarrow{-H_2} CH_3CN{-}Ag{-}NCCH \xrightarrow{-H_2} Ag(NCCH)_2$$

Keywords: Mechanism, DFT, Silver cluster

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A DFT study of the CO_2 adsorption on different cermet interfaces Ni-Ba*M*O_3 (*M* = Ti, Zr and Ce)

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Some ceramics, used as electrolytes for Protonic Conducting Fuel Cells (PCFC), are not chemically stable in presence of CO_2. An option which would constitute a breakthrough in this field would be to develop CO_2 tolerant ceramics. Perovskites are important ceramic materials exploited in a wide range of applications such as electrolyte for PCFC. The adsorption of CO_2 on different surfaces of cermets, such as Ni-Ba*M*O_3 (*M* = Ti, Zr and Ce) are investigated at the *ab initio* quantum mechanical level, using among others the CRYSTAL06 code. The calculations have been performed at the Hartree-Fock, density functional theory and hybrid levels.

This work focus mainly on the CO_2 adsorption on the (001) and (110) surfaces of the various perovskites with a BaO or *M*O_2 termination. The equilibrium geometries, surface stabilities, and CO_2 adsorption energies have been evaluated. For each compounds, it is found that the BaO termination is more stable than the *M*O_2 termination. Consequently, the adsorption energy of CO_2 is higher on the *M*O_2 terminated surfaces than the BaO ones. The relative energy of reactions with CO_2 of each surfaces are : $BaCeO_3 > BaZrO_3 > BaTiO_3$. The stability and the decomposition of CO_2 into various compounds, such as CO, has been evaluated. The role of Ni at the cermet surfaces Ni-Ba*M*O_3 is also commented.

Keywords: DFT, adsorption, CO_2, nickel and perovskites surface

POSTER PRESENTATIONS

Topic 7.

Large systems and biosystems

Icosahedral boron carbides under extreme conditions: an ab initio study.

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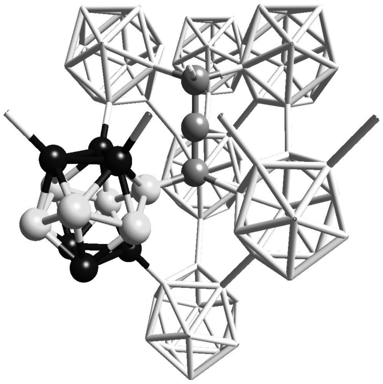
Boron carbides constitute a class of materials of industrial interest due to their remarkable mechanical properties, used in cutting tools for example. However, they can not be used as protective materials as they do not sustain shockwaves. In order to understand this behaviour, we have investigated the evolution of their physical properties under extreme conditions such as high pressure and high temperature with theoretical methods based on density functional theory (DFT) [1] and density functional perturbation theory (DFPT) [2].

The atomic structure of boron carbide (B_4C) mainly consists in $B_{11}C$ icosahedra (with C in polar site) linked by CBC chains [3,4,5]. We have investigated many other phases with various carbon concentrations and found that most of our structural models are metastable with respect to B_4C [6]. For some of them, we find that a structural modification does occur under pressure. Moreover, calculated transition pressure is in good agreement with experimental observations [7]. Occurence of these structures as defects in experimental samples yields an explanation about why boron carbides do not sustain shockwaves.



Keywords: boron carbides, structural defects, high-pressure, density functional pertubation theory

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QM/MM Meta-Dynamics Study of Asparagine Deamidation in Proteins

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Asparagine (Asn) residues in peptides and proteins are subject to spontaneous non-enzymatic deamidation to form aspartate or iso-aspartate at a rate determined by protein structure and environment [1]. Deamidation causes time-dependent changes in charge and conformation and limits the lifetime of peptides and proteins. This has led to the '*molecular clocks'* hypothesis [2], which suggests deamidation is a biological molecular timing mechanism that could be set to any desired time interval by genetic control of the primary, secondary, and tertiary structure surrounding the amide. A notable example is Bcl-x$_L$, an anti-apopotic protein that regulates cell death and undergoes a 'complete loss' of function upon deamidation; suppression of deamidation in Bcl-x$_L$ plays a pivotal role in the survival of tumor cells [1].

Deamidation occurs over a wide range of biologically relevant time intervals; this suggests that different mechanisms may be operative. While a succinimide-mediated deamidation pathway was originally suggested [3-5], two new 'competing' routes for deamidation of asparagine residues will be presented. In order to compare relative energetics and feasibilities of plausible routes, QM/MM molecular dynamics simulations, in a periodic water box, were performed on a model peptide. Free energies of competing pathways were calculated *via* meta-dynamics calculations utilizing the CP2K code [6], where the catalytic effect of water molecules was explicitly analyzed. These calculations have served as a stepping stone for QM/MM metadynamics calculations on deamidation of Bcl-x$_L$.

Keywords: Deamidation, asparagine, Bcl-x$_L$, meta-dynamics, QM/MM, CP2K

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Full Quantum Calculation of Horse Heart Carbonmonoxy Myoglobin

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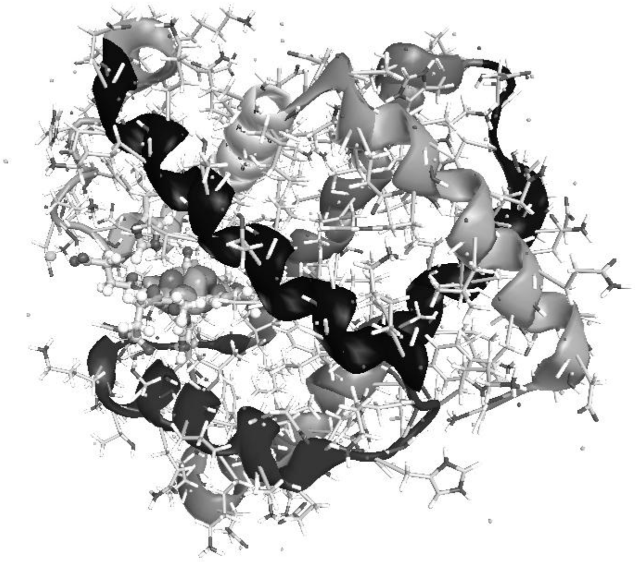
Myoglobin (Mb) is a typical hemoprotein which has a hetero molecule heme in its reaction center. The heme in Mb is an iron protoporphyrin IX and plays as the binding site of a small gas molecule, such as O_2, CO, and so on. Nowadays, all-electron wavefunctions of proteins can be estimated by high performance computing [1], but it is still difficult to lead SCF to successful convergence especially for hemoproteins like Mb, because the structural environment strongly influences the amount of orbital element mixing among an Fe, porphyrin, and apo-protein. Electron distribution changes over the wide range according to the computational models. In this study, we carried out the full quantum calculations on horse heart carbonmonoxy Mb (MbCO) by our Gaussian basis DFT program, ProteinDF [2], and established a successful treatment of its SCF convergence.

Steady SCF convergence could be achieved by the QCLO method [3]. Reasonable initial guess for full quantum calculation was constructed from localized orbitals of nine polypeptides that consisted of efficiently divided apo-protein and heme moiety including important residues interacting with the reaction center strongly.

As the result, two important orbitals having back bonding character from Fe $3d_{t2g}$ to carbonyl π^* orbitals that determined the Fe-CO bond strength and could be easily affected by external electrostatic field were observed at just below the highest occupied eigenstate which consisted chiefly of Fe $3d_{xy}$ orbital. Analysis among the several different computational structures of Mb showed that electrostatic potential caused by distal histidine significantly influenced on those bonding states and brought about orbital level shifts of up to 0.5 eV. A comparison of the results between our full protein model and the conventional partial models indicated that quantum chemical study to take apo-protein fully into consideration was indispensable in the representation of the electronic structure of active site in MbCO.



Keywords: Carbonmonoxy Myoglobin,
full quantum treatment on protein, Gaussian basis density functional calculations

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Multiscale Density Functional Treatment of Nanosized Solutes

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The conventional QM/MM procedure based on molecular simulations of solvent provides self-consistent calculations of molecular solutes, but it is usually applied only for few-atomic species due to huge computational costs required for the simulations. An alternative reference-interaction-site-model-self-consistent-field (RISM-SCF) approach uses the integral equations theory of molecular liquids to obtain the information encoded in the solvent distribution functions that reduces costs of computations by 3 orders with respect to simulations. But applications of the approach are at present limited by solutes with dozens of atoms, since it treats the solvent with the use of a uniform grid, whereas the number of grid points rises fast as solute size increases. What is why the state-of-the-art of the method is restricted only the classical treatment of nanosized solutes.

I have developed a multi-scale computational tool for self-consistent DFT calculations of the electronic structure of nanosized solutes and the density distribution of solvent molecules around them.[1] The aim of the tool is to combine the advantages of the RISM-SCF methodology with the power of multi-scale algorithms based on wavelets. The problem can be formulated as follows. The multi-resolution analysis provides a methodology to select the region of interest. The distribution function are expanded into a series in a multi-scale basis set instead of search of data on distribution functions in the grid points, and the problem reduces to the evaluation of the approximating coefficients for the chosen basis set. Wavelets are used to treat the distribution functions, while hierarchal algorithms used in the approach can convert the original concept into a powerful computational tool and will allow me to construct a robust computational scheme for the self-consistent calculations. These findings together with the novel method of extracting and parameterization of the data on the bridge functional will make realistic accurate calculations of various properties of nanosized solutes.

The benchmarks have been provided on the basis of calculations of J-aggregates consisted of several thousands atoms. I found the ladder-like H-aggregates to be the most stable in vacuum. However, the complexes formed by more than 4 monomers change their arrangement while self-assembling in water and form brickwork structures typical for J-aggregates. The calculated binding and dimerization energies of the aggregates are in agreement with available experimental data. The developed computational tool bridges the gap between quantum and statistical mechanics, providing a deep insight and understanding on detailed arrangements of the electron and the solvent distributions.

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Application of Linear Scaling DFT to the Stability of G-Quadruplexes in DNA and RNA

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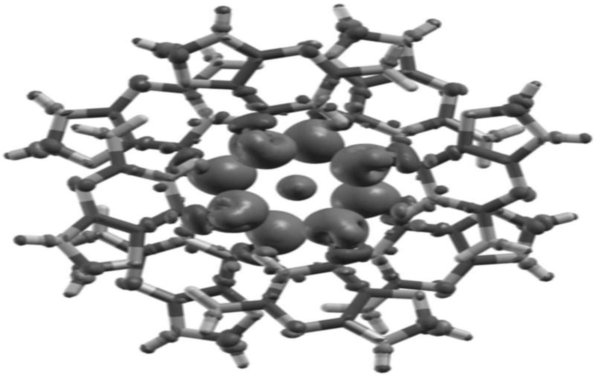
Guanine-rich regions of DNA can form four-stranded structures known as G-quadruplexes [1]. These consist of stacked, hydrogen-bonded quartets of guanine bases, stabilised by monovalent metal ions running up the central axis. G-quadruplexes are found in biologically significant genomic regions, such as telomeres, and are considered to be an important drug target. However, for the rational design of drug molecules, an understanding of the structures of G-quadruplexes under different physiological conditions is vital.

The MM-PB/SA approach [2] is a well-established technique for the study of relative free energies of complex biomolecules. Trajectories of the biomolecule in solution are generated and then post-processed by decomposing the free energy of the structure into gas phase energy, solvation free energy and entropy. Here, we reduce the reliance on the classical force field by calculating the gas phase energies using the linear scaling DFT code, ONETEP [3]. We also discuss the future possibility of calculating the free energy of solvation from first principles. The combined MM-PB/SA and *ab initio* approaches give us both more reliable relative free energies of complex biomolecules and also new information on the electronic structure of the different structures.

Here, we apply a combination of classical molecular dynamics simulations and linear scaling DFT to study the relative free energies of parallel and anti-parallel structures of G-quadruplexes believed to exist in the telomeric regions in human chromosomes. We show that stability is dependent on both long time scale motion of metal cations and polarisation effects within the quadruplex structure, supporting the case for this combined methodology. The effect of the radius of the metal cation is discussed and factors influencing the experimentally observed increased stability of G-quadruplexes in RNA are examined.



Keywords: Linear scaling DFT, G-Quadruplex, MM-PB/SA

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Modeling radiation-damage processes in organic solids via DFT calculations of EMR parameters

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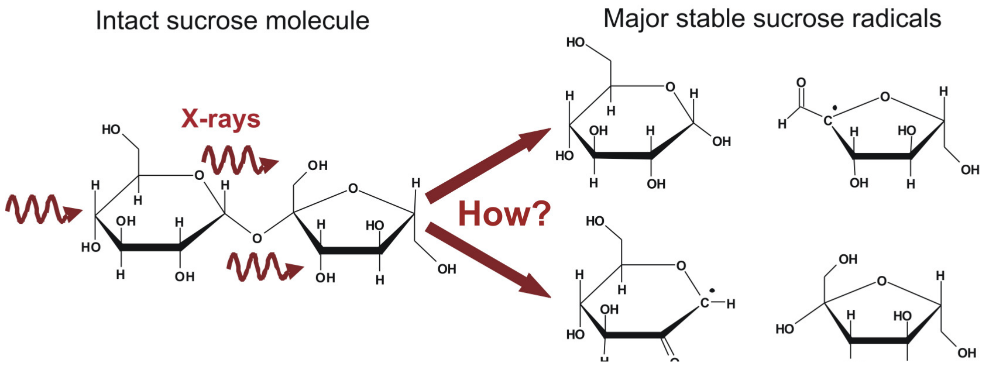
High-energy radiation induces radicals in organic materials. When created in biological macromolecules such as DNA, these can cause harm to living organisms. This detrimental effect is also exploited for the sterilisation of e.g. foodstuffs, and radiation-induced radicals are used for dosimetry purposes. Knowledge of the structure of the radicals and their formation mechanisms is therefore of fundamental importance.

In particular, radiation-induced radicals in solid sugars are studied (i) as model systems to gain insight into the precise role of the deoxyribose unit in the radiation chemistry of DNA and (ii) because of their potential as (emergency) dosimeters. X-irradiation typically gives rise to a variety of primary radicals in these systems, which then transform into stable radicals or diamagnetic species via one or more radical reactions. A prerequisite for unraveling the formation mechanisms is the identification of the different intermediate (semistable) radicals.

Experimentally, solid-state sugar radicals can be characterised in detail by electron magnetic resonance (EMR) experiments. These allow determination of *EMR parameters* which describe the interaction of the unpaired-electron spin with its lattice environment, e.g. with (nearby) nuclear spins. Theoretical calculations of EMR parameters with DFT codes are increasingly being used to help clarify, interpret and explain experimental results.



Recently we have managed, in a combined experimental and theoretical approach, to identify the structure of the major radiation-induced stable radicals in solid sucrose [1,2,3] (see Figure). We currently are investigating their formation mechanism, also via both EMR experiments and DFT modeling. A summary of the results obtained so far are presented.

Keywords: magnetic resonance, DFT, radiation, radicals, organic, solid state

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Elucidation of the acetamide hydrolysis mechanism using QM metadynamics simulations as a model for amide hydrolysis in proteins

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The reaction mechanism for the hydrolysis of amide bonds is a much debated topic in literature. This is not surprising when considering the variety of biologically significant domains in which this reaction is of interest, ranging from peptide bonds to protein side chain degradation. For instance, asparagine (Asn) and glutamine (Gln) residues are known to undergo spontaneous nonenzymatic deamidation in water to form aspartic acid and glutamic acid residues under physiological conditions. Deamidation could be the result of a hydrolysis reaction, either via a concerted or a stepwise mechanism.[1]

Gas phase calculations have shown that explicit water molecules play an important role in this reaction, but to date, no simulations of hydrolysis pathways using a periodic water model have been performed.

In this work, we perform quantum mechanical metadynamics simulations on the hydrolysis of acetamide as a model compound for Asn or Gln. The periodic simulation cell consists of one acetamide molecule and 90 water molecules in a cubic 15 Å box.

From all previously suggested pathways and a new, alternative route, the most competitive pathway can be identified. These results give a clearer insight in deamidation processes on proteins and polypeptides and show that an adequate description of the natural surroundings of the active species is necessary for obtaining a realistic image of biological processes.

Keywords: hydrolysis, deamidation, metadynamics

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On the performance of various DFT functionals in the description of periodic systems: from quasi-1D-materials to aluminosilicates.

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The performance of twelve DFT functionals (LDA, GGA and hybrids) in describing structural, electronic, energetic and vibrational properties of various classes of materials, from quasi-1D[1] (*i.e.* nanotubes) to 3D structures[2] (aluminium hydroxides, aluminosilicates, oxides) are discussed. The list of Hamiltonians includes the recently proposed GGA[3] (PBEsol, WC, SOGGA) and hybrid[2,4] (WC1LYP and B1WC) functionals.

Calculations were performed with a development version of the periodic *ab initio* CRYSTAL code by using all-electron Gaussian-type basis sets of various sizes. The full exploitation of the symmetry (translational, helical and point symmetries) in the mono- and bi-electronic integrals calculation and in the Fock matrix diagonalization allows to simulate large size systems (*e.g.* garnets, chrysotile and carbon nanotubes) at low computational cost.

The least deviation from experimental structures is obtained with the hybrid PBE0 functional. Vibrational frequencies are more accurate when computed with hybrids, in particular for systems containing H atoms, where B3LYP gives the best description of the H-modes. The vibrational spectra of H-free systems computed with PBEsol, SOGGA-PBE and WC-PBE are of the same quality as the ones provided by PBE0 and B1WC. Band gaps exhibit a strong dependence on the functional; also in this case hybrids yield the best results.

The relative stability of polymorphs is well reproduced with the twelve functionals when the compared systems have about the same density *(e.g.* gibbsite *vs* bayerite, graphene *vs* carbon nanotubes). In the other cases (*e.g.* boehmite *vs* diaspore, kyanite *vs* andalusite, diamond *vs* graphite), LDA, the recently proposed GGA[4] and B1WC functionals tend to stabilize the most dense phases, whereas the other GGA and hybrid functionals destabilize them.

Keywords: hybrid funtionals, nanotubes, aluminosilicates

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Formation of the active species in catalase and peroxidase: Insight from QM/MM calculations

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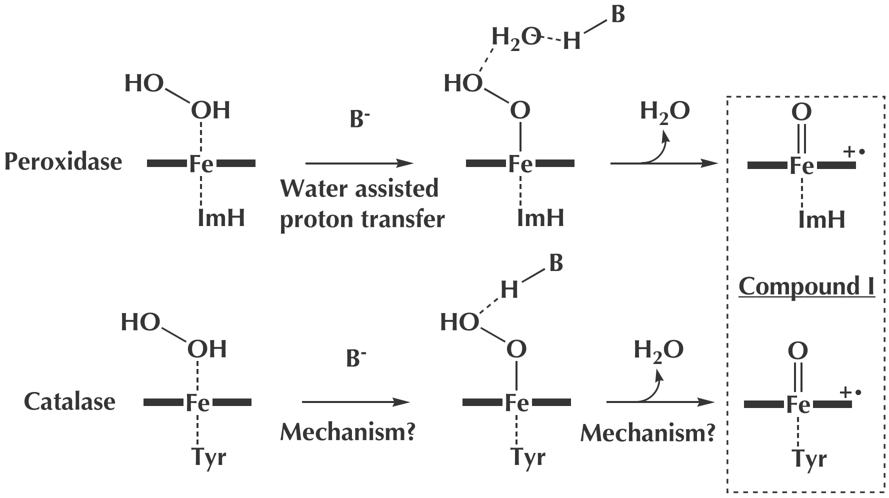
Heme enzymes represent a class of particular importance, catalyzing many reactions. The best known example, including non-scientists, is myoglobin, which allows the transport of oxygen in the blood. But there are many other examples with functions as important for living organisms. Two of them are catalase and peroxidase. These enzymes exist in all organisms in which they participate to the defense against toxic derivatives oxygen, namely H_2O_2. Catalase acts for peroxide concentrations higher than peroxidase.



In this communication, we will present QM/MM calculations made in order to elucidate the mechanism of formation of the enzymes active species (see Figure above). Peroxidase and Catalase share the same one, called Compound I. The enzymes active site environment is quite different. In catalase, contrary to peroxidase, there is no arginine in the neighbouring of the porphyrin. The proximal ligand is also different: tyrosine for catalase and histidine for peroxidase. We will discuss how these differences affect the enzyme reactivity.

Keywords: QM/MM, Enzymes, Catalase, Peroxidase

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QM/MM investigation of DNA damage: methodological aspects.

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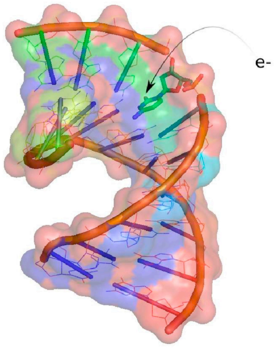
DNA is continuously exposed to endogenous and exogenous agents that compromise its integrity. The study of DNA damage, either by experimental or theoretical means, embraces an immensely large set of reactions: ca. 70 lesions have been characterized so far. There is a real need to determine their mechanisms of formation, notably for complex ones with a less efficient reparation pathway.

In that respect, DFT has proven its usefulness to gain insights into the often complex (radical) mechanisms involved (e.g. to rationalize marked regioselectivities [1]). Its intrinsic reliability to properly describe weak interactions typically ascribed to biomolecules (dispersion, hydrogen bonds, π-stacking...) constitutes a recurring question. This has motivated recent developments (see for instance [2,3]) to overcome the most serious pitfalls of DFT (lack of dispersion, self-interaction error...). We provide a comparison of energetic quantities for two DNA damage reactions (electron affinities and barrier heights): the electron induced single strand break, and the formation of cross-linked adducts.

Once the reaction is well apprehended on a model system, we examine the effects of inclusion of nucleotides at the MM level. This provides a more faithful description of DNA reactivity, with mechanical constraints and electrostatic effects that can drastically tune the ease of lesion formation. The conditions upon which such an inclusion is possible, within a QM/MM framework, is discussed in depth: link-atom or frozen orbitals scheme, partition along a polarized bond... One of our objectives is to identify reactions that can be described with a non-hybrid functional, using an artefact free QM/MM partition, and are thus well suited for ab initio molecular dynamics simulations.



Keywords: DNA damage, single-strand break, electron attachment, reaction path, hybrid methods.

