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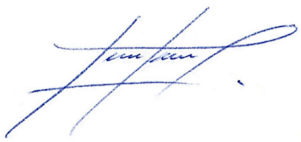
Presentation of the XL Edition

2014 will be remembered as a significant year for the Community of Theoretical Chemists of Latin Expression, because the QUITEL congress is held in Ecuador for the first time. In order to celebrate the incorporation of Ecuador to the QUITEL hystory, the ecuadorian Local Organizing Committee has chosen San Cristobal Island in the Galápagos Archipelago to host the XL Edtion of the Congress. We hope that all the attendees of QUITEL2014 will have fruitful scientific discussions while enjoying the natural beauties of the so-called enchanted islands.

We would like to thank all the members of the QUITEL community for the great number of contributions submitted to be presented in the current edition. We have selected the best papers to guarantee the high standards that characterize the scientific program of the QUITEL congresses.

On behalf of the organizing commitee



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From photosynthesis to sensors, solar cells and photovoltaics: How is theoretical chemistry helping us to understand how they work and control the design of devices

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Abstract. Understanding complex physico-chemical process occurring at nano–interfaces has become a key element in expanding our technological capabilities to be able to fabricate new optical, electronic and magnetic devices. It is also crucial in artificial photosynthesis and other alternatives for energy and charge storage and production, including solar cells and photovoltaics. Molecules at nano-interfaces behave as open quantum systems coupled to an environment of mesoscopic size with which energy, spin and charge can be exchanged. In addition, many systems of interest include exposure to an electromagnetic field, such as a laser or sunlight, that induces excitation and transfer processes and the possibility of chemical reactions of enormous importance for mankind such as CO_2 activation and water splitting. Using our own research in spin, energy and charge transfer at nano-interfaces as a guiding example, we will explore some of the fundamental challenges in the field, and the use of novel and traditional theoretical approaches to explore the dynamics of charge, energy and spin transfer. We will also examine the question of how our improved understanding of the fundamental chemistry and physics involved in this dynamics is helping the design of devices, and expanding the fields of energy, electronics, spintronics, nano-photonics and nano-catalysis in ways that can have a fundamental impact in our lives.

Keywords. Energy transfer, charge transfer, spin transfer, devices, nano-interfaces.

Recent advances in computational proteomics

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Abstract. During this talk I will summarize the most recent developments in computational proteomics that are taking place within our group. The talk will focus on two subjects. The first will be the calculation of enzyme reaction mechanisms with QM/MM techniques, emphasizing the methodological aspects that have to be taken into consideration to achieve accurate and reliable results. The role of enzyme exibility on catalytic rates will be addressed as well. The second subject will be computational proteomics, where methods for accurate calculation of the efect of point mutations in proteins and for protein-protein docking will be presented and discussed.

Keywords. QM/MM, enzyme catalysis, computational mutagenesis, protein-protein docking.

Theoretical study of the effect of heterogeneous medium in the electronic properties of molecules with biophysical interest

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Abstract. Solvent effects are of essential importance in many different aspects of physics, chemistry, biology and material sciences. The developments of quantum chemistry methods originally devised for studying isolated molecules have been extended to study the properties of atoms and molecules interacting with the environment. This led to the continuum methods that treat the solvent by means of average macroscopic constants, such as the dielectric constants. Very successful in different applications these continuum methods lack the consideration of the microscopic details and the necessary statistic representation of the thermodynamic molecular system. The natural extension has been to incorporate some molecular mechanics methods to generate solute-solvent structures and couple this with the quantum mechanical methods to obtain the solvent effects in the solute properties. This is the essence of the so-called QM/MM methods where part of the system is treated by molecular mechanics (MM) whereas the remaining is treated by quantum mechanics (QM). We have been involved in the developments of a sequential procedure (S-QM/MM) [1] where the MM simulations are used to obtain the structures of the solution for subsequent QM calculations. In this presentation we report some developments [2, 3] of this methodology and we address to some applications in electronic polarization and spectrum for some organic molecules in different environments, such as homogeneous liquid [4-5], mixtures [6] and phospholipid membranes [7].

