

**WHICH MATERIAL IS BEST FOR ORGANIC PHOTOVOLTAICS? A  
MASSIVE QUANTUM CHEMISTRY SEARCH BY MEANS OF THE HARVARD  
CLEAN ENERGY PROJECT**

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In this talk, I will describe our group's efforts related to *The Clean Energy Project*, a large-scale volunteer-donor distributed computing project to find the best donor and acceptor materials for organic photovoltaics. I will describe our progress towards the goal of an automated search for high-performance materials. We have currently computed the electronic structure of 2.8 million candidate oligomer building blocks, and successfully carried out a related theory to experiment demonstration jointly with the group of Zhenan Bao at Stanford. I will describe the status and plans for the project, including the release of our top candidate list of compounds. I will relate this briefly to our studies of quantum coherence in photosynthesis.

## Isotope effects in molecular ionization

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The use of nuclear molecular orbitals, besides of the usual electronic molecular orbitals, allows for extension of wave function methods like Hartree-Fock [1] and the orbital based density functional theory approach of Kohn-Sham [2]. Taking advantage of these previous developments we are working on the further extension for electron propagator theory [3] and auxiliary density perturbation theory [4]. The purpose is to recover adiabatic corrections, isotopic effects and new molecular descriptors related to the molecular ionization processes. Among these descriptors are electron binding energies, hydrogen binding energies, polarizability, hardness, Fukui functions and vibronic coupling constants. The new developments are outlined and a few numerical and graphical examples will be shown in this presentation.

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[1] S. González, N. Aguirre, A. Reyes, *Int. J. Quantum Chem.* **108**, 1742 (2008).

[2] F. Moncada, R. Flores-Moreno, A. Reyes, *submitted* (2011).

[3] J. Linderberg, Y. Öhrn, *Propagators in Quantum Chemistry*, (Academic, London, 1973).

[4] R. Flores-Moreno, A. M. Köster, *J. Chem. Phys.* **128**, 134105 (2008).

## CHEMICAL ACCURACY IN NOF THEORY

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The idea of a one-particle reduced density matrix (1-RDM) functional appeared few decades ago [1]. The 1-RDM functional is called Natural Orbital Functional (NOF) when it is based upon the spectral expansion of the 1-RDM [2]. An approximate NOF requires an expression of the two-particle reduced density matrix (2-RDM) in terms of the 1-RDM. Such reconstruction of the 2-RDM has been achieved using the cumulant expansion leading to the Piris NOF (PNOF) [3]. The PNOF is based on an explicit ansatz of the two-particle cumulant  $\lambda(\Delta, \Pi)$  satisfying the D-, Q- and G-necessary positivity conditions for the 2-RDM [4]. Appropriate forms of matrices  $\Delta(\{n_p\})$  and  $\Pi(\{n_p\})$  lead to different implementations of the PNOF [5]. In this presentation, the theory behind the PNOF is outlined. Special emphasis will be put on the spin conserving NOF theory [6] and on the recent proposed algorithm [7] which yields the natural orbitals by an iterative diagonalization of a generalized Hermitian matrix. The theory is applied to atoms and selected molecules formed with them. Several reactions are also investigated to illustrate the potentiality of NOF theory to yield the correct topology of potential energy surfaces that are sensible to electron correlation. Our NOF yields a remarkable accurate description of the homolytic dissociation of selected diatomic molecules. It is found that the method describes correctly the dissociation limit yielding an integer number of electrons on the dissociated atoms. Compounds with full or partial diradical character have been also considered. We have found that PNOF shows a promising description of these species, and yield the correct trends in occupation numbers as compared with wave-function methods such as CASSCF. The calculations carried out by our implementation, the PNOFID code [8], have produced very accurate values as compared to high level wave function methods and available experimental data.

[1] T. L. Gilbert, *Phys. Rev. B*, **12**, 2111 (1975); M. Levy, *Proc. Natl. Acad. Sci. U.S.A.*, **76**, 6062 (1979);

S. M. Valone, *J. Chem. Phys.*, **73**, 1344 (1980).

[2] M. Piris, *Adv. Chem. Phys.*, **134**, 387 (2007).

[3] M. Piris, *Int. J. Quantum Chem.*, **106**, 1093 (2006).

[4] D. A. Mazziotti, *Adv. Chem. Phys.*, **134**, 21 (2007).

[5] M. Piris, X. Lopez, J. M. Ugalde, *J. Chem. Phys.*, **126**, 214103 (2007); M. Piris, J. M. Matxain, X. Lopez,

J. M. Ugalde, *J. Chem. Phys.*, **132**, 031103 (2010); *J. Chem. Phys.*, **133**, 111101 (2010); M. Piris, X. Lopez,

F. Ruipérez, J. M. Matxain, J. M. Ugalde, *J. Chem. Phys.*, **134**, 164102 (2011)..

[6] M. Piris, J. M. Matxain, X. Lopez, J. M. Ugalde, *J. Chem. Phys.*, **131**, 021102 (2009).

[7] M. Piris, J. M. Ugalde, *J. Comp. Chem.*, **30**, 2078 (2009).

[8] M. Piris, PNOFID, downloadable at <http://www.ehu.es/mario.piris/#Software>.

# Chemical bonding in supermolecular flowers

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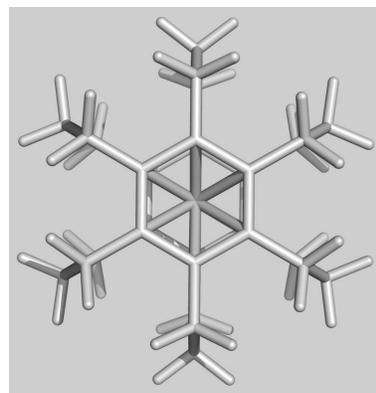
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Metal-ligand bonding patterns play an important role in the stability of transition-metal complexes and their spin state preferences. In previous studies<sup>[1,2,3]</sup> we have looked at several TM-complexes, and found that covalent bonding is often the most important factor to distinguish different metals, and different spin states. In terms of bonding energy, the electrostatic interactions and Pauli repulsion contributed significantly, but these contributions were more or less constant for different metals.

The past studies focused on metallocenes,<sup>[1]</sup> metalloporphyrins<sup>[2]</sup> and dibenzene-species.<sup>[3]</sup> Here we extend the series by looking at several supermolecules, which have the form of ice-flowers (see Figure). We have investigated the stability, electronic structure and spin ground-state for a number of alkaline-earth and transition metals using the recently developed SSB-D functional.<sup>[4]</sup> The supermolecules show resemblances to the systems studied before, but also some striking differences were observed. Similar to our previous study,<sup>[2]</sup> we have also investigated how the metal-ligand interactions influence the aromaticity of these interesting clusters.



## References

- [1] M. Swart, *Inorg. Chim. Acta* ("Inorganic Chemistry - The Next Generation" issue) **2007**, *360*, 179-189
- [2] F. Feixas, M. Solà, M. Swart, *Can. J. Chem.* (Tom Ziegler issue) **2009**, *87*, 1063-1073
- [3] M.P. Johansson, M. Patzschke, *Chem. Eur. J.* **2009**, *15*, 13210-13218
- [4] M. Swart, M. Solà, F.M. Bickelhaupt, *J. Chem. Phys.* **2009**, *131*, 094103

# STRUCTURE AND BONDING IN SMALL HYDROGEN BONDING NETWORKS

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## ABSTRACT

We study several cases of small clusters stabilized via hydrogen bonding networks (HBN). Pure HBN systems (water tetramer, pentamer, hexamer, methanol tetramer, carbonic acid dimer) as well as microsolvation effects in charged solutes ( $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{e}^-$ ) are discussed in detail. Equilibrium geometries are obtained after gradient following based optimization of randomly generated Markov chains of cluster candidate structures that populate the vicinities of local minima in quantum conformational spaces. We present and discuss evidence to support the following main results:

(i) Very rich and complex Potential Energy Surfaces are obtained (ii) Electrostatic interactions in the form of cooperative polarization seem to be the driving forces behind cluster stabilization and configuration (iii)  $n = 6$  is the transition point in planar to 3D geometrical preferences for water microclusters; this number is related to the topological complexity of the charge distributions in the clusters: only after the water hexamer, cage critical points are predicted (iv) Cyclic, compact structures are preferred, unless temperature and entropy are taken into account: at sufficiently high temperatures, more open, less stable structures are preferred, eventually leading to the existence of individual molecules (v) High levels of electron correlation and extended basis sets are needed for accurate prediction of relative energies: for the water hexamer, not even CCSD(T) calculations can resolve the global minimum (vi) Relative energies correlate linearly with the electron densities and its Laplacians at the bond criticalpoints (vii) The length of the hydrogen bonds correlate in a logarithmic fashion with the electron densities and its Laplacians at the hydrogen bond critical points (viii) The number of hydrogen bonds does not dictate stability of the clusters (ix) There is partial water dissociation in the first solvation shell of  $\text{Mg}^{2+}$ ,  $\text{F}^-$  but not in the  $\text{Li}^+$  (not enough charge) nor  $\text{Ca}^{2+}$  (highly screened valence electrons) cases.

# RESONANCES IN ULTRAFAST LASER ASSISTED MOLECULAR PROCESSES: FROM THEORY TO EXPERIMENT.

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Intense laser fields produce strong internal distortions in molecules and induce selective dynamical effects that can be exploited in designing control strategies. These strategies rest on some resonances and their underlying basic mechanisms which act either in complementary or antagonistic ways. In the high frequency visible-UV wavelength regime, the molecule feels an optical cycle-averaged force field. Its dynamics is described through a Floquet representation based on light-induced potentials. The strong radiative interaction generally facilitates fragmentation through the Bond Softening (BS) process, which results from the lowering of some potential barriers accomodating *shape resonances*. More unexpectedly, the dissociation may, under specific conditions, be delayed or even suppressed through the complementary, non-intuitive, Vibrational Trapping (VT) that occurs for *Feshbach resonances* supported by some “upper” adiabatic potentials. In the low frequency IR wavelength regime, a quasi-static adiabatic picture is appropriate. The molecular vibrational motion follows the field’s oscillations. An appropriate synchronization, either completely suppress potential barriers, or produces reflection of the wavepacket on them. This is the Dynamical Dissociation Quenching (DDQ) mechanism. BS and VT have been well documented in the literature [1,2], whereas a first experimental confirmation has only been recently given for DDQ [3,4]. The interpretation, control and imaging of a variety of molecular processes ranging from photofragmentation (ionization/dissociation), to alignment/orientation, molecular vibrational transfer and cooling, electron diffraction, high order harmonic generation or attosecond pulse production can be done by referring to and appropriately combining these basic multiphoton mechanisms [5,6]

Very recently, not only intense but ultrashort laser pulses (in the attosecond time scale) have been used in pump-probe experiments to reach real-time imaging of ultrafast molecular phenomena. Here we report a theory versus experiment comparison on the dissociative ionization of  $H_2$  in a two-color extreme ultra-violet (XUV attopulse pump) + infrared (intense probe) field, where variation of the pulse duration of the IR laser affects the adiabaticity of the multiphoton dissociation, as manifested in the proton kinetic energy distributions that can be measured, as a function of a variable delay between the two pulses. A detailed interpretation is worked out, based on resonances and their underlying basic mechanisms. We show, in particular, that the dynamics depends considerably on the properties of the IR radiation and whether or not the IR laser is already present when the molecule is ionized by the XUV pulse [8].

