14th deMon Developers Workshop

From Quantum Chemistry to Molecular Simulation

Los Cabos, Baja California Sur, Mexico
April 27th to 30th, 2014

PROGRAM

Organizers:

Patrizia Calaminici

Andreas M. Köster

Alberto Vela

Sponsored by:

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PROGRAM

Sunday, April 27

19:00 – 20:00 **Registration and welcome cocktail**

PROGRAM

Monday, April 28

Session 1

Chair: P. Calaminici

09:00 – 09:30 Organizers**: Opening**

09:30 – 10:00 D.R. Salahub: **deMon quo vadis**

10:00 – 10:30 G.Geudtner: **The status of the deMon2k program**

10:30 – 11:00 L.G.M. Pettersson: **Real-Time Observation with an X-ray Laser of Surface Bond Breaking and Reactions**

11:00 – 11:30 **Coffee Break**

Session 2

Chair: A. Vela

11:30 – 12:00 D. Cremer: **Electron Correlation as described by WFT and DFT**

12:00 – 12:30 J.V. Ortiz: **Propagator Concepts for the Interpretation of Spectra, Energetics and Transport**

12:30 – 13:00 J.M. del Campo: **Assessment of Hybrid Functionals within deMon2k**

13:00 – 15:00 **Lunch Break**

PROGRAM

Monday, April 28

Session 3

Chair: A.M. Köster

15:00 – 15:30 S.B. Trickey: **Outlook for Lower-rung Exchange-Correlation Functionals for Faster Simulations**

15:30 – 16:00 M.E. Casida: **Beginners' Introduction to What DFTB Might Be Able to Do for Organic Electronics**

16:00 – 16:30 H. Anderson Duarte: **Investigation of Nanotubes With Well Defined Structures using a New SCC-DFTB Parameterization Method**

16:30 – 17:00 A. Posada-Amarillas: **Computational modelling of mono- and bimetallic nanoparticles through semi-empiric potentials**

17:00 – 17:30 **Coffee Break**

Session 4: Round Table

Chair: R. Flores-Moreno

17:30 – 18:00 **Round Table I:** Methods in deMon2k

PROGRAM

Tuesday, April 29

Session 5

Chair: M.E. Casida

09:00 – 09:30 I.L. Garzón: **Optical and Chiroptical Properties of Organometallic Nanomaterials**

09:30 – 10:00 B.A. Zúñiga Gutiérrez: **Magnetic Properties in deMon2k**

10:00 – 10:30 D. Mejía-Rodríguez: **Towards linear scaling molecular response theory**

10:30 – 11:00 R. Delgado-Venegas: **Analytic Second Derivatives in ADFT**

11:00 – 11:30 **Coffee Break**

Session 6

Chair: H. Anderson Duarte

11:30 – 12:00 C.M. Zicovich-Wilson: **Full exploitation of symmetry in periodic LCAO ab initio calculations**

12:00 – 12:30 P. Calaminici: **Canonical Dynamics in deMon2k**

12:30 – 13:00 L.F.L. Oliveira: **Investigation of atomic and molecular cluster with DFTB: Energetics and thermodynamics**

13:00 – 15:00 **Lunch Break**

PROGRAM

Tuesday, April 29

Session 7

Chair: G.Geudtner

15:00 – 15:30 A. Álvarez Ibarra: **Born-Oppenheimer molecular dynamics of biological systems in deMon2k**

15:30 – 16:00 J.M. Vásquez Pérez: **Computation of partition functions with the Multiple Histogram Method**

16:00 – 16:30 R. Flores-Moreno: **Non-Born-Oppenheimer post-Hartree-Fock calculations with deMon2k**

16:30 – 17:00 **Coffee Break**

Session 8: Round Tables

Chairs: A. de la Lande & A.M. Köster

17:00 – 17:30 **Round Table II** Molecular Properties in deMon2k

17:30 – 18:00 **Round Table III** Molecular Simulation in deMon2k

18:00 – 20:00 **Poster Session and Canapes**

PROGRAM

Wednesday, April 30

Session 9

Chair: J.M. del Campo

09:00 – 09:30 D.Q. Wei: **QM/MM Studies of Enzymatic Catalysis**

09:30 – 10:00 T. Mineva: **Dynamics of hybrid organic-inorganic interfaces**

10:00 – 10:30 A. de la Lande: **The hydroxylation mechanism of noncoupled copper oxygenases**

10:30 – 11:00 C.Z. Gómez-Castro: **The role of Asp1 in the coordination of Cu(II) to the amyloid-beta peptide**

11:00 – 11:30 **Coffee Break**

Session 10

Chair: R. Flores-Moreno

11:30 – 12:00 M.R. Beltrán: **Theory and Anion Photoelectron Studies of Transition Metal Clusters**

12:00 – 12:30 M. Rapacioli: **Extensions of DFTB to treat long-range interactions**

12:30 – 13:00 A. Vela: **GGA exchange with correct asymptotics**

13:00 – 13:30 A.M. Köster: **From Quantum Chemistry to Molecular Simulations**

PROGRAM

Wednesday, April 30

13:30 – 16:00 **Lunch Break**

Session 11: Round Table & Action Items

Chairs: S.B. Trickey & D.R. Salahub

16:00 – 16:30 **Round Table IV** Documentation and Tutorial

16:30 – 17:00 **Action Items**

ABSTRACTS

ORAL

PRESENTATIONS

deMon quo vadis?

Dennis Salahub

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I will give a bird's-eye view of some of the progress that has been made over the years and try to point out some interesting new directions. I will then show briefly the Action Items from the Toulouse workshop, in preparation for this year's wrap-up session.

The status of the deMon2k program

Gerald Geudtner

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In this talk an overview of the changes made in the deMon2k program over the last year will be given. This includes modifications on existing parts as well as changes due to new features which have been recently incorporated. Also the plans for upcoming developments will be presented.

Real-Time Observation with an X-ray Laser of Surface Bond Breaking and Reactions

L. G. M. Pettersson

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We use the Linac Coherent Light Source free-electron x-ray laser to probe the electronic structure of CO molecules as their chemisorption state changes upon exciting the Ru(0001) substrate using a femtosecond optical laser pulse [1,2]. We observe electronic structure changes consistent with a weakening of the CO interaction with the substrate, but without significant desorption. This indicates that a large fraction of the molecules becomes trapped in a transient precursor state prior to desorption. The free energy of the molecule as a function of the desorption reaction coordinate is estimated using density functional theory including non-local correlation to describe van der Waals interactions. We find two distinct adsorption wells, chemisorbed and precursor state, separated by an entropy barrier which explains the anomalously high prefactors often observed in desorption of molecules like CO from metals. The present work is the first direct spectroscopic transient observation of a precursor state in desorption and, by time-reversal, in adsorption, and shows that the precursor is characterized by bonding CO states that interact weakly with the metal while the anti-bonding $2\pi^*$ states still couple significantly. Furthermore, the oxidation of CO to CO_2 on O/Ru(0001) and hydrogenation of CO on H/Ru(0001) have been studied experimentally at LCLS and theoretically through DFT calculations of the reaction path and associated x-ray spectra for each step in the reactions. The importance of a close interplay between experiment and theory will be emphasized.

[1] M. Dell'Angela *et al.*, *Science* **2013**, *339*, 1302-1305
[2] M. Beye *et al*., *Phys. Rev. Letters* **2013**, *110*, 186101

Electron Correlation as described by WFT (Wave function Theory) and DFT (Density Functional Theory) Methods

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An advantage of WFT methods is that, with the help of the orbitals and their properties, different electron correlation effects can be distinguished and the accuracy of a WFT description estimated according to the presence or absence of a given correlation effect. This is demonstrated in the case of Rayleigh-Schroedinger Many Body Perturbation Theory (MBPT) with the Møller-Plesset (MP) Perturbation operator. Different orders n of MPn describe specific correlation effects, which will be discussed up to order n = 6. So-called uncoupled correlation effects often lead to an unbalanced description. This problem ceases to exist at the coupled cluster level since for a given excitation level all infinite order (coupling) effects are included provided that no approximations to the cluster expansion of the wave function are made. - Standard DFT accounts for correlation effects via the XC functional. It is shown that some correlation effects are a result of the self-interaction error (SIE), which leads to the inclusion of non-dynamic electron correlation. The consequences of the SIE for practical applications and the merging of DFT with WFT methods are discussed.

Propagator Concepts for the Interpretation of Spectra, Energetics and Transport

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Electron propagator theory is the foundation of several one-electron concepts that facilitate interpretation of a variety of experiments. This theory also underlies several efficient approaches to the calculation of spectroscopic, thermodynamic and transport properties. One-electron, self-energy operators in the Dyson equation that describe many-body effects in electron binding energies, Dyson orbitals, one-electron properties and total energies may be systematically improved up to an exact limit. Calculations on the electron binding energies of large molecules such as fullerenes, metallo-macrocyclic compounds and DNA fragments, on the energetics of acid-base chemistry and on electric currents in molecular wires provide examples of the versatility of *ab initio* implementations of propagator theory.

Assessment of Hybrid Functionals within deMon2k

Jorge M. del Campo[a], Xiaomin Huang

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In this work the implementation of B3LYP [1-5] and PBE0 [6,7] hybrid funtionals within deMon2k will be presented. The implementation has been performed using the recently developed extension of Auxiliary Density functional Theory [3] to evaluate the exchange like expression with Kohn-Sham orbitals, a comparison against NWChem [8] implementation will be presented.

1 C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
2 A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
3 A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
4 A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
5 P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).
6 M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).
7 C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
8 M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, and W. de Jong, Comput. Phys. Commun. **181**, 1477 (2010).

Outlook for Lower-rung Exchange-Correlation Functionals for Faster Simulations

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Growth of system size and complexity causes the quest for chemical accuracy to come into near-prohibitive conflict with the need for fast simulations to screen many systems and properties. Dependence upon computer speed improvements as the sole solution is a doomed strategy: in addition to the difficulty of using massively parallel machines at truly massive levels, there is always Amdahl's law. Method simplification with minimal loss of accuracy therefore is always a meritorious goal.