Keywords. Electronic properties, heterogeneous medium, mixture, bilayer.

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A new path for nanoparticles: Toward fully synthetic protein mimics and beyond

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Abstract. Drug-delivery depends crucially on the ability to translocate drugs across the cell membrane. While some drugs do this naturally, most of the promising new therapies require a vehicle (or vector) that will deliver the drugs into the cytosol. The most common approach to enter the cell is to use the natural process of endocytosis, yet this poses serious challenges because the carriers are trapped in endosomes within the cell. Recently, it was discovered that a particular class of nanoparticles can enter the cell through non-endocytotic pathways without disrupting the membrane. These nanoparticle are composed of Au protected with a multi component ligand shell. Such nanoparticles essentially behave a "nano chamaleons" altering on-the-fly their surface chemistry to mimic that of the membrane. In this talk I will discuss the origins of such behavior and uncover the pathway by which such nanoparticles enter cells. In particular, I will explain in detail how one can control the interfacial properties of the nanoparticle and potentially target different membrane compositions. These nanoparticles can mimic several different functions performed by membrane proteins such as fusion proteins and lipid shuttling proteins, opening new possibilities in delivering drugs, as well as serving as artificial proteins themselves. Thus, understanding and controlling such a system can potentially be utilized in a wide variety of medical and biological technologies.

Keywords. Nanoparticles, bionano interfaces, lipid membranes, drug-delivery.

Acknowledgements. This work has been partially supported by the National Science Foundation.

Finding renewable-energy organic materials using high-throughput computational discovery approaches

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Abstract. A transition to a renewable energy economy is required for insuring a sustainable future for humanity and avoiding climate change. Organic materials have the potential to revolutionize energy generation (photovoltaics) and storage (flow batteries) due to their low costs of synthesis and of device fabrication. Our research group and collaborators have embarked on several projects that seek to accelerate the computational discovery of organic molecules and materials by employing a multipronged approach. First, intimate collaboration with experimentalists is a requirement for success. Second, the use of experimental and theoretical data on an equal footing, as well as embracing the use of tools such as machine learning allows for rapid progress in the discovery process. Third, a database-centric high-throughput computational framework is required to analyze the tens of thousands to millions of molecules required for screening the appropriate materials [1, 2]. I will talk about our group's approach to these problems, as well as the application to organic photovoltaic materials (http://cleanenergy.harvard.edu) [3, 4] as well as the discovery of new molecules for organic flow batteries [5]. If time permits, I will talk about or work on organic semiconductors and light-emitting diodes using similar molecular discovery tools.

Keywords. Photovoltaics, flow batteries, renewable energy.

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A new justification for hybrid functionals in DFT

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Abstract. In hybrid functionals, the local potential of the Kohn-Sham equations is modified to allow for mixed exchange functionals where in addition to the OEP local potential (or an approximation devised at some rung of Jacob's ladder in DFT) a Hartree–Fock non–local contribution is added. Similarly, in double hybrid functionals, in addition to the above changes in the exchange potential, the local correlation potential is replaced by a mixture of a non-local potential derived from a second-order term in perturbation theory and a local term approximated in the context of DFT. In what follows we show that the same variational principle used to derive the exact local exchange potential (OEP), and which can be extended to derive *ab initio* DFT, can be used to derive Kohn–Sham–type equations with arbitrary hybrid potentials [1]. As a simple example, we generate a simple hybrid potential for the exchange-only case. In addition we illustrate this procedure for double hybrid potentials.

Keywords. Hybrid functionals, DFT, local exchange potential.