- [1] A. Giusti-Suzor, X. He, O. Atabek and F.H. Mies, *Phys. Rev. Lett.* **64**, 515 (1990)
- [2] P.H. Bucksbaum, A. Zavriyev, H.G. Muller and D.W. Schumacher, *Phy. Rev. Lett.* **64**, 1883 (1990)
- [3] F. Châteauneuf, T.T. Nguyen-Dang, N. Ouellet and O. Atabek, *J. Chem. Phys.* **108**, 3974 (1998)
- [4] H. Nikura, P.B. Corkum and D.M. Villeneuve, *Phys. Rev. Lett.* **90**, 203601 (2003)
- [5] O. Atabek, R. Lefebvre, C. Lefebvre and T.T. Nguyen-Dang, *Phys. Rev. A* **77**, 043413 (2008)
- [6] R. Lefebvre, O. Atabek, M. Sindelka and N. Moiseyev, *Phys. Rev. Lett.* **103**, 123003 (2009)
- [7] O. Atabek, R. Lefebvre, M. Lepers, A. Jaouadi, O. Dulieu and V. Kookouline, *Phys. Rev. Lett.* (in press)
- [8] F. Kelkensberg, C. Lefebvre, W. Siu, O. Ghafur, T.T. Nguyen-Dang, O. Atabek, A. Keller, V. Serov, P. Johnsson, M. Swoboda, A. L’Huillier, G. Sansone, M. Nisoli, E. Benedetti, F. Ferrari, F. Lépine, M.F. Kling and M.J.J. Vrakking, *Phys. Rev. Lett.* **103**, 123005 (2009)

# New approximation to the $n$ -order reduced density matrix and its application to multicenter bond indices

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There has been renewed interest in the calculation of multicenter bond indices based on the electron density matrices.<sup>1-12</sup> Multicenter indices have been employed in a number of situations such as the analysis of conjugation and hyperconjugation effects,<sup>7</sup> to identify agostic bonds,<sup>8</sup> to account for electron distributions in molecules<sup>4-5</sup> or to study aromaticity in both organic<sup>10</sup> and all-metal compounds.<sup>11</sup> The general formula of the multicenter index involves the intuitive  $n$ -order central moment of the electron population used in probability theory.<sup>13,14</sup>

$$D(A_1, \dots, A_n) \sim \left\langle \left( \hat{N} - \bar{N} \right)^n \right\rangle_{A_1, \dots, A_n},$$

which depends on the  $n$ -order reduced density matrix ( $n$ -RDM). The calculation of the  $n$ -RDM is overwhelmingly expensive for correlated wavefunctions and, therefore, the studies of multicenter indices available in the literature have used at most the 3-RDM. In this talk we analyze different multicenter indices suggested in the literature, which depend either on the corresponding  $n$ -RDM or their approximation in terms of lower-order densities. We also suggest new approximations for the  $n$ -RDM, which we use in the calculation of three- and four-center bond indices.<sup>15</sup>

[1] M. Giambiagi, M. S. d. Giambiagi, C. D. dos Santos Silva, and A. P. de Figueiredo, *Phys. Chem. Chem. Phys.* **2000**, 2, 3381. [2] P. Bultinck, R. Ponec, and S. Van Damme, *J. Phys. Org. Chem.* **2005**, 18, 706. [3] J. Cioslowski, E. Matito, and M. Solà, *J. Phys. Chem. A* **2007**, 111, 6521. [4] A. M. Pendás, E. Francisco, and M. A. Blanco, *Phys. Chem. Chem. Phys.* **2007**, 9, 1087. [5] A. M. Pendás, E. Francisco, and M. A. Blanco, *J. Chem. Phys.* **2007**, 127, 144103. [6] R. Ponec and I. Mayer, *J. Phys. Chem. A* **1997**, 101, 1738. [7] F. Feixas, E. Matito, J. Poater, and M. Solà, *J. Phys. Chem. A* DOI:10.1021/jp205152n. [8] F. Feixas, E. Matito, J. Poater, F. Maseras and M. Solà, *in preparation*. [9] P. Bultinck, *Faraday Discuss.* **2007**, 135, 347. [10] F. Feixas, E. Matito, M. Duran, J. Poater, and M. Solà, *Theor. Chem. Acc.* **2011**, 128, 419. [11] F. Feixas, J. O. C. Jiménez-Halla, E. Matito, J. Poater, and M. Solà, *J. Chem. Theory Comput.* **2010**, 6, 1118. [12] F. Feixas, E. Matito, J. Poater, and M. Solà, *J. Comput. Chem.* **2008**, 29, 1543. [13] M. Giambiagi, M. Giambiagi, and K. Mundim, *Struct. Chem.* **1990**, 1, 423. [14] E. Francisco, A. M. Pendás, and M. A. Blanco, *J. Chem. Phys.* **2007**, 126, 094102. [15] F. Feixas, M. Solà, J.M. Barroso, J.M. Ugalde, E. Matito, *in preparation*.

## **Muon alchemy: Transmuting elements with the inclusion of negative muons**

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Recent experiments have revealed that the chemical nature of helium atom is changed into that of hydrogen by the inclusion of a negative muon [1]. In this talk we explore the effects of replacing electrons by negative muons in atoms with  $Z = 1-20$ . These studies have been performed with the non-relativistic any particle molecular method implemented on the LOWDIN software. Results for atomic and molecular properties of these exotic systems are presented.

[1] D. G. Fleming, et al. Science 331, 448 (2011)

# PROTEINS IN MOTION

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Structural biology has played a major role in the way we understand the way protein operates and work. Still the knowledge of the structure alone offers a limited insight into the protein dynamics. In this respect molecular dynamics can play a major role in complementing the experiments and in getting precious dynamical information. However biomolecules are characterized by complex and rough landscapes and their functionality relies in a delicate balance between enthalpy and entropy. Accurate sampling of the phase space is therefore necessary but the limited time scale that is accessible with modern commercially available computers hampers it. Accelerated sampling techniques are therefore necessary. Here we discuss metadynamics which allows efficient sampling and permits an accurate reconstruction of the free energy landscape. In metadynamics, sampling is accelerated by a time dependent bias that acts on a small number of collective variables. An appropriate choice of the collective variables leads to some spectacular success that will be illustrated with a number of examples. We shall also describe a novel variant of metadynamics, which we call reconnaissance metadynamics in which machine learning techniques are used to find automatically the collective variables and reconstruct the free energy landscape.

# The Reaction Electronic Flux in Chemical Processes\*

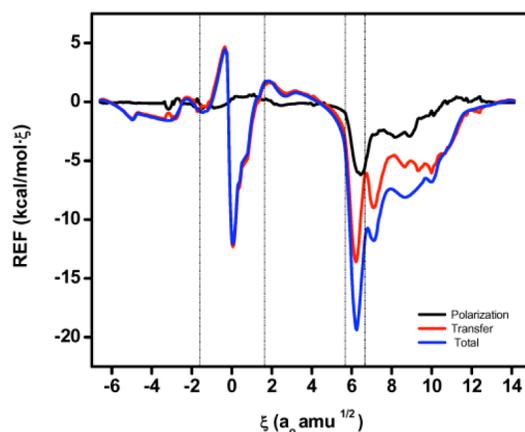
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The mechanism of a chemical reaction can be characterized in terms of chemical events that take place during the reaction, these events are bond weakening/breaking and/or bond strengthening/forming. The reaction electronic flux (REF)<sup>1-3</sup>, a new concept that identifies and rationalizes the electronic activity taking place along the reaction coordinate has emerged recently as a powerful tool for characterizing the mechanism of chemical reactions. In this talk, a quantitative theory introducing new descriptors for characterizing reaction mechanisms is presented. The theory is then illustrated with few representative examples in which special attention is devoted to the quantification of the energetic cost associated to specific electronic activity and the phenomenological characterization of the REF in terms of electronic polarization and transfer effects. The Figure displays the contributions to the REF in the methanol decomposition reaction catalyzed by copper oxide<sup>4</sup>.



## References

- [1] B. Herrera and A. Toro-Labbé. *J. Phys. Chem. A*, **111** (2007) 5921.
- [2] E. Echegaray and A. Toro-Labbé. *J. Phys. Chem. A*, **112** (2008) 11801.
- [3] S. Vogt-Geisse and A. Toro-Labbé. *J. Chem. Phys.*, **130** (2009) 244308.
- [4] M.L. Cerón, B. Herrera, P. Araya, F. Gracia, and A. Toro-Labbé. *J. Mol. Mod.*, **17** (2011) 1625.

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# Non-empirical global hybrids based on PBE exchange-correlation

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Global hybrids combine a fraction of the exact exchange with an approximate exchange-correlation energy functional. In the present work, the combination<sup>1</sup>

$$E_{XC}^{\text{hyb}} = E_{XC}^{\text{GGA}} + a_0 (E_X^{\text{exact}} - E_X^{\text{GGA}}),$$

where  $E_{XC}^{\text{hyb}}$  and  $E_{XC}^{\text{GGA}}$  are the hybrid and the generalized gradient approximation (GGA) exchange-correlation functionals, respectively,  $E_X^{\text{GGA}}$  is the exchange part of the GGA,  $E_X^{\text{exact}}$  is the exact exchange, and  $a_0 = 1/4$ ,<sup>2,3</sup> will be used to validate several non-empirical parameterizations of the PBE GGA functional through the calculation of 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, using specific test sets designed for these properties.

The results indicate that although PBE0,<sup>4</sup> which makes use of the original parameters of PBE, provides a rather good description of these properties, the predictions of several of them are improved when different constraints are used to fix the values of the parameters contained in the expression of the PBE exchange-correlation energy functional.

## References

1. A. D. Becke, J. Chem. Phys. **104**, 1040 (1996).
2. J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
3. C. Adamo and V. Barone, Chem. Phys. Lett. **274**, 242 (1997).
4. C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).

# Symmetry Breaking and Restoration

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We have derived and implemented symmetry-projected Hartree-Fock-Bogoliubov (HFB) equations and apply them to the molecular electronic structure problem. All symmetries (particle number, spin, spatial, and complex conjugation) are deliberately broken and restored in a self-consistent variation-after-projection approach. We show that the resulting method yields a comprehensive black-box treatment of static correlation with effective one-electron (mean-field) computational cost. The ensuing wave function is of multireference character and permeates the entire Hilbert space of the problem. The energy expression is an independent quasiparticle density matrix functional. All reduced density matrices are expressible as an integration of transition one-particle density matrices over a gauge grid. I will present several proof-of-principle examples demonstrating the compelling power of this new method for electronic structure theory [1].

[1] Projected Quasiparticle Theory for Molecular Electronic Structure, G. E. Scuseria, C. A. Jimenez-Hoyos, T. M. Henderson, J. K. Ellis, and K. Samanta, *J. Chem. Phys.* to appear 7-Oct-11.

# DESCRIBING THE REACTIVITY OF COMPLEX MOLECULAR SYSTEMS: THE BALANCE BETWEEN ELECTRON TRANSFER AND ELECTROSTATIC EFFECTS.

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When a reaction is only electron transfer controlled, the chemical potential and hardness explain most of the electron transfer and the Fukui function determines the reactive sites. If the reaction is totally electrostatically controlled, the electrostatic potential is often enough to determine the active site. But, how does one know if a reaction is electron transfer or electrostatically controlled? Even worse, what if one is interested in reactions where both effects are important? In this talk I would address these problems by presenting a computational method able to describe not only the balance between electron transfer and electrostatic effects, but even complicated situations where polarizability and higher-order effects could be decisive. The method relies entirely on the design of simplified pseudoatomic probes (a perturbing agent) that share (mimic) important properties with the reactive site of actual reagents. I expect a broad applicability of this approach, including gas phase molecules important in environmental atmospheric chemistry, small organic molecules, organometallic catalysts, nanostructures, and biological applications

## ENERGY ADDITIVITY IN LINEAR MOLECULES

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Several properties of some linear molecules, both macroscopic and microscopic, show regular trends with respect to the chain length. The linear behavior of the total molecular energy of linear alkanes and other families of linear molecules can be rationalized by using the Kohn-Sham method of density functional theory. Applying a space partitioning scheme and a fragment approach to the Kohn-Sham functional, one can show that, under a fragment transferability assumption, the total molecular energy of linear molecules, like the n-alkanes and other related compounds, is a monotonically increasing function of the chain length.

# APPLICATIONS OF ELECTROPHILICITY AND NUCLEOPHILICITY INDICES IN ORGANIC CHEMISTRY

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The electrophilicity and nucleophilicity descriptors defined within the conceptual DFT are very useful theoretical tools that allow for a rationalization of the reactivity for an important number of organic reactions.

In this talk we review recent developments and applications of theoretical scales of electrophilicity and nucleophilicity for a series of chemical reactions in organic chemistry, including Diels-Alder reactions and 1,3-dipolar cycloadditions.

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# Metal Cluster Structures and Properties

## from Born-Oppenheimer Molecular Dynamics

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Density functional theory (DFT) Born-Oppenheimer molecular dynamics (BOMD) simulations of metal clusters are presented. The calculations have been performed with the deMon2k [1] code employing all-electron basis sets and local and non-local functionals. The capability of reasonable long (~ 100 ps) first-principle BOMD simulations to explore potential energy landscape of metallic clusters will be presented [2,3]. The evolution of the cluster structures and properties such as polarizability and heat capacity [2,4-6], at different temperature, will be discussed.

[1] A.M. Köster, P. Calaminici, M.E. Casida, R. Flores-Moreno, G. Geudtner, A. Goursot, T. Heine, A. Ipatov, F. Janetzko, J.M. del Campo, J.U. Reveles, A. Vela, B. Zuniga and D.R. Salahub, *deMon2k*, Version 2, The deMon developers, Cinvestav, Mexico (2006), <http://www.demon-software.com>;

[2] G.U. Gamboa, P. Calaminici, G. Geudtner, A.M. Köster, *J. Phys. Chem. A* **112** 11969 (2008);

[3] J.M. Vásquez-Pérez, G.U. Gamboa-Martínez, A.M. Köster, P. Calaminici, *J. Chem. Phys.* **131** 12412 (2009);

[4] G.U. Gamboa, J.M. Vásquez-Pérez, P. Calaminici, A.M. Köster, *Internat. J. of Quantum Chem.* **110** 2172 (2010)

[5] P. Calaminici, A.M. Köster, J.M. Vásquez-Pérez, G.U. Gamboa Martínez, ICCMSE Conference Proceedings, edited by G. Maroulis and T. Simos, in press (2011);

[6] J.M. Vásquez-Pérez, G.U. Gamboa-Martínez, A.M. Köster, P. Calaminici, *to be submitted*.

## DFT CALCULATIONS APPLIED TO THE STUDY OF

- the reaction mechanism of DIALKYL DIALCOXY STANNANE with CO<sub>2</sub> for the catalytic DIALKYL CARBONATE synthesis,

- the fragmentation mechanism of DNA bases.