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Computational Modeling Study on the Inactivation Mechanism of GABA-AT by γ-vinyl-GABA

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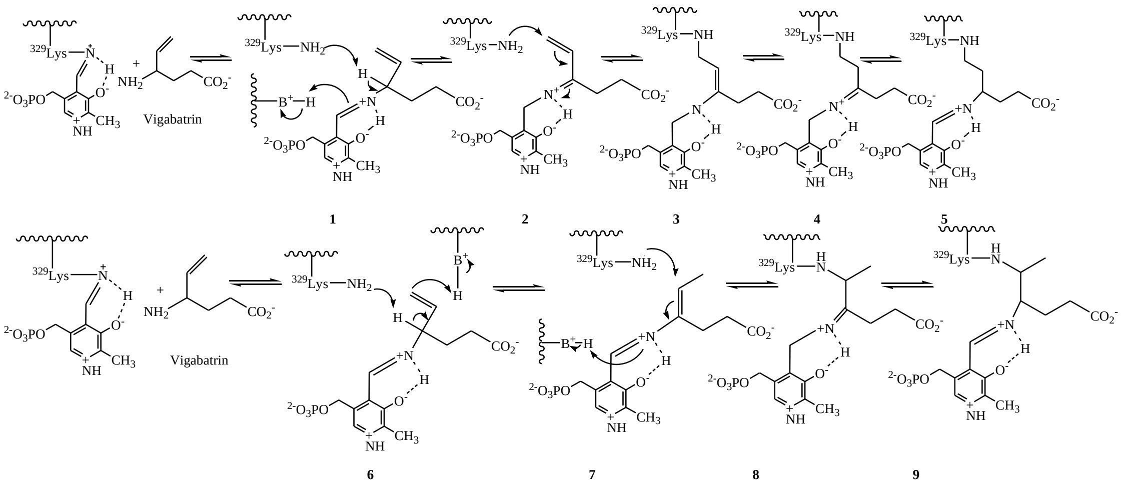
GABA-AT is a pyridoxal 5'-phosphate-dependent enzyme responsible for the degradation of the inhibitory neurotransmitter γ-Aminobutyric acid (GABA). When the concentration of GABA diminishes below a threshold level in the brain, convulsions result. Raising the brain GABA levels terminates the seizure [1]. A reduction in GABA concentration also observed in several other neurological diseases such as Parkinson's disease, Alzheimer's disease [2]. Introducing GABA via cardiovascular system is ineffective, as GABA, under normal conditions, cannot cross the blood-brain barrier. In order to increase GABA concentration level in brain, other approaches are proposed. One of them is the use of a compound that crosses the blood-brain barrier and then selectively inhibits or inactivates GABA-AT, thereby causing a buildup of GABA. γ-vinyl-GABA (Vigabatrin) is a drug which is used for this specific purpose.

Based on the experimental studies, supported by the spectroscopic and radiolabeling evidences, three different inactivation mechanisms for γ-vinyl-GABA were proposed [2]. De Biase et al. suggested that the experimental data were consistent with the formation of either 5 or 9 (Scheme 1). However, no computational analysis for mechanisms of any of the substrate analogues is found in the literature.

The aim of this study is to identify the probable reaction path on a model compound for the inactivation of γ-Aminobutyric acid aminotransferase (GABA-AT) by γ-vinyl-GABA (Vigabatrin). The B3LYP/6-31+g** method has been used to locate all the stationary points along the reaction coordinate.



Keywords: GABA-AT, vigabatrin, density functional theory

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DFT optimisations of Gallium clusters

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Gallium is a poor metal, structurally composed of Ga_2 molecules. It has a very low melting temperature, 30°C, below which it supercools. Why then have its clusters been observed to superheat [1]? Metallicity at the nanoscale is a poorly defined concept, although 'good' metals such as sodium exhibit metal-like behaviour already at very small numbers of atoms ($N < 5$) [2,3]. Gallium metal, in contrast, has molecular character in the bulk system: it has a very unusual structure - an orthorhombic 8-atom unit cell composed of dimers which have a bond distance 15% shorter than the next nearest neighbour distance. Clusters of 30-50 atoms heat to many hundreds of °C before melting [1,4]. This is in contrast to what is expected for nano-particles: it is generally expected that the melting temperature should decrease with size [5-8]. The number of energetically-close solid-state modifications of Ga with either covalent (boron-like) or metallic (aluminium-like) characteristics is definitely correlated with the rich behaviour of the element at the nanoscale. In this paper we describe the performance of density functional theory in describing the rather complicated potential energy surface of gallium, and present results for the optimised structures of both neutral and cationic small gallium clusters. We also provide a comparison with coupled-cluster results for the smallest sizes.

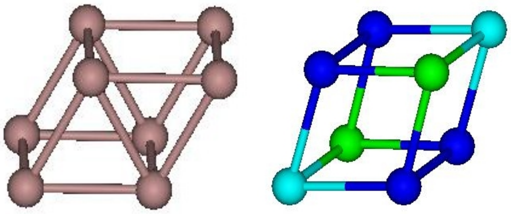

Figure 1: Left, Ga_8, Right, Ga_8^+.

Keywords: Clusters, Superheating, DFT

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Inactivation Mechanism of GABA-AT by 5-amino-2 fluorocyclohex-3-enecarboxylic acid: A Computational Study

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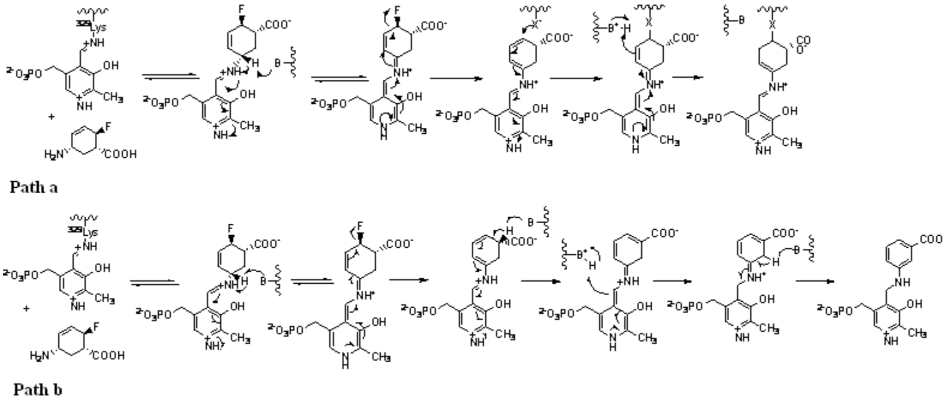
γ-aminobutyric acid is one of the inhibitory neurotransmitter in the mammalian central nervous system which has a pathway of degradation via transamination with R-ketoglutarate by catalization of pyridoxal 5-phosphate (PLP)-dependent enzyme GABA aminotransferase.[1] However it is observed that a reduction in GABA concentration in brain causes several neurological diseases. Increasing the concentration of GABA by inhibition of GABA aminotransferase, will lead treatment of epliepsy. Moreover, inhibition of this enzyme will be helpful for therapeutic applications in other neurological disorders, like Parkinson's disease, Huntington's chorea, and Alzheimer's disease. [2,3] Silverman et al. reported several fluorine-containing conformationally restricted analogues of GABA as potential mechanism-based inactivators of GABA-AT. One of them is 5-amino-2 fluorocyclohex-3-enecarboxylic acid, which was introduced as a non-commercial drug for inhibition of GABA aminotransferase.

5-amino-2 fluorocyclohex-3-enecarboxylic acid is an composite structure which has the form of cyclohexene analogue of (1*R*,4*S*)-(+)-4-amino-2-cyclopentene-1-carboxylic acid but with an added fluorine atom.[3] This compound could go through enzyme-catalyzed elimination that inactivates GABA aminotransferase either by an aromatization mechanism which produces a modified coenzyme or Michael addition that leads to a covalently modified active site residue (Scheme 1).

The ultimate aim of this study is to elucidate the inactivation mechanism of GABA-AT with 5-amino-2 fluorocyclohex-3-enecarboxylic acid in conjunction with experimental results. Methylamine was used to mimic the Lys329 in calculations. The stationary structures throughout the experimentally proposed pathways have been optimized at the B3LYP/6-31+g** level of theory.



Scheme 1. Path a. Inactivation of GABA-AT with 5-amino-2 fluorocyclohex-3-enecarboxylic acid via Michael addition. Path b. Inactivation of GABA-AT with 5-amino-2 fluorocyclohex-3-enecarboxylic acid via aromatization

Welcome to Lyon!

Keywords: GABA-AT, DFT, inhibition mechanism

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Theoretical study of piezoelectric materials in the presence of an external static electric field.

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α-quartz-type crystals such as SiO_2, $AlPO_4$, $FePO_4$, $GaPO_4$ and $GaAsO_4$ are piezoelectric materials. The direct investigation of the structural distorsion induced by an applied electric field should help to clarify the relevance of the structural contribution to these piezoelectric properties. In this work, the response properties of the α-quartz-type crystals to an external static electric field are investigated in the framework of the LCAO-DFT method for periodic systems implemented in the CRYSTAL06 package[1], using the hybrid exchange and correlation functional B3LYP. The elastic and piezoelectric tensors are first calculated from the Berry phasis method, as well as the high-frequency dielectric constant from the coupled perturbed Kohn-Sham method (CPKS) adapted recently for periodic systems [2]. The values obtained for these properties are in good agreement with experiments, showing the accuracy of the electronic structure calculation. Then, atomic displacements are determined by optimizing the geometry of each compound in the presence of an external finite field described by a "saw-tooth" electric potential [3]. The calculated variation of structure factors has been related to the relative scattering X-ray intensities experimentally observed on SiO_2 by R. Guillot et al.[4] with a field of 30kV/cm.

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All-electron DFT Study of the Photosynthesis Reaction Centre in the *Rhodobacter Sphaeroides*

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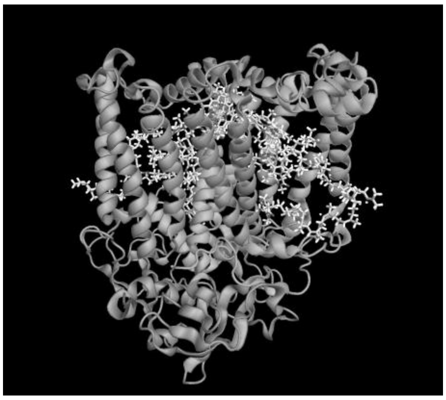
Some of the highlight facts in the photosynthetic reaction centre (PSRC) protein of purple bacteria are high efficiency of charge transfer (CT) reactions, and the striking contrast between structural pseudo-symmetry and CT functional asymmetry. The remarkable interests are attributed to not only the chlorophylls and pheophytins, but also the peripheral proteins, which built up by the H, M, and L subunits in the PSRC. Several computational studies focused on restricted regions of PSRC were carried out to describe the functions. One of the promising ways is treatment of the pigments and proteins as equivalent quantum region, but it is very difficult to achieve because of the limited computational resources. We have developed a density functional (DF) simulation program for large-scale proteins, ProteinDF, on the basis of the Gaussian base resolution of identity DF method [1]. In this presentation, we will talk about the challenge and prompt report of all-electron DF calculation of the whole PSRC protein using ProteinDF.

The calculation structure of PSRC was prepared from X-ray structure of *Rhodobacter sphaeroides* (PDB ID: 2JBC) [2] (illustrated below). The calculation procedure was based on quasi-canonical localized orbital (QCLO) method, which prepared a precise initial guess for SCF calculation [3]. All molecular orbital (MO) calculations in the QCLO method were carried out by the direct SCF method in the framework of the restricted KS equation. The B3LYP functional was used with an SG-1 grid to estimate the exchange-correlation potential. The convergence thresholds for the maximum deviation of density matrix elements and for the deviation of the total energy were 10^{-4} and 10^{-5} a.u., respectively. Finally, in the whole model which is consist of three protein subunits (H, L, M), four bacteriochlorophylls, and two bacteriopheophytins, the number of atoms, electrons and basis are almost 14 000, 52 000 and 77 000, respectively.

Progress results are summarized, as follows: In the previous step of the whole model computation, MO calculations of the pigments and proteins were separately carried out, which has already been extremely large system. In the results on the pigments and several residues, which had four bacteriochlorophylls (P_A, P_B, B_A and B_B) and two bacteriopheophytins (H_A, H_B), the HOMO spread over the special pair (P_A and P_B) and the LUMO over the H_A. The energy level distribution was very congestion, and the gap between HOMO and HOMO-1, and between LUMO and LUMO+1 were negligible small. The calculation of pigments with proteins is in process.



Keywords: large system, biomolecule, photosynthetic reaction center, all-electron calculation, Gaussian base DFT

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First principles studies of the electronic and magnetic structures of [Fe(pz)2]*x* complex.

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In recent years, there has been a growing interest in preparing and characterizing "molecular material" for their possible application in a number of different fields. In this respect, polybis(pyrazolato)iron(II), [Fe(pz)2]*x* is characterized by doubly bridged iron with pyrazolate ligands [1]. An original DFT study at both the molecular and extended solid levels is carried out for this complex system with the purpose of identifying the magnetic interactions and chemical bonding characteristics [2]. From molecular calculations, the exchange parameter J is obtained, pointing to the expected weakly antiferromagnetic ground state. The IR and Raman spectra have been calculated with relevant assignments, namely for the stretching modes. Computations for the extended solid in different magnetic configurations point to the total moment of 4 μB.fu−1, identifying Fe as divalent in high spin configuration, in accordance with a weak tetrahedral crystal field. From relative energies the ground state is antiferromagnetic. Analyses of the chemical bonding (COOP) and of electron localization function (ELF) illustrate the interactions between Fe and the cycle as well as within the *pz* cycle.

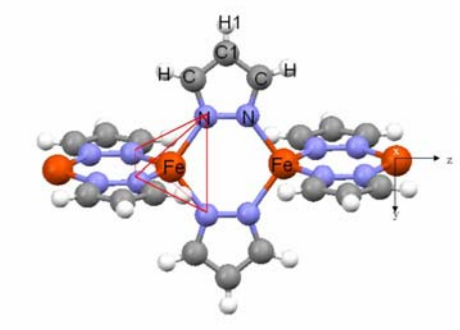

Figure 1 : Extended fragment view of [Fe(pz)2]*x*.

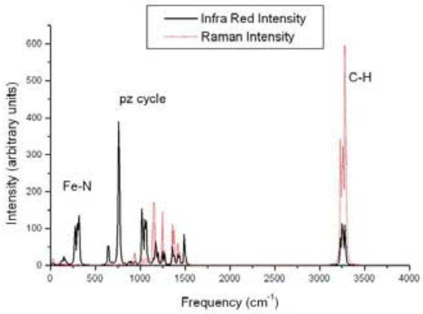

Figure 2 : Infra Red (full) and Raman (dot) spectra of [Fe(pz)2]*x*.

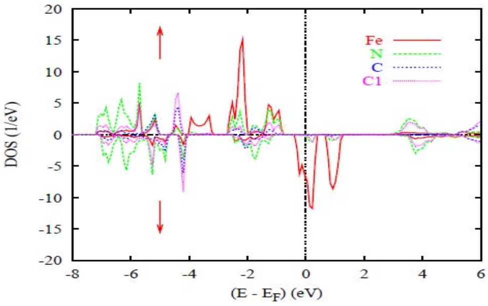

Figure 3 : Site and spin projected density of states of [Fe(pz)2]x in the magnetic configuration.

Keywords: DFT, exchange parameters, antiferromagnets, Gaussian03, IR, Raman, ASW.

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Solvatochromic shifts obtained from combination of orbital-free embedding formalism with 3D-RISM-KH method.

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We introduce a self-consistent field combination of the orbital-free embedding potential of Wesolowski and Warshel [1] with the statistical-mechanical, three-dimensional molecular theory of solvation (also know as 3D-RISM-KH) [2]. The orbital-free embedding potential [1] is used in multi-scale simulations, where the influence of the environment on the electronic structure of the embedded molecule is the subject of interest. This method has been already shown to be adequate to model the solvatochromic shifts of chromophores in polar and non-polar solvents [3,4]. In this approach the environment is represented only by its electron density which in practice is obtained from methods working at atomic resolution. This creates a bottleneck in calculations for large systems consisting of thousand of atoms. In the present work we propose a new way of generating the density of the environment by using the 3D-RISM-KH [2] method. Situated between explicit solvent and polarizable continuum models, it significantly reduces the computational effort of generating the density of the environment compared to the all-atom description and provides proper, more accurate treatment of the chemical specificity of the solvent than implicit solvation models. We demonstrate that such combination of the orbital-free embedding formalism with 3D-RISM-KH method predicts the solvatochromic shifts of several model chromophores in very good agreement with the experimental data.

Keywords: orbital-free embedding, molecular theory of solvation, 3D-RISM, solvatochromism

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Low-speed fracture instabilities in a brittle crystal

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Brittle materials under mechanical load fail by nucleation and propagation of cracks, and these cracks show well known instabilities at high crack speeds. In this work we show that new instabilities caused by the atomic structure of the crack tip can occur at low crack speeds as well [1]. Using the 'Learn on the Fly' [2] method to couple *ab initio* quantum mechanical accuracy at the crack tip with an interatomic potential further away, we perform simulations which reveal atomic rearrangements at a silicon crack tip on the (111) cleavage plane that occur preferentially on one side of the crack, but only at low crack speeds. Experiments using a novel technique for applying low tensile loads show that real silicon cracks form distinctive features on one side of the exposed crack surface. A mesoscopic model explains how the microscopic atomic rearrangements lead to the observed macroscopic features. We present extensive results on silicon and preliminary results on other brittle materials including sapphire, diamond, and silicon carbide. We conclude that even very brittle single-crystal materials can have a complex crack tip atomic structure, and that atomic scale rearrangements can lead to macropscopic changes in crack morphology.

Keywords: fracture, brittle, cleavage, silicon, ab initio, LOTF, hybrid, QM/MM

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A role of long-range interaction in ILM properties and defects creation in ionic crystals

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This is a well-known fact that in perfect classical anharmonic lattice can exist strongly localized excitations [1]. These excitations are called intrinsic localized modes (ILMs) because of their similarity to defect impurity modes.

The main approach, which has been used for the study of these excitations is based on the direct numerical integration of the equations of motion of the lattice with a finite number of the degrees of freedom. However this approach requires very lengthy computations in the case of 3D lattices due to a rapid growth of the number of numerical operations with the increase of the number of the degrees of freedom. The new method was developed [4], which gives a possibility to calculate the nonlinear local dynamics for macroscopically large lattices of arbitrary dimensions with realistic interaction potentials. The method is based on the consideration of small variations of the ILM. The equations for these variations include the characteristics of a ILM. This allows us to reduce the nonlinear problem of a ILM to a linear problem of the perturbed phonon dynamics; the perturbation comes from the ILM and it is determined self-consistently. To demonstrate how the method works, we considered ILMs and linear localized modes (LLM) in monatomic and diatomic chains. In parallel the molecular dynamics simulations were carried out. The results of both calculations are in a very good agreement [2,3,4].

We applied the method to different real systems (alkali halides and other ionic crystals). The harmonic lattice dynamics was calculated by direct methods [5] (Interatomic forces for tiny atomic displacements, calculated by DFT packages VASP. Phonon dynmical matrix, frequences and polirization vectors, for further Green's functions calculations, were obtained by *fropho* packages). In parallel the ab-initio molecular dynamics (by VASP) were carried out. It was demonstrated that in 3D ionic lattices with realistic interaction potentials the ILMs may have frequencies above the phonon spectrum. The long-range (Coulomb) interaction play a very important role in this effect. It was indicated that the minimal energy needed for crystal defects formation, is relatively small (~ 1 eV for inonic crystals).

Keywords: defects, phonon, molecular dynamics

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A combined DFT/Green's function study on electrical conductivity through DNA duplex between Au electrodes

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DNA has attracted much attention as a primary candidate for next-generation nanowires that possess outstanding qualities such as high self-organizing capability and electrical conductance. Although a number of experimental studies have been conducted, its electrical conducting properties remain to be fully elucidated in terms of the structural details. Recently, we [1] attempted to elucidate the effect of environmental factors on the electrical conducting properties of DNA duplexes sandwiched between Au electrodes by using a combined method of classical molecular dynamics (MD) and Green's function based on extended Hückel MO calculations. The results clearly indicated that the electrical conductivity through DNA duplex depends most strongly on the surface structure of Au electrodes. However, the extended Hückel MO method was unable to account for the effect of DNA base sequence on the electrical conducting properties: the conductivity was experimentally shown to decrease when an AT base pair was inserted into GC rich domain of DNA duplex.

In the present study, we employed density-functional theory (DFT) calculations to elucidate the effect of base sequence on the electrical conducting properties in DNA duplex. By using the DFT program SIESTA, we have succeeded in calculating the electronic properties for an extended system consisting of a DNA duplex with four base pairs plus two Au electrodes. In order to investigate the effect of DNA base sequence, we considered two types of DNA base sequences 5'-d(CGCG)$_2$-3' and 5'-d(CATG)$_2$-3'. At first, the most stable structures of these DNA duplexes were obtained by means of classical MD simulations using the AMBER9 program. Subsequently, two Au electrodes composed of 44 Au atoms were each attached to the 3' and 5' terminal bases of the DNA duplex along the helical axis as shown in Fig. 1. To evaluate the electrical conductivity in DNA duplexes from the DFT-computed electronic states, we employed the program developed by Meunier and Sumpter [2] based on the nonequilibrium Green's function and Landauer theories.

The results indicate that G bases mainly contribute to the hole transfer, and that the energy level of HOMO localized on G is higher in CGCG compared with that in CATG, resulting in greater hole transfer in CGCG. The computed transmission probabilities as well as current-voltage curves for the duplexes clearly indicate that CGCG has greater electrical conductivity than CATG. This result is in qualitative agreement with experiment. The detailed results will be displayed in our poster presentation.

Keywords: electrical conductivity in DNA, DFT, Green's function

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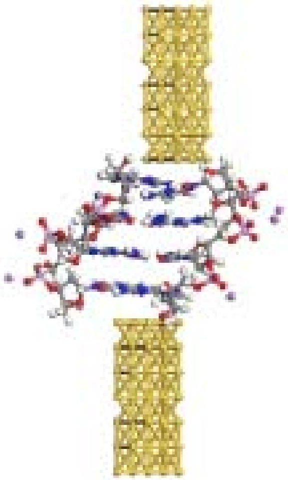

Figure 1

Puckering of modified nucleosides ready to be inserted in double helices.

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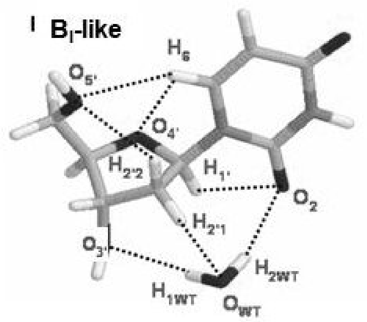
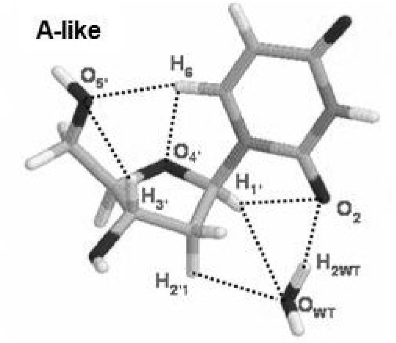
We used B3LYP quantum mechanical calculations to determine the pucker (north or south type) of various natural and modified nucleosides: position 2’ may have a simple H as in a deoxynucleoside or a hydroxyl as in a ribonucleoside[1]. Although the dihedrals of the backbone are set close to their experimental values in double-stranded nucleic acids, calculations of different theory levels show that in vacuo or in a continuum mimicking the dielectric properties of water, the south puckering of uridine is favoured. These computations contrast to experimental data: most ribonucleosides inserted in a duplex have the north puckering. We show that the north puckering is favoured when an explicit water molecule is introduced in the calculation. The role of hydration the energy barrier between the minima and the flexibility of the nucleoside are further discussed when the substituent group at the 2’ position is H, OH, OCH3 or NH2 in the ribo or arabino orientations [2].





Keywords: solvent, explicit water, H-bonds

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Spectral variations of photoactive biological molecules and related model compounds

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Conjugated polyene chromophores such as, for instance, retinal and various carotenoids play important role triggering functions of photoactive proteins such as, for instance, bacteriorhodopsin or photosynthetic pigment-protein complexes. Here we present results of theoretical studies of the spectral variation of such molecules depending on their surrounding by means of time dependant density functional methods.