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N-representable 1-RDM Theory

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Abstract. Since the Hamiltonian operator contains only one- and two-electron operators, the energy of a molecule can be determined exactly from the knowledge of the one- and two- particle reduced density matrices (1- and 2-RDMs). In 1974, Gilbert proved for the 1-RDMs an analogous theorem to the Hohenberg-Kohn theorem for the density. Accordingly, one can employ the exact functional with an approximate 2-RDM that is built from the 1-RDM using a reconstruction functional. The major advantage of a 1-RDM formulation is that the kinetic energy is explicitly constructed and does not require a functional. Like for the density, the ensemble N-representability conditions of the 1-RDM are well-known, but this does not overcome the N-representability problem of the energy functional. The 1-RDM functional is called Natural Orbital Functional (NOF) [1] when it is based upon the spectral expansion of the 1-RDM. An approximate reconstruction, in terms of the diagonal 1-RDM, has been achieved by imposing necessary N-representability conditions on the 2-RDM [2]. Appropriate forms of the two-particle cumulant have led to different implementations [3], being the most successful the PNOF5 [4] and its extended version PNOF5e [5]. On the other hand, antisymmetrized product of strongly orthogonal geminals (APSG) with the expansion coefficients explicitly expressed by means of the occupation numbers have been used to generate these NOFs [6], which demonstrates strictly the N-representability, size-extensivity and size-consistency of the functionals. Moreover, it opens the possibility of using a perturbation theory to recover the missing dynamic correlation. In this presentation, the theory behind this method is outlined, and some examples are presented to illustrate its potentiality. Special emphasis will be done on strong correlated problems. Our results are accurate values as compared to high level wavefunction methods and available experimental data.

Keywords. N-representability, reduced density matrices, natural orbitals, APSG wavefunction.

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Leveraging machine learning and stream processors for computational chemistry

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Abstract. Novel computational architectures and methodologies are revolutionizing diverse areas ranging from video gaming to advertising and espionage. In this talk, I will discuss how these tools and ideas can be exploited in the context of theoretical and computational chemistry. I will discuss how insights gleaned from recommendation systems (such as those used by Netflix and Amazon) can lead to reduced scaling methods for electronic structure (solving the electronic Schrödinger equation to describe molecules) [1–4], how the algorithms in electronic structure can be adapted for commodity stream processing architectures such as graphical processing units,[5–8] and how nonlinear dimensionality reduction methods can be used to extract chemical knowledge from the resulting data [9]. I will also show how these advances can be harnessed to progress from traditional "hypothesis–driven" methods for using electronic structure and first principles molecular dynamics to a "discovery–driven" mode where the computer is tasked with discovering chemical reaction networks. Finally, I will show how these can be combined with force–feedback (haptic) input devices and three–dimensional visualization to create molecular model kits that carry complete information about the underlying electrons. This interactive first principles molecular dynamics method (molecular computer–aided design) opens the door to novel ways of teaching chemistry and may also be of use in applied chemical research.

Keywords. GPU, tensor contraction, quantum chemistry, *ab initio* molecular dynamics.

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Ab-initio methods for time-resolved attosecond dynamics of laser-driven many-electron molecules

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Abstract. Ultrafast spectroscopic [1, 2] and imaging [3, 4] schemes using short and intense laser pulses hold great promises in Chemical Physics, as the matching of the durations of these pulses with the characteristic periods of molecular motions means that one can take snapshots and videos of these motions on their natural time-scales. Molecular and/or electronic processes unfolding under an ultrafast intense laser pulse are highly non-linear however, and their descriptions require new non-perturbative theoretical and computational tools to be developed. After reviewing these new challenges in theoretical chemistry, we will focus on the description of time-resolved multi-electron, attosecond dynamics by an *ab-initio* approach, highlighting in particular the way a number of powerful tools of stationary-state Quantum Chemistry can be adapted to suit the new context, that of time-dependent non-perturbative electron dynamics [5, 6]. Results of calculations on a number of few electron systems, in particular ionic-channel-resolved photoelectron spectra resulting from strong field molecular ionizations under a few-cycle NIR and/or XUV pulse, will be shown to illustrate the concepts and methodological ideas developed throughout the talk.