Ab initio molecular dynamics (AIMD) is computationally tractable today mostly because of density functional theory (DFT), in particular, effective exchange-correlation (XC) approximations. Most of the recent effort at bettering the XC functionals makes explicit use of the Kohn-Sham (KS) orbitals. Such "third- and fourth-rung" XC functionals worsen the computational scaling of AIMD from being proportional to N^3 (N = number of electrons) to scaling at fourth or higher power. For simple systems needing only a few simulations, the increase is not a difficulty. But large-scale AIMD-DFT studies over a wide range of physical or chemical conditions are different. Each AIMD-DFT run may have tens-of-thousands MD steps, with N=100 - 1,000. Many runs are required. Observe that the same problem arises in geometry optimization extremely large, complicated clusters.

Thus we have continued to focus on lower-rung functionals. Those depend on the density gradient and the kinetic energy density at most. We have made significant progress on constraint-based (non-empirical), higher accuracy, lower-rung X functionals including PBE-LS, PBEmol, VT{8,4}, and VMT at rung 2 and meta-VT{8,4} at rung 3. Some of these are in deMon2k. After a brief summary of these functionals, I shall report recent work of our own and relevant other work just announced which, together, holds the promise of further improvement of lower-rung functionals.

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Reprints at http://www.qtp.ufl.edu/ofdft

Beginners' Introduction to What DFTB Might Be Able to Do for Organic Electronics

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Organic electronics is a rapidly emerging field which promises to revolutionize some applications through light-weight, flexible, and most especially *printable* electronics. We are interested in improving our understanding and modeling of organic solar cells in particular. A key aspect is what happens in a nanometric interface region where excitons are caught and separate into conduction charges. On the one hand, “understanding” what happens in this region means seeking *quantitative* agreement between theory and experiment for simple devices and, on the other hand, it also means identifying key steps in the mechanism underlying complex devices using more *qualitative* exploratory methods such as density-functional tight binding (DFTB) that can be then further explored using more quantitative methods developed for small systems. In particular, we think that it is time to rethink these key processes from the point of view of photochemistry [1] rather than holding on to the conventional solid state physics first approximation of neglecting nuclear motion. In order to do this we plan to go beyond recent applications of DFTB in this area [2] to be able to apply mixed time-dependent DFTB/classical trajectory surface hopping [3] to obtain a better educated guess as to how nuclei move during key photovoltaic events.

[1] M.E. Casida, B. Natarajan, and T. Deutsch, in *Fundamentals of Time-Dependent Density-Functional Theory*, edited by M. Marques, N. Maitra, F. Noguiera, E.K.U. Gross, and A. Rubio, *Lecture Notes in Physics*, Vol. 837 (Springer Verlag: 2011), p. 279. "Non-Born-Oppenheimer dynamics and conical intersections." Preprint http://arxiv.org/abs/1102.1849
[2] R. Scholtz, R. Luschtinetz, G. Seifert, T. Jägeler-Hoheisel, C. Körner, K. Leo, and M. Rapacioli, *J. Phys.: Condens. Mater*, **2013**, *25*, article number 473201. “Topical Review: Quantifying charge transfer energies at donor-acceptor interfaces in small-molecule solar cells with constrained DFTB and spectroscopic methods.”
[3] M. Barbatti, J. Pitner, M. Pederzoli, U. Werner, R. Mitric, V. Bonacic-Koutecky, and H. Lischka, *Chem. Phys.*, **2010**, *375*, 26-34. “Non-adiabatic dynamics of pyrrole: dependence of deactivation mechanisms on the excitation energy.”

Investigation of Nanotubes With Well Defined Structures using a New SCC-DFTB Parameterization Method.

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We have applied SCC-DFTB method for investigating the clay mineral nanotubes (NTs) such as halloysites, imogolites and chrysotiles. The SCC-DFTB method requires the so-called Slater-Koster files and the parameterization of the atomic pairs. A set of parameters are available elsewhere (www.dftb.org). However, for some of the systems studied the SCC-DFTB parameterization was necessary. The parameterization normally involves intensive manipulation of files, chemical models and programs in order to set up the correct parameters that describe reasonably the target system.

In order to avoid human error in handling files and other data and increase the quality of the parameters, we developed the FASP (Framework for Automatization of SLAKO Parameterization) program. FASP is a framework that automates the procedure of finding the best polynomial fit (based on statistical criteria) that describes the E_{rep} of atomic pairs for a set of interception points of the band (E_{bnd}) and reference (E_{ref}) energy. The quality of the parameters is evaluated based on the description of the structural properties of desired molecules, clusters and solids (obtained from experiment or any quantum chemistry method) set in a database. The user is responsible for setting the initial data (E_{ref} and E_{bnd}) from molecular and/or solid models in an input and for analysing the output to choose, among the E_{rep} fit polynomials for each interception points, the best E_{rep}. The FASP program decreases the human intervention and minimizes the possibility of errors. The quality of the parameters are much improved since different models can also be used concomitantly to obtain the E_{rep}.

The new parameters were used to investigate NTs with well defined structure such as imogolite-like NTs. These NTs are monodisperse with well-defined diameter, length and chirality, which has been observed experimentally and predicted by theory. We have shown that the Ge-imogolite derivative can form double-walled tubes with the strongest stabilization found for tube indexes with nine units of difference around the circumference. The minimum structure is found for the (12,0)@(21,0) tube. In this presentation we intend to show the strategy used to develop the FASP program and the SCC-DFTB parameterization. The results obtained for the Ge-imogolite NTs will be also presented and discussed.

(Acknowledgments: INCT-ACQUA, CAPES, FAPEMIG, CNPq).

[1] M. P. Lourenço, L. Guimarães, M. C. da Silva, C. de Oliveira, T. Heine, H. A. Duarte, *J. Phys. Chem. C*, 2014, 118 (11), pp 5945–5953.

Computational modelling of mono- and bimetallic nanoparticles through semiempiric potentials

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Theoretical and experimental approaches have been utilized throughout the world to understand the role of shape, size and chemical composition of mono- and bimetallic nanoparticles. The current and potential technological applications, e.g. in catalysis and medicine, highlight the importance of these nanosystems driving basic knowledge to new scientific frontiers. Computational modelling has been a relevant tool in predicting new, amazing structures by exploring nanoparticles' energy landscape through optimization algorithms to find local and global minima of a number of potential-energy functions defining the interatomic bonding. The basic rules of the basin hopping method [1,2] are presented in this talk, showing a menagerie of clusters obtained for the Gupta potential in the study of mono- and bimetallic nanoparticles realized at Universidad de Sonora. A comparison to the threshold energy [3] and genetic algorithm [4] methods is also presented.

Acknowledgments. To CONACyT for financial support through project 180424.

[1] Wales, D. J.; Doye, J. P. K., *J. Phys. Chem. A*, **1997**, *101*, 5111−5116.
[2] Borbón-González, D.J., Fortunelli, A., Barcaro, G., Sementa, L., Johnston, R.L., Posada-Amarillas, A., *J. Phys. Chem. A*, **2013**, *117*, 14261−14266.
[3] Schön, J. C., *Ber. Bunsen-Ges.*, **1996**, *100*, 1388−1391.
[4] Johnston, R. L., *Dalton Trans.*, **2003**, *32*, 4193−4207.

Optical and Chiroptical Properties of Organometallic Nanomaterials

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Research on thiolate-protected gold clusters [$Au_n(SR)_m$, SR being a thiolate group] has shown important advances during the last few years mainly due to the success in their crystallization, allowing X-ray total structure determination and further experimental characterization, as well as to the reliability of theoretical studies on their physicochemical properties, using *state of the art* density functional theory calculations. We report results of a theoretical study, based on density functional theory (DFT), on the structural, electronic, optical, and chiroptical properties of small thiolated gold clusters, [$Au_n(SR)_m$, (n=12-15,16-20; m=9-12,12-16)]. Some of these clusters correspond to those recently synthesized with the surfactant-free method [1,2].

Structure and optical properties of a set of R-1,1´-binaphthyl-2,2´-dithiol (R-BINAS) monosubstituted A-$Au_{38}(SCH_3)_{24}$ clusters were also studied by means of time dependent density functional theory (TD-DFT). While it was proposed earlier that BINAS selectively binds to monomer motifs (SR-Au-SR) covering the Au_{23} core, our calculations suggest a binding mode that bridges two dimer (SR-Au-SR-Au-RS) motifs. The more stable isomers show a negligible distortion induced by BINAS adsorption on the $Au_{38}(SCH_3)_{24}$ cluster which is reflected by similar optical and Circular Dichroism (CD) spectra to those found for the parent cluster. The results furthermore show that BINAS adsorption does not enhance the CD signals of the $Au_{38}(SCH_3)_{24}$ cluster [3].

Electronic, vibrational, optical, and chiroptical properties of copper(II) complexes with amino-alcohol chiral ligands were also studied by means of density functional theory (DFT) and time-dependent DFT. The calculations are compared with experimental results of the absorption and circular dichroism spectra for an uncoordinated pseudoephedrine derivative, as well as for the corresponding mononuclear and trinuclear copper(II)-coordinated complexes [4].

[1] A. Tlahuice, I. L. Garzón, *Phys. Chem. Chem. Phys*. **2012**, *14*, 3737.
[2] A. Tlahuice, I. L. Garzón, *Phys. Chem. Chem. Phys*. **2012**, 14, 7321.
[3] B. Molina, A. Sánchez-Castillo, S. Knoppe, I. L. Garzón, T. Bürgi, A. Tlahuice-Flores, *Nanoscale* **2013**, *5*, 10956.
[4] I. Valencia, Y. Availa-Torres, N. Barba-Behrens, I. L. Garzón, **2014**, submitted.

Magnetic Properties in deMon2k: Implementations and Applications

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An update of the implementations of magnetic properties within the framework of auxiliary density functional theory (ADFT) in deMon2k [1] is presented. The main advantage of employing ADFT for these property calculations is the high computational performance reached without losing accuracy in the results compared to the conventional DFT framework. So far, the modules for the computation of magnetic shielding and magnetizability tensors are available in deMon2k [2,3]. More recently, we also implemented the rotational g-tensor [4] and the spin-rotation tensor. Furthermore, an efficient implementation of the module for computing the nuclear spin-spin constants is now available. The validation of the ADFT results for these three properties are presented as well as benchmark calculations on molecular systems containing hundreds of atoms.

The importance to have an efficient implementation of these properties is shown for the prediction of the chemical shifts in an organic molecule with several conformations. The calculated chemical shifts have a strong dependency on the spatial arrangement of the atoms. Thus, the simulation of these spectroscopic parameters must consider all feasible conformations in order to obtained a reliable prediction of the observed NMR spectra. This can be achieved by calculating chemical shifts along Born-Oppenheimer molecular dynamic trajectories. Some representative show case applications are presented.