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### ABSTRACT TEXT

The insertion of CO<sub>2</sub> into the Sn-OCH<sub>3</sub> bond of dialkyldimethoxystannanes is recognized as the first step to dimethyl carbonate (DMC) formation from methanol and carbon dioxide. The identification of the subsequent steps is crucial for activity improvements and is still under debate as the tin species have the propensity for oligomerization. For the purpose, we undertook a modeling study on the system (CH<sub>3</sub>)<sub>2</sub>Sn(OCH<sub>3</sub>)<sub>2</sub>/CO<sub>2</sub>/ CH<sub>3</sub>OH for determining reaction channels to DMC formation. Further calculations have been performed with n-butyl, isopropoxy and ethoxy ligands and pointed out a unique step where a steric effect occurs, leading to an improved efficiency of the reaction. DFT calculations were performed with ADF software, a TZP basis set, and PBE as GGA exchange – correlation functional.

The study of the radiation and fragmentation of DNA bases is an important field of research in radiobiology where it is essential to understand the mechanism leading to the cell death or cell transformations. Experimental studies have been carried out by using ionic impact techniques and mass spectroscopy on DNA/RNA bases. Systematic investigations at DFT/GGA level on the various DNA base fragmentations have been undertaken. The electronic and geometric data analyses of both of the ionized and radical fragments allow one to predict the weakest bonds that might be broken first, leading to a limited number of particular fragments, the cations being experimentally detected.

# The Profiles of electron delocalization indices characterize the nature of chemical interactions

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The Quantum Theory of Atoms in Molecules (QTAIM) developed by R. Bader and coworkers [1], based on a partitioning of the real space through the gradient of the electrons density, is one of the most fruitful theories of the chemical bond developed in the last few decades as alternatives to the dominant molecular orbital (MO) paradigm [2]. Recently, the well known result of the theory that identifies the existence of a bond critical point (BCP) with a pair of bonded atoms [3] has been put into question, for BCPs are found where chemists will not place them, and vice versa [4,5]. A lively debate, in our opinion far from over, has arisen regarding the meaning of BCPs in situations commonly referred to steric or repulsive [5,6]. Based on the Interacting Quantum Atoms (IQA) approach [7], some of us have tried to shed some light on the matter by a reinterpretation of the meaning of the BCPs [8], whereby bond paths of the QTAIM signal privileged exchange-correlation ( $x_c$ ) channels between pairs of atoms that always provide a locally stabilizing energetic term ( $V_{xc}$ ) to the total energy. Since  $V_{xc}$  is just one of the terms in the IQA approach, this view makes the presence of BCPs fully compatible with global destabilizations. The close relationship of the topology of the electron density to the energetic properties of a system offers an important contribution to the physical meaning of the BCPs and to the partitioning of space provided by the QTAIM. Following these ideas, we believe that by using global or domain-integrated properties useful insights about the nature of chemical interactions will be found. In this work, we analyze the behavior of one of these domain-integrated properties, the shared electron delocalization index (SEDI or DI), to reveal an important connection between its profile along a reaction coordinate and the nature of chemical change associated with it.

## REFERENCES

- [1] R. F. W. Bader, *Atoms in Molecules*; Oxford University Press: Oxford, 1990.
- [2] B. M. Gimarc, *Molecular Structure and Bonding. The Qualitative Molecular Orbital Approach*; Academic Press: New York, 1979.
- [3] R. F. W. Bader, *J. Phys. Chem.* 1998, **102**, 7314.
- [4] L. J. Farrugia, C. Evans, and M. Tegel, *J. Phys. Chem.* 2006, **110**, 7952.
- [5] A. Haaland, D. J. Shorokhov, and N. V. Tverdova, *Chem. Eur. J.* 2004, **10**, 4416.
- [6] R. F. W. Bader and D.-C. Fang, *J. Chem. Theory Comput.* 2005, **1**, 403; J. Poater, M. Solà, and F. M. Bickelhaupt, *Chem. Eur. J.* 2006, **12**, 2889; J. Poater, M. Solà, and F. M. Bickelhaupt, *Chem. Eur. J.* 2006, **12**, 2902; R. F. W. Bader, *Chem. Eur. J.* 2006, **12**, 2902; J. Poater, R. Visser, M. Solà, and F. M. Bickelhaupt, *J. Org. Chem.* 2007, **72**, 1134.
- [7] A. Martín Pendás, M. A. Blanco, and E. Francisco, *J. Comput. Chem.* 2007, **28**, 161; M. A. Blanco, A. Martín Pendás, and E. Francisco, *J. Chem. Theory Comput.* 2006, **1**, 1096; E. Francisco, A. Martín Pendás, and M. A. Blanco, *J. Chem. Theory Comput.* 2006, **2**, 90.
- [8] A. Martín Pendás, E. Francisco, M. A. Blanco, and C. Gatti, *Chem. Eur. J.* 2007, **13**, 9362.

# **De la Chimie théorique explicative à la chimie prédictive :**

## **L'exemple de la modélisation des spectres vibrationnels**

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### ABSTRACT

Depuis longtemps la chimie théorique a permis d'expliquer et comprendre des faits expérimentaux et d'interpréter ainsi les données issues de l'expérience. Ces expériences ne sont pas toujours facilement réalisables dans des conditions de laboratoire aussi est-on tenté de se demander si les résultats issus de la modélisation ne peuvent être, à terme, considérés comme aussi fiables que ceux issus de l'expérimentation et les remplacer. Cette chimie théorique prédictive est utilisée aujourd'hui pour guider l'expérimentateur et dans ce domaine la spectroscopie, notamment vibrationnelle, en est un exemple marquant.

Dans cette conférence sera présentée une approche comparative de modélisation des spectres vibrationnels (essentiellement IR) à partir d'un processus quantique indépendant du temps prenant en compte les termes anharmoniques de la fonction potentielle et d'une approche de dynamique moléculaire dans laquelle la matrice densité est propagée (ADMP).

Les avantages et les inconvénients de ces deux traitements seront brièvement analysés en considérant des systèmes moléculaires de type semi-rigide et des molécules flexibles pour lesquelles des mouvements de grande amplitude sont attendus.

Quelques exemples de calculs seront présentés afin de montrer que ces calculs restent d'une grande utilité pour guider les interprétations des spectres expérimentaux mais aussi d'une grande fiabilité pour les prédire de manière, quand cela est possible, de les revisiter expérimentalement.

# CHARGE TRANSFER AND SPIN POLARIZATION WITHIN THE SPIN-POLARIZED VERSION OF DENSITY FUNCTIONAL THEORY.

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Charge transfer and spin polarization are central aspects of any description of chemical reactivity. In this context *reactivity* is simply understood as the intrinsic response of a given chemical system against perturbations.

In this talk we review and discuss recent developments and applications of theoretical approximations focused on rationalize and predict the magnitude and intensity of both charge transfer and spin polarization phenomena. These advances are based on the so-called spin-polarized version of density functional theory, contributing to extend the building of a more complete picture of reactivity based on global, local and non-local electronic and nuclear reactivity descriptors.

**Acknowledgements.** We thank to FONDECYT (CHILE) by continuous support through of our research on formal and applied aspects related to the development of a chemical reactivity theory founded on the density functional theory framework. Particularly, contract grants Nos. 1100278, and 1100277 are acknowledged. E. Ch. And P. P also thank the Universidad Andres Bello for support through Projects DI 57-11/R and DI 35-10/R, respectively.

## Estudios computacionales revelan diferencias entre cationes mutagénicos e inhibidores en la ADN polimerasa $\lambda$

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Las ADN polimerasas requieren dos cationes metálicos en el sitio activo para realizar la reacción de polimerización. El  $Mg^{2+}$  ha sido confirmado como el catión mas probable usado por la mayoría de las polimerasas *in vivo*. Otros iones metálicos pueden ser potentes agentes mutagénicos o inhibidores. Presentaremos resultados de análisis topológico basados en cálculos híbridos QM/MM de la ADN polimerasa  $\lambda$  con diferentes metales en el sitio activo. Nuestros resultados muestran cambios estructurales menores cuando cationes mutagénicos o inhibidores ocupan el sitio activo. Los análisis topológicos de la función de localización electrónica (ELF) revelan una “separación” de la densidad electrónica de la capa exterior para todos los metales excepto  $Na^+$  y  $Mg^{2+}$ . La población electrónica y análisis multipolar en las cuencas de la ELF muestran que la polarización e hiper-polarización electrónica es completamente diferente para los metales mutagénicos e inhibidores comparadas con el catión natural. Nuestros resultados muestran las diferencias sutiles al nivel electrónico de los efectos de diferentes metales en el sitio activo de las ADN polimerasas. Estos resultados proveen una correlación entre la distribución electrónica de los cationes en el sitio activo y las posibles consecuencias en la síntesis de ADN.

# Obtaining the Free Energy for Unravelling a Protein by Adaptive Steered Molecular Dynamics (ASMD)

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The behavior and function of proteins necessarily occurs during nonequilibrium conditions such as when a protein unfolds or binds. The high-dimensionality of these systems—because of the large number of atoms in the proteins and their environments—presents significant challenges to theoretical or computational methods. The present work attempts to reign in this complexity by way of capturing the dominant energetic pathway in a particular protein motion. In particular, the energetics of an unfolding event can be formally obtained using steered molecular dynamics (SMD) and Jarzynski's inequality but the cost of the calculation increases dramatically with the length of the pathway. An adaptive algorithm has been introduced\* that allows for this pathway to be nonlinear and staged while reducing the computational cost. The potential of mean force (PMF) obtained for neuropeptide Y (NPY) in water along an unfolding path confirmed that the monomeric form of NPY adopts the pancreatic-polypeptide (PP) fold. Adaptive SMD can also be used to reconstruct the PMF obtained earlier for stretching decaalanine in vacuum<sup>#</sup> at lower computational cost. The PMF for stretching decaalanine in water solvent (using the TIP3P water potential) at 300K has now been obtained using adaptive SMD. Not surprisingly, the stabilization from the water solvent reduces the overall work required to unfold it. However, the PMF remains structured suggesting that some regions of the energy landscape act partially as doorways. This is also further verified through a study of the hydrogen-bond breaking and formation along the stretching paths of decaalanine in vacuum and solvent.

## References

\*G. Ozer, E. Valeev, S. Quirk and R. Hernandez, *J. Chem. Theory Comput.* **6**, 3026-3038 (2010), doi:10.1021/ct100320g.

<sup>#</sup>S. Park and K. Schulten, *J. Chem. Phys.* **120**, 5946 (2004).

## METALS IN PROTEINS

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We present computational studies on the characterization of existing metal coordination spheres in proteins looking at aspects such as the number of metal coordination spheres, coordination numbers, ligands present and their combination, thermodynamic stability and molecular electrostatic potential<sup>1</sup>. We have resorted to QM, MD and hybrid QM/MM calculations as well as to bioinformatics methodologies in our studies<sup>2,3</sup>, which have been very successful in reproducing the existing experimental data.

### References:

- [1] S.F. Sousa, A.B. Lopes, P.A. Fernandes, M.J. Ramos, *Dalton Transactions*, **2009**, 38, 7946-7953
- [2] S.F. Sousa, P.A. Fernandes, M.J. Ramos, *J. Am. Chem. Soc.*, **2007**, 129, 1378-1385
- [3] S.F. Sousa, P.A. Fernandes, M.J. Ramos, *Chem. Eur. J.*, **2009**, 15, 4243-4247

# **Climbing the Perdew's ladder on the cleanest line: the parameter-free functionals**

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The longstanding quest for representing the unknown part of the Kohn-Sham (KS) total energy in Density Functional Theory (DFT), that is the exchange-correlation term, has produced a relevant number of models, which can be grouped following the Perdew's ladder [1], a pictorial yet effective ranking of DF approximations (DFAs). This ranking is associated, in a rather heuristic way, with an improvement of the numerical performances so that higher rungs should correspond to more accurate functionals. However, the best "climbing line" on this ladder is not defined and two routes have been explored: a semi-empirical approach, where functionals are parameterized over a defined number of properties and systems, and first-principle models, which do not contain any fitted variables. Here we show that the latter approach, which can be defined as "the cleanest line on the steepest part of the face" [2], leads to the definition of robust exchange-correlation functionals belonging to the highest rungs of the ladder. In particular, starting from the work of Perdew, Burke and Ernzerhof (PBE) [3], global (PBE0) [4] and double (PBE0-DH) [5,6] hybrids will be derived and tested for a large number of systems and properties .

[1] J. P. Perdew, A. Ruzsinszky, L.A. Constantin, J. Sun and G. I. Csonka J. Chem. Theory Comput. 5, 902 (2009)

[2] Y. Chouinard, leading alpinist, fly fisher and CEO (1968)

[3] J. P. Perdew, M. Ernzerhof and K. Burke, J. Chem. Phys. 105, 9982 (1996).

[4] C. Adamo, V. Barone J. Chem. Phys. 110, 6158 (1999)

[5] E. Brémond, C. Adamo J. Chem. Phys. 135, 024106, (2011)

[6] J.Toulouse, K. Sharkas, E. Brémond, C. Adamo J. Chem. Phys. 135, 101102 (2011)

# METHANE ACTIVATION BY $\text{Cu}^+$ SPECIES

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The activation of alkanes by transition metal cores is a hallmark in catalysis and attracts continuous interest. In particular, the activation of methane and its subsequent conversion into more valuable feedstocks at ambient conditions are regarded as one of the major challenges in contemporary catalysis, due to its thermodynamically strong and kinetically inert C-H bond.