Photoinduced proton transfer from the Schiff base, which is a linker of retinal and the protein, to the nearest surrounding is considered by analyzing a model molecule (2-(N-methyl-α-iminoethyl)-phenol (MIEP)) in various surroundings. It was demonstrated that the hydrogen bonding network play a crucial role in determining the initial proton location in the vicinity of the Schiff base [1]. As follows from our calculations the inter-molecular proton transfer is driven by reorganization of the hydrogen bonding network after electronic excitation of the MIEP molecule. This effect is expected in the case when molecules capable to arrange the hydrogen network are present, while in vacuum the proton remains localized at the oxygen atom both in the ground and the excited states. The proton transfer to the nitrogen atom is substantially enhanced with the amount of water, ethanol or methanol molecules present in the vicinity of the Schiff base of the MIEP molecules. Computations where performed by means of CI SD, DFT, TD-DFT methods.

Photosynthetic light-harvesting complexes have been identified for most of the chlorophyll-based photosynthetic organisms. Their major function is absorption of light energy and its delivery to the reaction centers. Some of these complexes in plants are also involved in the excess energy quenching (so-called nonphotochemical quenching – NPQ). It is plenty of evidencies that carotenoids (either lutein [2] or zeaxanthin [3]) are responsible for the NPQ.

Doubly excited configurations are essential in order to achieve first excited singlet state of lutein and zeaxanthin (it is dark state for all planar configurations). The account of the influence of double excited configurations was reached by using Tamm-Dancoff approximation density functional theory method (TDa-DFT/blyp) [4]. Computations by means of CI SD, CI SDTQ and MCSCF PT2 methods were used for testing computations for several lutein conformations. Lutein conformations and spectra are highly dependant on surrounding environment. The structure of lutein is differently deformated as follows from the crystallographic data of specific light-harvestin complexes. The influences of deformation of polyene chain and aromatic rings and the possible effect of the surrounding environment on energy positions of the S1 and S2 electronic excited states have been investigated by means of TDa-DFT/blyp and QM/MM methods.

Keywords: lutein, carotenoid, retinal, proton transfer, Schiff base, excited states, environment

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DFT Based Conformational Analysis and Phase Transition Temperatures of Monomers of Phosphatidylcholine Lipids

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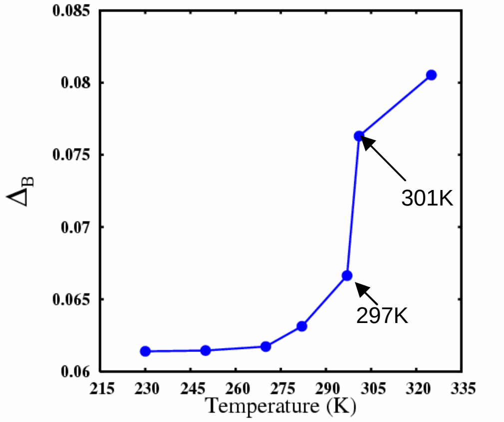
The longstanding interest to study the conformations, dynamics and packing of the phospholipid assemblies (micelles, bilayers and liposomes) is mostly due to the phospholipids bilayers role in the formation of biological membranes. Together with the continuously improving understandings of the bilayer properties, it was suggested that the knowledge of the structure of a phospholipid monomer within an assembly is essential for understanding the bilayer dynamics and its functional role in bio-membranes.

Due to the large size of phospholipid assemblies, quantum mechanical (QM) modeling has been so far limited. In this communication we will report our recent results from DFT based study of the potential energy surface [1] and dynamics [2] of the monomer of three phosphatidylcholine lipids, which differ by the length of their diacyl chains, i.e. dilauroyl (DL), dimyristoyl (DM) and dipalmitoyl (DP) phosphatidylcholines (PC). The dispersion interactions between the two alkyl chains are described by using a DFT method augmented by a damped London dispersion energy (DFT-D) and energy gradient term.



Large number of conformers is found in the range of 0 – 3 kcal/mol. Infrared and NMR calculations compared to the available experimental data (available for different lipid aggregates at different hydration rates) are used to validate the monomer structures. The evolution of the DLPC, DMPC and DPPC molecules as a function of time is also explored using Born-Oppenheimer molecular dynamics, showing that these molecules undergo phase transitions at temperatures similar to the bilayer phase transition temperatures. The first-order phase transition, such as the lipid melting, is quantified using density of states distribution and normalized interatomic distance fluctuation criteria, Δ_B, as function of temperature, as it is shown in the above Figure for a DMPC molecule.

Keywords: phospholipids; phase transitions, DFT-D

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Trans Hoogsteen/Sugar Edge Base Pairing in RNA Structures, Energies, and Stabilities from Quantum Chemical Calculations

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Recognition of the principles governing RNA base pairing [1,2] is a milestone in structural biology, which had a tremendous impact on the understanding of the structure and catalytic function of the ribosome. Due to the presence of the 2'-OH group of ribose, RNA base pairing is more versatile than DNA base pairing and gives rise to a great structural variety of the RNA molecules, necessary to operate the complete machinery of the protein synthesis.

Trans Hoogsteen/Sugar Edge (H/SE) pairing patterns are of key importance at stabilizing loop geometries in RNA. Here we provide a detailed quantum chemical characterization of the intrinsic structures and interaction energies of this base pair family, along with the evaluation of solvent screening effects via continuum solvent approach. We report DFT-optimized geometries and MP2 interaction energies for all ten crystallographically identified members of the family, for a representative set of them using the Complete Basis Set extrapolation. We confirm that the remaining, hitherto undetected, possible members of this family do not have appropriate steric features required to establish stable base pairing in the trans H/SE fashion. The interaction patterns in the trans H/SE family are very diverse with gas phase interaction energies within the range from -1 kcal/mol to -17 kcal/mol. Except of the C/rC and G/rG H/SE base pairs, the interaction energy is roughly evenly distributed between the electrostatic and correlation components. Thus, in the trans H/SE base pairs the relative importance of the electron correlation is noticeably smaller than in the cis WC/SE [3] or cis and trans SE/SE [4] base pairs, but still larger than in canonical base pairs. The trans H/SE A/rG basepair is the intrinsically most stable member of this family. This base pair is also known as the sheared AG base pair and belongs to the most prominent RNA base pairs utilized in molecular building blocks of functional RNAs. For all trans H/SE base pairs we identified, besides the conventional base pairing, viable alternative structures stabilized via amino-acceptor interactions.

Keywords: Hoogsteen, Sugar Edge, rRNA, isostericity

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Progress in Integrated Environment for Quantum Chemical Simulation of Biomolecules: ProteinEditor

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We have developed an integrated environment "ProteinEditor" to attain the canonical wavefunction of biomolecules based on the DFT program ProteinDF [1,2]. Since the manipulative data and simulation becomes huge and complicated in all-electron calculations on biomolecules such as proteins, it is important for the self-consistent field convergence to prepare the delicate processing methods to the structural modeling, the initial guess construction, the simulation control, as well as the computational results analyses. The ProteinEditor unifies those processing and supplies the interactive control methods to the users [3]. In this study, we will report the interactive visualization functions of ProteinEditor.

In general, structural data distributed by Protein Data Bank (PDB) [4] is available as initial structure at protein simulations. It is well known that the structural data obtained by X-ray analysis often requires some supplemental processing for the lacking information such as hydrogen atoms and missing amino residues. In addition, it is necessary for the quantum simulation to relax distorted and/or indistinct geometries including collisions between non-bonded atoms since stereo-chemically abnormal structures often give the highly molecular orbital energy, which will mislead the computational results. Adoption of a proper computational structure is especially essential for the DFT calculations of proteins [5]. In order to reduce these tasks, we have proposed the approach for the interactive modeling of protein structures suited for quantum chemical calculation in the ProteinEditor.

Furthermore, a large amount of the calculation results is output by the quantum chemical calculation. These results include not only bottom line of the calculation but also the progress information of the simulation. Therefore the processing becomes complicated. For this reason, we have implemented original molecular graphics to support various kinds of expression for complex physical quantities in ProteinEditor. As one of the examples, we introduced the rapid electrostatic potential (ESP) estimation function based on the all-electron wavefunction of large molecules [6]. In this work, we developed the practical method to calculate QM ESP by GPGPU. Combining this method and the proper grids generation on the real protein surface which was defined by the isosurface of electron density, we succeeded to draw the accurate QM ESP map on the true protein surface very rapidly.

These detailed methods and the implemented functions will be discussed.

Keywords: protein, density functional method, all-electron calculation, graphical user interface, integrated environment, electrostatic potential

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The Study of Quasi-Canonical Localized Orbital Method for Huge Canonical Molecular Orbital Calculation

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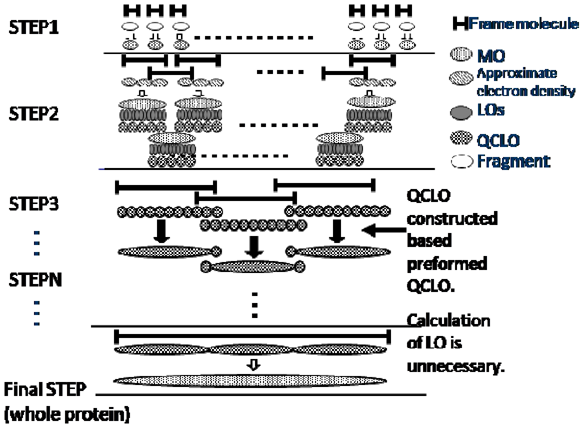
We have developed a density functional (DF) program, ProteinDF [1] and Quasi-Canonical Localized Orbital (QCLO) method [2, 3] program for all-electron calculation on proteins. We have achieved the all-electron calculation of insulin hexamer (306 residues) using those programs [4]. Generally saying, the achievement of the DF calculation on protein is very difficult because of huge elements that should be optimized and the narrow HOMO-LUMO gap. In the case of the calculation on small molecule, a reasonable approximation to the Fock matrix based on extended Hückel [5] or the Harris functional is applied for DF calculations [6]. However, in the case of huge and complex molecule such as proteins, those methods cause a significant error of the guess for SCF calculation.

In order to overcome difficulties of the SCF convergence problem in large-scale molecules, highly accurate initial guess is inevitably required. Therefore we have proposed QCLO method based on protein structure, which is named structure-based QCLO method, for more precise initial guess construction [7]. The QCLO is a kind of localized orbital (LO), which is not only localized in a certain region (fragment) of the molecule but also canonical in that region. Collecting QCLOs that have been obtained from the subsystems allow the formulation of a high-precision initial guess for the bigger corresponding region. However, even though the initial guess construction by the conventional QCLOs is very precise, it takes long time to create QCLO. The rate-determining process to create QCLO is calculation of LOs. The amount of calculation of LOs is proportional to N_{basis}^4. In this new method, to speed up QCLO method for the large system, the previously estimated QCLOs are used as transform matrices. The Kohn-Sham matrix for the elongated fragment is evaluated by the coefficient matrices of orthogonalized QCLOs. Therefore LO calculation is skipped. In this presentation, we will report the result of calculation using this new QCLO method.



Outline of the calculation using This new method

Keywords: initial guess, SCF, QCLO

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DFT study of Cu(II) complexes of Aminoguanidine, Pyridoxamine, Amadori compound, Ascorbic acid and LR-74 like AGE inhibitor.

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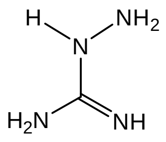
The Maillard reaction is a spontaneous non-enzymatic aminocarbonyl reaction between reducing sugar and long-lived proteins and lipids that are a major form of chemical modifications of biomolecules that compromise their functions. This reaction initially involves the reversible condensation of a terminal NH_2 group of protein or an amino-phospho-lipid and a C=O group of the sugar to give a Schiff base. The later is unstable and undergoes a rearrangement to yield a more-stable Amadori compound. The Amadori compound can undergo various complex processes to form the *advanced glycation endproducts* (AGEs) and *advanced lipoxidation endproducts* (ALEs). Glycation is one of the primary sources of *reactive oxygen species* (ROS) and reactive dicarbonyl intermediates, which can induce tissue and organ deterioration through natural aging processes and also some diseases such as diabetes, atherosclerosis and chronic inflammation.

The inhibitory action of advanced glycation endproducts has been ascribed to their scavenging carbonyl and radical species and also to their hindering the oxidation of Amadori compounds by chelating metal ions such as Cu^{2+} and Fe^{3+}, which catalyse their autoxidation. However, inhibition by AGEs seemingly results mainly from metal chelating rather than carbonyl trapping effects. The knowledge of the chelating properties of AGE as inhibitors is essential with a view to understanding the mechanism of action of some drugs and the potential benefits of chelation therapy [1].

Hereby, DFT calculation with UB3LYP/6-31+G* level of theory and the solvent effect simulated by using the Cosmo Polarizable Continuum Method (CPCM) were used to examine the formation, stability and potential biological implications of some complexes of Cu^{2+} ion with aminoguanidine (AG), pyridoxamine (PM), model Amadori compound (AMD) and ascorbic acid (ASC). These copper complexes have been compared with a new AGE inhibitor like LR-74 [1,2].



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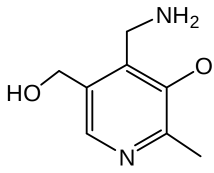

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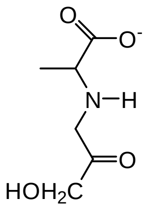

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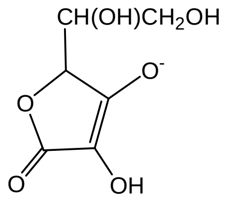
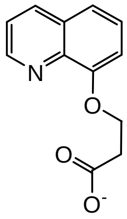


ASC



LR-74

Keywords: DFT, AGE-inhibitors, Cu(II) complexes.

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A DFT study of carbohydrate-π interactions

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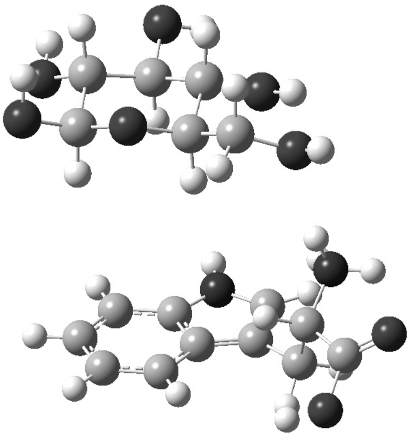
In many biological processes, as bacterial cell wall recognition, viral and bacterial infections, or fertilization, the carbohydrate-protein interactions play an important role.[1] The most cited noncovalent forces that participate in carbohydrate-protein recognition are hydrogen-bonding and ionic interactions. In addition, a widespread, but poorly understood, structural motif found between carbohydrates and proteins is the carbohydrate-aromatic stacking interactions.

The density functional theory (DFT) methods is clearly an atracctive alternative to the very expensive *ab initio* methods in order to describe these weak interactions. However, the standard functionals, as B3LYP, do not produce good results. An alternative strategy is to augment standard functionals with an empirical R^{-6} interatomic pairwise term in order to describe the dispersive interactions. This model is known as DFT-D method. Using this method, we are going to study the interactions between some examples of carbohydrates and the aromatic residues of aminoacids.



Keywords: carbohydrate-π interaction, DFT-D methods

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An Insight into the Selectivity in the DNA Replication Mechanism

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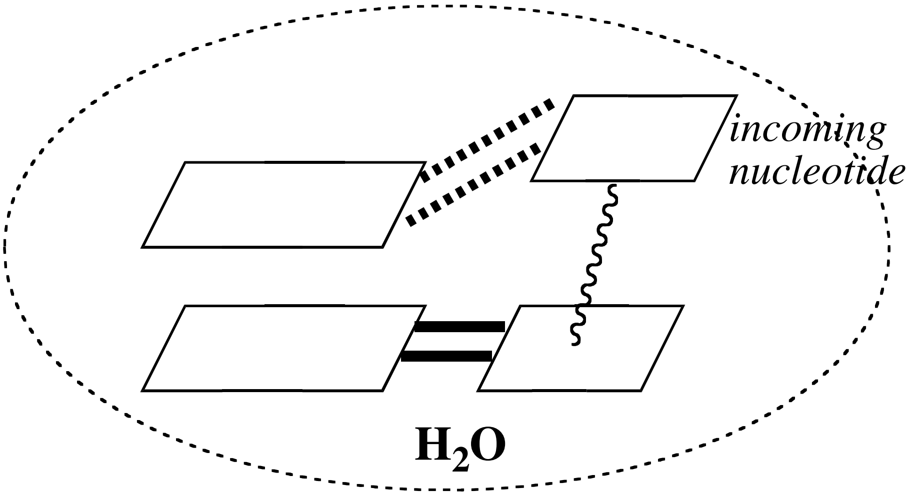
DNA replication is at the core of life and an increasing number of studies aims at unraveling the mechanism of this complex biochemical reaction that, in spite of much effort, is still incompletely understood. In the present study, we aim at obtaining a better understanding of how the selectivity for the formation of a Watson-Crick over a mismatched base pair is achieved during DNA replication. We uncover and quantify the effects on this process of solvation, π-stacking and hydrogen bonding. This is done using state-of-the-art density functional theory in a QM/QM approach. Our work confirms that a certain extent of selectivity remains even in the absence of the polymerase enzyme. At the same time, we also provide evidence for an amplification of selectivity through a steric mechanism that has been attributed to the working of polymerase.



Keywords: DNA replication, DFT, solvation

The electronic structure and dielectric properties of liquid acetonitrile under ambient conditions within density-functional-theory

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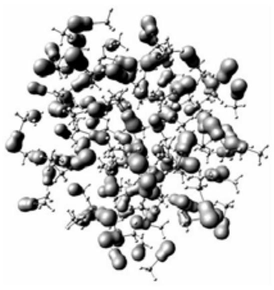
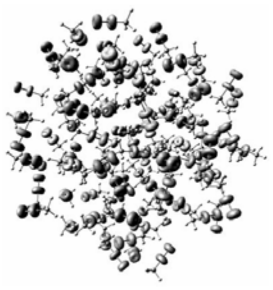
Acetonitrile (CH_3CN) is a very important solvent in which many hydrophobic and hydrophilic materials can be dissolved under ambient conditions [1]. Furthermore, neat liquid CH_3CN has been recognized as an interesting dielectric medium to investigate excess electron localization [2]. Although the solvation process relies on the dielectric behavior of the liquid, the dielectric function of acetonitrile is not yet fully understood in the electronic absorption region. Usually, the solvent effects are interpreted in terms of dielectric properties of the medium. In spite of this, we propose an efficient scheme to obtain the complex dielectric function of the liquid system using first-principles density-functional-theory (DFT) calculations.

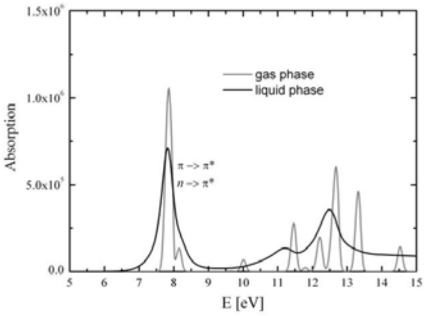
In this communication, we present a large scale efficient computational simulation to generate the appropriate liquid structure of a complex disordered system such as acetonitrile. We exploit a sequential protocol [3], combining *NPT* Monte Carlo (MC) simulation and gradient-corrected DFT calculations to describe the electronic structure of the bulk acetonitrile at ambient conditions [4]. Thus, using uncorrelated structures containing 100 CH_3CN molecules, we obtain average electronic properties of the liquid.



HOMO



LUMO



It becomes evident that condensation leads to a conduction band with large degree of dispersion, which is consistent with the description of dipolar liquids. This allows an interpretation of the dielectric spectrum based on the electronic structure of liquid CH_3CN, and clearly shows the influence of intermolecular interactions in the absorption features. The optical response is obtained using first-order time-dependent perturbation theory to calculate the dipolar transition matrix elements between occupied and unoccupied self-consistent Kohn–Sham eigenstates, considering corrections due to the non-locality of the pseudopotentials. We find that the lowest-lying excitation of the condensed phase occurs at 7.8 eV.

Keywords: liquid phase, optical absorption, dielectric function

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Ab initio Study of Peptide Stacking in an Amyloid Fibril

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[1] *Cavendish Laboratory, University of Cambridge, CB3 0HE, UK*

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Amyloid fibrils are filamentous peptide aggregates associated with the group of protein deposition diseases known as amyloidoses. One such fibril forming peptide is the fragment 105-115 of transthyretin (TTR), the structure of which is known to high resolution in its fibrillar form [1]. Though the fibril is known to exhibit long range order the nature of how the peptides stack within the protofilament has remained elusive. Taking the structure of the TTR fragment a number of possible models of peptide stacking have been constructed. These have been optimised and ranked using the linear-scaling density-functional theory code ONETEP [2] to obtain a 'potential well' of polymorphs. Using the GIPAW method [3] for reconstructing core properties from the pseudopotentials, chemical shifts may be found for each polymorph. By averaging these computed chemical shifts over an ensemble of structures the long time-scales present in the dynamics of the fibril can be accessed. Comparing these ensemble averaged *ab initio* chemical shifts to experiment provides a route to predicting the atomic structure of the TTR fibril.

Keywords: amyloid fibril, linear-scaling, NMR

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Predicting Drug Metabolism in Cytochromes P450: How DFT can Improve Both Speed and Accuracy

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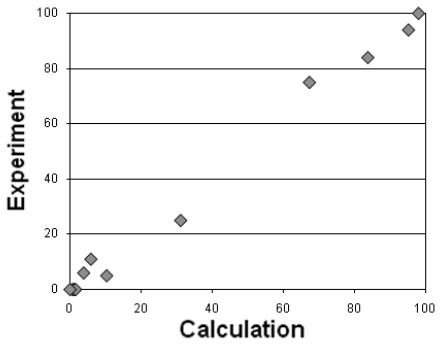
Today, a strategy which takes ADMET (absorption, distribution, metabolism, excretion, toxicity) properties into account is often used throughout the entire drug development process. The metabolism aspect is difficult to predict because it does not involve equilibrium properties but instead is heavily dependent on reactivities. In phase I metabolism molecules are made more polar, mainly by oxidation reactions that are catalyzed by cytochrome P450 enzymes (CYPs). These enzymes contain a heme group in the active site and in the active compound I, an oxygen is bound to the iron atom. CYPs can perform a number of different types of reactions, such as hydroxylation of aliphatic carbon atoms, hydroxylation and epoxidation of aromatic carbon atoms, oxidation of sulphur and nitrogen atoms, sulphur and nitrogen dealkylations, etc.

Currently, available prediction software are based upon semi-empirical calculations of bond dissociation energies and properties of substrates and radical intermediates. However, it has been shown that semiempirical calculations of bond dissociation energies only correlate to the activation energy if the radical in the intermediate is not distributed among several atoms.[1] Semiempirical methods do also perform poorly with regard to oxidations of aromatic carbon atoms.[2]

Instead of working with the current methods which rely on parameterization of data from semiempirical results to reproduce experimental results, we have chosen to work from a more physical point of view. We start by computing the activation energies using DFT (B3LYP functional and large basis sets) for different types of reactions, using a porphyrin ring with a SCH_3^- group bound to the iron atom (SCH_3^- models the cysteine amino acid bound to the iron atom in the enzymes) . These energies are shown to reproduce the trends of experimental data with high accuracy for several types of CYP reactions.

From the DFT data, we create rules which predict the activation energies depending on the types of neighboring atoms that the reactive site has. These rules can combined with the solvent accessibility predict the site of metabolism with a high accuracy.