[1] See www.demon-software.com
[2] B. Zuniga-Gutierrez, G. Geudtner, A. M. Köster, J. Chem. Phys. , **2011**, 134, 124108.
[3] B. Zuniga-Gutierrez, G. Geudtner, A. M. Köster, J. Chem. Phys. , **2012**, 137, 094113.
[4] B. Zuniga-Gutierrez, et al. submitted.

Towards linear scaling molecular response theory

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Semi-classical treatments of small perturbations in quantum chemical calculations, where the perturbation field is treated classically and the response of the system quantum-mechanically, have proven to be extremely useful for the direct comparison between experiment and theory.

Auxiliary density perturbation theory (ADPT) [1] is a non-iterative approach to treat, analytically, perturbations within the auxiliary density functional theory [2] framework. The non-iterative problem to be solved in ADPT has the size of the auxiliary function set. This is different to the coupled-perturbed Kohn-Sham method, where the problem has the size of the number of single excitations. This drastic reduction of the problem size provides the possibility to calculate properties for large molecular systems and/or along large time scales. However, the direct implementation of ADPT equations includes a formal N^5 step that hinders to some extent such applications.

In this talk, we will present the development of a new method for solving the response equations via an iterative procedure valid for general non-symmetric matrices [3]. In this manner, the formal N^5 step is completely avoided, being substituted by two formal N^3 steps. Furthermore, the memory demand of the new steps is similar to the self-consistent field memory demand. Also, the N^3 steps are completely equivalent to the well optimized calculations of the Kohn-Sham matrix and the Coulomb vector in deMon2k [4]. The new ADPT solver takes advantage of such optimizations, achieving near linear scaling behavior. Validation and benchmark calculations of this implementation will also be shown.

[1] R. Flores-Moreno, A.M Köster, *J. Chem. Phys.*, **2008**, *128*, 134105.
[2] A.M. Köster, J.U. Reveles, J.M. del Campo, *J. Chem. Phys.*, **2004**, *121*, 3417.
[3] T. Eirola, O. Nevanlinna, *Linear Algebra Appl.*, **1989**, *121*, 511.
[4] see www.demon-software.com

Analytic Second Derivatives in Auxiliary Density Functional Theory: Implementation in deMon2k and Perspectives

Rogelio Delgado-Venegas[a] , Roberto Flores-Moreno[b], Patrizia Calaminici[a],
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Calculations of second energy derivatives are crucial for many applications in computational chemistry. Among them are structure optimization, vibrational frequency analysis and potential energy surface exploration [1]. For the calculation of second derivatives in the framework of the KS-DFT methodology, the Coupled Perturbed Kohn-Sham Equations (CPKS) must be solved. Recently, a non-iterative alternative to CPKS in the framework of ADFT was developed in our group [2]. So far, Auxiliary Density Perturbation Theory (ADPT) has been applied to both time-independent and time-dependent molecular property calculations [3-8]. In second derivative calculations, the Coulomb response matrix is needed. This increases substantially the computational demand [9]. In order to circumvent this bottleneck a new approach for the calculation of the perturbation vector is presented. In combination with the newly developed iterative solver for the ADPT equations the explicit calculation of the Coulomb response matrix can be avoided. A preliminary implementation in deMon2k at the Hartree level is presented and further perspectives are discussed.

[1] P. Calaminici, V.D. Dominguez-Soria, R. Flores-Moreno, G. U. Gamboa, G. Geudtner, A. Goursot, D. R. Salahub, A. M. Köster, Auxiliary density functional Theory : From Molecules to Nanostructures, in Handbook of Computational Chemistry. Editor: J. Leszczynski, Springer-Verlag, Berlín, Heidelberg, **2011**
[2] R. Flores-Moreno, A.M. Köster, *J. Chem. Phys*. **2008**, *128* , 134105
[3] J. Carmona-Espíndola, R. Flores-Moreno, A. M. Köster, *J. Chem. Phys*. **2010**, *133*, 084102
[4] B. Zuniga-Gutierrez, G. Geudtner, A. M. Köster, *J. Chem Phys*. **2011**, *134*, 124108
[5] J. Carmona-Espíndola, R. Flores-Moreno, A. M. Köster, *Int. J. Quantum Chem*. **2012**, *112*, 3161
[6] B. Zuniga-Gutierrez, G. Geudtner, A. M. Köster, *J. Chem. Phys*. **2012**, *137*, 094113
[7] S.V. Shedge, S. Pal, A.M. Köster, *Chem. Phys. Lett*. **2012** ,*552*, 146
[8] J. Carmona-Espíndola, A.M. Köster, *Can. J. Chem*. **2013,** *91*, 795
[9] G. Guzmán-Ramírez, R. Flores-Moreno, *J. Mex. Chem. Soc*. **2012**, *56*, 325

Full exploitation of symmetry in periodic LCAO ab initio calculations.

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Symmetry can dramatically reduce the computational cost (running time and memory allocation) of Self-Consistent-Field ab initio calculations for crystalline systems. Crucial for running time is use of symmetry in the evaluation of one- and two-electron integrals, diagonalization of the Fock matrix at selected points in reciprocal space, reconstruction of the density matrix. As regards memory allocation, full square matrices (overlap, Fock and density) in the Atomic Orbital (AO) basis are avoided and a direct transformation from the packed AO to the SACO (Symmetry Adapted Crystalline Orbital) basis is performed, so that the largest matrix to be handled has the size of the largest sub-block in the latter basis. We here illustrate the effectiveness of this scheme, following recent advancements in the CRYSTAL code, concerning memory allocation and direct basis set transformation. Quantitative examples are given for large unit cell systems, such as zeolites (all-silica faujasite and silicalite MFI), garnets (pyrope) and 1D periodic nanotubes. It is shown that the full SCF of 3D systems containing up to 576 atoms and 11136 Atomic Orbitals in the cell can be run with a hybrid functional on a single core PC with 500 MB RAM in about 8 hours.

Canonical Dynamics in deMon2k

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Canonical simulations are the method of choice for obtaining caloric curves from Born-Oppenheimer molecular dynamics (BOMD) simulations. To get good accuracy the coupling equation between the system and the thermostat must be solved analytically. This involves the inversion of a matrix which makes very demanding the calculations of large systems. It will be shown how this problem has been solved and the effect of this improvement in terms of computational time, statistics and phase space distribution. BOMD simulations of metals clusters are then presented. It will be shown how the accuracy of the electronic structure method can cause a shift in the main peaks of the caloric curves. Nevertheless, relative values are not affected.

Investigation of atomic and molecular cluster with DFTB: Energetics and thermodynamics.

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Our goal is to develop new tools for the simulation of atomic and molecular clusters with the Density Functional based Tight Binding potential energy surface. Different methods to explore the potential energy surface, to extract either structural or thermodynamical properties, have been recently implemented in the deMonNano code, as for example, Molecular Dynamics Parallel Tempering [1], Monte Carlo Parallel Tempering [2] and smart Monte Carlo [3]. These methods can for instance be used to compute heat capacities based on the multiple histogram methods

In this presentation such methods will be briefly presented with examples from noble metal clusters (Ag, Cu, Au) to water clusters.

Additionally, results from a preliminary study of the adsorption of hydrogen on the metallic clusters will be presented focusing on the DFTB parameterization benchmarked on the basis of comparison with ab initio calculations.

[1] Y. Sugita and Y. Okamoto, *Chem. Phys. Lett.*, **1999**, 314, 141.
[2] R. H. Swendsen and J.-S. Wang, *Phys. Rev. Lett.*, **1986,** 57, 2607.
[3] P. J. Rossky, J. D. Doll, and H. L. Friedman, *J. Chem.Phys.*, **1978** 69, 4628.

Born-Oppenheimer molecular dynamics of biological systems in deMon2k

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Molecular dynamics is a useful tool to analyze a variety of phenomena in biochemistry. Thanks to the constant development in computer hardware, it is possible to perform studies on larger and larger systems. It is even possible to go beyond the classical molecular mechanics simulations and access the more accurate world of Born-Oppenheimer molecular dynamics (BOMD) in which electronic structure is taken into account in the calculation of the potential energy surface. However, the computational cost of BOMD simulations has been a major drawback due to the repeated calculation of the self-consistent fields (SCF) when systems of several dozens of atoms are analyzed.

A new SCF scheme implemented in deMon2k, *the mixed SCF* [1], reduces the electron repulsion integral (ERI) computation time up to 90% using a combination of ERI storage in RAM and the double asymptotic expansion [2]. Benchmarks on mono-, bi- and tri-dimensional carbon systems, as well as a Na_{55}^{+} cluster are presented, showing that BOMD simulation times for small- to medium-sized systems can be reduced by half. In this regard, BOMD simulations of a variety of phosphatidylcholines (PC), the building bricks of the membranes around our cells, are presented. An interesting feature of this system is that cell membranes are formed by bilayers of PC molecules held by non-covalent interactions. This creates a situation in which a separation of the bilayer in individual molecules is feasible to address the system calculation in a simplified, efficient way. An approach in this direction using a QM/MM scheme [3] is proposed.

[1] A. Alvarez-Ibarra, Asymptotic expansion of molecular integrals in self-consistent auxiliary density functional methods. PhD Thesis, Centro de Investigación y de Estudios Avanzados del I.P.N.: Mexico City, August **2013**.
[2] A. Alvarez-Ibarra, A.M. Köster, *J. Chem. Phys.*, **2013**, *139*, 024102.
[3] A. Alvarez-Ibarra, A.M. Köster, R. Zhang, D.R. Salahub, *J. Chem. Theory Comput.*, **2012**, *8*, 4232–4238.

Efficient computation of partition functions with the Multiple Histogram Method

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Thermodynamic property calculations of finite systems has became a very active research field triggered by the recent availability of experimental heat capacities and latent heats of metallic nanoclusters [1-4]. Theoretical determination of thermodynamic properties are based on Monte Carlo or Molecular Dynamics simulations aimed to reproduce the probability distribution of the system microstates. That distribution is then used to calculate thermodynamic properties using different techniques, standing out the Multiple Histogram Method (MHM) and its generalizations. However, to reach acceptable convergence, these methods often require arbitrary parameters or least square fittings which can lead to artifacts.