$\text{CuO}^+$  cores have been suggested as the catalytic center in several enzymes and synthetic bioinorganic systems, performing the activation of C-H bonds in methane and small hydrocarbons. Regrettably, this activity has not been proven until very recently, mainly due to the difficulty to produce sufficient amounts of active species to demonstrate the bond activation processes. Furthermore, the methane activation by  $\text{CuOH}^+$ , one of the side products of this reaction, has also been observed.

Such highly elaborate matrix isolation and mass spectrometric techniques enable studies on intrinsic reactivity patterns of isolated TM-ligand cores under well defined conditions.

Quantum chemistry is ideally suited to complement these studies, providing reliable predictions of the thermodynamics, reaction barriers, and electronic structures of many of these species by post Hartree-Fock or density functional theory.

The theoretical study presented here provides a thorough quantum chemical description of the reactive  $\text{CuL}^+$  species, together with a molecular level insight into the elementary steps of the experimentally observed reactions. This has thus permitted us to unravel detailed electronic and mechanistic aspects that will be crucial for elucidating and predicting the chemistry of related active sites based on these building blocks.

# Excited state nonadiabatic molecular dynamics: energy funneling in light harvesting dendrimers

Adrian Roitberg

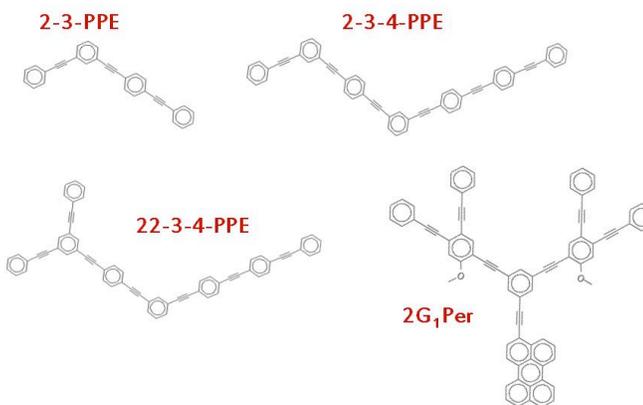
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Dendrimer macromolecules can be thought of as arrays of coupled chromophores with the energy of each unit depending on the backbone structure and conformation. There is a deep interplay between the strength of the coupling between units, dephasing and vibrational energy dissipation channels, and the nature of the energy transfer. Absorption of light in organic solar cells creates excitons that diffuse to a heterojunction, where charge separation occurs. For an efficient photon-to-current conversion, exciton transport process must occur in a time scale shorter than deactivation. It is then critical that we understand the mechanisms for exciton transport and explore the chemical and physical properties that can help speed the process.

Excited state nonadiabatic molecular dynamics simulations are used to study the nature of the energy transfer in different model dendritic molecules built from linear poly-phenylene ethynylene (PPE) units linked:

Dendrimers built from these building blocks have been experimentally shown to undergo, upon excitation, highly efficient and ultrafast unidirectional energy transfer. The simulations start by an initial vertical excitation to the  $S_4$  that is localized on the two-ring unit. We observe ultrafast and mostly one-directional



mostly one-directional  $S_4 \rightarrow S_3 \rightarrow S_2 \rightarrow S_1$  electronic energy transfer, concomitant with an also

ultrafast two-ring  $\rightarrow$  three-ring  $\rightarrow$  four-ring vibrational energy transfer. The  $S_{n+1}-S_n$  ( $n=3-1$ ) energy gaps and nonadiabatic couplings are strongly influenced by the different nuclear motions in the different potential energy surfaces. Subsequent to a significant  $S_{n+1} \rightarrow S_n$  electronic population transfer, a rapid increase of the  $S_{n+1}-S_n$  energy gaps and decrease of the corresponding values for  $S_n-S_{n-1}$  gaps are observed. In consequence, the  $S_{n+1}$  and  $S_n$  states become less coupled while the  $S_n$  while  $S_{n-1}$  become more coupled. This behavior guarantees the successful  $S_{n+1} \rightarrow S_n \rightarrow S_{n-1}$  unidirectional energy transfer associated to the efficient energy funneling in light-harvesting dendrimers.

# Local Quantum Chemistry

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## ABSTRACT

The recent discovery of new chemical bonds challenges conventional orbital and electron density analyses. While covalent bonding is the strongest and most stable, several other stabilizing interatomic interactions does not fit within the Langmuir-Lewis electron pair description. This is the case of van der Waals and noncovalent interactions in general, which are central to physicochemical processes such as the biomolecular recognition in proteins, nucleobase stacking in DNA, crystal packing, vapor-liquid condensation, polymer aggregation and fluid viscosity, among many others. In the present work we introduce a new local analysis of the electron density that provides insightful information about the bonding and valence regions in molecules. As a result, an intuitive portrait of the chemical structure emerges that makes possible to characterize all kind of interatomic stabilizing interactions in a consistent and unified way. We illustrate this assertion by discussing covalent bonds, ionic bonds, hydrogen bonds, van der Waals complexes and metallic bonds.

## Chalcopyrite Surface Reactivity – A DFT Study.

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Sulfide minerals have great environmental importance because they are associated with the acid mine drainage (AMD) which is a critical problem for regions near mining activities. The AMD is caused by the oxidation of the sulfide minerals on environment producing sulfuric acid and, hence, decreasing the pH of aquifers and releasing heavy metals to the environment. Chalcopyrite,  $\text{CuFeS}_2$ , is a sulfide mineral which, besides the environmental importance, has also a great economic relevance since 80% of the copper in earth is available as chalcopyrite.

However, extracting copper from chalcopyrite is a challenging process, since the technologically viable pyrometallurgical process is only effective for high grade ores. An alternative, especially for low grade ores, is the hydrometallurgical route which the mineral is leached in aqueous solution followed by the electrochemical reduction of copper (II) to metallic copper. However, the low kinetics for the leaching process is a moot question. Many experiments have been carried out and metal-deficient sulfides, polysulfides, elemental sulfur and jarosites are pointed as possible passivation agents, inhibiting the leaching process.

The reactivity of the chalcopyrite surfaces have been investigated by means of Density Functional Theory. Plane-wave calculations have been performed to investigate the surface reconstruction and the primary steps of the leaching process such as the adsorption of water and ions.

We advance that the chalcopyrite surfaces are reconstructed leading to the dimer sulfide formation followed by the reduction of the iron centers. We have also showed from our calculations that underneath of the sulfur dimer on the surface, metal-metal bonds are formed leading to bidimensional alloys. These findings are coherent with the XPS measurements on the pristine (001) surfaces and bring new insights about the leaching process of chalcopyrite at the molecular level. In our presentation we will show all the results and discuss in detail the consequences of these results for understanding the mechanism of the leaching process.

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References:

- Guilherme F. De Lima, Cláudio De Oliveira, Heitor A. De Abreu, Hélio A. Duarte, *J. Phys. Chem. C.*, 115 (7-8), 1395-1402, (2011).
- Cláudio de Oliveira, Hélio A. Duarte; *Appl. Surf. Sci.*, 257 (4), 1319-1324 (2010).

# UNDERSTANDING CHEMICAL REACTIVITY UNDER MICROWAVE IRRADIATION: DEVELOPMENT AND APPLICATIONS OF A MOLECULAR MODEL

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In the course of our research on microwave-assisted cycloaddition reactions, we have observed different stereochemical outcomes in 1,3-dipolar reactions depending on the heating conditions and/or the nature of the substituents<sup>1</sup> (Figure 1). More recently, we have developed a novel synthesis of 1*H*-pyrrol-2(5*H*)-ones that only proceeds under microwave irradiation.<sup>2</sup> In order to improve our understanding of these and related phenomena, we have developed a physicochemical model which describes the interaction between the microwave electric field and a given molecule in a solvent. This solvent is considered as a continuum dielectric medium.

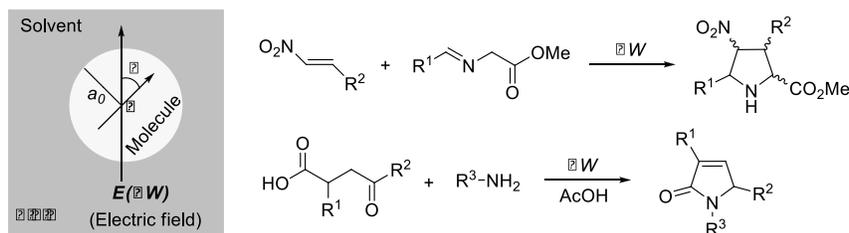


Figure 1

Under this theoretical framework, we have found that the power transferred from the microwaves to the molecule-solvent system depends on the dipole moment and the Onsager radius of the molecule (Figure 1) as well as on the viscosity of the medium and the effective electric field amplitude.<sup>3</sup>

## References

- (a) D. Otaegui, A. Zubia, F. P. Cossío, A. Díaz-Ortiz, A. de la Hoz, M. A. Herrero, P. Prieto, C. Foces-Foces, J. L. Pizarro, and M. I. Arriortua, *J. Org. Chem.* **2007**, *72*, 4313.  
(b) A. Zubia, S. Roper, D. Otaegui, E. Ballester, Fraga, M. F., M. Boix-Chornet, M. Berdasco, A. Martinez, L. Coll-Mulet, J. Gil, F. P. Cossío, and M. Esteller, *Oncogene* **2009**, *28*, 1477.
- M. Aginagalde, T. Bello, C. Masdeu, Y. Vara, A. Arrieta, and F. P. Cossío, *J. Org. Chem.* **2010**, *75*, 7435. M. Aginagalde, Y. Vara, A. Arrieta, R. Zangi, V. Cebolla, A. Delgado-Camón, F. P. Cossío, *J. Org. Chem.* **2010**, *75*, 2776.
- F. P. Cossío, A. Rivacoba, A. de Cózar, X. Lopez, Y. Vara, and E. Aldaba, *submitted*.

# **DFT study on the mechanism of $O_2 + 2NO$ reaction in gas phase and an explanation to the reaction rate constant increase in solution.**

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The reaction of NO with  $O_2$  has been the subject of numerous investigations to explain the unusual third order, second order for NO, without any apparent bimolecular reaction intermediate. For this reason it was believed to be termolecular (one of the exceptions) for a long time. From a theoretical point of view the last investigations do agree that the reaction is complex. However the variations in Gibbs free energies have not been proposed. There are no kinetic calculations in agreement with experiments either. In this work we use the M05 functional to explore the reaction potential energy surface and to locate the stationary points. We have performed kinetic calculations in excellent agreement with experiments in gas phase. The experimentally determined rate constant in solution is 385 times faster than in gas phase whereas the calculated one in usual way is 177 times slower. This discrepancy can be explained by the omission of the entropy loss in solution with respect to the ideal gas model. Using the correction proposed by S. W. Benson the calculated rate constant in solution is 144 times faster than in gas phase, in agreement with the experimental evidences.

# TRANSMEMBRANE NANOPARTICLES

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Designing nanomaterials that can mimic biological systems (e.g. proteins or viruses) is one of the major challenges in the field of nanomedicine and nanobiotechnology. In particular, creating synthetic soluble nanoparticles (NPs) that can fuse reversibly (or irreversibly) with the cellular membrane and behave as membrane proteins could allow us to insert and translocate materials across membranes, signal specific conditions, and even control the shape of cells or organelles. In this talk I will present our theoretical and computational work on designing transmembrane nanoparticles, which are a class of nanoparticles composed of a metallic core protected by a ligand shell with hydrophilic groups at the ends. Recently, it was discovered that these particles can insert themselves spontaneously into a lipid bilayer resembling their biological counterparts: transmembrane fusion proteins or cell penetrating peptides. By using a combination of analytical theory and simulations we find that the key to bilayer complexation is the rearrangement of ligands by bending to maximize hydrophobic matching and minimize charge exposure. Our results also indicate that one can design nanoparticles to fuse selectively with different lipids, and in principle be able to sculpt the bilayer. Finally, these results improve our understanding of transmembrane proteins and enable the design of nanoparticles for drug delivery and biosensing applications.

# Water from first-principles simulations

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Modeling water from first principles is very challenging, as physical effects beyond the reach of standard density functional theory based molecular dynamics are important. Only recently simulations have been able to assess the structural role played by hybrid functionals, dispersion interactions and quantum dynamics of the nuclei. These studies will be reviewed and compared to old and new experimental data.

In addition to diffraction (x-ray, neutron), core excitation spectroscopy has emerged as a powerful tool for investigating hydrogen bonded systems. However, the difficulty of simulating accurately the x-ray absorption spectra of disordered molecular materials has hampered the interpretation of experiments. Novel calculations of the x-ray absorption spectra of water, crystalline ice, low- and high-density amorphous ices, including the effects of nuclear quantum dynamics and of local field screening will be presented. These studies achieve unprecedented agreement with experiment and unveil electronic and structural features underlying the observed spectra.

Finally, new results on tunneling protons in high-pressure ice will be discussed to illustrate the challenge posed by correlations to effective single-particle quantum mechanical pictures.

## **On the antioxidant activity of representative compounds in edible oils**

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The free radical scavenging activity of main compounds present in canola, sesame and olive oils, is studied using the Density Functional Theory. The relative importance of different mechanisms of reaction on their antioxidant activity is analyzed, as well as the influence of the polarity of the environment and of the acid-base equilibria. The tested mechanisms are: single electron transfer (SET), sequential electron proton transfer (SEPT), sequential proton electron transfer (SPET), hydrogen transfer (HT), and radical adduct formation (RAF). Kinetic results are presented, as well as a comparison on the relative scavenging activity of the studied compounds. The reliability of the presented calculations is demonstrated, as well as the importance of theoretical calculations on the search for efficient strategies for chemically fighting oxidative stress.