Keywords: cytochromes P450, heme, porphyrin, metabolism, reaction energies

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Theoretical studies on the effect of π- π stacking on the Cu_2O_2 core in the active site of oxyhemocyanin

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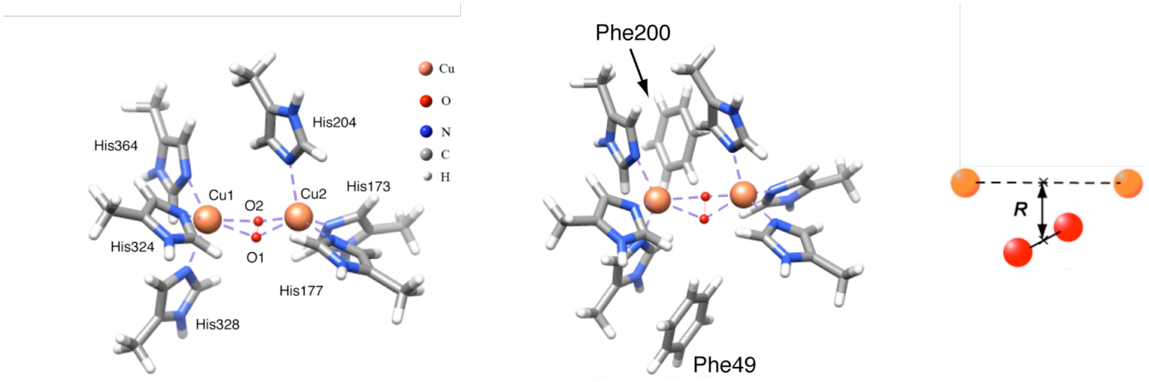
We examined the environmental effects on the geometry of the Cu_2O_2 core in type 3 copper proteins. Previously, we examined several conventional hybrid density functional sets with a broken-symmetry (BS) method on the geometry of the Cu_2O_2 core of the active site of oxyhemocyanin (oxyHc)[1, 2]. We found that the structure of the Cu_2O_2 core depends on the orientation of coordinated histidine residues (see Fig. 1(a)). Therefore, we constructed a larger model complex in order to constrain the orientation of His328 and His364, as shown in Fig. 1(b). The UM05-2X[3] and UX3LYP[4], which is designed to describe noncovalent interactions were used to predict the most stable coordination of oxygen molecule in the Cu_2O_2 and reaction coordinate $\boldsymbol{R}$ (see Fig1(c)). In order to evaluate their net accuracy, the spin contamination errors caused by the triplet (S=1) state for energy and energy gradient in the BS (S=0) state were replaced by our approximate spin projection (AP) procedure. The results will be presented on the day.



(a) (b) (c)

Fig. 1 model complexes (a), (b) denifition of $\boldsymbol{R}$ (c)

Keywords: Hemocyanin, type 3 copper protein, broken-symmetry, π-π stacking

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

On the Structure of the Oxygen-Evolving Complex of PS II: Density Functional Calculations on the EPR Parameters of the S_2 State

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Oxygen powers a substantial part of life on earth. While the biological production of oxygen in plant photosynthesis by photosystem II (PSII) may be viewed as a waste byproduct, the oxygen produced contains a significant amount of the chemical energy generated. The catalyst at which two water molecules are coupled in a four-electron oxidation to one O_2 molecule is known to be a tetranuclear manganese complex, known as the oxygen-evolving complex (OEC). The light-driven oxidation occurs through a cyclic sequence of five oxidation states $S_0 - S_4$.

Here we provide the first explicit quantum-chemical study of EPR parameters (^{55}Mn and ^{14}N HFCs and NQCs) for a substantial variety of model complexes of the S_2 state of the OEC, with the aim to compare different structural models suggested in the literature explicitly with experiment. Due to the complicated spin-coupling patterns of the formally $S = 1/2$ ground spin state of the S_2 state, a fully appropriate quantum-chemical treatment would require sophisticated multiconfigurational wavefunctions incorporating both dynamical and nondynamical electron correlation effects to a large extent. This is currently out of the question for a system of the complexity of the OEC. A possible alternative is to construct so-called broken-symmetry (BS) states within unrestricted Kohn-Sham density functional theory (DFT), followed by appropriate spin projection procedures. We have now been able to construct a wide variety of BS solutions for different models of the S_2 state. After spin projection, this provides access to hyperfine and nuclear quadrupole couplings, enabling us for the first time to evaluate the quality of molecular model complexes for the OEC by direct comparison with experimental EPR, ENDOR and ESEEM data.

Keywords: Broken-symmetry DFT, hyperfine couplings, nuclear quadrupole couplings, oxygen-evolving complex, spin-projection techniques.

Using WFT-in-DFT and DFT-in-DFT Embedding to Model Actinide Spectra in Condensed Phase

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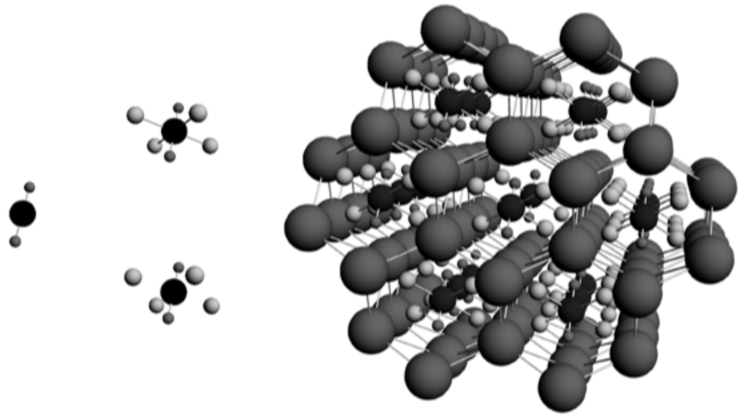
Theoretical modeling of actinide species' properties (such as their electronic spectra) require that environment effects are accurately taken into account, since most chemically interesting phenomena occur in condensed phase. This places severe strain on the available methodologies, since one usually must employ wavefunction-based (WFT) methods in order to properly describe electron correlation and spin-orbit effects[1]. These are, however, too expensive to use in calculations on large systems, such as solvated species, or in complexes with ligands used for Ln/Ac separation, where Density Functional Theory (DFT) is perhaps the only applicable method.

In this contribution we address how, by combining WFT and DFT in a fully QM/QM embedding scheme[2] based on a subsystem formulation of DFT[3], we can obtain accurate spectra for actinide-containing species while reliably describing the environment. We illustrate the performance of WFT-in-DFT embedding in calculations of the low-lying spectrum of NpO_2^{2+}[2] and UO_2^{2+} embedded in $Cs_2UO_2Cl_4$ (see figure).

Moreover, we compare the performance of WFT-in-DFT to that of time-dependent DFT (TDDFT) calculations based on both conventional Kohn-Sham DFT and on a DFT-in-DFT embedding treatment for UO_2^{2+}. While the main focus of this work is on crystal environments, we also address the use of embedding schemes to model the spectra of UO_2^{2+} in water, starting from microsolvated clusters such as those used in modeling the photoinduced O_{yl}-exchange reactions[4].



Keywords: Actinide Chemistry, Frozen Density Embedding, Electronic Spectra

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A QM/MM investigation of molecular factors influencing the properties of radical intermediates in a Fungal Versatile Peroxidase

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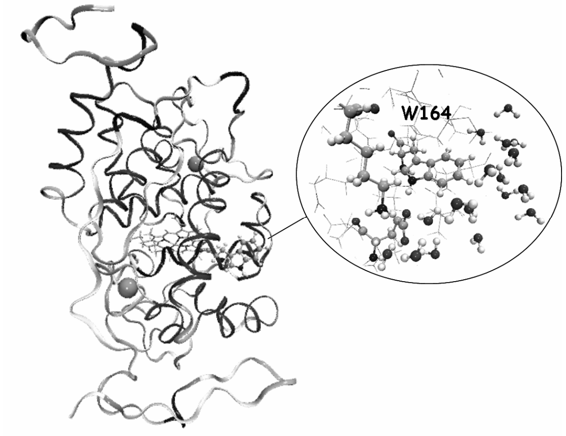
Versatile peroxidases (VP) represent a novel class of ligninolytic peroxidases, which combine typical properties of both manganese and lignin peroxidases. Such enzymes are able to oxidize large substrate molecules at an exposed radical species formed by a long-range electron transfer mechanism activated by H_2O_2.

Recently, the radical intermediates involved in the catalytic cycle of wild-type (wt) and W164Y mutant of a VP isolated from lignolytic fungus *Plerotus eryngii* have been characterized from the experimental point of view by multifrequency EPR and ENDOR spectroscopies supported by DFT/PCM computations [1-4]. These works demonstrated that for wt-VP a hydrogen bonded neutral tryptophan (W164) is the radical site. Similarly, in W164Y mutant, a stable free-radical is formed on the tyrosine residue (Y164), even if with a lower yield. Furthermore, W164Y showed a reduced activity in oxidizing substrates.



Here we show the results of a QM/MM (DFT/CHARMM) characterization of these radical species inside the protein matrix with the aim of elucidating the role of the environmental and molecular factors that may affect the side chain orientation and electronic nature of the involved radical species and, ultimately, getting an insight on the origin of the different catalytic behavior (wt-VP vs W164Y).

Keywords: QM/MM, Molcas/Tinker, radical intermediates, fungal versatile peroxidase

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An efficient approach to compute reduction free energy by the QM/MM method combined with a theory of solutions

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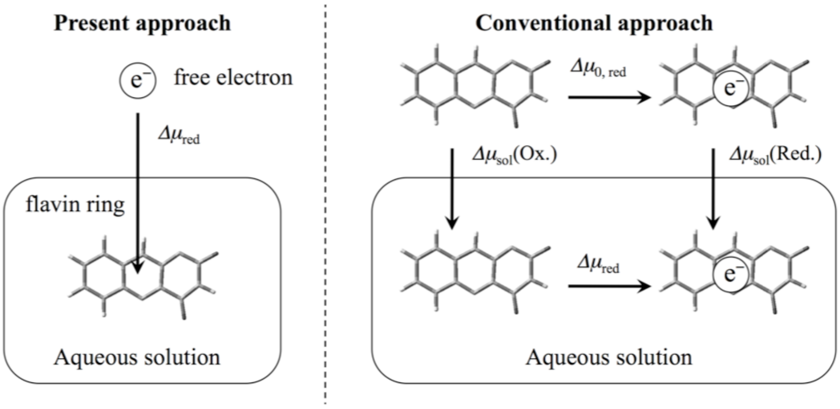
Electron transfer is one of the ubiquitous chemical events in biological systems. Hence, it is a matter of significance to develop an efficient and robust computational methodology to compute reduction or oxidation free energy of a biological molecule in water solution. The isoalloxazine ring (flavin ring) is a part of a coenzyme FAD (Flavin Adenine Dinucleotide) and it acts as an active site in various enzymes oxidizing substrates. We have computed the free energy change $\Delta\mu_{\mathrm{red}}$ associated with one-electron reduction of the flavin ring in water by the approach termed as QM/MM-ER method[1] which combines the quantum mechanical/molecular mechanical (QM/MM) method with the theory of energy representation (ER)[2]. In the QM/MM-ER approach, the distribution functions of the solute-solvent interaction potential, which play a fundamental role in computing the free energy change, are directly constructed through the QM/MM simulations. As a novel implementation of the QM/MM-ER method[3], we have identified the excess charge to be attached on the flavin ring as a solute, while the remaining molecules, i.e. flavin ring and surrounding water molecules, are treated as solvent species. This method allows us direct computation of $\Delta\mu_{\mathrm{red}}$. On the other hand, within the conventional approach, the free energy $\Delta\mu_{\mathrm{red}}$ is described in terms of the solvation free energies of the flavin rings before and after the reduction by the thermodynamic cycle. The illustrations for these methods have been presented in the figure below.

In the novel approach, the reduction free energy can be decomposed into the contribution $\Delta\mu_{\mathrm{red}}(\mathrm{QM})$ due to the oxidant described quantum chemically and the free energy $\Delta\mu_{\mathrm{red}}(\mathrm{MM})$ due to the water molecules represented by a classical model. By the sum of these contributions, the total reduction free energy $\Delta\mu_{\mathrm{red}}$ has been given as –80.1 kcal/mol, which shows an excellent agreement with the value of -81.0 kcal/mol given by the conventional method. This clearly suggests the efficiency of the present methodology for the computation of the reduction free energy.



Keywords: QM/MM, Theory of solutions, Biological system

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Computational Study of the Mechanism of Transamination Reactions Mediated by Metal Ions and the Stereoselectivity

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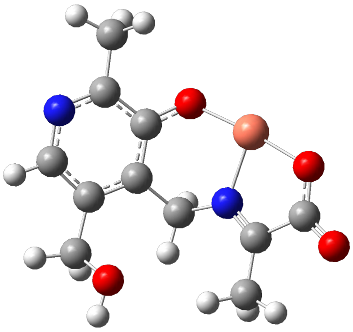
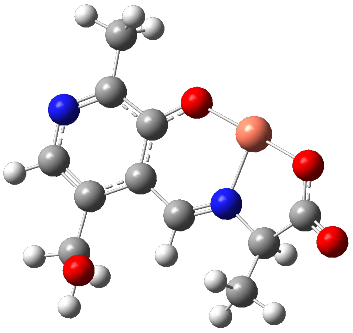
It is well-known that transamination reactions are accelerated by the presence of metal ions, e.g., Cu(II), Mn(II), Zn(II) ions, etc. Quite a few studies have so far been carried out for the purpose of clarifying the mechanism of these reactions [1]. Experimental works found that the complex formation of metal ions with vitamin B6 compounds (pyridoxal, pyridoxamine, and their phosphates), keto acids and amino acids is important. The Schiff-base complex formation with metal ions is reported to take an essential role in these reactions. First, pyridoxamine, keto acid, and a metal ion react to form a Shiff base complex (ketimine), and then this complex is isomerized to a different type of Shiff-base (aldimine) through an intermediate.

However, in spite of a huge number of experimental studies, the details of this reaction mechanism including the transition state are still unknown. In this work, we studied the transformation of two main Schiff-base metal complexes, i.e., ketimine and aldimine. The structures of these Schiff-base complexes having several conformational and rotational isomers were optimized and the energies of each structure were estimated by DFT. The populations of the structures were also calculated. The structures of ketimine (left) and aldimine (right) containing Cu(II) ions (and parts of pyruvic acid or alanine) are shown in the following figures.





The DFT computational search of optimum structures indicates that the stabilities of the conformers depend on the orientation of hydroxyl groups and methyl groups as well as the R substituents of keto acids or amino acids. Therefore, we picked up several stable conformational isomers for vitamine B6 parts and for these structures we optimized the rotational isomers of keto acid or amino acid parts. The calculated energy diagram coincides with the experimental results in which ketimine is preferentially transformed to aldimine through an intermediate (a plausible transition state) [2]. Furthermore, the stereoselective formation of chiral amino acids from keto acids was also predicted in the presence of optically active ligands by DFT calculations using B3LYP/6-31G* level functionals.

Keywords: transamination, metal ion, stereoselectivity

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Ab initio assessment of high-*P*,*T* thermodynamics in multi-component mineral systems: Application to postperovskite phase equilibria in the $MgSiO_3$–Al_2O_3 system

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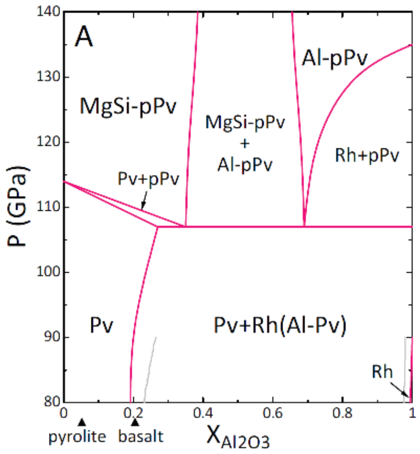
First principles density functional simulations have been applied with great success to investigate high-pressure crystallographic and thermodynamic properties of various classes of materials from elemental and molecular solids, oxides and other compounds to complex silicate minerals. It is definitely worthy to extend this powerful technique to high-*P*,*T* thermodynamics of multi-phase and multi-component systems, which are, in particular, of significant geophysical interest. Since such studies are so far limited mainly in the research field of relatively simple alloy systems, we try to develop the computation techniques for solid solution thermodynamics of Earth and planetary materials with much more complex structural and compositional degree of freedom, including both statistical effects and phonon effects by taking ensemble averages of hundreds of different configurations.

As the first example, we have assesed high-*P*,*T* post-perovskite [1] phase equilibria in the $MgSiO_3$–Al_2O_3 pseudobinary system [2], which is thought to be closely related to the deep mantle D” seismic discontinuity. Although earlier studies based on the static cationic substitution properties reported a significant divariant loop suggesting no sharp transition expected to occur in this system, present calculations demonstrate that Al_2O_3 produces a narrow perovskite-post-perovskite coexisting *P*,*T* area (ΔP~1 GPa) for the pyrolitic Al concentration, which is sufficiently responsible to the seismic discontinuity (Figure). We also found that the perovskite structure spontaneously changes to the Rh_2O_3(II) structure with increasing the Al concentration involving very small displacements of the Mg-site cations. Results suggest that the technique appears to work well even for complex mineral solid solution systems.



Keywords: solid-solution phase equilibrium, multiple configuration sampling, post-perovskite

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Adaptive QM/MM simulations in solution

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Hybrid quantum-classical molecular dynamics (QM/MM) simulations enable the study of chemical reactions in large systems. The small part of the system where the reaction is taking place is treated at quantum mechanical level, while the rest of the system with lower level of accuracy. However, although in many reactions and experiments solvent diffusion plays an important role, most hybrid methods do not allow material flow in and out of the quantum zone. Another problem that is related to this is that forces acting on the atoms near the boundary of the quantum and classical regions are inaccurate due to transferability problems between the quantum and classical force models.

We present a simple scheme that reassigns the quantum zone on the fly, thus allowing material flow across the border of the quantum zone during the simulation. We compare our scheme to existing adaptive QM/MM methods, and show how accurate forces are obtained, thus our adaptive QM/MM scheme has controllable boundary region errors and the transferability problems are alleviated.

Keywords: hybrid QM/MM, adaptive simulation

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DFT, from the understanding to molecular design. A study of Uranyl(V) Compounds.

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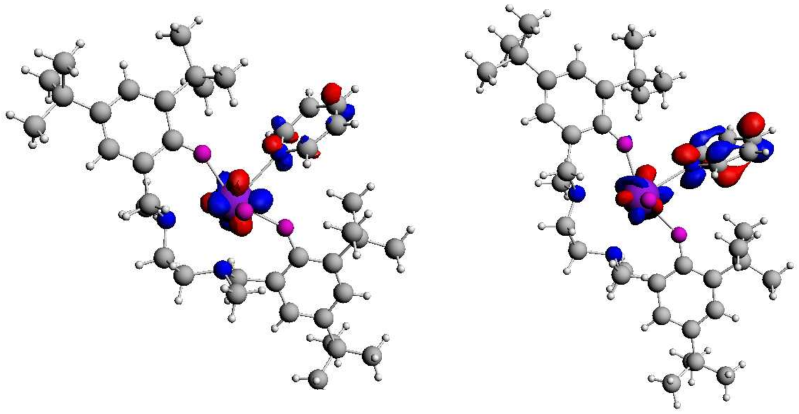
DFT techniques are really powerful for the understanding of molecular systems but they can also be useful for the design of new strucure with particuliar properties. We will show how this approach has been applied on the study of U(V) compounds.

For years the experimental and theoretical studies on uranium compounds have been applied on three major oxidation states, VI, IV and III. The oxidation state V, highly reactive towards dismutation process to U(VI) and U(IV), has been observed just in a carbonate uranyl structure $[UO_2(CO_3)_3]^{5-}$. Recently, new uranyl V structures have been synthesized [1-4] that are stable toward the dismutation process. The understanding of factors governing the stability towards dissociation and dismutation of such new structures is thus a crucial point.

A theoretical DFT study of the electronic structures of several uranyl(v) compounds will be presented[5]. In particular, we will focus our attention on the metal-ligand interaction. We will show also that apart from the metal-ligand interactions, other factors may govern the stability of uranyl V structures. In particular, we will discuss the role of counterions and solvent.

Thanks to the theoretical understanding of the synthesized structures, new theoretically studied ligands have been proposed giving stronger stabilization of the uranyl unit. This approach has been successful and led to the synthesis of more stable U(V) complexes.



Keywords: Theory, DFT, actinides, uranyl

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Approaching the mechanism of anticancer activity of a copper(II) complex through molecular modelling, docking and dynamic studies.

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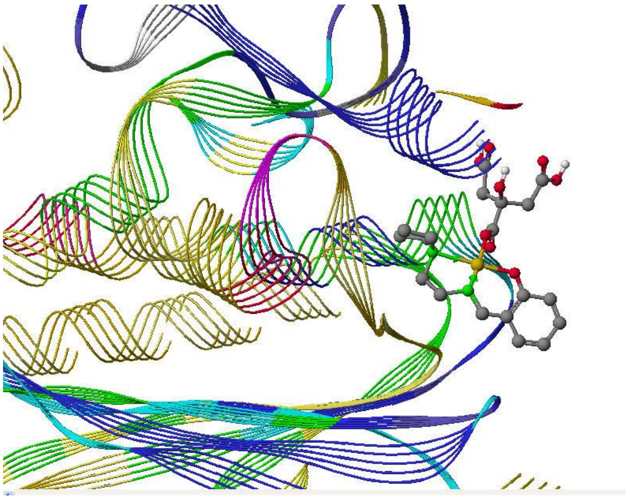
In an attempt to understand the molecular basis of the drug action of several copper(II) chelates, we studied theoretically their chemical interactions involved in the complex processes of drug delivery and their reactions with a variety of biological molecules.

We have focused in the theoretical study of copper(II) complexes of the formula Cu(SalNEt$_2$)-X, where SalNEt$_2$ stands for the anion of the N-(2-(diethylamino)ethyl)salicylidenaminato and X = citrate, tartrate, and salicylate anion, as well as their adducts with various biological molecules. The complexes have shown a potent cytotoxic activity against a panel of human cancer cell lines in vitro [1,2,3]. DFT calculations demonstrated that the mechanism of the cellular damage can be explained, at least in part, by the ability of the nucleobases and nucleotides to nucleophilic attack the complexes. It was also verified through molecular docking studies the hypothesis that the mechanism of action of complexes involves the binding to DNA and RNA and also the inhibition of DNA topoisomerases I and II. In order to explain the inhibition profile, we explored the interactions of each complex within the binding cavity of the aforementioned proteins' active site. Moreover, through molecular modelling we stepped forward to build new molecules with advanced properties. These findings represent a prompting to search systematically for the possible interaction of the complexes with other cellular elements, which is one of the most important goals in drug design.



Keywords: molecular modelling, docking, dynamics, copper(II) complexes

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POSTER PRESENTATIONS

Topic 8.

Nano and molecular devices

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Transport and Electronic Properties of One-Dimension Nanosystems

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For applications to molecular electronics, wire is a very important component because it can be used as the power supply line or the ground line, which connects a metal electrode with a single molecular device and creates a complex molecular circuit. Here, the several candidates for wire applications such as doped carbon nanotube and bismuth nanowires deposited on the Si(001) surface have been selected and their conductance properties has been investigated by the nonequilibrium Green's function formalism of quantum transport.

The realization of the CNT based electronic devices is a still complicated problem due to several limitations, such as the separation of metallic and semiconducting CNTs. These problems can, most likely, be solved by doping CNTs. Recently, the SWNT doping with different organic molecules has been reported experimentally [1], exemplifying the importance of estimating the electronic and conductance properties of doped SWNTs. The encapsulation effect of several organic molecules such as tetracyano-*p*-quinodimethane (TCNQ), anthracene, and tetrakis(dimethylamino)ethylene (TDEA) on electronic and transport properties of carbon nanotubes have been investigated. In the case of *p*-doping, the transport characteristics of both (10,10) and (17,0) SWNT remain similar to those of the undoped SWNT. However, in the case of *n*-doping, the calculated I/V curves show that organic molecules, especially TDAE, do not affect the conductance through metallic (10,10) SWNTs, but do significantly increase the conductivity through the semiconductor (17,0) SWNTs. The obtained results indicate, in particular, the following three possibilities: enhancing the metallic features of carbon nanotube mixtures while avoiding complicated separation processes, realizing complex electronic devices such as *p*-*n* junctions based on SWNTs doped by different types of molecules, and controlling these devices' characteristics by varying the concentration of the dopant.