In this work a modification of the standard Multiple Histogram Method is presented, based on cumulative histograms and a form of Gauss quadrature. This formulation is fully equivalent to the original one by Ferrenberg and Swendsen [5] but avoids the need of arbitrary parameters or fittings. Therefore this approach greatly improves convergence of the MHM equations without compromising the reliability of the calculated thermodynamic functions. Test calculations of metallic clusters will be presented to illustrate the advantages of the new formulation for the calculation of heat capacities.

[1] M. Schmidt, R. Kusche, B. von Issendorff, H. Haberland, Irregular variations in the melting point of size-selected atomic clusters, *Nature* **1998**, *393*, 238-240.
[2] A.A. Shvartsburg, M.F. Jarrold, Solid Clusters above the Bulk Melting Point, *Phys. Rev. Lett*. **2000**, *85*, 2530-2532.
[3] G.A. Breaux, R.C. Benirschke, T. Sugai, B.S. Kinnear, M.F. Jarrold, Hot and Solid Gallium Clusters: Too Small to Melt, *Phys. Rev. Lett.* **2003**, *91*, 215508.
[4] C.M. Neal, A.K. Starace, M.F. Jarrold, Melting transitions in aluminum clusters: The role of partially melted intermediates, *Phys. Rev. B* **2007**, *76*, 054113.
[5] A.M. Ferrenberg, R.H. Swendsen, Optimized Monte Carlo data analysis, *Phys. Rev. Lett.* **1989**, *63*, 1195-1198.

Non-Born-Oppenheimer post-Hartree-Fock calculations with deMon2k

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In this talk I will comment on the achievements for the computation of H+ propagator [1] with deMon2k. The software was first extended with a Hartree-Fock implementation for regular electronic structure calculations in order to have the usual reference state for propagator theory [2]. In a second stage non-Born-Oppenheimer extension was pursued in order to make possible the treatment of protons and not only electrons [3]. Currently we are working on higher order electron propagator methods in one side and ADPT [4] based GWA implementation on the other. The first is for accuracy tests and the second for making feasible the computation of systems with hundreds of atoms.

[1] M. Diaz-Tinoco, J. Romero, J. V. Ortiz, A. Reyes, R. Flores-Moreno, *J. Chem. Phys.* **2013**, 138, 194108.
[2] R. Flores-Moreno, J. V. Ortiz, *J. Chem. Phys.* **2009**, 131, 124110.
[3] J. Romero, E. F. Posada, R. Flores-Moreno, A. Reyes, *J. Chem. Phys.* **2012**, 137, 074105.
[4] R. Flores-Moreno, A. M. Koster, *J. Chem. Phys.* **2008**, 128, 134105.

QM/MM Studies of Enzymatic Catalysis

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We present a few examples of QM/MM studies of the enzyme-catalyzed reactions. The free energy barriers for glycosylation and deglycosylation are calculated to be 22.5±0.4 and 24.5±0.7 kcal/mol at 85°C, respectively. The barrier for deglycosylation is found to decrease with increasing temperature or as a result of the Y61→G mutation, consistent with experimental observations. The transition state for glycosylation and deglycosylation from the simulations is in an oxocarbonium state with the -1 glucose ring having an E_3 envelop (or $^4H_3$ half-chair) conformation. A unique characteristic of the *Tm*Cel12A structure is the existence of a stable moiety that may play a role in “holding” cellulose at the binding site with the correct orientation for the reaction even at 85°C. This stable moiety (comprising hydrogen-bonded E116, E134, E227 and an active-site water molecule) may be one of the important factors for the relatively high activity of *Tm*Cel12A at high temperature.

The molecular mechanism of this Hg transfer is explored, the transfer is found to be nearly thermoneutral and to pass through a stable tri-coordinated intermediate that is marginally less stable than the two end states. For the overall process, Hg2+ is always paired with at least two thiolates, and thus is present at both the C-terminal and catalytic binding sites as a neutral complex. Prior to Hg2+ transfer, C141 is negatively charged. As Hg2+ is transferred into the catalytic site, a proton is transferred from C136 to C559’ while C558’ becomes negatively charged, resulting in the net transfer of a negative charge over a distance of ~7.5 Å. Thus, the transport of this soft divalent cation is made energetically feasible by pairing a competition between multiple Cys thiolates for Hg2+ with a competition between the Hg2+ and protons for the thiolates.

The relevance of the pathway through which the second proton is delivered to the active site of P450cam and the subsequent coupling/uncoupling reactions has been investigated. Different from previous studies, a dynamic process of the last stage of coupling/uncoupling was observed. We found the peroxide bond cleavage in coupling, the Fe-O bond stretching in uncoupling, proton transfer and electron delivery take place spontaneously. Moreover, besides the intrinsic chemical differences between the two peroxide oxygen atoms, water molecules in the active site and the proton transfer pathway may play an important role in the determination of coupling/uncoupling. We conclude that by maintaining a specific proton transfer channel, Asp251–Thr252 channel, the wild-type enzyme could efficiently deliver the second proton to the ideal position for coupling reaction.

Dynamics of hybrid organic-inorganic interfaces: current advances and challenges for computational studies

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A combination of organic and inorganic entities at a molecular level led to the concept of hybrid organic-inorganic (HOI) materials, which opened the accesses to a wide spectrum of functionalities [1]. The HOI interactions are in the basis of synthesis of zeolites, MOFs, COFs, mesoporous materials, macrocellular solids, hierarchically structured materials, clathrates, membranes, carbon-related functional porous materials, etc. The process engineering is much ahead with respect to the fundamental understandings, which is strongly hindered by the HOI complexity, due to the intrinsic spatial and dynamical disorder experienced by the chemical entities at the interface. The inorganic units are often oxide-based skeletons (silica or transition metal oxides) and very different amphiphile assemblies are used as organic templates.

Here, we will present an approach allowing computing dynamic NMR parameters from large time scale MD simulations, commensurable with the NMR measurement time scale, to account for the inter-chain interactions as well as for the electrostatic interactions between the polar heads and the counter-ions, and the effect of explicit water solvent. Validation of this methodology against more precise BOMD/DFT results obtained with deMon2k will be also presented. These results allow bringing new understandings about the factors influencing ^{14}N quadruple coupling parameters. Finally, it will be shown how a better interpretation of the NMR experimental data aided by computational modelling, based on the combination between quantum and classical approaches, can be applied to study the charge distribution in zeolite frameworks [2].

References:

[1] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.*, **2006**, 45, 3216-3251.

[2] E. Dib, T. Mineva, P. Gaveau, B. Alonso, *Phys Chem Chem Phys*, **2013**, 15, 18349 – 18352.

Computational investigation of the hydroxylation mechanism of noncoupled copper oxygenases

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In Nature peptidylglycine α-hydroxylating monooxygenase (PHM) is known to achieve the dioxygen-dependent hydroxylation of aliphatic C-H bonds using two uncoupled copper sites.[1] In spite of many investigations, either biochemical, chemical or computational, the details of the C-H bond oxygenation mechanism remain elusive; conflicting proposals have been advanced in the recent literature for the enzymatic catalytic cycle.

I will present an investigation of the hydroxylation mechanism of PHM using *ab initio* Molecular Dynamics simulations based on hybrid Density Functional Theory-classical potentials (*ie*. DFT/MM). DFT calculation were carried out with deMon2k, the QM/MM interface being handled with the program CUBY. This computational scheme permits the inclusion of the intrinsic dynamics of the active site into the modeling strategy. The major result of this study has been an extremely fast (picoseconds timescale) rebound after the initial H-abstraction step promoted by the cupric-superoxide adduct. The H-abstraction/Rebound sequence leads to the formation of an alkylhydroperoxide intermediate. A long range electron transfer from the remote copper site subsequently triggers its reduction to the hydroxylated substrate.[3] The characteristic time scale of the rebound step (ps) suggests that it is very probably the fastest reactive pathway over the previously advanced proposals. Moreover, our proposal finds favorable echoes with recent experimental results obtained on biomimtic complexes.

[1] Osborne R.L.; Klinman, J. P. "Copper Oxygen Chemistry", pp 1-22; **2011**, Ed. Karlin, K. D.; Itoh, S. Pub. J. Wiley & Sons.
[2] Melía C., Ferrer S., Řezáč J., Parisel O., Reinaud O., Moliner V., de la Lande A. *Chem. Eur. J.* **2013**, *19*, 17328 – 17337.
[3] Thiabaud, G. Guillemot, G., Schmitz-Afonso, I., Colasson, B. Reinaud, *Angew. Chem. Int. Ed.* **2009**, *48*, 7383 –7386.

The role of Asp1 in the coordination of Cu(II) to the amyloid-beta peptide

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The amyloid-beta (Aβ) protein is the major component of amyloid plaques and is causative of the neurodegeneration in Alzheimer’s disease (AD). This protein has the ability to coordinate transition metals such as copper or zinc; however, the role this process plays in either diseased or healthy brains is not fully understood. Although the copper coordination to the N-terminal region of this protein has been extensively studied there is no consensus on the precise assignment of the ligands in the coordination shell, in particular the identity of oxygen-based ligand which involves the Asp1 residue. In this work, we construct a set of model complexes of Cu^{2+} with peptides including 3, 6 or 17 amino acids of the Aβ sequence at the N-terminus. Using the deMon2k code, we optimized these models exploring the different Cu ligands, as well as different possible conformations of the Asp1 side chain. Through this procedure we were able to distinguish the ligands and conformers that best favors the coordination to Cu^{2+}. The structures and predicted parameters of the most stable complexes were compared with several experimental measurements including EXAFS-derived geometries and X-ray structures as well as EPR parameters finding a good agreement with our results in all cases.