Keywords. Ultrafast dynamics, *ab-initio* electron dynamics, strong-field ionization, time-dependent Quantum Chemistry.

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The chemical bond overlap polarizability and covalency. Concepts and applications: From diatomic molecules to solids

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Abstract. The concepts of chemical bond overlap polarizability (OP) and ionic specific valence (ISV) have been introduced, about a decade ago (2002), in the context of the ligand field theory applied to lanthanide compounds. These concepts led to relevant conclusions on the interpretation of the non-spherical ligand field interaction in terms of covalency. They have also been explored in a more general context outside the scope of ligand field theory. Thus, they have proven to be useful in the case of diatomic molecules, allowing to establish a new covalency scale in excellent agreement with Pauling's scale and analytically quantifiable in terms of the OP. An analysis on this subject in 2005, in which the overlap region is regarded as a localized plasmon-like mode of oscillation (chemical bond overlap plasmon – CBOP), characterized by the OP, has raised the possibility of absorption and inelastic scattering of radiation, specifically by the overlap region, in an oscillation mode distinguishable from the collective plasmon of the system. Predicted oscillator strengths and scattering cross sections for diatomic molecules are considerably high and can be measured in the UV up to the near soft-X-rays spectral regions. The possibility of detecting the CBOP in diatomic molecules by electron energy-loss measurements has also been analyzed. Different treatments by using the Valence Bond Theory and a Localized Molecular Orbital approach have been evoked to describe de OP concept and the CBOP proposal, in polyatomic molecules and hydrogen bonding. The CBOP has been shown as a promising tool for quantifying covalency also in solid-state materials, opening a way to classifying materials in terms of average covalent fractions. Interesting questions could be raised on possible relationships between macroscopic properties of materials and the OP concept. For instance, a good correlation has been found between the non-linear index of refraction (n2) and the OP, though the comparison has been made between the precursor diatomic molecule and the solid-state material. Some unassigned bands in the electron energy-loss and absorption spectra of crystalline alkaline-earth chalcogenides and some alkali and alkali-earth metals in solid-state systems have been discussed in terms of the CBOP, raising the possibility of new assignments alternative to exciton or band-to-band transitions [1].

Keywords. Polarizability, covalency, chemical bond.

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The "converse" method for the calculation of NMR and EPR parameters: Theory and *ab-initio* calculations

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Abstract. The electric polarization (**P**) and the orbital magnetization (**M**) are well known textbook topics in solid state physics. While it is easy to compute their derivatives in an extended system, **P** and **M** themselves are not easy to formulate, due to the unboundedness of the position operator. The problem of the electric polarization has been solved in the '90s by the Modern Theory of Polarization (MTP) [1-2], which relates the electric polarization to the electrons Berry phase. Only recently, two independent groups found a formula for the orbital magnetization in periodic systems [3-5]. I will briefly review our derivation, which is based on Wannier functions, and I will present first principles calculations of the orbital magnetization by the plane wave pseudopotential method. As an application, I will show that the NMR chemical shifts and the EPR g-tensor can be calculated from the orbital magnetization by a "converse" approach. The advantages of the new approach are: (1) it avoids any linear response calculation, (2) it is not plagued by the gauge-origin problem of most quantum chemistry methods.

Keywords. Berry phase, GIPAW, pseudopotential, NMR/EPR parameters.