The development of scanning tunneling microscopy (STM) and the recent remarkable progress in its application toward atom manipulation and surface modification allow one to fabricate various atomic-scale artificial structures. For instance, bismuth nanowires with 1.5 nm wide and length of several hundreds of nanometers have been deposited on a Si(001) surface. In order to integrate bismuth nanolines into complex molecular circuits, it is important to measure the conductance characteristics of such wires. One of the challenges that can arise with these measurements is to understand surface effects on the value of current flow through these wires and thus to prevent the possible current leakage. The results of calculation show that the conductance properties of deposited bismuth wires depend on the morphology of the silicon surface and the existence of dangling bonds on the surface, which may lead to current leakage across these bonds [2]. Thus, in order to use the bismuth lines as atom-wire interconnections for molecular electronics applications it is important to use the hydrogenated Si(001) surface. Despite the fact that Bi nanowires exhibit semiconductor features, the current through these nanowires can be operated within a given voltage region. Moreover Bi nanowires may possibly be used as a nanoline template for other metals.

Keywords: Carbon nanotube, Bi-atomic nanoline, NEGF, DFT

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Modulation of the Electronic and Physical Properties in Organometallic Molecular Wires: Some Theoretical Aspects

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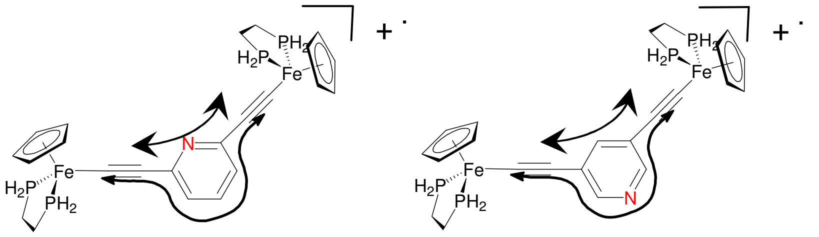
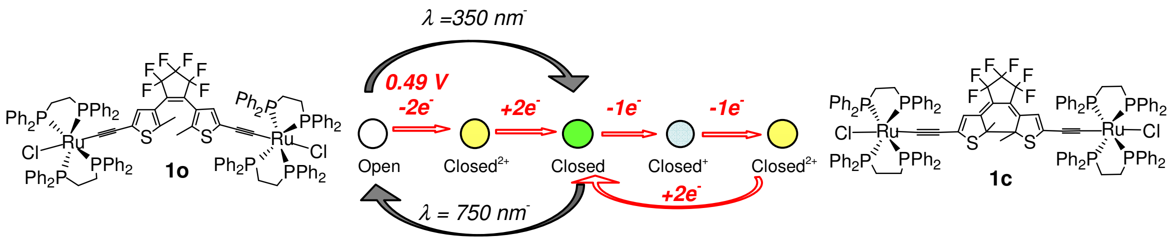
Molecular materials based on the assemblage of organometallic fragments and conjugated organic ligands are among the most studied compounds in coordination chemistry. This is due to their relatively good stability combined with their excited-state and redox properties which confer them interesting physical properties in several domains (magnetism, optics, electrochemistry…). These multifunctional systems are promising candidates to be incorporated in nanoscale devices for molecular electronics and/or spintronics.

The control and manipulation of the interactions between the metal termini of such systems are of great practical importance, but present considerable conceptual challenges. These challenges can be met by combining experimental and theoretical studies. Using results obtained from theoretical calculations of density-functional theory (DFT) type, some physical properties of representative compounds will be discussed. Particular emphasis will be put on the electronic reasons of the changes in structural and physical properties upon oxidation or reduction, or upon structure modification of metallic moieties and of the conjugated ligands.

Two examples will be particularly dicussed: (1) The case of di-iron-(bis)acetylide-pyridine species which shows an unprecedent example of bistability of its mixed-valent form;[1] (2) The multifunctional behavior of Ru(II) acetylide compounds containing a bistable photochromic unit which is sketched below.[2]



(1)



(2)

Keywords: Organometallic chemistry; Multifunctional molecules; Applied DFT

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Structural Properties of Aluminosilicate Nanotubes

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Imogolite [1] and Halloysite [2] are naturally occurring aluminosilicate minerals with a predominantly hollow structure. Imogolite is composed of single walled nanotubes with stoichiometry of ($Al_2SiO_3(OH)_4$), where silanol (Si-OH) groups are in the inner part of the tube. Halloysite have a 1:1 structure with stoichiometry ($Al_2Si_2O_5(OH)_4.nH_2O$), with silicate groups in the outside part of the tube (Figure 1).

The use of halloysite and imogolite offers significant advantages over other nanotubes. They are low cost clay materials that can be mined from deposits as raw mineral. Such materials are attractive due to the vast range of applications, e.g., as catalyst support, molecular sieving material for membranes and adsorbents.

In this work, structure, stability, electronic and mechanical properties of *zigzag* and *armchair* imogolite [3] and halloysite nanotubes have been calculated using the self-consistent charge density-functional based tight-binding (SCC-DFTB) method. Periodic boundary conditions were applied to the cells along the tube axes.

The highest stability of all studied imogolite tubes has (12,0) chirality, in contrast to halloysite and conventional nanotubes where the stability decreases for larger radii. This is in agreement with experimental data, as shown by comparison with simulated XRD spectrum. Analysis of the electronic density of states shows that all tubes are insulators with a wide band gap. The nanostructure formation mechanism will be briefly discussed.

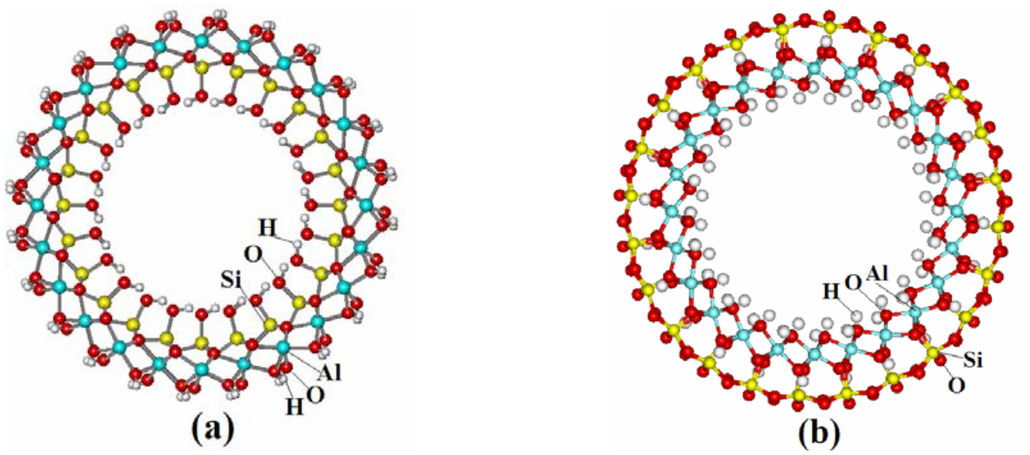

Figure 1- Imogolite (a) and Halloysite (b) Nanotubes

Keywords: SCC-DFTB, Imogolite, Halloysite, Nanotubes

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STRUCTURE AND BONDING IN ELECTRON-RICH EDGE-BRIDGED TUNGSTEN CHLORIDE OCTAHEDRAL CLUSTERS

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Several theoretical studies have shown that the optimal metallic electron (ME) count, *i.e.* the number of electrons that are available for metal-metal bonding, is generally equal to 16 for $M_6L^i_{12}L^a_6$ octahedral transition metal clusters (a = apical, i = inner according to the Schäfer and Schnering notation[1]).[2] Indeed, the metallic electrons of such clusters occupy a set of eight metal-metal bonding molecular orbitals (spanning a_{1g}, t_{1u}, t_{2g} and a_{2u} in the ideal O_h symmetry). For the electron count of 16 MEs, the HOMO is of a_{2u} symmetry. The energy of this orbital is governed by a fine tune between its modest $(\pi+\delta)$ M-M bonding character and π^* M-L antibonding character. Because of its overall non-bonding character, 15 and 14 ME species have been characterized.

Surprisingly enough, H.-J. Meyer *et al.* synthesized few years ago W_6Cl_{18}. Its crystal structure contains molecular octahedral W_6Cl_{18} units arranged in a cubic close packing.[3] Later, the same group synthesized $(Me_4N)_2[W_6Cl_{18}]$ and $Cs_2[W_6Cl_{18}]$.[4] Their structures can be considered as derivatives of that of W_6Cl_{18} in which 2/3 of the W_6Cl_{18} molecules are substituted by Me_4N^+ ions and Cs^+ ions, respectively. Interestingly, with 18 MEs for W_6Cl_{18} and 20 MEs for $(Me_4N)_2[W_6Cl_{18}]$ and $Cs_2[W_6Cl_{18}]$ the usual number of 16 MEs per cluster is exceeded in these compounds. Recently, few compounds containing 19 ME and 20 ME-W_6Cl_{18} clusters have also been synthesized.[5] In order to understand these "unexpected" electron counts and rationalize their physical properties, the electronic structure of these cluster compounds has been studied using molecular and periodic density functional theory calculations. The main results which were obtained will be discussed.

Keywords : transition metal clusters, electron count

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Role of aluminum atoms for hydrogen adsorption on graphene sheets

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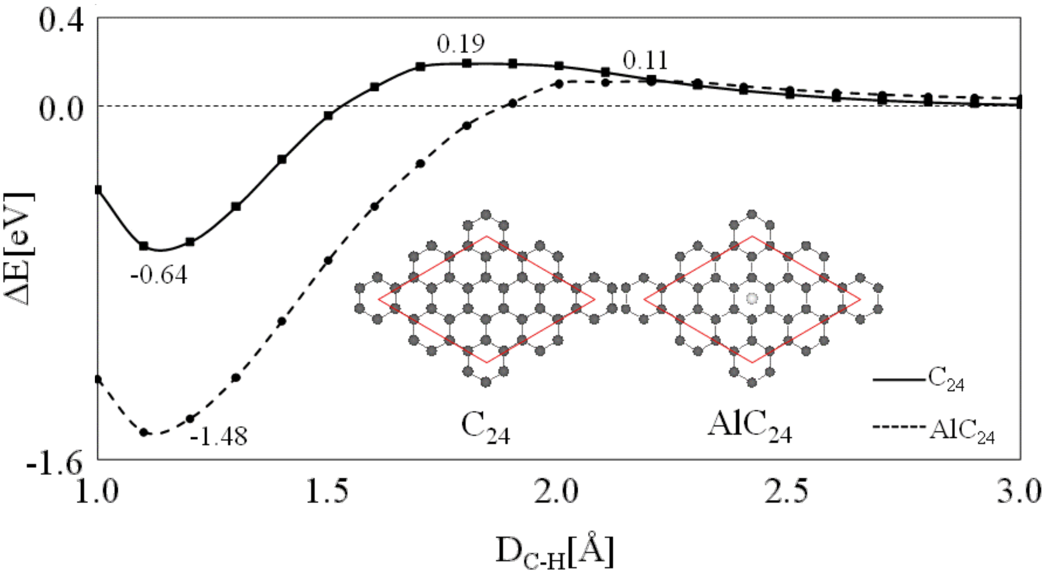
In this work, the effects of aluminum atoms for hydrogen adsorption on graphene sheets are investigated. Carbon materials are considered as a good candidate for the materials of the fuel cell due to their light weight [1]. Flat carbon surfaces, e.g. graphene and carbon nanotubes with large radius, are known to have high potential barrier for the hydrogen adsorption [2, 3]. In this work, we show that the activation energy of the hydrogen adsorption on graphene sheets stuck by aluminum atoms is significantly smaller than that without the aluminum atoms by using the computational simulation by density functional theory with periodic boundary conditions. The figure in this abstract shows one of our results. The activation energy of a pure graphene model was 0.19eV and that of AlC_{24} model was 0.11eV. Hence, for example, we speculate that wrapping an aluminum species in a carbon nanotube improves the property of the hydrogen adsorption. On the other hand, the adsorption energy of AlC_{24} model is much larger than the pure graphene model, and hence, the aluminum doping may not be favoured for the detachment of hydrogen atoms. In order to clarify the effects of aluminum atoms, we investigate electronic states of these models in detail and compare these effects of the aluminum atoms with those of lithium and magnesium atoms. This figure means potential energy curves for the hydrogen adsorption. Solid (Dashed) lines show the result of C_{24} (AlC_{24}) model. $D_{C\text{-}H}$ is the distance between the nearest C atom and the H atom. In the legend, the models we used are shown.



Keywords: Graphene, Hydrogen adsorption, Energy density

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Chemistry and Physics, DFT09, Lyon, France.

Double-wall carbon nanotube interacting with aminoacid: first-principles calculation of electronic properties

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In last years, interest in materials at the nanoscale is increasing dramatically, primarily due to their potential application in various scientific and technological fields. Through the improvement of experimental techniques and the development of ever more sophisticated computers. Theoretical and experimental researchers have had the opportunity and ability to work together. Within the materials at nanometric scale, the discovery of carbon nanotubes provided a new area of research and since then has attracted much interest due to their intrinsic properties and potential applications in the field of materials science and in medicine and biology, and that many in the last two tests may be performed from the knowledge of their interactions with various biological systems. Much attention has been given to single-wall carbon nanotubes (SWCNT) and multiple-wall carbon nanotubes (MWCNTs), but the interesting in studying double-wall carbon nanotubes (DWCNTs) has increased recently. Their systems are interesting structures are intermediated between the SWCNT, and MWCNTs systems have only two nanotubes, and external diameters of nanotubes are often similar to that of the SWCNT and the effect of quantum confinement of internal nanotubes are remarkable because of the small diameter. Experiments by aminoacid functionalization of DWNT and analysis were performed by Raman spectroscopy, and they suggested protected by internal external nanotubes [2]. In this work we study the structural and electronic properties of carbon nanotubes interacting with double layer of the aminoacid lysine by first principles calculations, we used the theory of the density functional (DFT) implemented in software Siesta [3]. Our goal is to see how the structural and electronic properties are affected when the aminoacid lysine interacts with the external and internal walls of DWCNTs.

Keywords: carbon nanotube, DFT,

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Exploring the Superionic Phases of Water at Giant Icy Planet Conditions by Free Energy Surface Trekking

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The interiors of giant icy planets such as Neptune and Uranus have been expected to have a thick intermediate ice layer which consists of water, methane and ammonia [1]. The ice layer is considered to exist in the range from 20 GPa and 2000 K to 600 GPa and 7000 K along the planetary isentrope and to be the source of strong magnetic fields measured by the Voyager 2 spacecraft [2]. To maintain such magnetic fields, the planetary dynamo mechanism has been considered in the ice layer with electrical conductivities of the order of 10 $\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$ [3]. In 1999, Cavazzoni *et al.* estimated the phase diagrams of water in the pressure range from 30 GPa to 300 GPa and the temperature range from 300 K to 7000 K by Car-Parrinello molecular dynamics simulations and observed a superionic phase in the condition of the outer part of the ice layer [4]. The predicted superionic phase is reported to have a crystal structure in which oxygen atoms form a body-centered cubic lattice and hydrogen atoms diffuse extremely rapidly via a hopping mechanism through different molecular sites. They have concluded that the large proton mobility in the superionic phase could produce the large electrical conductivity expected in the outer part of the ice layer.

The superionic water has been observed so far only for the ice phases with the body-centered cubic oxygen lattice [5, 6]. Then, in this study, first we explore the other stable or metastable structures with the superionic state at the high-P,T conditions relevant to the interiors of Neptune and Uranus, and then we estimate the proton mobility for the obtained structures. For the exploration of the structures, we use our originally developed algorithm, Free Energy Surface Trekking (FEST). FEST enables us to efficiently find many local minima located around an initial local minimum on the free energy surface with the finite temperature effect taken into account. In the presentation, we will explain the details of FEST and show the obtained structures and the calculated proton mobilities.

Keywords: high pressure, high temperature, phase transition, superionic state, water

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A computational study on [2]rotaxane self-assembled monolayer molecular electronics components

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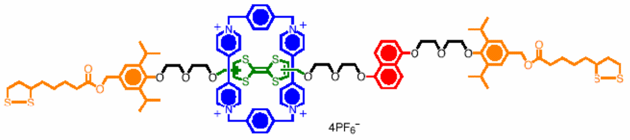
A programmable [2]rotaxane molecular switch consists of a ring-shaped shuttle encircling a two-station finger. It was shown that redox-controlled movement of the shuttle between the two stations turns on and off electric conductivity when assembled between two electrodes, opening a possibility to build up molecular-scale electronics devices. However, further development has been hampered due to the complexity in the molecular and self-assembly structure of such small devices. Thus we carried out a multi-step molecular modeling study on [2]rotaxane molecular junction devices: (1) we carried out density functional theory quantum mechanics calculations on key components of rotaxane (shuttles and stations) and explained the switching mechanism from the calculated electronic structure, and (2) we carried out molecular dynamics simulations to obtain the self-assembled monolayer structure of rotaxane on gold electrode; and then (3) we built model molecular junctions (electrode-rotaxane-electrode) and observed the switching behavior from calculated current-voltage curves. From this series of molecular modeling study we were able not only to reproduce their overall properties in good agreement with experiments but also to provide detailed molecular-level information on their structure and switching mechanism, which were hardly accessible from experiments.



Keywords: molecular switch, molecular junction, molecular electronics, [2]rotaxane, density functional theory quantum mechanics calculation, molecular dynamics simulation, non-equilibrium Green's function formalism

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An effective algorithm for the investigation of structure of clusters from DFT based Potential Energy surface : the exemple of Ga_nAs_m.

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The study of atomic clusters has become an increasingly active area of research in the recent years because of the fundamental interest in studying a completely new area which can bridge the gap between molecular and solid state physics. Owing to their peculiar and size tuned magnetic, electric and chemical properties, clusters, have been the subject of numerous studies in the past and their role in the area of nanotechnology has been well established [1,2].

Beyond any doubt, the first and most important step in the study of the properties and dynamics of atomic or molecular clusters is the determination of their microscopic structure. However, the reliable determination of the cluster structures is an extremely difficult task mainly due to the numerous minima, that exist in a cluster Potential Energy Surface (PES). Monte Carlo [3-7], Genetic Algorithm [8] and molecular dynamics [9] are the method generally used for the PES exploration.

The efficiency of these PES exploration methods is strongly connected to a reliable determination of the molecular energy. On this grounds, the ability of the DFT methods, well known to give good reliable results saving substancially the computation cost, to treat quantum effect such as Pseudo Jahn-Teller effect have been demonstrated [10]. Thus, we propose a DFT-based algorithm for finding the most stable isomers for any clusters. This algorithm includes the generation of the initial guesses and the selection scheme. Moreover, in order to save substantial computational time, instead of fully optimizing all the selected configurations, another way, presented here, consists of selecting the most reasonnable configurations during the optimization process. Finally, since the efficiency of this algorithm have been demonstrated in the case of Si_n clusters [11], this procedure have been used to study Ga_nA_m clusters.

Keywords: algorithm, cluster structure

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Tuning of Inelastic Transport by *Doping* for Single Molecular Junction and Analysis of Symmetry Propensity of IETS

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Electron transport in single molecules or in atomic wires connected to bulk electrodes, to which we refer shortly as molecular junctions, has attracted great interest because of the prospect for applications as new nanoscale devices. The non-equilibrium Green's function (NEGF) formalism is often adopted by combining the density functional theory (DFT) to yield a practical method for *ab initio* calculations.

In the development of the device by molecular junctions, the interaction between electron and nuclear vibrations (phonons) during the transport is one of the central issues because the resulting inelastic transport relates the local heating of the device, and it leads potentially to new functional device features such as molecular switching. In addition, the inelastic tunneling current can be a promising tool of the surface spectroscopy, which is called IETS (Inelastic Electron Tunneling Spectroscopy). However, the inelastic transport process correlates both of electron-phonon coupling strength and tunneling pathway itself in the bridge molecules, hence the symmetry propensity for "active vibrational mode" is more complex than the selection rule of the standard IR or Raman spectroscopy of molecules.

Recently, Kushmerick's group measured the IETS of alkanethiol and semifluorinated alkanethiol to show the relation between IR or Raman and IETS activity, where the dipole and polarizability are "tuned" by partial permutation of C-H to C-F.[1] In this presentation, we examine a similar idea of "tuning" more systematically by "doping" different affinity atoms into the backbone of the bridge molecule with first principle calculations.

We adopt the benzene-dithiol (BDT) with $\sqrt{2}\times\sqrt{2}$ structure of Au(001) electrodes as the template because the bridge part maintains (at least approximately) D_{2h} symmetry. In order to identify electron tunneling pathway for the ballistic transport, the calculated eigenchannels of transmission coefficient are decomposed into MOs (molecular orbitals) of MPSH (molecular projected state Hamiltonian), which we names as RMOs (restricted MOs) with assignment by the irreducible representation in D_{2h}. To analyze inelastic transport, we adopt fully *non-local* Holstein model and apply the *conventional lowest order expansion (LOE)* method within our "efficient NEGF-DFT" scheme. [2, 3] By the conventional LOE calculation, we assign the IETS activity for each symmetric and asymmetric mode. Furthermore, estimation of electron-phonon coupling matrix in the RMO basis is performed, and we compare the contributions of electron-phonon coupling with tunneling pathway to the IETS intensity.

To tune dipole and polarizability as well as the electron pathway, we fixed the N atom at the β position of the C atom then examine "doping of B atom" by putting B atom to ortho-, meta-, and para- C atomic positions, respectively. By this "tuning", the calculated (molecular) IR and Raman intensities are enhanced (or weekend) for several normal modes. Furthermore delocalized π RMO, which is the conduction state, is distorted by the above doping of different affinity atoms: thus the electron pathway can be also changed. By carrying out the same procedure for inelastic transport with the BDT, we discuss the IETS symmetry propensity as well as the correlation between IETS and IR/Raman activities.

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Theoretical study on the electronic conductivity of modified artificial Metal-DNA using Salen

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DNA is well known as the molecule to carry all of the genetic information necessary for all living organisms in the earth. The DNA double helix is stabilized by π-π stacking interaction between adjacent base pairs. The role of base pairing and π-π stacking in assembling the DNA double helix is an excellent example of supermolecular self-assembly. Using the programmable self-assembly, DNA will be one of the most promising materials. Seeman et. al. carried out pioneer studies of DNA nano-architectures . They made, for example, self-assembly of branched DNA molecules into a two-dimensional crystal and ligated DNA molecules form interconnected rings to create a cube-like structure. Using these structures, it is possible to create a new material to precisely arrange molecules in space.

As one of the excellent topic of arranging metals in space, Clever et. al. succeeded in allowing the complexation of up to ten Cu^{2+} ions using Salen as ligand inside an artificial DNA double helix (below transcribed **S**-Cu^{+2}-**S**) [1]. This advance is the replacement of Watson-Crick base pair in natural DNA by coordinate bond of metal.