Theory and Anion Photoelectron Studies of Transition Metal Clusters

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A combined study where both, Anion Photoelectron Sspectroscopy (PES) and far Infra Red Multiple adsorbed Photon(FIR-MPD) experimental spectra are combined with Density Functional Theory (DFT) calculations is presented to identify the unique structural, electronic, and magnetic properties of neutral and charged free standing clusters of Rh_n (n=1-9) as well as hydrogen saturated Co_nH_m n=2-6,m=1-6 clusters. Negative ion photoelectron spectra are presented for electron binding energies up to 3.493 eV. We discuss our computational results in the context of the PES experiment, in which the calculated electron affinities and vertical detachment energies as well as Infra Red (IR) spectra are in good agreement with the measured values. Theoretically, we investigate the low-lying energy structures and the spin isomers of each neutral and charged rhodium cluster and infer their magnetic moments by means of two functionals (PBE), and (B3LYP). Our results show that octahedral and tetrahedral motifs are favored in contrast to cubic motifs found in earlier studies when an hybrid functional is used. As for the study on Co_n clusters we found the adsorption of H_2 exclusively dissociative for all neutral Co_nH_m n=1-5, m=1-5 clusters. The twofold bridge site is identified to be the most favorable for adsorption on neutral Co_n (n>2). Therefore hydrogen adsorption in clusters is different than it is on surfaces, where it is known that hydrogen adsorbs in high coordination sites. We found that as we add H atoms: a structural transition from three to two dimensions occur in the cluster geometry, an enhanced, but non-monotonic change in their magnetic moments is observed, and the stability of the system is greatly increased. Both experimental and theoretical results obtained here are compared and discussed with previous experimental and theoretical studies on the same systems

Extensions of DFTB to treat long-range interactions

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Molecular complexes and clusters provide bridges between molecular and solid states physics. Containing tens to few thousands of atoms, such systems can hardly be approached via traditional ab initio wavefunction based methods at the moment. Density functional theory (DFT) and density functional based tight binding methods (DFTB) have strongly developed with respect to computational efficiency to cover this size range. However both DFT and currently implemented DFTB face difficulties to describe realistically and accurately the typical interactions met in molecular clusters, in particular long range interactions such as Coulomb interactions between distant charge fluctuations, charge resonance in ionic clusters, polarization and van der Waals interactions. I will give an overview of how extensions of DFTB can circumvent some of the above deficiencies and turn out to be realistic and efficient tool to investigate the properties of molecular clusters and complexes, focusing on structural, electronic, energetic, and spectroscopic properties of clusters of polycyclic aromatic hydrocarbons.

M. Rapacioli, A. Simon, L. Dontot, and F. Spiegelman. Physica Status Solidi (b), 2012, **249**, 2, 245 (2012)

GGA exchange with correct asymptotic behavior of its potential

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We present a non-empirical exchange energy functional of the generalized gradient approximation (GGA) type which leads to an exchange potential with the correct asymptotic behavior that in combination with the PBE correlation provides heats of formation, ionization potentials, electron affinities, proton affinities, binding energies of weakly interacting systems, barrier heights for hydrogen and non-hydrogen transfer reactions, bond distances, and harmonic frequencies competitive with those obtained from other GGA functionals that do not have to the correct asymptotic exchange potential behavior. We show that the proposed functional provides important improvements in the description of properties that depend upon response functions, such as static and dynamic polarizabilities and hyperpolarizabilities.

[1] A. Miller, B.C. Meier, B.C., *Journal*, **Year**, *Volume*, fist page – last page

From Quantum Chemistry to Molecular Simulations: Perspectives and Challenges for the deMon2k Development

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Over the last years ab-initio quantum chemistry methods have been used by several research groups to perform simple first-principle molecular simulations. Even though, the methods are still at a rather primitive stage their potential has been already well recognized. In this presentation I report about my experiences with these first-principle simulations in the field of cluster science [1]. The challenges for the further development of deMon2k are highlighted. The presentation will conclude with the formulation of possible perspectival milestones for first-principle molecular simulations.

[1] J.M. Vásquez-Pérez, P. Calaminici, A.M. Köster, *Comp. Theor. Chem.*, **2013**, *1021*, 229-232.

ABSTRACTS

POSTER

PRESENTATIONS

The implementation of time correlation functions in deMon2k

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The prediction of power spectra from molecular dynamics simulations is important because they provide a link between experiment and theory. The power spectra can be calculated taking the Fourier transform (FT) of a signal of interest. A special case is when one takes the FT of the dipole moment autocorrelation function (ACF) associated with the infrared spectra[1], or the FT of the polarizabilities ACF, associated with the Raman spectra. From the chemical point of view, the spectra can be used to understand the structure of molecules. Transport properties such as shear viscosity and thermal conductivity can be calculated with an ACF.

The implementation for the calculation of infrared spectra from the dipole moment ACF was perfomed in the deMon2k code. The algorithm was taken from Frenkel[3] and the FT algorithm of the FT was implemented as proposed by Goertzel and Reinsch[4]. In this poster details of these implementations will be presented as well as a series of test calculations considering different molecular systems. As examples, the power spectrum of small molecules such as HCl and H_2O and undissociated $HCl(H_2O)_n$ (n=4,5,6) clusters are presented. The theoretical results are analysed and compared with experimental data[2] and results from vibrational analysis (VA). The influence of temperature in the behavior on these spectra is investigated, too.

[1] M. Thomas, M. Brehm , R. Fligg , *Phys. Chem. Chem. Phys.* , **2013**, 15, 6608-6622
[2] M. Masia., H. Forbert, D. Marx, *J. Phys. Chem. A*, **2007**, 111 (49), 12181–12191
[3] D. Frenkel, B. Smit, Understanding molecular simulation: from algorithms to applications, Academic Press, 2001, 107-112
[4] J. Stoer, R. Bulirsch, Introduction to Numerical Analysis, 3rd ed., Springer, 2002, 88-91

Molecular Symmetry for TD-ADFT

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A convenient approach to calculate electronic excitations in molecular systems is given by time-dependent auxiliary density functional theory (TD-ADFT) [1]. The selection rules for these excitations are based on molecular symmetry considerations of the electronic states involved. In the framework of TD-ADFT, these selection rules can be directly obtained from the symmetry of the molecular orbitals. To assign calculated electronic transitions according to the molecular symmetry will allow a reliable and more detailed comparison with experimental results, that is our primary interest. Moreover, symmetry considerations can also be used to reduce the computational effort.

In order to proceed along this lines we aim to incorporate a molecular symmetry analysis into the new deMon2k [2] TD-ADFT branch of Carmona-Espíndola [3]. To this end we generalize the molecular orbital symmetry analysis suggested in [4]. The actual implementation is based on the molecular symmetry analysis in StoBe [5] and deMon2k. In this poster, the working equations along with an implementation scheme are presented.

[1] J. Carmona-Espíndola, A. M. Köster, Canadian Journal of Chemistry, **2013**, 91, 795-803.
[2] See http://www.demon-software.com
[3] J. Carmona-Espíndola, PhD thesis, Cinvestav, México City, **2012**.
[4] A. A. Martínez-Carranza, Bachelor thesis, U. de G., Guadalajara, Jalisco, México, **2014**.
[5] deMon version of Stockholm & Berlin http://www.fhi-berlin.mpg.de/KHsoftware/StoBe/

Energy curvature as a function of the electron number.

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During the last decades, the Kohn-Sham (KS) formalism of the Density Functional Theory[1,2] has become the most popular and powerful method to study the electronic structure of complex systems. Despite the success of KS, a contribution to the energy, yet to be known, the exchange and correlation energy, $E_{xc}[\mathbf{n}]$, still remains being a functional whose exact contribution is unknown. In particular, it has been proved that the energy depends linearly to the electron number when a fractional occupation is used[3], result known as the ensemble theorem. In this manner, any deviation from the lineal behaviour is a measurement of the approximation degree[4,5] in $E_{XC}[\mathbf{n}]$.

In this work, the software package deMon2k[6] has been used to measure the deviation from the lineal behaviour; which is denoted as the curvature of the energy, and it was used to estimate the approximation degree of LDA and GGA functionals.

Understanding the origin of these deviations, measured by the curvature, will be of great utility to help improve existent functionals

[1] P.Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, B864.
[2] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.
[3] J. P. Perdew, R. G. Parr, M. Levy, J. L. Balduz Jr., *Phys. Rev. Lett.* **1982**, *49*, 1691.
[4] P. Mori-Sánchez, A. J. Cohen, W. Yang, *Phys. Rev. Lett.* **2008**, *100*, 146401.
[5] A. J. Cohen, P. Mori-Sánchez, W. Yang, *Science* **2008**, *321*, 792.
[6] A.M. Koster, G. Geudtner, P. Calaminici, M.E. Casida, V.D. Dominguez, R. Flores-Moreno, G.U. Gamboa, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J.M. del Campo, J. U. Reveles, A. Vela, B. Zuniga-Gutierrez and D.R. Salahub, deMon2k, Version 3, The deMon developers, Cinvestav, Mexico City (2011).

ELECTRODONATING POWER AND ITS RELATIONSHIP TO THE PROTON AFFINITY AND BASICITY

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In this work we show the thermodynamic calculation in gas phase of the proton affinity (ΔH°) and basicity ($-\Delta G^\circ$) of a series of alkyl amines (RR'R''N). Also we use the electrodonating power (ω^-) which is derivated in the chemical reactivity in DFT (CRDFT) [1], to explain and connect the ability of the amines to donate charge with these thermodynamics properties.

[1] J. L. Gázquez.; A. Cedillo.; A. Vela. *J. Phys. Chem. A*, **2007**, *111*, 1966 – 1970

THEORETICAL STUDY (QSAR) OF DIHYDROPYRIDINES ANALOGUES WITH EFFECTIVE HYPOTENSIVE APPLYING DFT METHODS

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Cardiovascular diseases (hypertension) are the 1st cause of death worldwide and a major cause of disability. Hypertension occurs when blood is driven through the heart with excessive force against the walls of the arteries, because of this, probability of having a heart attack, stroke or even death increases exponentially[1]. These aspects encourage us to develop a new project to predict hypotensive effect with organic compounds that can subsequently be used as reducing high blood pressure drugs (Hypertensive).

We use as molecular descriptors properties like: hardness, softness, volume, log P, atomic charges, hydrophilic Factor, Molecular Orbital (HOMO, LUMO) molecular graphs, critical points, the analysis is performed is determined at dimensionless density gradient and the generalized gradient for the exchange of energy, etc., all of these properties could be responsible for the biological activity (log(1/IC50)), in dihydropyridine derivatives. The structural and electronic properties were obtained with the exchange-correlation functional PBE[2] with DZVP basis and Gen-A2 as auxiliary basis in deMon2k[3]. Subsequently, a quantitative structure-activities relationship is performed[4], which allows to discern what factors are involved in the hypotensive effect, this QSAR model was performed with 36 molecules[5] and was validated statistically, the mathematical model of Multiple Linear Regression (MLR) presented the following statistical values $R^2=81.43\%$, $Q^2=76.80$ and F=34.0 t=2.01[6,7], this model suggests that the hypotensive effect is a function of molecular orbital (HOMO), the partition coefficient (log P), the volume and the critical point (CP) of the interaction distance $H_{di} \cdots X$.