# MECHANISM OF SURFACE REACTIONS: INSIGHTS FROM FIRST PRINCIPLES CALCULATIONS

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Although surface reactions are ubiquitous in chemical processes, their mechanisms are far from being understood. Commonly, the experimental chemist faces too many variables and possibilities to propose and assess a given mechanism, making it almost impossible to go further than a reasonable hint. The knowledge of the reaction sites as well as the involved species bring details that when mixed together with the experimental data allows a deeper view of the elementary steps that usually are related with a surface chemical transformation. In this talk we focus on the water gas shift reaction, WGS, a chemical process that allows for obtaining clean molecular hydrogen:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ . Bulk like phases or extended surfaces of coinage metals show low catalytic activity that improves when supported on a metal-oxide. The mechanism involves several steps that can take place at different sites of the catalyst: the metal, the support or the interface. Besides the dispersion effect, the role of the support is to increase the interaction with water and facilitate its dissociation. DF calculations show that supported  $\text{CeO}_x$  nanoparticles (NPs) are highly efficient in water splitting (Fig 1, left). Furthermore The  $\text{M}/\text{CeO}_x/\text{TiO}_2$  (110) surfaces display outstanding activity for the WGS, in the sequence:  $\text{Pt} > \text{Cu} > \text{Au}$  (Fig 1, right). Such a high catalytic activity reflects the unique properties of the mixed-metal oxide at the nanometer level. STM and DF calculations show that Ce deposition on  $\text{TiO}_2$  (110) at low coverage gives rise to  $\text{Ce}_2\text{O}_3$  dimers specifically aligned, indicating that the substrate imposes on the ceria NPs unusual coordination modes enhancing their chemical reactivity.

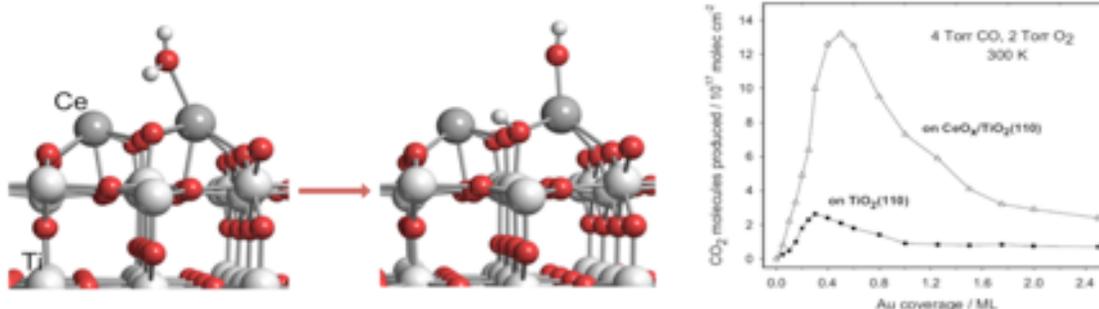


Fig. 1. Left: water dissociation on  $\text{CeO}_x/\text{TiO}_2(110)$ . The process is exothermic by 0.70 eV and the activation barrier is of only 0.04 eV. Right: catalytic activity of gold NPs supported on  $\text{TiO}_2(110)$  and  $\text{CeO}_x/\text{TiO}_2(110)$ .

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# Modeling and understanding structure and reactivity of ceria; from bulk to surfaces and nanoparticles

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Ceria ( $\text{CeO}_2$ ) is an interesting material of paramount importance in various technologies and, in particular, in catalysis. One of the key properties responsible for the special function of ceria-based heterogeneous catalysts is the facile reducibility of  $\text{CeO}_2$ , which involves the  $\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$  process. This redox process can be triggered either by direct electron transfer from metals adsorbed over a ceria surface or by oxygen release. Both processes result in the appearance of  $\text{Ce}^{3+}$  cations with highly localized Ce ( $4f^1$ ) electrons. This is precisely the main reason for the difficulties encountered when attempting to describe the electronic structure of ceria based materials using standard computational methods derived from Density Functional Theory. In fact, the usual Local Density Approach (LDA) and the Generalized Gradient Approach (GGA) forms of the universal exchange-correlation potential are unable to properly describe the localized character of the Ce  $4f^1$  electrons in  $\text{Ce}^{3+}$  cations [1]. Other approaches such as the so-called LDA+U (or GGA+U) or hybrid functional which contain a fraction of non-local Fock exchange provide a more physically sound description of partly reduced ceria ( $\text{CeO}_{2-x}$ ) bulk and surface [1] although this is not free of problems. This is illustrated taking the oxidation state of Au on  $\text{CeO}_2(111)$  as a case study [2,3]. The study of ceria nanoparticles introduces yet several additional complications due to the difficulty to predict the most stable structure of a given particle and, for non-stoichiometric samples, of handling the electronic isomers differing in the position of the  $\text{Ce}^{3+}$  cations. The combined use of global optimization procedures using interatomic potentials and of DFT calculations offers a physically sound description and permits one to make important predictions about the properties of these interesting systems [4-6].

## References

- [1] C. Loschen, J. Carrasco, K. M. Neyman and F. Illas, *Phys. Rev. B*, 75 (2007) 035115
- [2] N. J. Castellani, M. M. Branda, K. M. Neyman and F. Illas, *J. Phys. Chem. C*, 113 (2009) 4948
- [3] M. M. Branda, N. J. Castellani, R. Grau-Crespo, N. H. de Leeuw, N. C. Hernandez, J. F. Sanz, K. M. Neyman F. Illas, *J. Chem. Phys.*, 131 (2009) 094702
- [4] A. Migani, K. M. Neyman, F. Illas and Stefan T. Bromley, *J. Chem. Phys.*, 131, (2009) 064701
- [5] A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas and K. M. Neyman, *Chem. Commun.*, (2010) 5936-5938
- [6] A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas and K. M. Neyman, *J. Mater. Chem.*, 20 (2010) 10535

# Orbitales simétricamente localizados y su relevancia para el diseño de métodos químico cuánticos de sólidos cristalinos.

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En esta presentación se discute la posibilidad formal de existencia y obtención de bases de funciones de onda cuyas componentes presentan óptimas propiedades de localización espacial y relaciones de simetría entre ellas. A diferencia de las usuales bases adaptadas a la simetría, como bases de las representaciones irreducibles del grupo correspondiente, estos *orbitales simétricamente localizados (OSL)* son bases de representaciones inducidas,<sup>1</sup> lo que permite que muestren características propiedades de equivalencia por simetría entre ellas y, a la vez, óptima localización espacial.

Por otro lado, siendo las representaciones irreducibles un caso particular de representaciones inducidas, los OSL son una forma general de orbitales adaptados de simetría. De hecho, se puede demostrar que el teorema de Wigner que relaciona bases de representaciones irreducibles con autovectores de operadores invariantes por simetría se generaliza en un nuevo teorema que relaciona bases ortogonales de representaciones inducidas con autovectores simultáneos de un conjunto de operadores simétricamente equivalentes.

Se muestra también como estas bases de orbitales pueden ser convenientemente optimizadas respecto a algún funcional mediante transformaciones unitarias, lo que favorece su uso general en métodos variacionales para la estructura electrónica.<sup>2</sup> La combinación de localización y simetría resulta de particular utilidad para el estudio de sistemas cristalinos, ya que permite extender los métodos periódicos con bases atómicas ya implementados en códigos públicos como CRYSTAL<sup>3</sup> hacia aproximaciones de la función de onda que, por ejemplo, pueden incluir explícitamente la correlación electrónica.<sup>4;5</sup>

## Referencias

- [1] Cloizeaux, J. D., *Phys. Rev. A* **1964**, *135*, 698–707.  
[2] Zicovich-Wilson, C. M.; Erba, A., *Theor. Chem. Acc.* **2010**, *126*, 165. doi 10.1007/s00214-009-0619-8.  
[3] Dovesi, R.; Saunders, V. R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civaleri, B.; Doll, K.; Harrison, N. M.; Bush, I. J.; Arco, P. D.; Llunell, M., CRYSTAL06 User's Manual, Università di Torino, Turin 2006, see <http://www.crystal.unito.it>.  
[4] Casassa, S.; Zicovich-Wilson, C. M.; Pisani, C., *Theor. Chem. Acc.* 2006, *116*, 726–733, on line ed.: <http://dx.doi.org/10.1007/s00214-006-0119-z>.  
[5] Pisani, C.; Busso, M.; Capecchi, G.; Casassa, S.; Dovesi, R.; Maschio, L.; Zicovich-Wilson, C. M.; Schütz, M., *J. Chem. Phys.* **2005**, *122*, 094113.

# The polarizability and hyperpolarizability of nanotubes and polyacetylene. A quantum-mechanical simulation.

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The polarizability, the first and second hyperpolarizability of BN and Carbon nanotubes of the (n,0) family have been evaluated by using a quantum-mechanical approach, a Gaussian basis set and the CRYSTAL code [1]. The Coupled Perturbed Hartree-Fock or Kohn-Sham Self Consistent perturbative schemes [2-3] have been implemented and applied to tubes of increasing radius (from (6,0) to (60,0)) [4,5]. The pure electronic and the ionic contributions have been evaluated, the latter through the FF-NR (finite field nuclear relaxation) scheme proposed by Bishop and Kirtman [6,7]. Longitudinal and transverse components of the three tensors are considered. Five different Hamiltonians (Hartree-Fock, LDA, PBE, PBE0 and B3LYP) are compared. The evolution with the tube radius is considered, and the trend towards the limit of infinite radius (that is, the hexagonal BN or the graphene monolayer) explored. The so called “DFT overshoot” is discussed with reference to these systems and to polyacetylene.

- [1] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C.M. Zicovic-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, P. D’Arco, and M. LLunell, CRYSTAL 2009
- [2] M. Ferrero, M. Rérat, R.Orlando and R. Dovesi, *J. Comput. Chem.* 29, 1450 (2008); *J. Chem. Phys.* 128, 014110 (2008)
- [3] M. Ferrero, M. Rérat, B. Kirtman and R. Dovesi, *J. Chem. Phys.* 129, 244110 (2008)
- [4] M. Ferrabone, B. Kirtman, M. Rérat, R. Orlando and R. Dovesi, *Phys. Rev. B*, in press (2011)
- [5] M. Ferrabone, B. Kirtman, V. Lacivita, M. Rérat, R. Orlando and R. Dovesi, *Int. J. Quantum Chem.*, in press (2011)
- [6] D. M. Bishop, M. Hasan and B. Kirtman, *J. Chem. Phys.* 103, 4157 (1995)
- [7] B. Kirtman, J. M. Luis and D. M. Bishop, *J. Chem. Phys.* 108, 10008 (1998)

## Aluminum Interaction with Biological Ligands

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Aluminium is one of the most abundant elements in earth, but living systems have utterly avoid the use of this metal in their metabolism. Due to its various industrial applications, Aluminium has dramatically increased its bioavailability in the last decades, and the presence of this metal has been linked to various human diseases. Although the effects of Aluminium toxicity are still far from being understood, its primary effect is the formation of strong complexes with a variety of bioligands, which can lead to a profound alteration of their own structure and protonation state. Besides, aluminium can substitute metals of similar size, but lower charge, in metalloenzymes.

In the present communication, we investigate several aspects of the Aluminium biochemistry by the use of different theoretical approaches. Various quantum mechanical methods, and both QM/MM and classical molecular dynamic techniques are employed to unveil interesting aspects of Aluminium speciation in vivo. In particular, using CASSCF, CASPT2 and DFT methods we will analyse the pro-oxidant activity of aluminium, by formation of Al-superoxide complexes. Besides, we will analyse the possibility of Aluminium to interact with oxygen containing aminoacid sidechains and how this interaction alters the pKa of these species. DFT in its B3LYP implementation is used for this purpose. We will also analyse a variety of Aluminium complexes with citrate, one of the main low weight mass bioligands responsible for Aluminium speciation, and the interaction of Aluminium with serum transferrin, the main Aluminium carrier in blood. For the latter, a variety of QM/MM and classical molecular dynamics methods have been used. Finally, we will also analyze how the use of theoretical methods to calculate excited states can help in the design of organic molecules to act as selective Aluminum sensors in solution.

# The problem of hole localization in inner-shell states of N<sub>2</sub> and CO<sub>2</sub> revisited with CASSCF approach

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The problem of core-hole localization has been debated for decades since the work of Bagus and Schaefer<sup>1</sup> has shown that the localization of core-hole lowers the energy of the O<sub>2</sub><sup>+</sup> (1s<sup>-1</sup>) ion, resulting in a better agreement with experiment. The problem with this approach is that it breaks the symmetry of the final wave function and, consequently, cannot reproduce the whole hamiltonian spectrum. This problem was circumvented for N<sub>2</sub> by Bielschowsky et al<sup>2</sup> by using the Generalized Multistructural function (GMS), in which two structures are optimized, one with a core-hole on the left and the other with core-hole on the right nitrogen atom and the full symmetry of the system is recovered by a CI calculation based on a nonorthogonal orbital basis set. This approach is quite accurate but the nonorthogonality of orbitals is quite demanding on computational grounds. In the present work, we present an alternative approach, in which core orbitals can be localized or delocalized but in both cases they are simultaneously optimized in a multiconfigurational approach. This is possible since the collapse of the wave function to a low-lying state is avoided by a sequence of constrained optimization in the orbital mixing step, a procedure recently develop to treat core-shell states<sup>3</sup>. The method was named inner-shell CASSCF (IS-CASSCF). The problem of localization of K-shell states is revisited by calculating them at CASSCF level based on both localized and delocalized orbitals. The localized basis presents the best results at this level of calculation. Transition energies are also calculated by perturbation theory, by taking the above mentioned MCSCF function as zeroth order. Values for transition energy are in fairly good agreement with experimental ones. Bond dissociation energies for N<sub>2</sub> are considerably high, which means that these states are strongly bound. Potential curves along normal modes of CO<sub>2</sub> indicate the occurrence of Renner-Teller effect in its inner-shell  $\pi$  states.