On the other hand, electronic properties of natural B-DNA by the π-π stacking, such as electronic conductivity, have been studied in recent years. But unfortunately, there is no consecutive consequence about this problem. Especially, for the artificial metal-DNA, there is no an experimental date at all on electronic conductivity. It is important for Bio-Environmental Chemistry to investigate electronic conductivity of DNA because we can understand differences between the artificial and the natural systems and can also understand electronic conductivity occurring inside living body. In our presentation, we report theoretical investigation on electronic conductivity of the artificial metal-DNA (**S**-Cu^{+2}-**S**). Study on electronic conductivity of the artificial metal-DNA is the first approach.

Specifically, I adapt the method developed by Luo et. al. [2] using Kubo formula (below equation) in order to estimate electron conductivity of the artificial metal-DNA.

$$i_{SD} = \sum_{\eta} \frac{emk_B T}{2\pi^2 \hbar^3} \int_{eV_D}^{\infty} dE \left|T(E)\right|_{\eta}^{2} \left\{ \ln\left[1+\exp\left(\frac{E_f + eV_D - E}{k_B T}\right)\right] - \ln\left[1+\exp\left(\frac{E_f - E}{k_B T}\right)\right]\right\}$$

The artificial metal-DNA (**S**-Cu^{+2}-**S**) is an open shell system. For this reason, I expect that it is possible to give various behaviors depending on alpha and beta spins. I investigate electronic conductivity due to difference of a binding pattern of molecule and electrode because electronic conductivity changes by a binding pattern.

Keywords: artificial metal-DNA, kubo formula, salen

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13th Intern. Conf. on the Applic. of Density Functional Theory in
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Structural Determination of Transition Metal Doped Silicon Clusters: DFT Calculations and Far Infrared Spectrometry in Concert

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Silicon-based clusters have received a great deal of attention from both experimental and theoretical researchers, due to their technological applications [1]. In the miniaturization trend of electronic devices, understanding of structural and electronic properties of small clusters is essential. The structure of small vanadium- and copper-doped silicon clusters, Si_nV and Si_nCu, with n = 1-11, has been investigated using infrared multiple photon dissociation (IR-MPD) of their complexes with an argon atom, in combining with density functional theory calculations. We found the surprising performance of the BP86 functional [2] in providing good agreement with far infrared experiments.

In most cases, the calculated IR spectrum of the ground state fits well with the experimental counterpart, even when various low-lying isomers are very close in energy. In a few cases, the assigned isomer is not the energetically lowest, but it is still in excellent agreement with the growth mechanism of the whole series such as Si_9Cu^+, $Si_{11}Cu^+$ and $Si_{10}V^+$, $Si_{11}V^+$. This indicates the large error of the applied computational methods in evaluating relative energies.

In some systems, a combination of few isomers should be considered to recover the experimental spectra. For example, Si_9V^+ has been assigned for two isomers where one silicon atom moving around on the core which is a bicapped pentagonal bipyramid.

A clear picture of the impact of different impurities to host silicon clusters has been shown. Vanadium atom prefers to substitute to a high-coordinate position of the bare silicon clusters, whereas copper atom favors to adsorb to the bare clusters and has lower coordination number. The change from pentagonal bipyramid to trigonal prism motif is expected at n = 10 for copper dopant and n = 11 for vanadium dopant.

Although copper and vanadium have similar behavior at the transition size from *exo*- to *endo*-hedral structure, they are following different growth mechanisms.

Keywords: Density functional theory, Infrared multiple photon dissociation (IR-MPD), Far-infrared spectrum, Vanadium-doped silicon cluster, Copper-doped silicon cluster

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Metadynamics algorithm applied to study reduced form of 1-amide-4,4` bipyridinium dimer complex with DFT methods.

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Bipyridinium units have been widely incorporated into many supramolecular systems due to their diverse chemical properties. Their role is mainly based on the electronaccepting and electrostatic properties resulting from positive charges on the nitrogen atoms.

Reduced form of 1-amide-4,4`-bipyridinium dimer molecule (see figure 1 below) presents two conformers the open and closed conformations, whereas the non-reduced form exhibits only the open conformation. This change of behavior is quite interesting for the conception of nanodevices.

Firstly, we have studied the energy difference between the open and closed conformations of the reduced form using different levels of calculations: MP2, DFT and DFT + dispersion correction. Secondly, the dynamics of the opening process has been studied using metadynamics[1]. Metadynamics is a relatively new method that can be used for accelerating rare events and for reconstructing the free energy surface. In metadynamics, the evolution of the system is biased by a history-dependent potential constructed as a sum of Gaussians centered along the trajectory in the set of collective variables and at the end, because the added Gaussians, we can see that the system is forced to escape from local minima using the lowest saddle points and to visit new wells.

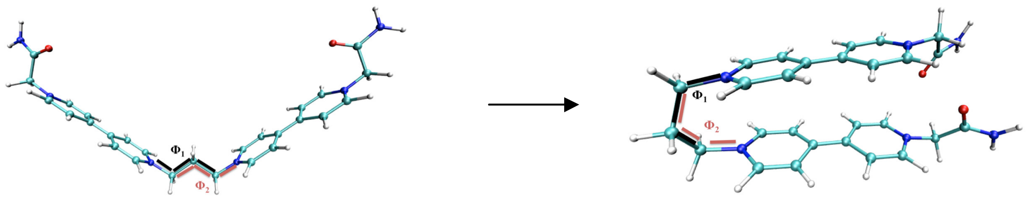

Fig.1 Reduced form of 1-amide-4,4`-bipyridines dimer molecules. Open and closed conformations

Keywords: Metadynamics, DFT-D, free energy

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Poster Abstracts for DFT09

Ligand and solvation effects on the redox properties of Au_{55} and applications to molecular logic.

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Passivating ligand and solvation effects on the electronic properties of the Au_{55} nano cluster are studied using density functional theory for $Au_{55}(PH_3)_{12}Cl_6$, neutral, positively and negatively charged. In all charged states, the distorted icosahedral lowest conformer of the bare and ligated Au_{55} clusters is found to be more stable than the cubohedral one. The computations show that upon passivation, there is a significant charge transfer from the gold core to the ligand shell. In the gas phase, the ligands PH_3 and Cl bind to a one and three coordination site of the Au_{55} respectively. Upon geometry optimization in the presence of an explicit water shell, the Cl and PH_3 ligands are solvated by the H_2O molecules and bind to one coordination sites only. The computed ionization potential, electron affinity and the charging energy reflect the strong interaction between ligand shell and Au_{55} core and their alteration by the explicit solvation with water molecules. We then show with simulations that the three redox states of the $Au_{55}(PH_3)_{12}Cl_6$ can be selectively addressed electrically and used to build logic machines.

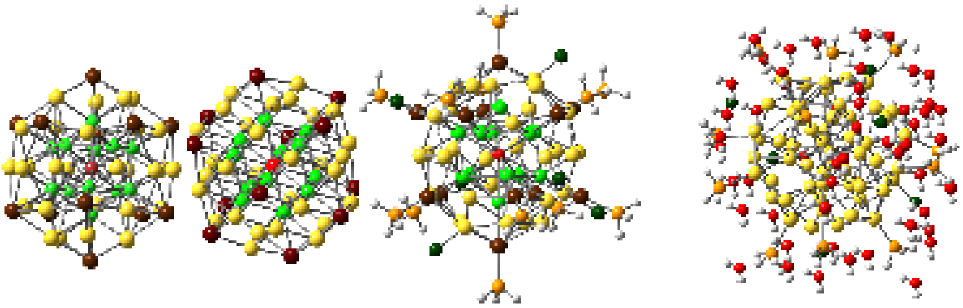

Figure : Distorted icosohedral and cubohedral bare Au_{55}, $Au_{55}(PH_3)_{12}Cl_6$ and $Au_{55}(PH_3)_{12}Cl_6 \cdot 54\ H_2O$.

Keywords: Molecular logic, gold cluster, DFT

Optical properties of photochromic molecules functionalized by gold clusters: towards nano-hybrid switches.

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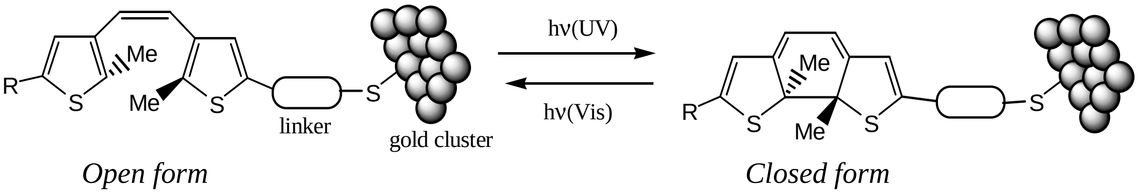
There is a great interest in the development of electronic devices at the molecular level. In this context, organic photochromes are promising candidates since specific changes in their electronic and structural properties occur under light irradiation. Among the various families of organic photochomes, diarylethene molecules are the most promising candidates for optical, electronic and plasmonic applications due to their interesting photochromic properties, *i.e.* good fatigue resistance and high thermal stability of closed and open forms [1].



Photochromic equilibrium in diarylethene series (R=SH, phenyl-SH, thiophene-SH, C≡CSH…; linker= phenyl, thiophene…)

However, in order to use these photochromic compounds within an active electronic device, it is necessary to make sure that their commutation properties are preserved when they are in contact with metallic electrodes. Recent studies have shown that the molecular structure of the diarylethene has a great impact on the reversibility mechanism. Thus, Dulic et al. [2] studied the optical properties of photochromic molecules assemblies on a gold surface. UV-Vis spectroscopic measurements show that in the case of photochroms with thiophene linkers functionalized by gold, the reaction of ring-opening was always possible whereas the cyclization reaction was inhibited.

Within the framework of the Density Functional Theory (DFT) and Time-Dependent DFT, we determined the spectroscopic properties of diarylethenes grafted on small gold clusters. The analysis of molecular orbital interactions established between the photochromic molecule and the gold cluster made it possible to rationalize these experimental findings.

Keywords: photochromism, gold cluster, optical spectra

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Optical Properties of Pure Silver and Bimetallic Silver-Nickel clusters

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The absorption spectra (UV-Visible) of small pure Ag_n ($n \leq 22$) clusters and bimetallic Ag_mNi_p ($m+p \leq 14$) clusters are investigated in the framework of the time-dependent density functional theory (TDDFT). For Ag_n clusters, the calculated spectra compare well with recent experimental ones obtained for clusters embedded in an argon matrix [1]. The analysis of the molecular transitions indicates that the *s* electrons are responsible for the optical response in the very small clusters ($n \leq 8$) while *d* electrons play a crucial role in the optical excitations for larger n sizes. The present study shows that the use of a small core (i.e. 19 electrons treated as valence electrons) is suitable for accurate calculations of the excited states [2].

The structure of Ag_mNi_p clusters is essentially governed by the formation of a Ni-core surrounding by silver atoms [3]. The calculated absorption spectra of these core/shell clusters are found to be broadened, and blue-shifted with increasing nickel proportion as compared to those of pure silver clusters [4,5]. These results are consistent with experimental ones obtained for the large Ni/Ag nanostructures of 2-5 nm of size for which a damping, broadening, and blue-shift of surface plasmon resonance band with increasing nickel proportion were observed as compared to pure silver clusters[6]. The transitions are essentially due to excitations from *d* orbitals of nickel atoms to outer region with hybrid *s-p* orbitals distributed on wide areas involving several silver atoms. This leads to a charge transfer from nickel to silver atoms.

Keywords: silver clusters, bimetallic clusters, TDDFT

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Effect of annealing on the dynamics and structure of hot giant fullerenes in presence of buffer gas: DFTB/MM MD simulations

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Abstract

Annealing of hot giant fullerenes in presence of buffer gas is performed using density functional tight binding (DFTB)/molecular mechanics (MM) molecular dynamics simulations. Cluster size and structural changes are analyzed and discussed considering different buffer gases and with different temperatures and pressures. A comparative study on the performance of thermostat vs explicit use of buffer gas is also presented. It is observed that the explicit use of buffer gas with sufficient initial energy helps to shrink the giant fullerenes faster and a continued controlled annealing eventually may form smaller fullerenes, e.g., C_{60}, C_{70}. The shrinking process occurs almost exclusively via emission of C_2 unit from the fullerenes. Ring transformations and subsequent C_2 fragmentations occurred mainly following either general Stone-Walls (GSW) or non-SW type transformation and thus the defects due to 7 or higher membered rings are healed up. Cage opening and re-closing also occurred following GSW or non-SW type transformations. It is also observed that the appearance of sp3 carbon has an important role in the fragmentation process. These simulations suggest that continued annealing might have important role in the formation of smaller fullerenes and thus shed light on the high yield of C_{60}.

Binding Energy Estimation of Hydrogen Storage Materials MOF by All-Electron Mixed-Basis Program TOMBO

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[2] Department of Materials Science and Engineering, Delft Univ., Mekelweg 2, 2628, *Delft*

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In 2004, for automobile onboard storage system, the U.S. Department of Energy (DOE) set the target that hydrogen storage capacity should be higher than 6wt.%. Metal-Organic Frameworks (MOFs) are one of the promising candidates for hydrogen storage materials [1]. In the present study, we estimated the binding energy of hydrogen molecules to MOFs by introducing a simple model with lithium cation doping to expand hydrogen storage capacity and clarify the mechanism of enhancing hydrogen adsorption energy. We use TOhoku Mixed-Basis Orbitals *ab initio* simulation package TOMBO [2, 3] developed by our research group, which enables us to study based on ”all-electron mixed-basis approach” with smaller number of plane waves.

In the presentation, at first we demonstrate to show the advantage of the present simulation using some simple molecules with hydrogen and MOFs. We found that the adsorption of Li atoms on benzene unit of MOF-5 improves hydrogen storage function properties of these systems by 1.74 wt% and makes binding energy much higher than the systems without lithium doping. This work has been supported by New Energy and Industrial Technology Development Organization (NEDO) under "Advanced Fundamental Research Project on Hydrogen Storage Materials".

Keywords: all-electron mixed-basis approach, hydrogen storage materials, binding energy

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Density-functional theoretical study combined with integral equation theory on wet-DNA: hydrated structures and electronic properties

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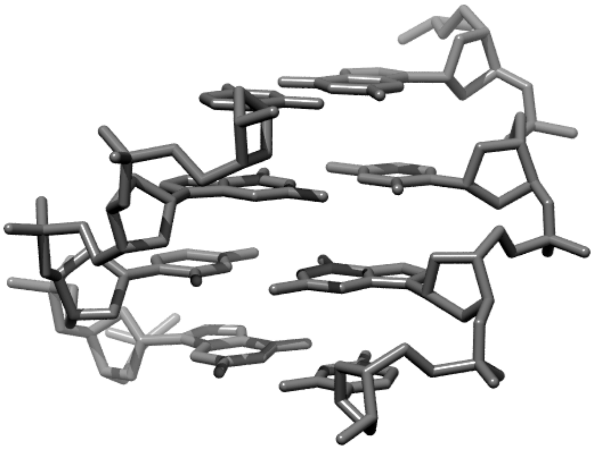
It is well known that a DNA has high electronic conductivity in wet condition, while it doesn't in dry condition. Therefore, the solvent effects on the electronic properties of DNA got much attention in the field of biology, chemistry and physics.

In the present study, we employ three-dimensional reference interaction site model method combined with Kohn-Sham DFT (3D-RISM-DFT) theory to investigate the electronic structure and solvent distribution around DNA.[1,2] We also introduce quantum-mechanics and molecular mechanics (QM/MM) method to treat the large DNA chain. In this study, we consider one DNA chain in water solvent. The DNA chain consists of 4 to 10 base pairs. The system can be divided to three regions. Two or four base pair of DNA are treated by KS-DFT, and the remaining part of DNA is calculated by molecular mechanics region. Distribution of solvent water can be evaluated by 3D-RISM theory. By this theory, the electronic structure of QM part of DNA and solvent distribution around DNA are determined simultaneously.

The results indicate that the solvent effects on the HOMO and LUMO orbital of G-C and A-T base pair are quit different. HOMO-LUMO gap of G-C base pair become shorter by solvation. This is originated that the water molecule strongly binds to guanine. The change of electronic structure contributes to high electronic conductance of DNA.



Keywords: QM/MM, 3D-RISM-SCF, DNA, charge transfer

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

A DFT Study on the reaction mechanisms of some TTF derivatives obtained by coupling reactions

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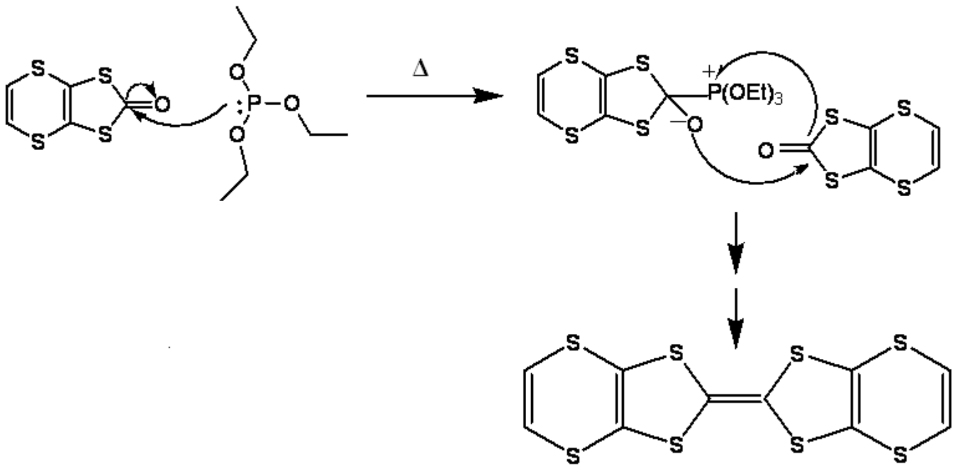
Tetrathiafulvalene (TTF) and its derivatives has been subject of many studies due to the fact that they exhibit superconducting property upon oxidation[1]. In this study, the coupling reaction mechanisms leading to the TTF derivatives synthesized recently by our group, are studied theoretically by using the Density Functional Theory (DFT) method with B3LYP hybrid functional and 6-311+g** basis set. The transition state geometries of two different competing pathways are modeled and the activation energy of these reactions is used to shed light the experimental product distribution.



The figure above shows the schematic representation of self coupling reaction mechanism of oxo compound in the presence of triethyl phosphite catalyst to yield a TTF derivative.

Keywords: DFT**,** TTF, reaction mechanism

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POSTER PRESENTATIONS

Topic 9.

Conceptual DFT

13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Development of CAS-SCF-DFT approach: application to dissociation of binuclear systems

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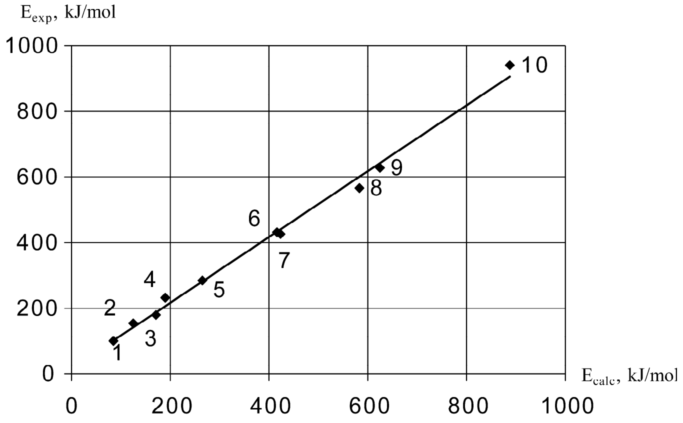
The CAS-SCF-DFT (Complete Active Space Self Consistent Field Density Functional Theory) is introduced as the combination of KS–DFT and conventional CASSCF approaches: the flexible active space is chosen by inspection of corresponding KS–orbitals that are initial guess for variational treatment of MCSCF method. We present the new hybrid CAS–SCF–DFT approach as a method that allows accounting for both the non–dynamical and dynamical correlation.

The traditional approaches (MR–MP2 and CASPT2) are frequently plagued by intruder states incipient from application of perturbation theory. In these cases, the non–dynamical and dynamical correlation effects are treated in an imbalanced way. We suppose that CAS-SCF-DFT approach is free from these difficulties because the KS reference is probably better than the HF guess which is known [1] to be sometimes qualitatively incorrect. If the KS-orbitals are used as input quantities, the central problems of the CAS-SCF-DFT method are the double counting of dynamical correlation effects and the self–interaction error (SIE). Variational treatment of KS–orbitals reduces or fully removes the above errors. Using the new approach, we determined the potential energy curves of some test binuclear systems (Li_2 (1), F_2 (2), LiH (3), $HeH^{+\prime}$ (4), B_2 (5), H_2 (6), OH (7), HF (8), C_2 (9), N_2 (10)). The comparison between the calculated bond dissociation energies and the corresponding experimental values are shown in Figure.



The method is size extensive if the active space is properly chosen and free of inversion symmetry breaking problem (see Bally [2]) for all the considered DFT functionals. All calculations were performed with the Gaussian03 program suite via non-standard route sections.

This work is supported in part by the Russian Foundation for Basic Research (project No.07-03-00390).

Keywords: hybrid method, multireference DFT, dissociation energy

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

A DFT Study on Tautomerism and Vibrational Analysis of 1-(2-Benzothiazolyl)-3-methyl-5-pyrazolone

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In this study the computational calculations of 1-(2-Benzothiazolyl)-3-methyl-5-pyrazolone have been carried out by using the Becke-3-Lee-Yang-Parr (B3LYP) functional [1,2] supplemented with the 6-31+G(d) basis set. The geometry optimization calculations shown that of the conformers for the possible tautomers the most stable one is illustrated in Figure 1. The calculations have been performed using Gaussian 03 package program.

Fundamental frequencies of the most stable configuration have been calculated. The total energy distributions (TED) of the vibrational modes have been calculated by using Scaled Quantum Mechanical (SQM) method. Calculated frequency values have been found to be in consistent with the experimental ones.

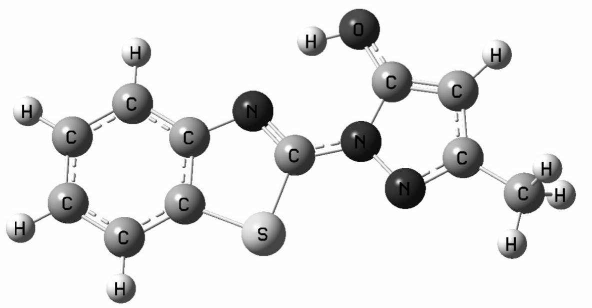

Figure 1. The geometry optimized structure of 1-(2-Benzothiazolyl)-3-methyl-5-pyrazolone

Keywords: DFT; Tautomerism; Vibrational frequencies; SQM

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P903

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Thermodynamic extension of spin density-functional theory.