References:
[1] Agewall S, et, al; The Risk Factor Intervention Study Group, Apr; (4) 2001 305-314.
[2] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77 (1996) 3865-68.
[3] The deMon2k., the International deMon Developers Community..,Version 3.0. Cinvestav-IPN. Mexico (2011)
[4] A.Cerda.,et al "Evaluacion de la susceptibilidad a la oxidación microsomal de análogos de nifedipina."(2000) 375-280.
[5] Yuji Takahata., et, al;, J. Chem. Inf Comput. Sci., Vol 43, (2003) 540-544.
[6] R. Todeschini, D. Ballabio, V. Consonni, A. Mauri, M. Pavan, MobyDigs, User Manual 2004-2005 by Talete srl, Milano, Italy.
[7] Todeschini, V. Consonni, A. Mauri, M. Pavan, Anal. Chim. Acta 515 (2004) 199- 208.

14th deMon developers workshop
From Quantum Chemistry to Molecular Simulation
Los Cabos, Baja California Sur, Mexico
April 27th to 30th, 2014

Adsorption of $H2O$ on sites of Pd nano-surface: a Theoretical and Experimental Study

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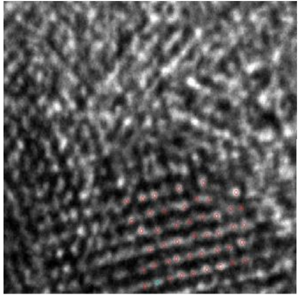
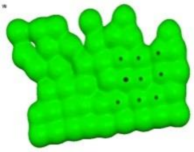
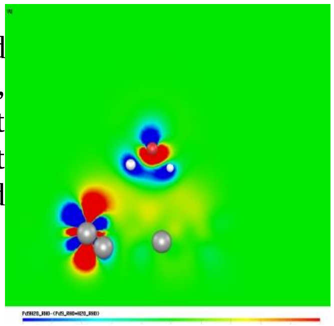
Palladium nano particles were prepared using a modified sol-gel method[1]. The samples were characterized using xray diffraction and high resolution transmission electron microscopy(HRTEM)[1]. From the HRTEM micrography, a 46 atom Pd nano crystal surrounded by a Pd quasi-liquid inter-phase was chosen. The position of Pd atoms were determined, and a DFT electron density calculation was performed. To calculate the adsorption energy of a H_2O molecule on a surface site, a cluster of nine atoms was selected and a geometry optimization was carried out. To check the reliability of our calculations, the dipole moment of water was calculated using dzvp, tzvp, and aug-cc-pvdz. The aug-cc-pvdz obtained dipole moment of water was 1.86 that compares well with the experimental value of 1.85. The adsorption energy was calculated using dzvp and aug-cc-pvdz. For dzvp we found an adsorption energy of 3 kcal/mol and for the aug-cc-pvdz we found an adsorption energy of 1 kcal/mol, this values for the adsorption energy can be related to hydrogen bonds.





Finally, a difference of densities analysis were done to the optimized water molecule on the Pd9 cluster. In our last figure, green is zero, colors toward red indicates that electron density was transfer to that area, and colors toward blue indicates that electron density leave that area. Here we can see the bare H protons interacting with the Pd surface, as is expected for an hydrogen bond.



1. **Synthesis of new hybrid material based on copolimer and Pd-nanoparticles.** M. Ugalde, E. Chavira, M. T. Ochoa, M. A. Canseco, E.A. Zaragpza Contreras, **C. Quintanar**, M Gutierres Nava. Mater. Res. Soc. Proc. Vol. 1483 **2012** Material Research Society DOI 10.1557/opl.2012.1622.

A density functional investigation of structures, stability and energy properties of $(Mo_2C)_n$, n=1-7 clusters

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Metal carbides research has grown significantly in recent years due to the fact that these materials have a potential use as catalysts in the petroleum industry [1]. However, this industry generates negative impact in the environment. For this reason, different studies have been done in the area of catalysis, which aim to reduce emissions of pollutants generated by fossil fuels [2].

In order to solve the addressed problem the molybdenum carbide is being studied in form of clusters monitoring the change of structures and different energy properties with the size. This research has great relevance and importance since it helps to understand the catalytic processes involving these metal carbides, i.e. the extraction of oil from tar sands [3]. For this reason we carried out a theoretical study focusing on the $(Mo_2C)_n$ with n=1-7 compounds. For this investigation the density functional theory (DFT) method was employed as it is implemented in the deMon2k code [4]. The PBE functional in combination with the DZVP basis set for the C atom and the RMCP12|LK basis set for the Mo atom were respectively employed. For each cluster size different initial structures in different multiplicities were considered for the geometry optimization. In order to generate a large variety of initial structures to start the geometry optimization Born-Oppenheimer molecular dynamics (BOMD) simulations were performed at different temperatures for each clusters size. All structures were fully optimized without including any symmetry restriction. The optimized structures were characterized by frequency analysis in order to discriminate them in terms of minima or transition states. Structures and energetic properties such as dissociation energy, ionization potential and HOMO-LUMO gap of the found ground states are presented. The obtained results are compared with data available from the literature.

[1] A. Hynaux, C. Sayag, S Suppan, J. Trawczynski, M. Lewandowski, A. Szymanska Kolasa, G. Djéga-Mariadassou, *Catalysis Today* **119**, 3 (2007).
[2] M.L. Frauwallner, F. Lopez-Linares, J. Lara-Romero, C.E. Scott, V. Ali, E. Hernandez, P. Pereira-Almao. *Appl. Catal. A-Gen.* **394**, 62 (2011).
[3] N. Berkowitz, J.G. Speight, *Fuel* **54**, 138 (1975).
[4] A.M. Koster, G. Geudtner, P. Calaminici, M.E. Casida, V.D. Dominguez, R. Flores-Moreno, G.U. Gamboa, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J.M. del Campo, J.U. Reveles, A. Vela, B. Zuniga-Gutierrez and D.R. Salahub, deMon2k, Version 3, The deMon developers, Cinvestav, México City (2011).

Global optimization using BOMD with Bi_2O_3 cluster as an example

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In the presentation will show a scheme for finding minimum structures using Born-Oppenheimer Molecular Dynamics (BOMD) calculations. The idea is to use BOMD calculations as a kind of 'scanner' in order to find valleys in the potential energy surface. These valleys are then further investigated separately via geometry optimization. By this scheme one gets a set of structures which then can be studied further for their vibrational properties. As an example we choose $(Bi_2O_3)_n$ clusters with n ranging from 1 to 7. These results for the found minimum structures will be presented along with the geometrical relationship between clusters of different sizes.

This study was performed in the framework of the BisNano project funded by European Union FP7-NMP EU-Mexico programme under Grant Agreement No. 263878 and cofunded by CONACYT No. 125141.

A Density Functional Theory Based Study of Structures and Properties of Pd_nM_n (M=Fe, Co, Ni and n=1-7) Clusters

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Over the last decades the interest in transition metal clusters has grown considerably, both experimentally and theoretically, because these systems have several applications, standing out its possible function as catalysts. Also these systems present a strong dependency of their physical, chemical, electronic and magnetic properties with respect to their size and geometrical shape. In this work a theoretical study of Pd_nM_n (M=Fe, Co, Ni and n=1-7) clusters using the Linear Combination of Gaussian-Type Orbital Density Functional Theory (LCGTO-DFT) deMon2k program was performed [1]. The calculations were performed using the PBE-98 functional [2], in combination with the DZVP-GGA basis sets for the cobalt, the nickel and the iron atoms [3] and a quasi-relativistic effective core potential (QECP|SD) for the palladium atom [4], respectively. The auxiliary functions set GEN-A2* was employed as well [3]. For each size of the systems under study several starting geometries were optimized considering various spin multiplicities. All optimized structures underwent a frequency analysis to discriminate between situations of minima and transition states on the potential energy surfaces. Calculated structures and energy properties such as ionization potential, electron affinity and binding energy are presented.

[1] A.M. Koster, G. Geudtner, P. Calaminici, M.E. Casida, V.D. Dominguez, R. Flores-Moreno, G.U. Gamboa, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J.M. del Campo, J. U. Reveles, A. Vela, B. Zuniga-Gutierrez and D.R. Salahub, deMon2k, Version 3, The deMon developers, Cinvestav, Mexico City (2011).
[2] Y. Zhang, W. Yang, *Phys. Rev. Lett.*, 1999, 80, 890.
[3] P. Calaminici, F. Janetzko, A.M. Köster, R. Mejia-Olvera, B. Zúñiga-Gutiérrez, *J. Chem. Phys.*, 2007, 126, 044108.
[4] http:://www.theochem.uni-stuttgart.de

Structures, vibrational frequencies and energy properties of clusters of (Fe3O4)n (n=1-4) neutrals, cationics and anionics in the density functionals theory.

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In this work are presented structures of energy minimum of nanoclusters of iron oxide (Fe3O4) n with n = 1-4. The search for the minimums was done through the analysis of a trajectory of molecular dynamic Born-Oppenheimer type[1] (BOMD). Subsequently were selected the structures obtained for performed both estimates of local optimization and analysis of vibrational frequencies in order to know which structures are really minimal in the potential energy surface (PES). The respective cations and anions of each minimum were also calculated. These calculations were performed with the functional of exchange and PBE correlation[2], the bases set DZVP and GEN-A2 auxiliary bases[3]. Apart from the structures, the followings energetic properties are presented: ionization potential, electron affinities and energies of polymerization. All calculations were performed in the framework of the theory of the density functionals auxiliary included in the deMon2k code[4].

[1] M. Born, J. R. Oppenheimer, Ann. Phys., 1927, 84, 457
[2] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett.,1996, 77, 3865
[3] P. Calaminici, F. Janetzko, A. M. Köster, R. Mejia-Olvera, B. Zuniga-Gutierrez, J. Chem. Phys.,2007, 126, 044108
[4] A. M. Köster, G. Geudtner, P. Calaminici, M. E. Casida, V. D. Dominguez, R. Flores-Moreno, G. U. Gamboa, A. Goursot, T. Heine, A. Ipatov, et al., deMon2k, Version 3, The deMon developers, Cinvestav, Mexico City, 2011.