<sup>1</sup> P. S. Bagus, H.F. Schaefer III, J. Chem. Phys. **56**, 224 (1972).

<sup>2</sup> C. E. Bielschowsky, M. A. C.Nascimento, E. Hollauer, Phys. Rev. A **45**, 7942 (1992).

<sup>3</sup> A. B. Rocha, J. Chem. Phys. **134**, 024107 (2011)

## **Explicit Solvent Effects on the Visible Absorption Spectrum of Chlorophyll *c* and Photosynthetic Pigments**

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The absorption of visible light by chlorophylls is the first step to photosynthesis and as such it is one of the most important mechanisms in nature. Extensive theoretical and experimental investigations have been devoted to the understanding of their absorption spectra. In this work we analyze the absorption spectrum of chlorophyll *c* in methanol (MeOH). Chlorophyll *c* is perhaps one of the most simple pigments, present in marine algae, but still showing all the essential characteristic of the absorption spectrum: the intense Soret band and the two low-lying Q bands. The absorption spectrum measured in MeOH exhibits a clear Soret band located at 451 nm and the two Q bands at 586 and 633 nm. This absorption spectrum in MeOH is then investigated theoretically, using different approximations to include the solvent effects. Special attention is devoted to the explicit role of the solvent in the absorption spectrum. Using explicit solvent molecules an excellent description of the absorption spectrum is obtained. Additional considerations made are the coordination of the Mg atom, the adequacy of the Gouterman four-state model, the role of solute-solvent hydrogen bonds and the existence and location of dark states.

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# Many-Body van der Waals Interactions in Biology, Chemistry, and Physics

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Van der Waals (vdW) interactions are ubiquitous in nature, playing a major role in defining the structure, stability, and function for a wide variety of molecules and materials. Thus, the accurate description of vdW interactions is essential for improving our understanding of many biological, chemical, and (hard and soft) condensed matter.

We have developed an efficient method to obtain an accurate description of the long-range vdW interactions in terms of adding simple, pairwise  $C6[n]/R^6$  terms, where  $C6[n]$  is a functional, calculated from ground-state molecular electron density [1]. Recently, we have extended this approach to the calculation of full non-additive many-body vdW energy [2]. We demonstrate that many-body effects play a significant role even for rather small molecules, becoming crucial for an accurate treatment of conformational energies in biomolecules, and binding of molecular crystals. Our method achieves accuracy close to that of the "gold standard" of quantum chemistry, namely CCSD(T). However, the computational cost of our method is negligible compared to the underlying DFT calculation, enabling calculations for thousands of atoms.

Examples to be discussed include (hard and soft) bulk crystals [3,4], organic/organic and organic/inorganic interfaces [5], and the unfolding dynamics of polypeptides [6]. In all these cases it is found that vdW interactions play a noticeable, if not crucial role, not just for quantitative values but also for the qualitative behavior.

[1] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 073005 (2009).

[2] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, Phys. Rev. Lett., submitted.

[3] G. Zhang, A. Tkatchenko, J. Paier, H. Appel, and M. Scheffler, Phys. Rev. Lett., submitted.

[4] N. Marom et al., Cryst. Growth Des. 11, 3332 (2011).

[5] N. Marom et al., Phys. Rev. Lett. 105, 046801 (2010).

[6] A. Tkatchenko, M. Rossi, V. Blum, J. Ireta, and M. Scheffler, Phys. Rev. Lett. 106, 118102 (2011).

## Hybrid Quantum Mechanics/Effective Fragment Potential (QM/EFP) Studies of P-O Bond Cleavage of Phosphate Esters in Solution.

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In the last years the Effective Fragment Potential (EFP) [1] has emerged as a powerful method to study organic reactions in solution. In this presentation an overview of the hybrid QM/EFP method will be given and its potential to study organic and organometallic reactions in aqueous solution is discussed and exemplified through the results of recent studies involving the cleavage of P-O bonds of phosphate monoesters and diesters, promoted by biomimetic compounds of Purple acid Phosphatase (PAP) and also by alpha nucleophiles [2].

[1] (a) I. Adamovic, M. A. Freitag, M. S. Gordon, *J. Chem. Phys.*, **118**, 6725 (2003). (b) I. Adamovic, M. S. Gordon, *J. Chem. Phys. A* **109**, 1629 (2005).

[2] D. E. C. Ferreira, B. P.D. Florentino, F. Nome, W. R. Rocha, *J. Phys. Chem. B.*, **113**, 14831 (2009).

# THE GSAM CODE: A GLOBAL SEARCH ALGORITHM OF LOCAL MINIMA ON A POTENTIAL ENERGY SURFACE FOR FINDING THE PHYSICALLY REASONABLE STRUCTURES OF CLUSTERS AT A GIVEN TEMPERATURE. EXAMPLES AND APPLICATIONS.

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The study of clusters has become an increasingly active area of research in the recent years because of the fundamental interest in studying a completely new area that can bridge the gap between atomic and solid state physics. Owing to their peculiar and size tuned properties, their role in the area of nanotechnology is well established.

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 structures. Since the standard experimental techniques that allow to determine the atomic positions in crystals and molecules are not applicable to clusters, the determination of cluster structures relies mainly on theoretical methods.

However, even in this case, there are many issues that make the reliable determination of the cluster structures an extremely difficult task mainly due to the numerous minima that exist in a cluster potential energy surface (PES).

We propose an algorithm for finding the most stable isomers for any cluster. This global search algorithm of minima exploration includes (i) the generation of an initial guess (ii) a selection scheme and (iii) an optimization step that fully optimize the physically reasonable configurations only. The efficiency of the algorithm in terms of computational cost, number of isomers found, capability to allow the determination of an overall value of a property, is illustrated through several examples of monoatomic, binary and molecular clusters, up to 60 atoms.

This paves the route toward a more predictive chemistry, such as design of nano-material.

# A THEORETICAL APPROACH OF THE REDOX CHEMISTRY OF CO<sub>2</sub> WITH LANTHANIDE AND ACTINIDE COMPLEXES

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The transformation of CO<sub>2</sub> and especially its reduction is an important environmental issue. In the last ten years, molecular systems involving either Samarium(II) or Uranium(III) centers have been reported to be efficient to reduce CO<sub>2</sub>. However, depending on the nature of the metal and of the ligands, formation of either carbonate or oxalate complexes have been experimentally observed. In this presentation, after briefly discussing the relative influence of the f electrons in the reactivity of organolanthanide and actinide complexes as well as a methodology to compute oxidation of f-element complexes, I will discuss the reaction mechanism for CO<sub>2</sub>, COS and CS<sub>2</sub> reduction by Cp\*<sub>2</sub>Sm, (Cp\*)(COT)U and N-anchored aryloxide U(III) complexes. It will be demonstrated that this difference of reactivity is mainly explained by steric effects

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## Reference

<sup>1</sup> Liang, L.-C. Liang; Chien, P.-S.; Huang, Y.-L. *J. Am. Chem. Soc.* **2006**, *128*, 15562-15563.

# THE ROLE OF DISPERSION IN FULLERENE REACTIVITY

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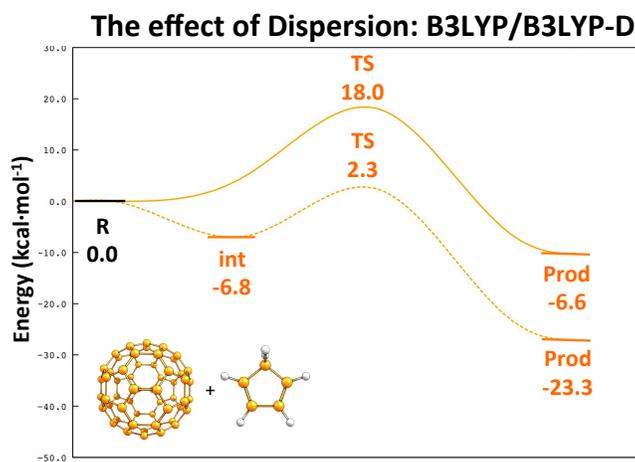
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In a recent paper we analyzed theoretically the Diels-Alder cycloaddition between cyclopentadiene and C<sub>60</sub> for which experimental results on energy barriers and reaction energies are known.<sup>1</sup> One of the main conclusions reached was that the two-layered ONIOM2(B3LYP/6-31G(d):SVWN/STO-3G) method provides results very close to the full B3LYP/6-31G(d) ones. Unfortunately, however, both the exothermicity of the reaction and the energy barrier were clearly overestimated by these two methods. In the present work, we analyze the effect of the inclusion of Grimme's dispersion corrections in the energy profile of this reaction. Our results show that these corrections are essential to get results close to the experimental values. We have also tested the performance of M06-2X, which includes medium-range correlation. Although M06-2X gives accurate reaction energies, somewhat less accurate activation barriers are obtained. In addition, we have performed calculations both with and without dispersion corrections for the Diels-Alder reaction of C<sub>60</sub> and several dienes, for the Diels-Alder cycloaddition of a (5,5) single walled carbon nanotube and 1,3-*cis*-butadiene, and for the Diels-Alder of the metal carbide endohedral metallofullerene Ti<sub>2</sub>C<sub>2</sub>@D<sub>3h</sub>-C<sub>78</sub> and 1,3-*cis*-butadiene.<sup>2,3</sup> The results obtained indicate that inclusion of dispersion corrections is extremely important to accurately reproduce the experimental reaction and activation barriers of cycloaddition reactions of large systems such as fullerenes and nanotubes.



<sup>1</sup>Osuna, S.; Morera, J.; Cases, M.; Morokuma, K.; Solà, M. *J. Phys. Chem. A* **2009**, *113*, 9721.

<sup>2</sup>Osuna, S.; Houk, K. N. *Chem. Eur. J.* **2009**, *15*, 13219.

<sup>3</sup>Garcia-Borràs, M.; Osuna, S.; Luis, J. M.; Swart, M.; Solà, M. *submitted for publication*.

# FROM CHEMICAL BONDS TO ALKALI HALIDE NANOTUBES

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The driving force for chemical binding is the quantum-mechanical interference effect among one-electron states. [1-7]. Previous approaches for the partition of the energy to calculate the interference contributions to the energy [1-3] run into some difficulties and calculations were only carried out for a few diatomic molecules. We have recently developed a general approach of partitioning [5] based on Generalized Product Functions with Generalized Valence Bond at the Perfect Pairing approximation and Spin-Coupled groups, which should allow the investigation of a broader array of molecules, and hopefully, shed light on the nature of the chemical bond in molecules with unusual chemical features. Among other things, this approach lends itself naturally to the investigation of interference in individual bonds or groups of bonds in a molecule. In the first part of this talk we will illustrate the applicability of the developed approach by examining the chemical bond in simple diatomic molecules, polyatomic (saturated and unsaturated hydrocarbons) molecules, in addition to reactions to double-bonds and also in the description of some electrocyclic reactions.

In the second part of this talk we will introduce a new family of nanotubes, namely, the alkali halide (LiF, NaCl, KBr) nanotubes. The relative stability of  $(MX)_{n=2,28}$  structural isomers was studied at the DFT (B3LYP/LAVCV3P\*\*) and CCSD/SDD (LAVCV3P\*\*) levels of calculation. Quantum dynamics calculations, at room temperature and atmospheric pressure, were also performed for  $(LiF)_{28}$ . The results obtained for the  $(LiF)_n$  clusters show that overall the cubic series is highly stable as expected from the structures that are debris of a crystalline bulk. Surprisingly, however, nanotubes with hexagonal and octagonal cross-sections present similar or higher stability than the corresponding cubic clusters. The fact that similar stable structures were found for the  $(NaCl)_n$  and  $(KBr)_n$  clusters indicate that nanotubes represent a new possibility for the macro assembly of alkali halide  $M^+X^-$  clusters (CNPq, FAPERJ, Instituto Nacional de Materiais Complexos Funcionais).

- [1] K. Ruedenberg, *Rev. Mod. Phys.*, **34**, 326 (1962).
- [2] C. W. Wilson Jr. , W. A. Goddard III, *Chem. Phys. Letts.*, **5**, 45 (1970).
- [3] F. Driessler and W. Kutzelnigg, *Theo. Chim. Acta*, **43**, 1 (1976).
- [4] M.A.C. Nascimento, *J. Braz. Chem. Soc.* **2008**, *19*, 245.
- [5] T.M. Cardozo, M.A.C. Nascimento *J. Chem. Phys.* **2009**, *130*, 104102
- [6] T.M. Cardozo, M. A. C. Nascimento. *J. Phys. Chem. A*, **2009**, *113*, 12541
- [7] T. M. Cardozo, G. N. Freitas, M. A. C. Nascimento *J. Phys. Chem. A* **2010**, *114*, 8798.