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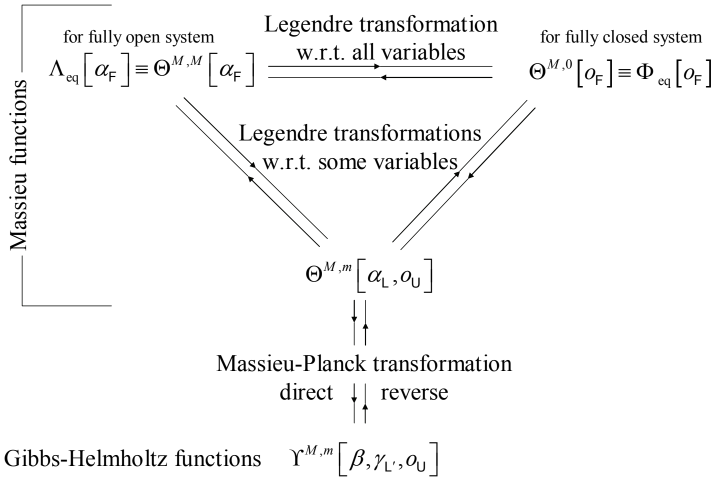
The formalism of the presented theory, based on the maximum entropy principle, describes the equilibrium state of a many-electron system in terms of a (mixed-state, ensemble) density matrix operator in the Fock space. Various characteristic functions/functionals are defined and investigated: the basic Massieu function for fully open thermodynamic system (ensemble), its Legendre transform — the effective action function — for the fully closed (isolated) system, and a series of their partial Legendre transforms — the Massieu functions — for partially open/closed systems. Other characteristic functions — the Gibbs-Helmholtz functions — are obtained from previous ones as their Massieu-Planck transforms, i.e. by specific transformation of arguments (which involves the temperature) and by applying the temperature with the minus as a prefactor. Such functions are closer to traditional (Gibbs, Helmholtz) thermodynamic potentials.[1]



This formalism is applied to two thermodynamic systems: (i) of three global observables (the energy, the total electron number and the spin number), (ii) of one global observable (the internal electron energy) and two local (position-dependent) observables (the total electron density and the spin density). The two-component potential of the many-electron system of interest is constructed of a scalar external potential and a collinear magnetic field (coupled only with the spin operator). Various equilibrium characteristics of two systems are defined and investigated. Conditions for the equivalence between two systems (the same equilibrium density matrix demanded) are presented and thoroughly discussed.[2] Obtained results provide a rigorous mathematical foundation for future derivation of the zero-temperature limit of this theory and determination of its chemical reactivity indices.

Keywords: spin DFT, spin Kramer function, spin Massieu function, spin grand potential, spin Helmholtz function, fractional occupation, fractional spin

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[1] R. Balawender, A .Holas, arXiv:0901.1060
[2] R. Balawender, A .Holas, arXiv:0904.3990

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Computing chemical reactivity indices in thermodynamic spin density-functional theory.

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Based on the thermodynamic extension of the density functional theory (see the poster *Thermodynamic extension of spin density-functional theory*) [1,2] the chemical reactivity indices are introduced. Global (non-local) and local (position-dependent) indices in chemical-softness and chemical-hardness representations for both the closed system and the open one are explored. Properties of these indices, using the dimensionless representation (i.e., in terms of the Massieu functions) and the energy-dimension representation (i.e., in terms of the Gibbs-Helmholtz functions), are investigated, their dependence on the temperature is included. The fundamental relations between all defined basic quantities are summarized and interpreted.

The calculation scheme for the indices, using the first- and second-order coupled perturbed equations, is proposed (as the extension of the scheme presented in [3,4]). The illustrative examples which include both the global and local resolutions for externally closed and open molecules are presented.

Keywords: spin DFT, spin Kramer function, spin Massieu function, spin grand potential, spin Helmholtz function, fractional occupation, fractional spin

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[1] R. Balawender, A .Holas, arXiv:0901.1060
[2] R. Balawender, A .Holas, arXiv:0904.3990
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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Combined DFT and NMR study of stannylenes and germylenes in interaction with organic solvents

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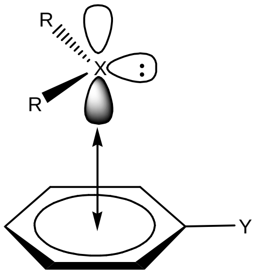
Stannylenes, R_2Sn:, and germylenes, R_2Ge:, are tin and germanium analogues of carbenes [1], containing divalent tin and germanium centers respectively. These electrophilic compounds are instable and highly reactive, but can be stabilized by introducing sterically demanding functional groups (e.g. bulky phenyl and isopropyl groups), or/and with π-electron-donating substituents, like the heteroatoms N, O and S, on the central metal atom.

In solution, electrophilic stannylenes and germylenes interact with (aromatic) π-electron-donating organic solvents. The aromatic π-electron complexation is depicted in the figure below. Disubstituted (R= -F, -Cl, -Br or -I) stannylenes (X=Sn) or germylenes (X=Ge), in the singlet state, interact with an aromatic solvent (Y = -H, $-CH_3$, $-OCH_3$, $-CF_3$ and $-NO_2$).



The strength of this interaction can be quantified by the overall complexation energy, $\Delta E_{complexation}$.

This study combines quantum chemical DFT calculations and experimental NMR work.

In the experimental approach, we have studied several samples of three stannylene compounds, dissolved in the following organic solvents: toluene-d_8, cyclohexane-d_{12} and THF-d_8. Several NMR techniques were applied to investigate intermolecular stannylene solvent complexation interactions (^1H, ^{13}C, ^{117} Sn and ^{119}Sn NMR, heteronuclear (^1H-^{119}Sn) 1D HMQC, (^1H-^{13}C) 2D HMQC and (^1H-^{13}C) 2D HMBC correlation NMR).

In the theoretical study, following the methodology from [2], simple stannylene and germylene complexes were computed. The dihalogenated stannylenes and germylenes are combined with a range of organic solvent molecules: benzene, toluene, anisole, tetrahydrofurane, trifluoromethylbenzene, nitrobenzene and furan. NBO (Natural Bond Orbital) analyses [3] are performed on the optimized complex structures to study specific orbital interactions.

The strongest complexation interaction is observed with THF. A difference in complexation is observed upon changing the substitution pattern on the aromatic ring (e.g. anisole versus nitrobenzene). The results are in good agreement with the expected trends.

Keywords: Stannylenes, Density Functional Theory, π-complexation

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[3] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, **88**, 899-926 (1988)

13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Fukui Functions for Degenerate Ground States oman

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The Fukui function, defined as the derivative of the electron density with respect to the number of electrons, plays a central role in the density-functional theory of chemical reactivity because it describes how a molecule accepts/donates electrons. Despite its widespread use, some fundamental issues remain unsolved. Chief among these is the nonexistence of the Fukui function for systems with degenerate ground states, cations, and/or anions. Because the functional derivative of the energy respect to the external potential does not exist for degenerate ground states, the Fukui function cannot be written as the derivative of the electron density respect to the number of electrons. Here we show how to generalize the Fukui function to degenerate ground states by defining the Fukui function as a response function that depends on the form of the external potential. The Fukui function for degenerate systems is thus not an intrinsic property of the system, but depends on the specific perturbation (i.e., the reagent) the system encounters. This is true even in the limit of infinitesimal perturbations. Our practical results include bounds to the Fukui functions that do not depend on the perturbation and frozen-core approximations to the generalized, perturbation-specific, Fukui functions. Our results can be extended to any response function involving perturbations in the external potential.

Keywords: Fukui function, Degenerate states.

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Chemistry and Physics, DFT09, Lyon, France.

Differential solvation on the tautomers of the keto-enol equilibrium

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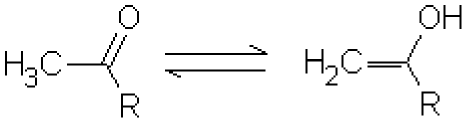
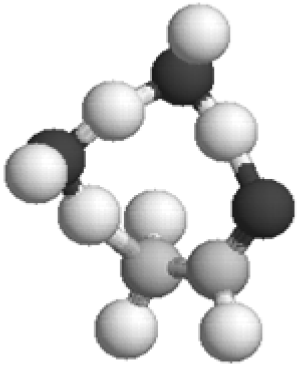
The keto-enol tautomeric equilibrium corresponds to an intramolecular proton transfer. In the gas phase, this reaction is energetically prohibited with an activation barrier close to 70 kcal/mol.



Water solvation significantly lowers the barriers. Hydration is simulated using microsolvation with one and two water molecules. The first solvent molecule reduces the activation energy in 30 kcal/mol, while the second one lowers the barrier in an additional amount of 10 kcal/mol. Solvent molecules greatly lower the activation barriers since they are involved in the proton migration. For this kind of reactions continuous solvent models show a negligible effect on the activation energy.



Reactivity descriptors are compared, both in solution and in the gas phase. Differences on the direction of the charge transfer between the solute and the solvent is analyzed in both tautomers.

Keywords: solvation, reactivity, proton shift

P908

Kinetic (Ir)reversibility from Conceptual DFT based Reactivity Descriptors within the Framework of the Reaction Force Concept

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[2] *Laboratorio de Química Teórica Computacional (QTC), Pontificia Universidad Católica de Chile, Santiago, Chile*
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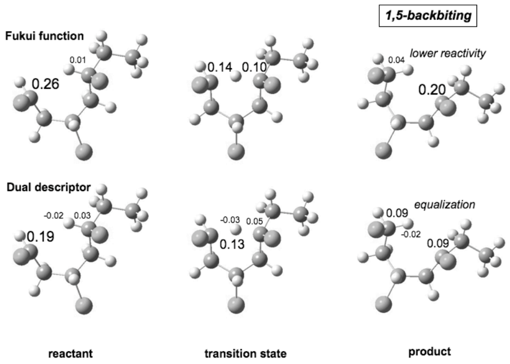
The kinetic (ir)reversibility of intramolecular reactions can be linked to changes in Conceptual Density Functional Theory (DFT) based reactivity descriptors[1], within the framework of the reaction force concept[2]. This idea was investigated for 4 intramolecular side reactions in the polymerization of poly(vinyl chloride): the 1,5- and 1,6-backbiting reactions and the 1,2- and 2,3-Cl shift; only the latter is considered to be kinetically reversible.[3] The (ir)reversibility concept is of great importance as controlling and even hindering side reactions play a major role in polymer chemistry.

It has been observed that more specifically the Fukui function and the dual descriptor can be used to rationalize the kinetic (ir)reversibility of the considered reactions. For all irreversible side reactions, the Fukui function value, i.e. the reactivity, of the original radical center was higher than that of the product radical center, thus the reverse reaction is less likely. In addition, for the backbiting reactions, an equalization of the dual descriptor for the original and product radical center was observed. Again, there is no driving force for the reverse pathway. The only reversible side reaction, i.e. the 2,3-Cl shift, shows different behavior: about the same difference in value of Fukui function and dual descriptor for the original radical center in the reactant conformation and the product radical center in the product conformation with respect to the chlorine atom is encountered.[4]



Keywords: Conceptual DFT, reaction force, (ir)reversibility, intramolecular reactions

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The Mechanism of the Schiff Base Formation between Methylglyoxal and *N*-α-Acetyl-lysine in the context of Advanced Maillard Reactions

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[3] *Departament de Fisicoquimica and Institut de Biomedicina (IBUB), Facultat de Farmàcia, Universitat de Barcelona, 08028 Barcelona, Spain*

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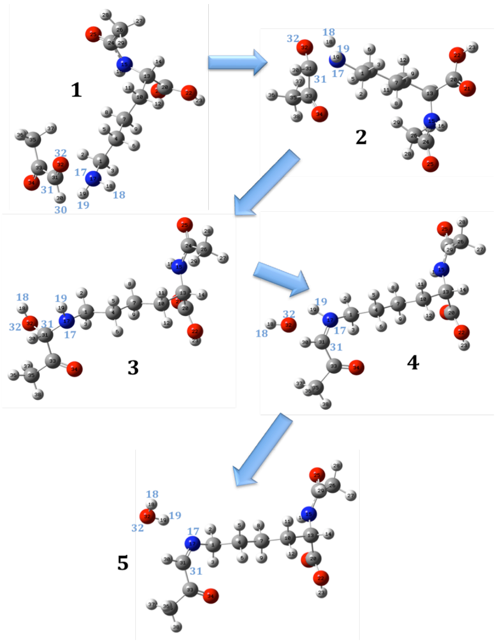
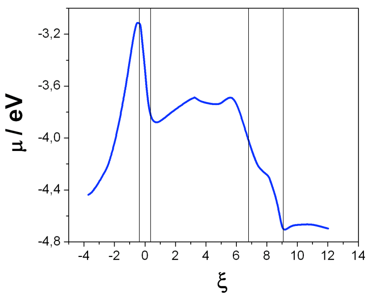
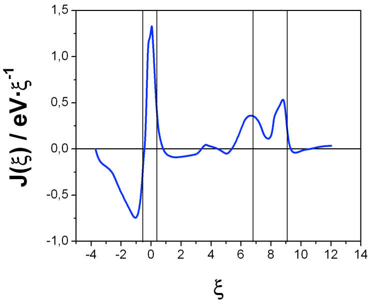
The mechanism of the Schiff base formation between metilglyoxal and N-α-acetyl-lysine has been described in terms of the Reaction Force and a new global descriptor, the Reaction Electronic Flux (REF) [1-3]. The reaction proceeds trough two proton transfers and a carbynolamine intermediate, and leads to the formation of an advanced Maillard product. In the first proton transfer, the structural rearrangements in at the interacting molecules are the most relevant contributions to the energy barrier, but in the second one, the electronic rearrangements overrule the structural ones. This behaviour denotes a change in the mechanism of the second proton transfer where the charge delocalization is enhanced by a decrease in the hardness. On the other hand, the Reaction Electronic Flux indicates that the first proton transfer is driven by the electronic transfer contribution whereas the polarization contribution drives the second proton transfer.







Keywords: Maillard reaction, Reaction Electronic Flux

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Conjugation of Allyl Systems on the Light of the Energy Decomposition Analysis

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Conjugation is quite an extended concept in chemistry. It is invoked to explain the special stabilisation of double bonds separated by just one single bond, as in the case of benzene. It is also used to understand the short C–C single bond distance in 1,3-butadiene or the special reactivity of 1,4-addition to enones. Nevertheless, although conjugation is very used for explaining structures and reactivity of unsaturated compounds, its theoretical estimation is still challenging; it is not an observable cuantity and cannot be defined without arbitrary assumptions.

The case of the allyl anion, cation and radical ($[CH_2CHCH_2]^{-,+,\bullet}$) is a clasical example to demonstrate the effects of conjugation. Wiberg *et al.* concluded that conjugation is significant in allyl cation and negligible in allyl anion [1], while Gobbi and Frenking [2] suggested that conjugation is present in the three systems, being more important for the ions. This is supported by Mo and Peyerimhoff [3] and Linares *et al.* [4], which actually determine that conjugation in allyl ions is twice stronger than for the radical species.

The present contribution is an attempt to clarify this open question. The Energy Decomposition Analysis (EDA) firstly proposed by Morokuma [5] and later developed by Ziegler and Rauk [6] is a method that can be employed for this purpose since it can directly estimate the π interactions in these systems and, hence, the conjugation. Previous results show that EDA analysis has proved to be a valid approach for determining conjugative and hyperconjugative interactions [7]. Consequently we will apply it to study the conjugation of the allyl anion, cation and radical ($[CH_2CHCH_2]^{-,+,\bullet}$). However, we do not only consider these systems but also the *all-sila, -gemanium and -tin* analogues ($[XH_2XHXH_2]^{-,+,\bullet}$ with X = Si, Ge, Sn) in order to investigate how the conjugation energy varies down in the group. We find that the latter systems present a very different chemistry from the all-carbon counterparts, showing how different is the chemistry of first-row elements.

Keywords: Density Functional Theory, Energy Decomposition Analysis, Bond Analysis, Conjugation, Allyl, Group 14 Elements

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Further Development of the Concepts of Electrodonating and Electroaccepting Powers

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Charge transfer processes are of fundamental importance in chemistry. Simple, though chemically meaningful, descriptions are based on the behavior of the energy as a function of the number of electrons. In particular, the smooth quadratic interpolation, that allows one to express charge transfer properties, such as the electrophilicity, in terms of the chemical potential and the hardness, has been amply used to explain the behavior of a wide variety of chemical systems. However, in the smooth quadratic interpolation, the response function for charge donation is equal to the response function for charge acceptance. Since from the chemical perspective it may be important to differentiate these responses, recently, the concepts of electrodonating and electroaccepting powers have been developed through an alternative interpolation procedure in which the first derivative of the energy with respect to the number of electrons is different as one approaches the reference state from the left or from the right [1]. In the present work an analysis of the energy change associated with the simultaneous charge donation and charge acceptance processes, when the system is immersed in an electron bath that represents the chemical environment, is performed in order to establish the net response. The applications of this analysis in donor-acceptor driven processes will be discussed.

Keywords: charge transfer, electrophilicity, electrodonating and electroaccepting powers

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Theoretical Study of the Mechanism of Hydrogen Transfer in Antioxidant Reactions

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Abstract

We study the hydrogen transfer from phenolic antioxidant compounds to free radical using Density Functional Theory. An exhaustive analysis of this reaction using a set of tocopherol-like compounds as antioxidant is performed through the characterization along the reaction coordinate of different electronic properties.

The adequate methodological elements for this investigation are provided by the reaction force analysis that partition the reaction coordinate in regions where different reaction mechanism may take place [1,2,3]. This research produce valuable information about the kinetic, thermodynamic and mechanisms of the hydrogen transfer reaction from the antioxidant to the free radical species. It also provide new criteria to characterize the antioxidant power of the systems under study.

Keywords: Reaction Force, DFT, Transition State

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The Role of *d*-Orbitals in the Bonds of Negative Ions

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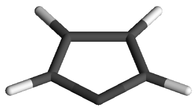
In the early 90's it has been shown that *d*-orbitals do not participate in the bonding of neutral molecules containing heavy atoms [1]. This founding is in agreement with the ionization energies of the pyridine-stibabenzene series obtained by photoelectron spectroscopy, where the A_2 ionized states have almost constant energy within the series [2]. Since the a_2 orbitals have two planar nodes through the heteroatom, they are relatively unperturbed by the heteroatom, and a *d*-orbital interaction would stabilize an A_2 cationic state. In contrast to this, the electron transmission investigation of the electron affinities of the same series [3] revealed that A_2 π^* anionic state of phosphabenzene is stabilized by about 0.5 eV with respect to pyridine, while it remains almost constant for arsabenzene and stibabenzene, i.e., in all those compounds where the heteroatom have *d*-orbitals in the valence shell.

We have investigated the *d*-orbital contribution in the semi-occupied molecular orbitals of the pyridine-stibabenzene and furan-tellurophene series in both low-lying $^2A_2$ and $^2B_1$ anionic states by means of a newly developed, powerful "potential wall confinement" technique [4]. We found a significantly increase in the heteroatom *d*-orbital contributions of the semi-occupied a_2 orbitals in the P, As, Sb and the S, Se, Te compounds, compared to the N and O compounds. Analogously, the Natural Bond Orbital analysis revealed in the possible NBO localized mesomer structures heteroatom *d*-carbon *p* π-style bonds in the P, As, Sb and the S, Se, Te compounds, while no similar bonds were found in the N and O compounds. The trends in the case of B_1 anionic states are the same, however, due to symmetry reasons the heteroatom perturbs the b_1 orbitals more significantly than the a_2 orbitals.

In the picture below, we show the total heteoratom orbital contributions to the semi-occupied a_2 orbitals in the anionic states.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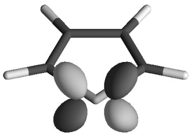
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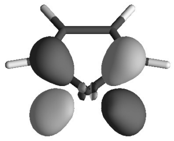
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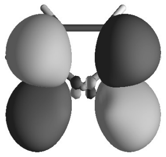
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Keywords: negative ions, *d*-orbital contribution, electron affinities

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Correspondence between information theory and the kinetic-energy functional: A combined theoretical and numerical approach

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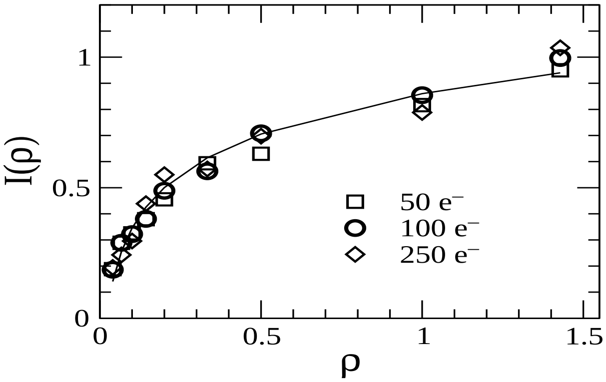
We strengthen the connection between information theory and quantum mechanical systems for the nearly uniform electron gas by employing the Levy-Lieb constrained search formalism [1] to obtain a decomposition of the kinetic energy into two universal terms. The first term is a functional of the electron density and we show that this functional is proportional to the Fisher information which is one cornerstone of information theory. The second term is a functional of the $N-1$ conditional electron density. [2] This term is evaluated via a statistically rigorous Monte Carlo procedure to obtain a Coulomb integral and a functional of the electron density. [3] We show that this functional is proportional to the Shannon entropy which is another cornerstone of information theory.



Keywords: kinetic-energy functionals, Fisher information, Shannon entropy

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The Mechanism of Methanol Decomposition. A Theoretical Study Based on the Reaction Force Analysis

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A theoretical study of methanol decomposition using a model system that represents the initial step of the reaction $CH_3OH + CuO \rightarrow CH_2O + H_2O + Cu$ is presented. Theoretical calculations using B3LYP/6-21G along with Lanl2DZ pseudopotentials on metallic centers were performed and discussed within the framework of the reaction force analysis. It has been found that the reaction takes place following a stepwise mechanism, in which electron transfer effects are predominant at the initial step of the reaction, whereas polarization effects takes over in the second step to promote a proton transfer that leads to the product formation.

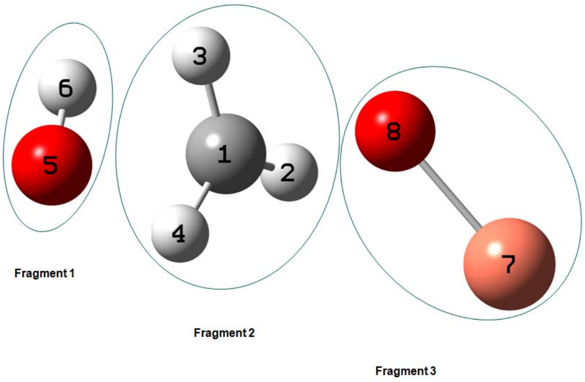

Figure 1: Description of the model used to represent the electronic flux decomposition.

Keywords: Reaction Flux, Reaction Force, Catalysis Mechanism,

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P916

Solvent and conformational effects in the Vibrational Circular Dichroism spectrum of $[Co(en)_3]^{3+}$

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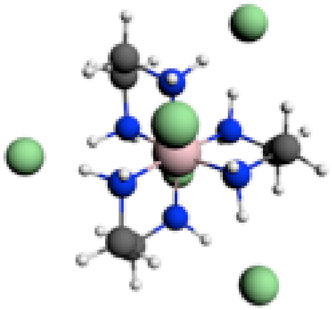
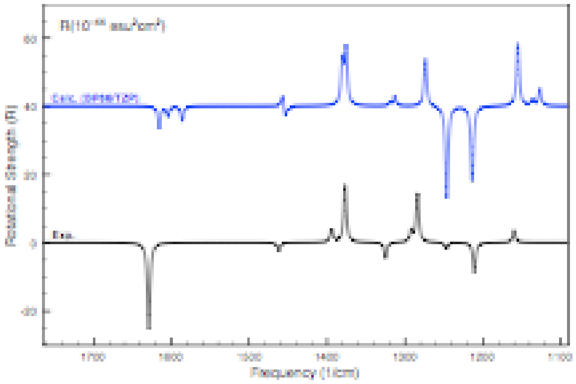
Vibrational circular dichroism (VCD), the differential absorption of left and right circularly polarized light for an infrared transition, is a probe of absolute configuration of chiral molecules. In general the different conformations that nonrigid molecules may have in solution is a complication, because of the different VCD spectra for the different conformers. Sometimes VCD can, however, be helpful for conformational analysis.