Atomistic simulation of phenylalanine assembly

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Phenylketonuria (PKU) is a metabolic disorder characterized by a mutation in the gene for the enzyme phenylalanine hydroxylase, rendering it nonfunctional. This enzyme is needed to metabolize phenylalanine to tyrosine. Failure to do this leads to accumulation of phenylalanine. Affected children are likely to develop mental retardation, epilepsy and other serius medical problems. Amyloid etiology in PKU was recently suggested, due to the observation of phenylalanine assembly into toxic fibrils [1]. The details of the assembly mechanism are still unknown, as is the nature of the interactions that stabilize the fibrils. This work presents the results obtained from an atomistic Molecular Dynamics simulation of a system of 10 zwitterionic phenylalanines in explicit water (Fig. 1). These results can shed insight into the aggregation mechanism of phenylalanine.

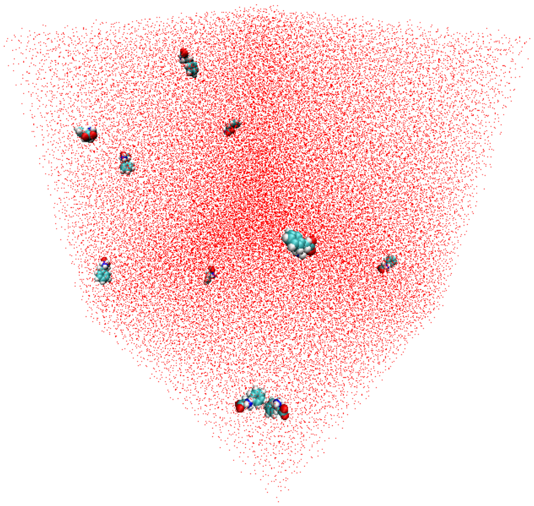

Figure 1. Snapshot of the system after 15 ns of simulation with explicit solvent.

[1] L. Adler-Abramovich, L. Vaks, O. Carny, D. Trudler, A. Magno, A. Caflisch, D. Frenkel, E. Gazit, *Nature Chemical Biology*, **2012**, *8*, 701 – 706

The oxidation of CO catalyzed by small Pd_n clusters through the Langmuir-Hinshelwood and Eley-Rideal mechanism

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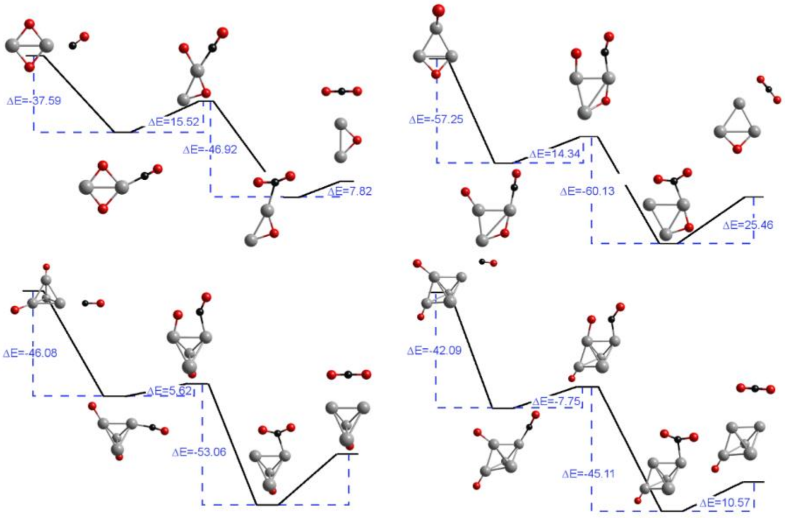
Human exposure to high concentrations of CO may cause health damage, from a simple irritation on the respiratory system to death. To oxidize CO, oxygen atoms are needed; these atoms usually come from a surface, which liberates oxygen atoms, or from the dissociation of molecular O_2. If oxygen atoms are pre-adsorbed on a metal catalyst, two reaction pathways are in competition: the Langmuir-Hinshelwood (LH) and the Eley-Rideal (ER) mechanism.

This study presents both reaction pathways treated under the Density Functional Theory and the Zero Order Regular Approximation (ZORA) to include the scalar relativistic effects. The energy barriers ($E_a < 10$ kcal/mol) to form CO_2 in the ER mechanism are less than in the LH. In the LH mechanism, the formed CO_2 molecule is adsorbed on Pd_n clusters, while in the ER mechanism, CO_2 is released. The CO lone pair of electrons is used to form a dative covalent bond with the atomic oxygen and produces CO_2.



Large s constraint included in PBE and RPBE functionals.

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We introduce two families of generalized gradient expansion approximation (GGA) functionals, which take as starting point the known GGA functionals PBE [1] and RPBE [2]. For both of them it was included an extra term to satisfy the correct asymptotic large ***s*** constraint [3]. This inclusion has the intention of mimic the enhancement form of PW91 [4], which has a complicated analytic form for the enhancement function. With this way of including an extra condition, we are also looking for an easier analytic form that can mimic the enhancement function. It's important to notice that only PW91, Lacks-Gordon [5], and VT{m,n} [6] are the only functionals that satisfies this large ***s*** constraint.

This functionals that we are calling lsX (where X can be PBE or RPBE), have been proved in several databases and the mean absolute deviations (MAD's) have shown for example, an improvement in the prediction of standard heat formation up to 65% in comparison to PBE and PW91 functionals and up to 42% with respect to RPBE.

All this new functionals have been implemented in deMon2k [7] code.

[1] J. P. Perdew, K. Burke and M. Ernzerhof; *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
[2] B. Hammer, L. B. Hansen and J. K. Norskov; *Phys. Rev. B* **1999,** *59*, 7413-7421.
[3] Levy, M.; Perdew, J. Perdew. *Phys Rev B* **1993**, *48*, 11638-11645.
[4] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais; *Phys. Rev. B* **1992**, *46*, 6671-6687.
[5] D. J. Lacks and R. G. Gordon; *Phys. Rev. A* **1993**, *47*, 4681-4690.
[6] A. Vela, J. C. Pacheco-Kato, J. L. Gázquez, J. M. del Campo and S. B. Trickey; *J. Chem. Phys.* **2012**, *136*, 144115.
[7] The deMon2k International Developers Community, Version 3.0. Cinvestav-IPN. Mexico (2011).

Calculating electron transfer kinetics between single graphite layer and iron atom.

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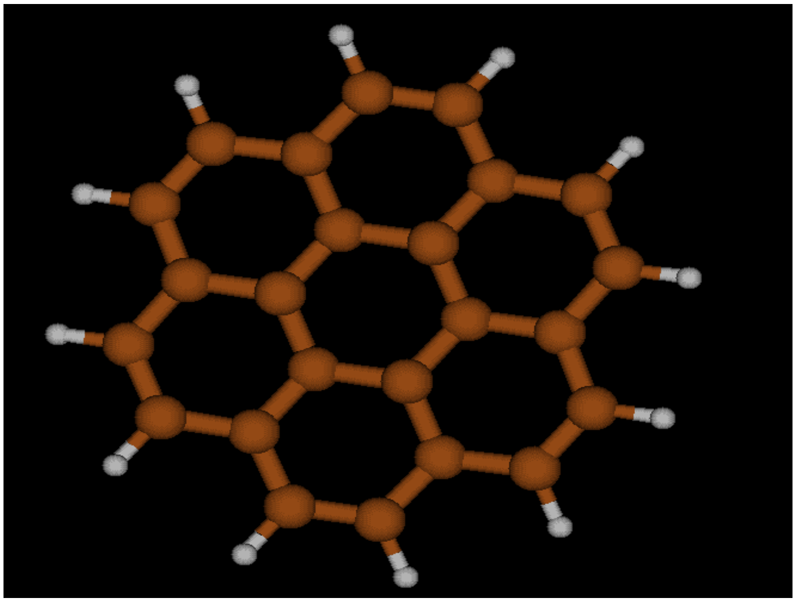
The electron transfer (ET) between redox moieties and electrode surface is of immense interest during the investigation of molecules in electrochemical sensors. Graphite materials are widely used as electrochemical sensors. However, the ET kinetics of graphite electrodes are slow when compared to metallic electrodes. To improve the performance graphite electrodes have been modified experimentally. Hence, understanding the heterogeneous ET reactions yields important information related to the effect of modifier on the kinetics. As a first step towards this goal. In this first study, we are doing an effort to calculate the electron transfer kinetics between a single graphite layer and the iron atom. The kinetics was studied using Marcus theory. Reorganization energy between graphite layer and the redox moieties plays a crucial role to determine the kinetics. To determine reorganization contribution the energies of the graphite and iron molecules were mandatory. The calculations are being performed with deMon2k software.



Theoretical study of some X-ray spectroscopy using DFT

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During recent development of synchrotron radiation facility, various core-level electron spectroscopies such as X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES), have been extensively studied, and understanding on electronic structures and chemical reactions of clusters and adsorbed molecules on surface have been advanced. By supporting theoretical approach, structures and chemical reactivity have been clarified at the gas and condense phases.

In this presentation, I show you our resent computational results about X-ray natural circular dycroism (XNCD) and double core hole electron spectroscopy. A new code for the former spectroscopy was implemented in density functional theory code StoBe. Our procedure was applied for some amino acids using cluster models. For the second spectroscopy, we have already some publications [1-4]. This type of spectroscopy can be realized not only synchrotron radiation instruments but also X-ray free electron laser (XFEL). Especially theoretical studies are one of hot topics in X-ray spectroscopy. I show basic idea and some resent results.

[1] O. Takahashi, M. Tashiro, M. Ehara, K. Yamasaki, and K. Ueda, Chem. Phys. **384** (1-3), 28-35 (2011).

[2] O. Takahashi, M. Tashiro, M. Ehara, K. Yamasaki, and K. Ueda, J. Phys. Chem. A **115** (44), 12070-12082 (2011).

[3] O. Takahashi, K. Yamasaki, S.-i. Nagaoka, and K. Ueda, Chem. Phys. Lett. **518**, 44-48 (2011).

[4] K. Ueda and O. Takahashi, J. Electron Spectrosc. Relat. Phenom. **185**, 301-311 (2012).