# An accurate DFT treatment of weak intra- and intermolecular interactions

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Standard density functional approximations fail to provide a consistent description of weak molecular interactions arising from small electron density overlaps. These intra- and intermolecular van der Waals interactions are responsible for many energetic and structural phenomena such as host-guest chemistry, crystal packing of organic molecules, protein folding, pi-pi stacking of nucleic acids in DNA and supramolecular assemblies. A simple remedy to correct for the missing interactions is to add *a posteriori* an attractive energy term summed over all atom pairs in the system. For general applicability, the dispersion coefficients used in such corrections should depend on the electron density, with no increase in the computational cost. The density-dependent energy correction, dDsC, presented herein, is constructed from dispersion coefficients computed based on a generalized gradient approximation to Becke and Johnson's exchange-hole dipole moment formalism.<sup>[1]</sup> dDsC also relies on an extended Tang and Toennies damping function accounting for charge-overlap effects.<sup>[2,-4]</sup> The density dependence of both the dispersion coefficients and the damping function makes the approach especially valuable for modeling redox reactions and charged species in general.

We will discuss general improvements obtained for standard and modern density functionals and present results for a broad variety of reaction energies and geometries.

[1] S. N. Steinmann and C. Corminboeuf, *J. Chem. Phys.* **2011**, *134*, 044117.

[2] S. N. Steinmann and C. Corminboeuf, *J. Chem. Theory Comput.* **2010**, *6*, 1990.

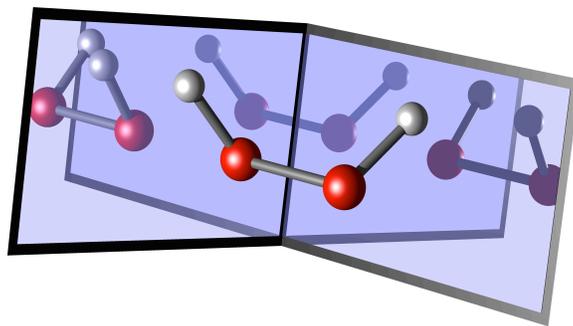
[3] S. N. Steinmann, M. D. Wodrich and C. Corminboeuf, *Theor. Chem. Acc.*, **2010**, *127*, 429.

[4] S. N. Steinmann and C. Corminboeuf, submitted

# PARITY VIOLATION IN CHIRAL MOLECULES

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Chirality is a fundamental concept in physics, chemistry and biology. In **physics** objects of opposite chirality are connected by the parity operation (P), which combines with charge conjugation (C) and time reversal (T) in the CPT theorem. Although the theorem states that the combined CPT symmetry is conserved by all physical processes and by the four fundamental forces (gravitation, the electromagnetic force, the strong and the weak force), individual symmetries may be broken. Of interest here is that parity may not be conserved in processes involving the weak force, as suggested by Lee and Yang in 1956 and soon after confirmed by experiment. In **biology** chirality is a hallmark of life in that Nature shows, with very few exceptions, a distinct preference for L-amino acids and D-sugars over their mirror images. For **chemistry** chirality is a challenge, notably in the development and synthesis of molecules for pharmaceuticals, agrochemicals, flavors and, more recently, nanotechnology. The development of catalysts for stereoselective synthesis is one of the most important tasks of modern chemistry, as demonstrated by the award of the Nobel Prize in Chemistry for 2001 to William S. Knowles, Ryoji Noyori and K. Barry Sharpless for the development of catalytic asymmetric synthesis.

The theoretical description of chemistry provided by conventional quantum mechanics considers only electromagnetic interactions. These forces conserve parity, which implies that a chiral molecule and its mirror image are degenerate. The Hamiltonian of electroweak quantum chemistry contains, on the other hand, a parity non-conserving component and therefore predicts a small energy difference between enantiomers, which may shed light on the origin of biochirality. I am partner in the project NCPCHEM [<http://dirac.ups-tlse.fr/ncpchem>], sponsored by the French research agency ANR, which aims at the first experimental observation of parity violation in chiral molecules, using high-resolution vibrational spectroscopy. In my talk I give a brief status report.

**Reference:** Radovan Bast, Anton Koers, André Severo Pereira Gomes, Miroslav Iliaš, Lucas Visscher, Peter Schwerdtfeger and Trond Saue, *Phys. Chem. Chem. Phys.* **13** (2011) 854

# TOPOLOGICAL ANALYSIS OF THE FUKUI FUNCTION AND SOME APPLICATIONS IN CHEMICAL REACTIONS

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In this work an alternative to the analysis of the Fukui function will be presented and compared with the traditional condensed function. The topological analysis of the Fukui function allows us to define basins corresponding to different regions of the space and the numerical integration of the density over those volumes gives a number amenable of a chemical interpretation in line with the Fukui function applications. Various examples are shown, a series of small molecules, a couple of clusters and aromatic molecules. The criteria of “maximum matching” between the Fukui functions to predict the best interaction between small silicon clusters to form larger ones is discussed. We tested the methodology in the formation of  $\text{Si}_4\text{-Si}_8$  using a set of small  $\text{Si}_2\text{-Si}_6$  clusters as building blocks in ground state structures in singlet and triplet multiplicities. In all the cases the Fukui function predicts the formation of the large cluster in their ground state structure, but the number of reaction channels increases with the cluster size.

## **Acknowledgements**

Our work was supported by Andres Bello (Grants: No DI-13-10/R), Fondecyt (Grants No 11090431).

## Density analysis applied to scalar fields

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The density analysis developed by Zupan<sup>1,2</sup> *et al.* is generalized to an arbitrary scalar field. In particular, it is used to analyze the electron localization function<sup>3</sup> (ELF), and the exchange and correlation dimensionless gradients.

Through this analysis, that we call phi-analysis, we will try to obtain the values of the scalar field at which the synapse effect is observed, for the case of the ELF function, and at which chemical interactions exist, for the case of the dimensionless gradients.

Additionally, we will also present the application of this methodology as an efficient alternative to perform volume integrations inside complicated surfaces.

(1) Zupan, A.; Burke, K.; Ernzerhof, M.; Perdew, J. P. *J. Chem. Phys.* **1997**, *106*, 10184-10193.

(2) Zupan, A.; Perdew, J. P.; Burke, K.; Causa, M. *Int. J. Quantum Chem.* **1997**, *61*, 835-845.

(3) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990** *92*, 5397.

## **The richness of the dynamic of clusters**

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Ab initio molecular dynamics for a variety of atomic clusters will be shown and discussed. In systems as small as  $M_3$  ( $M$ = alkali metal atom) there are some interesting phenomena like pseudorotation and transposing. The dynamics will be characterized by some geometric parameters and also energetic considerations. In some cases, especially  $Na_7$ , it was also possible to identify a transition state for the conversion between the two main isomers.

# **Predicciones *ab initio* de espectros fotoelectrónicos e interpretaciones basadas en orbitales de Dyson con el propagador del electrón**

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Las soluciones de la ecuación de Dyson producen energías de ionización, electroafinidades y orbitales de Dyson que corresponden a estas transiciones. Los efectos de la correlación electrónica diferencial y de la relajación de orbitales entre estados iniciales y finales son descritos sistemáticamente a través de la inclusión del operador de autoenergía en la ecuación de Dyson. Varias aproximaciones a este operador son capaces de producir datos precisos para moléculas e iones grandes y para sistemas que exhiben efectos fuertes de correlación. Los orbitales de Dyson facilitan el desarrollo de interpretaciones transparentes y rigurosas de resultados obtenidos con formas complicadas del operador de autoenergía. Algoritmos nuevos e eficientes permiten la aplicación de esta técnica *ab initio* a la asignación cuantitativa de espectros fotoelectrónicos de fullerenos grandes, de aniones metalomacrocíclicos con energías negativas de remoción electrónica, de fragmentos aniónicos de nucleótidos y de aniones en fase líquida. En cada caso, los orbitales de Dyson son indispensables para la interpretación cualitativa de los resultados.

## **HgCl<sub>2</sub> aqueous solvation. Cluster models vs. liquid phase**

### **Monte Carlo studies with refined *ab-initio* derived potentials**

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#### **ABSTRACT**

We address the aqueous solvation of HgCl<sub>2</sub> using two different approaches. First through a systematic DFT stepwise hydration study with aggregates of up to 24 water molecules and, secondly, through extensive Monte Carlo (MC) simulations for the liquid phase using MP2-derived interaction potentials. The interaction potentials are flexible, polarizable and include non-additive effects. In all cases the hydrogen bond network is crucial to allow orbital-driven interactions between Hg(II) and the water molecules. We conclude that a cluster description of the solvation mechanism is limited and biased when compared to the condensed phase model, the former yielding artificially large solvation energies. The molecular image derived from the MC simulations of the solution is peculiar, resembling that of a hydrophobic solute, which explains the rather easy passage of this neutral molecule through the cell membrane; however, it also shows an intermittent binding of one or two water molecules in the fashion of a hydrophilic solute. Thus our trans-membrane passage model proposes the diffusion of a non-polar molecule that easily loses its hydration shell and does not require a proteinic channel for trans-membrane transport

# Dyotropic and Double Group Transfer Reactions: Mechanisms, Aromaticity and Synthetic Applications

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Double group transfer (DGT) reactions are a general class of pericyclic reactions that occur through the simultaneous migration of two atoms or groups from one compound to another in a concerted reaction pathway.[1] The archetypal DGT process is the thermally allowed transfer of two hydrogen atoms from ethane to ethylene. The process is suprafacial on both reaction sites and therefore these [ $s_2s+s_2s+p_2s$ ] transformations may be considered to be a thermally allowed pericyclic reaction according to the Woodward–Hoffmann rules. Strikingly, DGT reactions share a common feature, namely, they proceed in a concerted and synchronous fashion through a transition state featuring a six-membered ring that is highly in-plane aromatic.[2]

Despite the aromatic character of these transition states, DGT reactions are associated with relatively high barriers. The origins of these barrier heights have been studied with the help of the so-called Activation Strain Model. We found that, similar to other pericyclic processes, the activation strain associated with the structural rearrangement of the reactants is also the controlling factor for the high energy of the DGT reaction barriers.[3]

In addition, we shall present recent applications of DGT and dyotropic reactions in organic and organometallic synthesis as well.[4]

## References:

[1]. (a) S. Sankararaman, *Pericyclic Reactions-A Textbook: Reactions, Applications and Theory*, Wiley, Weinheim, 2005; pp. 326 –329, and references therein. (b) I. Fernández, F. P. Cossío, M. A. Sierra, *Chem. Rev.* **2009**, *109*, 6687.

[2]. (a) I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* **2007**, *72*, 1488. (b) G. Frenking, F. P. Cossío, M. A. Sierra, I. Fernández, *Eur. J. Org. Chem.* **2007**, 5410.

[3]. (a) I. Fernández, F. M. Bickelhaupt, F. P. Cossío, *Chem. Eur. J.* **2009**, *15*, 13022. (b) I. Fernández, F. P. Cossío, *Curr. Org. Chem.* **2010**, *14*, 1578.

[4]. Some examples in the chemistry of Fischer carbenes can be found in (a) I. Fernández, F. P. Cossío, M. A. Sierra, *Acc. Chem. Res.* **2011**, *44*, 479.

## Nuclear size and QED effects on NMR spectroscopic parameters

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The two most useful NMR spectroscopic parameters, the nuclear magnetic shielding,  $\sigma$ , and the indirect spin-spin coupling,  $J$ , are quite sensitive to local electronic environment. This is the reason why they are powerful sensors for getting reliable information on the whole molecular structure (electronic and geometric).

In the last decade there was an extraordinary increase in the understanding of relativistic effects on molecular properties<sup>1</sup>, being that two spectroscopic parameters between the most influenced by such effects<sup>2,3</sup>. They can be so large that do produce the inversion of NR tendencies following experimental results, or convert diamagnetic shieldings in paramagnetic, for heavy elements. Then one can infer that the nuclear model one uses to describe the electron-nucleus interaction would be of importance in accurate calculations.

Few years ago it was predicted that QED effects may be as large as of 1% of relativistic effects<sup>4</sup>. At the moment there is no any implementation that permits to verify whether this is the actual order of magnitude.

In this presentation we will show recent advances in our studies of relativistic and QED effects on both NMR spectroscopic parameters. We will show that the effects of nuclear size and QED are as large that they must be included in accurate calculations. Preliminary values of QED effects on J-couplings will be exposed.

[1] P. Pyykkö, Annual Rev. Phys. Chem. **63** (2012) DOI: 10.1146/annurev-physchem-032511-143755.

[2] G. A. Aucar, R. H. Romero and A. F. Maldonado, Int. Rev. Phys. Chem. **83**, 1-64 (2010); A. F. Maldonado, C. A. Gimenez and G. A. Aucar, Phys Chem Chem Phys. Submitted.

[3] J. Autschbach and S. Zheng, Ann. Rep. NMR Spectrosc. **67**, 1 (2009).