In this poster we present a detailed analysis of the effects induced by 1) conformational freedom, and 2) solute-solvent complex formation, in the VCD spectrum of Tris(ethylenediamine)Co(III) complex, $[Co(en)_3]^{3+}$. First, we establish the signatures of the four conformations of $[Co(en)_3]^{3+}$ (δδδ, δδλ, δλλ, λλλ) by comparing their calculated spectra. Then, we compare the experimental spectrum [1, 2] to calculated spectra [3] for molecular complexes form between $[Co\ (en)_3]^{3+}$ and 2, 3 and 5 chloride ions, respectively.

The experimental spectrum [1, 2] is reproduced best by the calculated spectrum of the $[Co(en)_3]^{3+}$–$5Cl^-$ complex. However, signatures of the complexes involving 2 and 3 chloride ions can also be identified in the experimental spectrum.

Regarding the four conformations of $[Co(en)_3]^{3+}$, we found that they have little influence on the VCD spectra of the $[Co\ (en)_3]^{3+}$–$5Cl^-$ complex, but affect significantly the spectra of the complexes involving 2 or 3 chloride ions.





Keywords: solute-solvent complex formation, VCD, Tris(ethylenediamine)Co(III), conformation

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Information Theoretical Study of the Chirality of Enantiomers

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In this work [1] we probed the Kullback-Leibler information entropy as a chirality measure, as an extension of previous studies on molecular quantum similarity evaluated for different enantiomers (enantiomers possessing two asymmetric centra in [2], with a single asymmetric carbon atom in [3] and with a chiral axis in [4]). The entropy was calculated using the shape functions of the R and S enantiomers considering one as reference for the other, resulting in an information theory based expression useful for quantifying chirality. It was evaluated for 5 chiral halomethanes possessing one asymmetric carbon atom with H, F, Cl, Br and I as substituents. To demonstrate the general applicability, a study of two halogen-substituted ethanes possessing two asymmetric carbon atoms has been included as well. Avnir's Continuous Chirality Measure (CCM) [5] has been computed and confronted with the information deficiency. By these means we quantified the dissimilarity of enantiomers and illustrated Mezey's Holographic Electron Density Theorem in chiral systems [6]. A comparison is made with the optical rotation and with the Carbó similarity index.

As an alternative chirality index, we recently also calculated the information deficiency in a way which is consistent with experiments as VCD spectroscopy and optical rotation measurements. The entropy calculates the difference in information between the shape function of one enantiomer and a normalized shape function of the racemate. Comparing the latter index with the optical rotation reveals a similar trend.

Keywords: chirality, Kullback-Leibler information theory, enantiomers, Avnir's continuous chirality measure

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Solvent effects on global properties for neutral and charged systems using a sequential MC/QM model: Monte Carlo - quantum mechanics

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The energy of the frontier molecular orbitals and reactivity indices such as chemical potential[1], hardness[1] and electrophilicity[2] of neutral and charged molecules have been investigated in aqueous solution using explicit solvent model in the S-MC/QM methodology[3]. The supermolecular structures of the solute-solvent system in solution were generated by NVT Monte Carlo (MC) simulations. Statistically uncorrelated structures have been extracted for quantum mechanical calculations of the solute surrounded by the first solvation shell, using explicit water molecules, and the outer shells treated as atomic point charges. The supermolecular calculations treating both the solute and the solvent explicitly were performed within the density functional theory (DFT)[1]. The energies of the frontier orbitals, HOMO and LUMO, were used to calculate the reactivity indices in gas phase and in solution. The dependence of the results with respect to the number of explicit solvent molecules is also analyzed. It is seen that for the systems considered here, the energies of the HOMO and the LUMO show a strong dependence with the number of solvent molecules. However, the properties derived from these are relatively stable. In particular the results reported here[4] for the reactivity indices obtained using the first solvation shell are similar to those obtained for the limit bulk value. The delocalization of the solute orbitals over the solvent region is analyzed and its consequence to the reactivity indices are discussed. For comparison, the reactivity indices were also calculated using the polarizable continuum model (PCM). The molecules do not show significant changes in the reactivity indices between gas phase and PCM model. The S-MC/QM calculations reported here show considerable changes in the properties of the different solutes in aqueous environment in distinction to the simplified PCM model. The importance of including explicit solvent molecules and adopting a statistical approach for the liquid is emphasized.

Keywords: reactivity indices, solvent effects, Sequential MC/QM.

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Fukui Function Calculations Based on Atomic and Molecular Polarizabilities.

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The Fukui function represents a derivative of the local electron density $\rho(r)$ in the electronic system (a molecule) over the number of electrons (*N*), when the external potential $\upsilon(r)$ is kept constant or, alternatively, a functional derivative of the chemical potential $\mu = \partial E/\partial N$ over the electrostatic potential $\upsilon(r)$ in the closed system (*N=const.*), [1]

$$f(r) = \left[\frac{\partial\rho(r)}{\partial N}\right]_{\upsilon(r)} = \left[\frac{\delta\mu}{\delta\upsilon(r)}\right]_N$$

The Fukui function has long been recognized as a possible source of estimation of the molecular reactivity. Consequently, numerical values thereof have been a target of many efforts aiming in two general directions: (i) inventing a reasonable approximation for $f(r)$, starting for the very first educated guess $f(r) = \rho(r)/N$; (ii) proposing a version of condensed (or atomic) Fukui indices, that would carry some information on the reactivity of a specific site in a molecule. Numerous investigations in this area brought a little success – no generally recognized method has ever been proposed, although the results seem to confirm an expectation, that the Fukui function is worthwhile to study – it does tell something about the site reactivity and selectivity in a molecule [2].

Much interest in exploring the quantum chemical tools in calculations of the Fukui function has recently been observed [3, 4]. Although ingenious in details, they suffer to the same shortcoming as many others before – the lack of physical ground, that would allow for verification of $f(r)$ against a sound physical quantity, before it is applied as a prospective measure in some reaction path.

The authors of the present work have elaborated and tested a consistent quantum-chemical scheme, based on the work by Vela and Gazquez [5], in which the resultant Fukui functions are verified in calculation of the atomic (molecular) polarizability. This procedure adds much of the rigor to quantum chemical calculations. The resultant new Fukui functions have been additionally verified by studying properties of their derivatives $\partial f(r)/\partial N$ and $\delta f(r)/\delta\upsilon(r')$.

Keywords: Fukui function, Fukui index, polarizability.

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Can Alanes be described by PSEPT rules as Boranes? a DFT computational study of Al_nH_{n+2}.

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Along with boranes, alanes constitute nowadays an active field of investigation because of their promising applications in different areas such as in hydrogen storage and clean energy.

Taking into account the success of the Wade-Mingos (or Polyhedral Skeletal Electron Pairs Theory (PSEPT)) rules to determine structures of borane clusters, it has been suggested (1,2), for some modifications, to apply these rules to the isovalent alanes. A set of alanes of Al_nH_{n+2} general formula have been detected by a mass spectrometer equipped with a pulsed arc cluster ions discharge source (PACIS). These species were considered equivalent to $B_nH_n^{2-}$ by treating them by the (n+1) electron-pairs-repulsion rule.

In this work, we analyse the validity of the application of such rules by computing the total potential energy surface (PES) in order to predict the most stable structures and then to verify the applicability of the Wade-Mingos n+1 rule to Al_nH_{n+2} (n=4…, 8) series. Our results are not in complete agreement with the modified rules as is shown in the figure for the pentaalane. We propose to review the previous suggestions with the amended rules. We justify these conclusions by our calculations at high levels of theory such as B3LYP and B3PW91 using the extended basis sets as 6-311+G (3df, 2p).

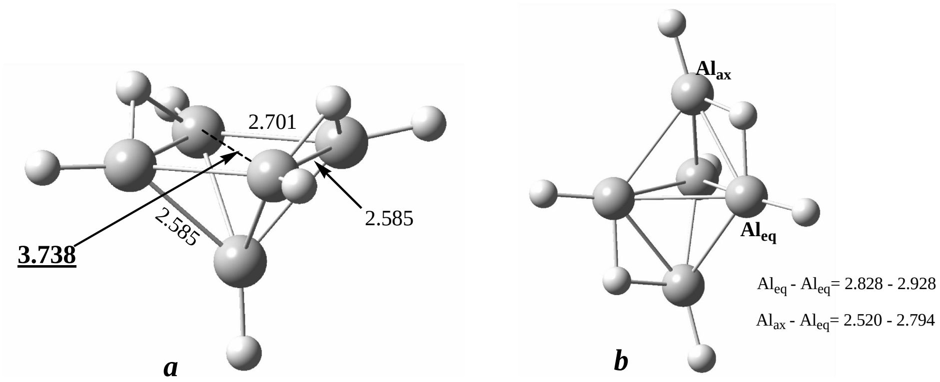

Figure: Al_5H_7: absolute minimum (a), PSEPT structure (b), bond length (Å)

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

Pauli potential from the differential virial theorem

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Recently, a first-order differential equation for the functional derivative of the kinetic energy functional is derived for spherically symmetric systems [1] using the differential virial theorem of Nagy and March [2]. Here a more general first-order differential equation for the Pauli potential (valid not only for spherically symmetric systems) is derived applying the differential virial theorem of Holas and March [3]. The solution of the equation can be given by quantities capable of fully determining every property of a Coulomb system.

Keywords: differential virial theorem, Pauli potential

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QSA(P)R Studies On Some Novel Drug Precursor 6-Acylbenzothiazolon Derivatives*

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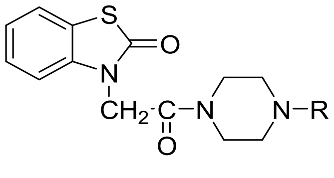
ABSTRACT

Out of 32 suggested target molecule 4 molecules were modeled and after conformational analysis the minimized energy geometries, thermodynamic and physical parameters were determined. QSAR parameter calculations were carried out by B3LYP method and 6-31G(d,p) basis set. The acidity and tautomeric equilibrium constants were determined by *ab initio* HF, DFT and semi-empirical AM1, PM3 and PM5 methods of Gaussian03, ChemOffice 2004 and CAChe 6.1 programs. The successes of the used methods in elucidation structure-activity and structure-property relations will be discussed.



R=Methyl,Ethyl,i-Propyl, Butyl

Figure. A general formula for studied molecules

Keywords: QSAR studies, QSPR studies, novel drug precursors, theoretical studies, modeling

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Electronic chemical potential of anions in gas phase.

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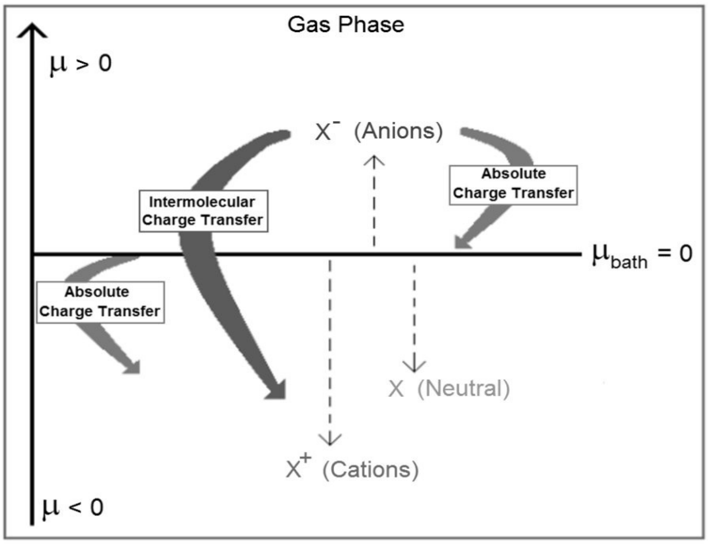
In contrast to the general belief that the electronic chemical potential of any species in the gas phase must be a negative number, we here demonstrate that for anions this property may reach positive values and the ocurrence of this results is a possible and meaningful outcome in ab initio calculations. The proof is based on the classical Pearson´s [1] conducting sphere model describing the absolute electronegativity and chemical hardness of neutral and charged atomic and molecular systems together with Politzer´s [2] model of electronegativity of atoms and groups in their valence state.

For instance, if intrinsic positive values for the electronic chemical potential of anions are allowed, then one has immediately the possibility of defining a sound scale of electrophilicity and nucleophilicity within a common framework, by keeping the properties of the environment fixed at a reference value, in a form consistent with classical thermodynamics. A computational analysis is detailed, this one establishes the mathematical conditions where the significant positive values of μ can be obtained. The implications that this result may have on the phenomenological chemical reactivity theory are described in detail, principally those related to the definition of the electron donating (nucleophilicity) [3] ability of anions in the gas phase.



Keywords: chemical potential, anions, nucleophilicity

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Chemistry and Physics, DFT09, Lyon, France.

Substituent and solvent effect on Radical Cation Diels-Alder reactions

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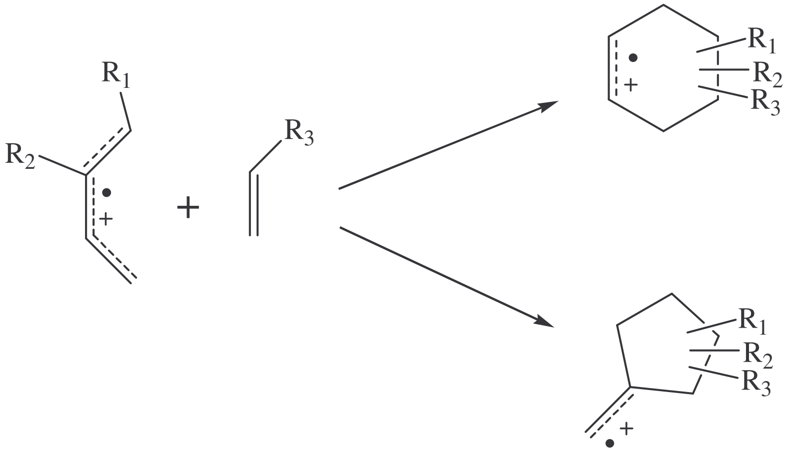
Electron transfer catalysis has a profound impact on the Diels-Alder (DA) reaction; the oxidized (by an oxidizing agent or by photoinduced electron transfer) diene easily undergoes cycloaddition with alkenes via a stepwise mechanism [1]. Generally, the radical-cation-mediated DA cycloadditions are highly regioselective with increasing rates over the neutral reaction by several orders of magnitude. This makes possible thermally forbidden or electronically disfavored cycloadditions.

The substituent and solvent effect on the photoexcited Radical Cation Diels-Alder (RCDA) were studied by *ab initio* and Density Functional Theory methods. The effect of different types of substituent on the regioselectivity (Scheme 1) was also investigated.



Scheme 1.

Next, the regioselectivity in the rate determining ring-closure step was determined within the framework of the spin-polarized conceptual Density Functional Theory [2]. Namely, we used spin-polarized Fukui functions which measure f_{NN} the initial response in the reorganization of the charge density upon removing (f_{NN}^{-}) or adding (f_{NN}^{+}) exactly the same fraction of the number of electrons to the spin-up and spin-down frontier molecular orbitals. It was previously shown that f_{NN} is suitable to describe charge-transfer processes without a change in the total spin multiplicity of the system [3, 4].

Keywords: Radical Cation Diels-Alder, regioselectivity, spin-polarized DFT

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Calculation of functional derivatives for the reactivity description of alkaline earth metal oxides

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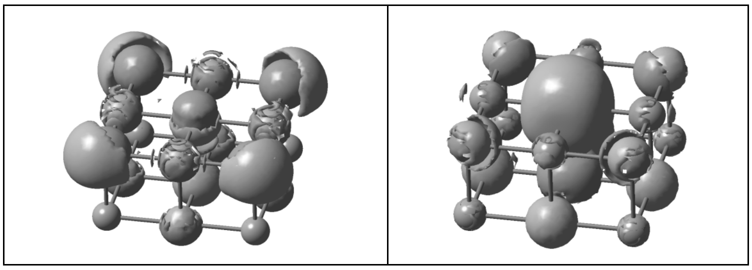
Apart from its many computational advantages, density functional theory (DFT) presents a conceptual framework for the reactivity and stability interpretation of chemical systems. The central idea in this conceptual DFT is to identify chemical concepts with first and higher order (functional) derivatives of the electronic energy E with respect to the number of electrons N and the external potential $v(\mathbf{r})$ [1-2].

The local interpretation of chemical reactivity is generally done with the Fukui function, a reactivity index which is usually calculated by a finite difference approach. Though this is entirely justified within an exact theory, the DFT concepts can only correctly be obtained by an effective evaluation of the electronic energy derivatives as practical DFT calculations make use of approximate exchange-correlation functionals.



A recently developed methodology for the calculation of functional derivatives with respect to the external potential $v(\mathbf{r})$ [3-5] is presented and applied to a reactivity description of the surface oxygen centres in the alkaline earth metal oxides series (MgO, CaO, SrO and BaO) [6]. The cumbersome periodic boundary conditions calculations [7], typically required to probe the reactivity of such systems, are avoided by the construction of a reliable cluster model. The standard Fukui function concept of conceptual DFT is generalised to include the contribution from not only the HOMO and the LUMO, but also from other chemically relevant orbitals. Results prove that this approach is a valuable and straightforward alternative to the reactivity calculation of extended systems [6].

Keywords: conceptual DFT, Fukui function, functional derivatives, alkaline earth metal oxides, clusters

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13th Intern. Conf. on the Applic. of Density Functional Theory in Chemistry and Physics, DFT09, Lyon, France.

On the spin-polarized states in unsaturated organic molecules

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In this work, we present one-determinant (Hartree-Fock (HF) and Density Functional Theory (DFT) types) and multi-determinantal calculations, of several organic non-saturated molecules. All HF calculations and many DFT show a spin-polarized ground state, anti-ferro magnetic, in agreement with previous calculations[1,2].

Nevertheless, the multi-determinantal calculations, maked with perturbatives and variational wave-functions, (MPn, CISD and CCSD(T)), show that the more stable state is the constructed from the non-polarized wave-function.

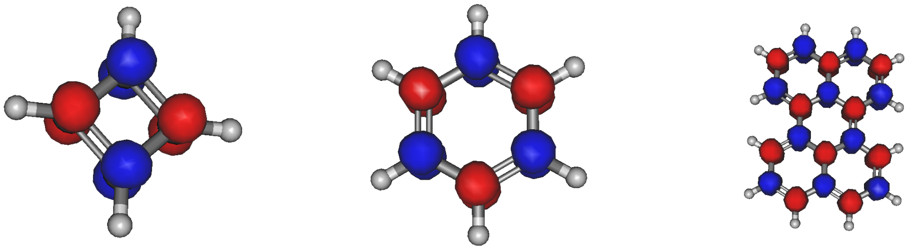

Figure 1: Spin density of spin-polarized unrestricted HF wave-function of cyclobutadiene, benzene and 1-periacene molecules.

Because the number of electrons is even, it is always assumed that S_z=0, though not all mono-determinantal wave-functions have $< S^2 >= 0$. An analysis of $< S^2 >$ is carried out also with a study of the results that arise from the annihilation of unwanted spin states[3].

Finally, the physical meaning of these solutions is analyzed.

Keywords: Spin-polarized states.

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

Local DFT Reactivity Descriptors for the Investigation of the Chemical Reactivity Involved in Covalent Toxicant-Peptide Binding

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The chemical reactivity of a compound, relating to the covalent binding between a small electrophilic molecule and a peptide or DNA target site, is increasingly considered as being important, since reactivity can be linked with various toxicological effects.

Global DFT descriptors, such as frontier orbital energies or electrophilicity indices, often fail to predict site-specific reactivity, especially if the molecule contains more than one possible reaction site. Therefore, local DFT descriptors were applied, which, amongst others, capture the site-specific electron acceptor affinity for electrophiles. These descriptors are based on the electronic ground-state properties of the single molecules, employing the prevalent B3LYP functional. Therefore, they avoid calculations for time-consuming electrophile-peptide complexes and transition-state calculations.

These physically meaningful reactivity descriptors were able to explain the variation in behaviour of toxicants with regard to different reference nucleophiles (glutathione, lysine, cysteine or histine). The results of the global descriptors were compared to those for the local descriptors. This approach allows for the formation of categories with similar reactivity. This could be applied for screening purposes based on structural information and the reactivity data used in elucidating mechanisms of toxic effects.

The funding of the EU FP6 InSilicoTox Marie Curie Project (MTKD-CT-2006-42328) is gratefully acknowledged.

Keywords: Local Reactivity Descriptors, Covalent Binding, Electrophile, Nucleophile, Toxicant, Electron Acceptor Affinity

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Deriving spin symmetric states and improved energies from unrestricted HF

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Unrestricted Hartee-Fock (UHF) gives states which are eigenstates of S_z but not of $\mathbf{S}^2$. The advantage of this method is that it gives ground state energies lower than those of the restricted Hartee-Fock (RHF) which are eigenstates of $\mathbf{S}^2$. As it was shown in previous work [1,2], one can analyse the UHF states as a sum of eigenstates of $\mathbf{S}^2$, i.e.

$$|\Phi_{\mathrm{M}}>=\sum_{S=M}^{N/2} C_M^S \,|\,\Psi_{\mathrm{M}}^S>$$

Some of the states $|\,\Psi_{\mathrm{M}}^S>$ correspond to energies lower that those of UHF, i.e. they include some correlation energy, because of the fact that they are not simple Slater determinants, but a linear combination of them.

We use the above analysis to derive the eigenstate energies $\mathrm{E}_{\mathrm{M}}^S=<\Psi_{\mathrm{M}}^S\,|\,H\,|\,\Psi_{\mathrm{M}}^S>$. At least one of these energies is smaller than the UHF energy $\mathrm{E}_{\mathrm{UHF}}=<\Phi_{\mathrm{M}}\,|\,H\,|\,\Phi_{\mathrm{M}}>$.

Keywords: Hartree-Fock

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13th Intern. Conf. on the Applic. of Density Functional Theory in
Chemistry and Physics, DFT09, Lyon, France.

On the applicability of the local softness and hardness

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The global hardness and softness and their hard/soft acid/base (HSAB) principle[1] have been used to explain many experimental observed reactivity patterns and their concepts can be found in textbooks of general or organic chemistry. In addition, local versions of these reactivity indices and principle have been defined to describe the regioselectivity of the systems.[2] In this framework, the local hardness and softness indicate the hardest and softest regions of the molecule, respectively, suggesting that the largest values of the local softness need to correspond to the smallest values of the local hardness.

The local hardness is a controversial descriptor,[3] although it can be evaluated using "simple" approximations of the hardness kernel.[4] In a very recent article,[5] the present authors have shown that the picture of these descriptors is incomplete and that the understanding of these reactivity indices must be "redefined". In fact, the local softness and hardness contain the "same potential" information (see Figure 1) and they have to be considered as "local abundance" or "concentration" of their corresponding properties. In this contribution, we will analyze the implications of this new point of view in the applicability of these well-know descriptors and the repercussions in the local version of the HSAB principle.[6]

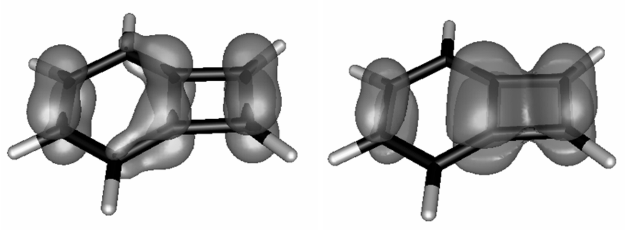

Figure1: Three-dimensional countour plots of local softness (left) and hardness (right) for the benzocyclobutadiene molecule.

Keywords: Density Functional Theory, hard and soft acids and bases principle, local softness, local hardness.

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