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Electronic and vibrational energy relaxation after photoexcitation in chlorophylls

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Abstract. Optical properties of chlorophylls have drawn considerable attention because of their fundamental and biological relevance. Chlorophylls play an essential role in the conversion of sunlight into chemical energy in green plants and various algae. Furthermore, they are also widely studied as candidates for molecular electronics applications. In this work, Non-Adiabatic Excited-State Molecular Dynamics simulations (NA-ESMD) [1] have been performed to study the internal conversion process in three different chlorophylls a, b, and d. We aim to achieve a detailed comprehension of the ultrafast intramolecular electronic and vibrational energy transfer that takes place after photoexcitation. Within our NA-ESMD framework, direct nonadiabatic molecular dynamics simulations can be applied to describe photoinduced dynamics in large organic conjugated molecules involving multiple coupled electronic excited states. Such NA-ESMD simulations are performed by combining the molecular dynamics with quantum transitions (MDQT) approach with "on the fly" analytical calculations of excited state energies, gradients, and non-adiabatic couplings terms. This is possible using the collective electron oscillator (CEO) method at the configuration interaction singles (CIS) level to describe correlated excited states [2–4]. Briefly, the method treats the electronic degrees of freedom quantum mechanically, while the motion of the nuclei is treated classically. The nuclei evolve on a potential energy surface (PES) that is defined by a single electronic state at a given time. Jumps from one electronic state to another are governed by the coefficients of the electronic wave function. Our results are in good agreement with femtosecond time-resolved spectroscopic experiments [5]. We present comparative results of the intramolecular redistribution of the electronic transition density during the internal conversion process in the three different chlorophylls. Besides, we identify the group of active middle-to-high frequency vibrational normal modes that participate in the electronic energy transfer process. There fore, we describe the vibrational modes that induce coupling between the electronic excited states.

Keywords. Non-adiabatic dynamics, excited electronic states, normal modes.

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Electron-molecule collisions: The influence of microsolvation on the shape resonance spectra and on the differential cross sections

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Abstract. Boudaïffa and co-authors [1] reported that low-energy electrons can cause single and double strand breaks in DNA. The strand breaks are caused by the occupation of an empty molecular orbital by the incoming electron, forming a transient negative ion (resonance). This resonance can initiate a dissociative process along some particular bond. The DNA is a large system to be treated computationally and the available studies consider small systems that in some way resemble the DNA (DNA subunits, acids, alcohols and water). Most calculations and experiments on electron-molecule collisions with these biological molecules were performed in the gas phase. Whereas it is far from the reality in life tissues, it was possible to obtain good insight into the dynamics of electron interactions with DNA. We considered the influence of microsolvation on the π^* resonance of formaldehyde [2] and of formic acid [3], and in the two lowest π^* resonances of phenol [4] through electron collisions with complexes formed by these molecules and one or two water molecules. Depending on the role of the water on the hydrogen bond, the resonance of the complex can stabilizes (if the water is proton donor) or destabilizes (if the water is proton acceptor). Here we will present the cross sections for electron collisions with the systems discussed above. We will also discuss the microsolvation signature looking at the differential cross sections. We employed the Schwinger multichannel method with pseudopotentials [5, 6] to compute the cross sections in the static-exchange and in the static-exchange-polarization approximations.

Keywords. Shape resonances, cross sections, elastic scattering, solvation effects.

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Spin states along the catalytic cycle of non-heme Fe-containing enzymes

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Abstract. Histone demethylases regulate the degree of methylation in lysine residues of histones. These enzymes play an essential role in epigenetics, namely heritable covalent changes in chromatin that do not modify the sequence of bases of DNA. Epigenetic phenomena are very relevant in cancer and therefore histone demethylases have emerged as very attractive therapeutic targets in oncology [1, 2]. In particular, JmjD domain-containing demetlylases are specially promising [3]. The structure of the active site of JmjD2A has been determined by X-ray diffraction analysis [4] and a plausible mechanism for the demethylation reaction has been proposed. However, the details of the reaction, the origins of the selectivity of JmjD enzymes, and the spin states along the catalytic cycle have not been determined. In this communication, we present our DFT results obtained for model systems that mimic the chief geometric and electronic features of the active site of JmjD domain-containing enzymes bound to model substrates possessing different methylation degrees. We have found that the demethlyation reaction catalyzed by these non-heme Fe enzymes consists of a two step process involving at least two spin states and one minimum energy crossing point (MECP) [5]. These results are compatible with the main features observed experimentally for these enzymes and suggest novel design criteria for the development of novel inhibitors.