[4] L. Labzowski *et al.* Phys. Rev. A **59**, 2707 (1999); P. Pyykkö Chem. Rev. **112** (2012) DOI: 10.1021/cr200042c

# Dephasing representation: Beating the efficiency of both quantum and classical simulations with semiclassics

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While rigorous quantum dynamical simulations of many-body systems are extremely difficult (or impossible) due to the exponential scaling with dimensionality, corresponding classical simulations completely ignore quantum effects. Semiclassical methods are generally more efficient but less accurate than quantum methods, and more accurate but less efficient than classical methods. We find a remarkable exception to this rule by showing that a semiclassical method can be both more accurate and faster than a classical simulation [1]. Specifically, we prove that for the semiclassical dephasing representation [2,3] the number of trajectories needed to simulate quantum fidelity is independent of dimensionality and also that this semiclassical method is even faster than the most efficient corresponding classical algorithm [4]. Analytical results are confirmed with simulations of quantum fidelity in up to 100 dimensions with  $2^{1700}$ -dimensional Hilbert space. Applications of the dephasing representation that will be discussed include evaluation of the nonadiabaticity of molecular quantum dynamics [5,6] and calculation of the ultrafast time-resolved electronic spectra [7].

[1] C. Mollica and J. Vanicek, "Beating the efficiency of both quantum and classical simulations with semiclassics," *Phys. Rev. Lett.*, in press (2011), arXiv:1108.3853v1.

[2] J. Vanicek, "Dephasing representation: Employing the shadowing theorem to calculate quantum correlation functions," *Phys. Rev. E* **70**, 055201 (2004);

[3] J. Vanicek, "Dephasing representation of quantum fidelity for general pure and mixed states," *Phys. Rev. E* **73**, 046204 (2006).

[4] C. Mollica, T. Zimmermann and J. Vanicek, "Efficient sampling avoids the exponential wall in classical simulations of fidelity," arXiv:1108.0173v1 [nlin.CD] (2011).

[5] T. Zimmermann and J. Vanicek, "Communications: Evaluation of the nonadiabaticity of quantum molecular dynamics with the dephasing representation of quantum fidelity," *J. Chem. Phys.* **132**, 241101 (2010).

[6] T. Zimmermann and J. Vanicek, "On the nonadiabaticity of molecular quantum dynamics," submitted, *J. Chem. Phys.* (2011).

[7] M. Wehrle, M. Sulc, and J. Vanicek, "Accelerating Calculations of Ultrafast Time-Resolved Electronic Spectra with Efficient Quantum Dynamics Methods," *Chimia* **65**, 334 (2011).

## **Theoretical Study of Non-Stoichiometric $\text{Li}_x\text{Si}_y^-$ Clusters for Development of Novel Lithium-ion Batteries**

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Rechargeable Li-ion batteries are the most promising energy storage devices for hybrid, plug-in hybrid electric, and all-electric vehicles. Lithium is an ideal material for batteries: it is the lightest metal in addition to having a high electric potential. Charging a lithium-ion battery usually means moving lithium ions from cathode into anode. There is an increasing interest in developing rechargeable lithium batteries with higher energy capacity and longer cycle life for applications in portable electronic devices and electric vehicles. Currently, the graphite anode is the most commercially used due to its good capacity ( $372 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ ) together with its rate capability and long life. Silicon has recently become very popular as a potential anode material for lithium batteries because it has a low discharge potential and the highest known theoretical charge capacity (which could be ten times that of graphite). However, silicon anodes have limited applications because of its large volume change upon lithium insertion or extraction. Silicon nanowires have been shown to be promising as high-performance lithium battery anodes because they can accommodate large strains derived from lithium charging or discharging. We would like to study lithium silicon nanoclusters  $\text{Li}_x\text{Si}_y^-$  as model systems to understand the structural changes and mechanisms of lithium intercalation and deintercalation in silicon nanostructures. We are interested in finding the maximum number of Li atoms that a given silicon nanocluster can accommodate with a charge transfer from Li to Si and how lithiation changes the native structures of the silicon clusters. Finding the maximum number of lithium atoms that can be bonded ionically to a silicon cluster will help evaluation of the charge capacity of silicon nanostructures, which can be directly related to the maximum energy density stored by a particular silicon nanocluster. In particular, we are interested in finding silicon nanoclusters with maximum capacity for lithiation with charge transfer and minimal structural changes. Such information will be highly valuable to guide the search for optimal silicon nanostructures to develop new lithium batteries with high-energy storage capacity. The recent results on this field will be presented in this talk.

# UNUSUAL RESONANCE STATES FOR A CONTROL OF MOLECULAR PROCESSES

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The interaction of a molecule with a cw laser field is described by a time-periodic Hamiltonian. The wave equation has solutions given by the Floquet formalism, with eigenvalues called the quasi-energies. If the field can lead to photodissociation of the molecule, these quasi-energies are complex, with an imaginary part yielding the photofragmentation rate. These resonance energies are in fact the poles of the scattering matrix. In the case of intense fields, there is a richness of new processes. Some of the resonances, when varying the intensity for a given wavelength, can present a zero width. This ensures the stability of the molecule even in the presence of an intense field. This can be turned into a filtration scenario, where all states presenting this property are the only surviving states at the end of a pulse [1]. There is also the possibility, with an appropriate choice of laser frequency and intensity, to provoke the degeneracy of two Floquet quasi-energies. The corresponding point in parameter plane is called exceptional. Such points have recently been studied in many areas of physics, either classical or quantum. They have a number of very important consequences. At an exceptional point the two resonance wave functions merge into a single one, which is "self orthogonal". The concept of self-orthogonality is due to the special scalar product valid for resonance wave functions. With an adiabatic variation of the parameters along a closed contour around an exceptional point, it is possible to go from one field-free vibrational state to another. In order to realize such a transfer, it is necessary to reach a compromise between two conflicting conditions: the laser pulse must vary slowly enough for an adiabatic transfer to take place, but fast enough to keep a fair amount of undissociated molecules. Cooling scenarios can then be formulated [2-3]. The two molecular species which are studied are  $H_2^+$  and  $Na_2$ , the latter being a strong candidate for molecular cooling.

[1] O. Atabek, R. Lefebvre, C. Lefebvre and T.T. Nguyen-Dang, Phys. Rev. A 74, 063412(2008).

[2] O. Atabek, R. Lefebvre, M. Lepers, A. Jaouadi, O. Dulieu and V. Kokoouline, Phys. Rev. Lett. 106, 173002(2011).

[3] R. Lefebvre, O. Atabek, M. Sindelka and N. Moiseyev, Phys. Rev. Lett. 103, 123003(2009).

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# THEORETICAL INVESTIGATION OF A HIGHLY STEREOSELECTIVE BISTHIOUREA ORGANOCATALYZED DIELS-ALDER REACTION

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Despite rapid progress in organocatalyst development, practical and efficient asymmetric approaches remain in high demand. An ideal asymmetric reaction would be atom-economical and rapid, performed under mild conditions to yield quantitative and enantiomerically pure products with catalyst and solvent recycling. Organocatalytic asymmetric Diels-Alder reactions have been approached using iminium, enamine, and bifunctional acid-base catalysis as well as hydrogen-bonding catalysis. Very recently, an unusually efficient organocatalytic asymmetric Diels-Alder reaction of 3-vinyl indole **1** and methyleneindolinone **2** using bisthiourea H-bonding catalyst **3** to yield carbazolespirooxindole skeletons **4** with up to three stereocenters, has been described<sup>1</sup> (Figure 1).

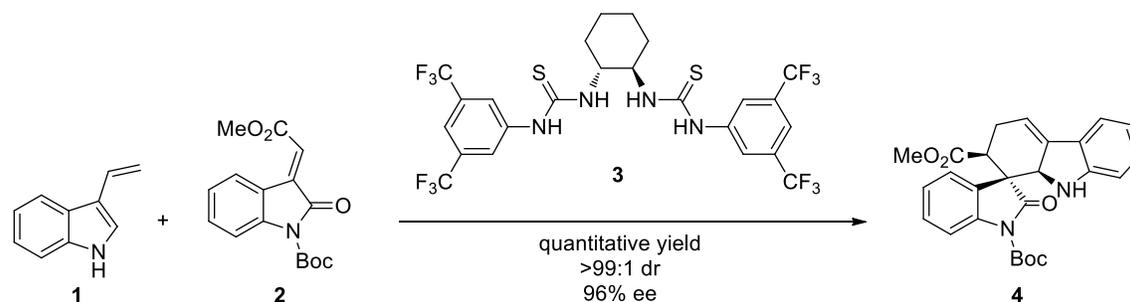


Figure 1. Asymmetric Diels-Alder reaction of 3-vinyl indole and methyleneindolinone

In this communication, a thorough theoretical study on the mechanisms of asymmetry induction is reported. A detailed conformational search of the rather flexible bisthiourea organocatalyst both in the free and complexed states, as well as the substrate-organocatalyst coordination modes, was necessary to account for the experimentally observed stereoselectivity levels. The inclusion of dispersion forces in the theoretical method was key to properly describe the reaction potential energy surface.

As a side project derived from this study, a new computational tool for the conformational and stereochemical diversification of transition structures, is currently under development.

<sup>1</sup> B. Tan, G. Hernández-Torres, C. F. Barbas, III, *J. Am. Chem. Soc.*, **2011**, *133*, 12354–12357.

# **Efectos de varios confinamientos sobre la estructura electrónica de sistemas atómicos y moleculares**

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En esta plática discutimos los efectos sobre sistemas atómicos y moleculares cuando están bajo confinamientos espaciales, impuestos por diversas situaciones. Mostramos la importancia del modelamiento del confinamiento para entender los mecanismos involucrados sobre la estructura electrónica de átomos o moléculas cuando estos sistemas se encuentran confinados. Usando varias paredes de confinamiento y la teoría de funcionales de la densidad podemos conectar algunos de nuestros resultados con una contraparte experimental. Entre las cantidades discutidas en esta plática se encuentran las energías totales y orbitales, polarizabilidades, densidad electrónica y energías de excitación.

## **Effects of several confinements on the electronic structure of atomic an molecular systems**

In this talk we discuss the effects on atomic and molecular systems when they are under spatial confinements, imposed by diverse situations. We show the importance of the confinement modeling in order to understand the mechanisms involved on the electronic structure of atoms or molecules when these systems are confined. By using several confinement walls and the density functional theory we can link some our results with an experimental counterpart. Total and orbital energies, polarizability, electronic density and excitation energies are among the quantities discussed in this talk.

# NATURE OF CHEMICAL BONDS BY MEANS OF PIRIS NATURAL ORBITAL FUNCTIONAL THEORY

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In this work the Natural Orbital Functional Theory (NOFT) is used for the first time in the analysis of different type of chemical bonds. Concretely, the Piris Natural Orbital Functional formulation, in its fifth version (PNOF5) has been used. It provides an a-priori localization scheme that yields a natural orbital picture that agrees very well with empirical Valence Shell Electron Pair Repulsion theory (VSEPR) and Bent Rule, along with other theoretical pictures provided by Valence Bond (VB) or Linear Combination of Atomic Orbitals Molecular Orbital (LCAO-MO) methods. In this context, the interpretation of PNOF5 natural orbitals and their occupation numbers provide a bridge connecting the VB and the LCAO-MO interpretation. Therefore, it introduces a novel tool for the chemical bond analysis. In this work this method is applied to selected molecules that cover from ionic, polar covalent, covalent, multibonds (sigma and pi), 2e-3c to 4e-3c bonds. Concretely, LiF, HF and N<sub>2</sub> have been chosen as diatomic ionic, polar covalent and covalent molecules. Some organic (HCN, H<sub>2</sub>CO, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) and inorganic molecules (H<sub>2</sub>O, NH<sub>3</sub>, and BF<sub>3</sub>) are studied for single and multiple bond-containing molecules. Finally, diborane and CH<sub>5</sub><sup>+</sup> cation are analyzed for 2e-3c systems and BrF<sub>5</sub> for 4e-3c systems (hypervalency).

# EVIDENCIA TEÓRICA DE LA FORMACIÓN DE POZOS ELECTRÓNICOS EN EL INTERIOR DE LOS COMPUESTOS MACROCÍCLICOS PIROGALOL[4]ARENOS

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Los pirogalol[4]arenos son compuestos macrocíclicos de gran importancia en el campo de la química supramolecular debido a su capacidad de adsorber selectivamente y transportar moléculas huéspedes de pequeñas y medianas dimensiones. Existe una gran cantidad de evidencia experimental que indica que la conformación que adoptan los pirogalol[4]arenos sintetizados mediante la condensación de 1,2,3-benzotriol (*i.e.*, C<sub>6</sub>H<sub>3</sub>(OH)<sub>3</sub>) con aldehídos (*i.e.*, R-CHO), depende exclusivamente del grupo R del aldehído empleado. A este respecto se ha determinado que aldehídos con grupos R arilo dan paso a la formación de pirogalol[4]arenos con conformación de silla (*rcff*) mientras que aldehídos con grupos R alquilo promueven la formación de estructuras con conformación de copa (*rccc*). El presente estudio cuanto-mecánico realizado a nivel B3LYP/6-311G(d,p) se enfoca en la descripción teórica de estas dos conformaciones que adoptan los R-pirogalol[4]arenos y muestra que aparte del control estructural que se puede lograr variando el aldehído usado como precursor, las propiedades electrónicas de estos compuestos también pueden ser modificadas. En particular, se muestra que se puede formar un *pozo electrónico* en el interior de la cavidad de los *rccc* R-pirogalol[4]arenos dependiendo de las características electro-donadoras o electro-aceptoras del grupo sustituyente R.