The role of the electron transfer on the O_2 dissociation catalyzed by clusters Au-Ag

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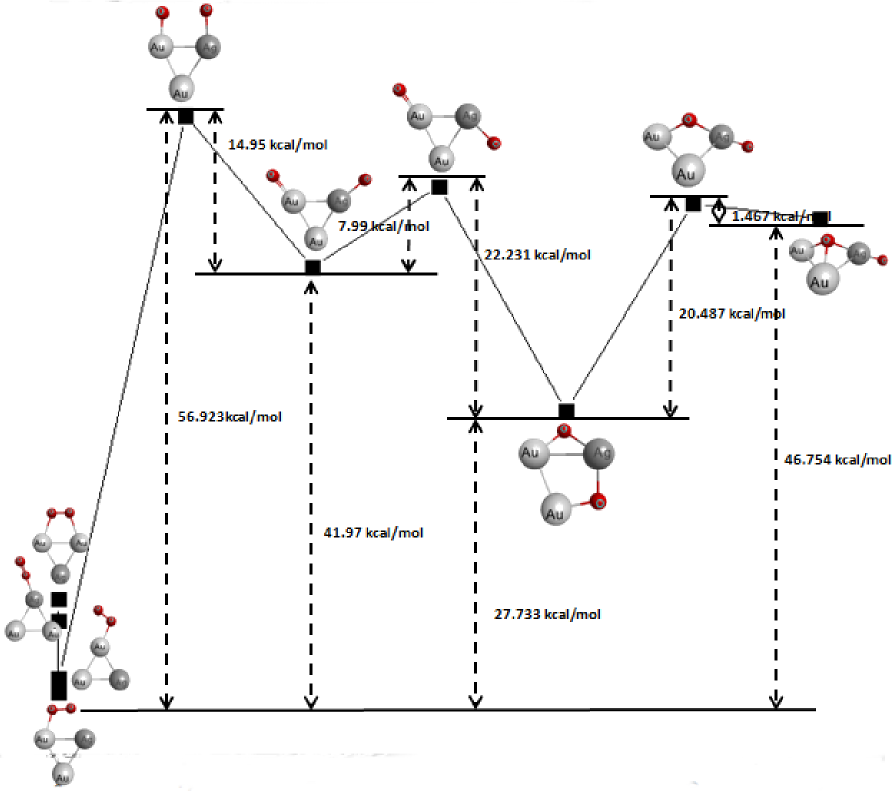
The oxidation of CO is dependent on prior dissociation of molecular oxygen O_2 catalyzed by transition metals. This work presents the activation of O_2 by bimetallic clusters Au-Ag using the density functional theory and the zero-order regular approximation (ZORA) to include scalar relativistic effects. The O_2 activation barriers are in the range of 20-60 kcal/mol. The adsorption of O_2 decreases the bond order from 2.0, when it is gas phase to a value of 1.2 when O_2 is adsorbed. The weakening of the bond O-O is due to electron transfer from the cluster Au-Ag to the antibonding orbital of O_2.



Identifying weak chemical interactions by quantum chemical topology

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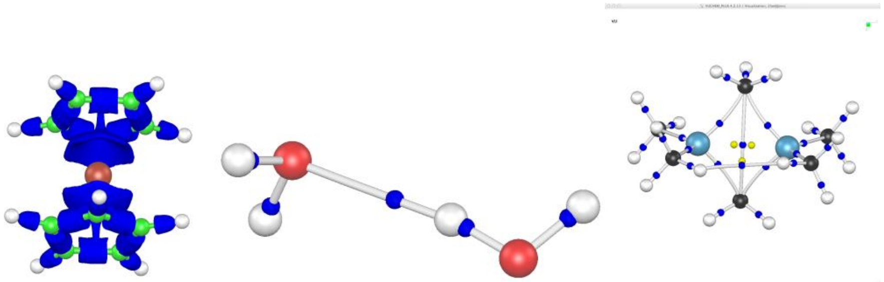
An analysis able to identify both strong and weak chemical interactions is presented. It is based on a generalization of the analysis presented by Zupan et. al [1,2] that consist in evaluating the integral

$$N_{\rho_k}(\varphi) = \iint \cdots \int d\vec{r}_1, d\vec{r}_2 \cdots d\vec{r}_k \ \rho_k(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_k)\theta\big(\varphi - \varphi(\vec{r}_1)\big)\theta\big(\varphi - \varphi(\vec{r}_2)\big) \cdots \theta\big(\varphi - \varphi(\vec{r}_k)\big)$$

where $\rho_k(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_k)$ is the diagonal element of the k-nt reduced density matrix and $\theta(\varphi)$ is the Heaviside function. $N_{\rho_k}(\varphi)$ represents the numbers of electrons in k-nt arrangement localized in the constrained by the φ scalar field isosurface $\varphi = \varphi(\vec{r})$. For k=1, the derivative with respect to the φ yields the correspondent density of states and, at the same time, its bounds allow to localize the values that are chemically relevant for the scalar field. Many examples to illustrate the behavior of this analysis are presented using the exchange and correlation dimensionless gradients and the normalized electron localization function [3].



[1] A. Zupan, J.P. Perdew, K. Burke and M. Causa. *Int. J. Quantum Chem*. **61**, 835 (1997)
[2] A. Zupan, K. Burke, M. Ernzerhof y J.P. Perdew, *J. Chem. Phys.* ***106***, 10184 (1997)
[3] Analysis of the generalized gradient approximation for the exchange energy. J. L. Gázquez, J. M. del Campo, S. B. Trickey, R. J. Alvarez-Mendez, A.Vela. Chapter in "Concepts and Methods in Modern Theoretical Chemistry, Vol. 1: electronic structure an reactivity". In honor of Professor B.M. Deb; S.K. Ghosh and P.K. Chattaraj eds. Taylor & Francis / CRC Press. (2013)

Theoretical and Experimental Study of Cu(I) Binding to the Fragment 106-115 of the Human Prion Protein

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Transmissible spongiform encephalopathies (TSEs) are a group of infectious neurodegenerative diseases that include mad cow disease, and Creutzfeldt-Jakob. These diseases are characterized by the conversion of normal cellular prion protein (PrP^{C}) into the infectious scrapie isoform (PrP^{Sc}) [1]. PrP^{C} is known to have several binding sites for Cu at its N-terminal region. Human PrP^{C} contains six Cu binding sites, two Cu binding sites are located at His96 and His111 [2, 3], in a domain that is key for the conversion of PrP^{C} to PrPSc. Moreover, the His111- containing fragment PrP(106-126) has properties similar to those of PrP^{Sc}, it is neurotoxic and generates H_2O_2 in the presence Cu(II), reducing agents and O_2 [4]. Cu(II) binding to this site has two coordination modes (3N1O and 4N) that are present at physiological pH [5, 6]. In this work, we study the coordination of Cu(I) to His111 in the PrP(106-115) fragment, both theoretically and experimentally. In particular, the structural properties of the PrP(106-115)-Cu(I) complex have been probed by X-ray absorption spectroscopy (XAS) and Nuclear Magnetic Resonance (NMR). Plausible coordination modes for the Cu(I) forms have been modeled with the full PrP(106-113) peptide, within the approximation of linear combination of Gaussian orbitals to solve Kohn-Sham equations (LCGTO-KS), as implemented in the program deMon2k [7]. Our results indicate that the PrP(106-115)-Cu(I) complex is also dependent on pH: at low pH it involves a NO2S coordination mode with the two sulphurs of Met109 and Met12, while at high pH a 2NOS coordination mode is favored, with a single Met residue bound to Cu(I). These results contribute to our understanding of the redox properties of this Cu binding site and provide insight into plausible mechanisms for copper transport by PrP^{C}.

[1] S. B. Prusiner, *Proc. Natl. Acad. Sci. USA*, **1998**, *95*, 13363-13383
[2] Jackson, G. S., et al. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 8531–8535.
[3] Klewpatinond, M. J., et al. *J. Biol. Chem.* **2008**, *283*, 1870–1881.
[4] Turnbull, S., et al. *Neurosci. Lett*. **2003**, *336*, 159–162.
[5] Rivillas-Acevedo, L., et al. *Inorg. Chem*. **2011**, *50*, 1956-1972
[6] Quintanar, L. et al. *Coord. Chem. Rev*. **2013**, *257*, 429-444.
[7] Köster, A., et al. deMon2k, 2.5.1; The International deMon Developers: Mexico D.F., Mexico, 2009.

Theoretical study of the catalytic dehydration of glycerol

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The catalytic dehydration of glycerol was investigated using the Density Functional Theory as it is implemented in the deMon2k code [1]. Dehydration of glycerol has been studied considering a step by step mechanism. Geometry optimizations and frequency analysis were performed with the non-local PBE [2] functional and the TZVP basis set. The uphill trust region methodology [3,4] was employed for the local transition state search. In order to generate the connectivity between reactants, transition states, intermediates and products, intrinsic reaction coordinate calculations were performed with González-Schlegel algorithm [5,6].

References:

[1] AM. Koster, G. Geudtner, P. Calaminici, M.E. Casida, V.D. Dominguez, R. Flores-Moreno, G.U. Gamboa, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J.M. Del Campo, J.U. Reveles, A. Vela, B. Zuniga-Gutierrez y D.R. Salahub, deMon2k, Version 3, *The deMon developers,* Cinvestav, Mexico City (2011).
[2] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett*., **1996**, 77, 3865
[3] P. Culot, G. Dive, V.H. Nguyen, J.M. Ghuysen, *Theor. Chim. Acta,* **1992**, 82, 189 .
[4] J.M. Bofill, *J. Comput. Chem*., **1994**, 15, 1 .
[5] C. Gonzalez, H.B. Schlegel, *J. Chem. Phys*., **1989**, 90, 2154 .
[6] C. Gonzalez, H.B. Schlegel, *J. Chem. Phys*., **1991**, 95, 5853.

Development of batteries making use of deMon2k and charge transfer theory

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In the current scenario, to develop a new methodology to design a battery, it is important to know about electrodes used. The material of the electrodes will determine the charge transfer properties and, therefore, the voltage and current of the battery. Redox reactions are usually employed together with many electrochemical techniques for experimental characterization. In this work we propose to complement with exhaustive use of Quantum Chemistry calculations for describing the basic charge transfer phenomena, aiming to achieve more effective development of new batteries. The deMon program will be used for developing a Ni-MH battery, where the M parameter is a metal or alloy. This software was choosed for theoretical analysis that leads to the selection of M due to is capability for treating properly transition metal properties and computing models with hundreds of atoms. However, an extension to GWA calculations is required in order to improve reliability of charge transfer calculations.