Keywords. DFT, two-state reactivity, histone demethylases, epigenetics.

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Gap behavior of Fibonacci molecular nanowire based on CH_2 and SiH_2 radicals

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Abstract. Recently, Fibonacci nanowires have attracted attention due of remarkable multifractal signature in their electronic spectra [1]. In this work, we report theoretical calculations of the electronic spectra of molecular nanowire where its molecular components are arranged in a Fibonacci quasi-periodic sequence. This nanowire is formed by CH_2, and SiH_2 radicals. We have used molecular mechanics with universal force field(UFF) for obtain the optimized initial structures, and semi-empirical quantum method based on Hückel extended model, and density functional based on tight-binding, as single point as full relaxation to obtain the electronic spectra. Although the calculations presented here are more complete than the models adopted in the literature which take into account the electronic interaction, up to the second and third neighbors, an interesting property that remains is their gap energy. We discuss the electronic gap behavior with the increasing of the nanowire Fibonacci generation in both approximations.

Keywords. Molecular mechanics, Hückel extended, density functional based on tight–binding, CH_2, SiH_2 radicals

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The reaction pathway leading to the formation of 2–aceto–2–hydroxybutyrate in the catalytic cycle of AHAS

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Abstract. The reaction between the intermediate HEThDP$^-$ and 2-ketobutyrate, in the third step of the catalytic cycle of acetodydroxy acid synthase (AHAS), is addressed from a theoretical point of view by means of hybrid quantum/molecular mechanical (QM/MM) calculations. The QM region includes one molecule of 2-ketobutyrate, the HEThDP$^-$ intermediate, and the residues Arg 380 y Glu 139; while the MM region includes the rest of the protein. The study includes potential energy surface (PES) scans in order to identify and characterize critical points on it, transition state search and activation barrier calculations. The results show that the reaction occurs via a two-step mechanism corresponding to the carboligation and proton transfer in the first stage; and the product release in the second step [1].

Keywords. AHAS, catalytic cycle, QM/MM.

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Finding reasons why two structural related enzymes catalyze distinct reactions

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Abstract. Trypanosoma *cruzi* trans-sialidase (TcTS) is a crucial enzyme for the infection of the protozoa responsible for Chagas' disease. It catalyzes the transfer of sialic acids from the host glycoconjugates to the parasite glycoconjugates. *Trypanosoma rangeli* sialidase (TrSA) is an enzyme of the same family, shares 70% of sequence identity with TcTS, the C_α-RMSD between them is only 0.59 Å and both enzyme active sites are surprisingly similar. In spite of these similarities, TrSA does not transfer sialic acids but only cleave it from sialyl-glyconjugates. Numerous single, double, triple and quintuple mutants have been experimentally tried in order to confer TrSA, transialidase activity. This goal was achieved in only one case (the quintuple mutant) and the activity was pretty low (1%). In this presentation we describe in detail the entire mechanistic pathway of both enzymes [1, 2], highlighting their most significant similarities and well as the apparently tiny differences. Our results are able to explain why they catalyze different reactions and reveal the reasons of the low activity found in the quintuple mutant. Besides, based on energetical and configurational analysis, we identify five extra mutations to be introduced in the quintuple mutant that would confer TrSA full TcTS activity [3].

Keywords. *Trans*-sialidase, sialidase, QMMM.

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Membrane binding of a curvature-sensing peptide of a lipid transport protein in yeast

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Abstract. This work presents the preliminary steps of the study of a peripheral membrane protein's (Osh4) binding mechanism and function. This protein is member of a family of seven homologue oxysterol binding proteins in yeast. It was previously shown, using molecular dynamics simulations, that Osh4 has six membrane binding regions [1]. Nonspecific interactions with anionic lipids are an important driving force for the Osh4 attraction to yeast membranes. The ALPS-like motif of Osh4, a 29 amino acid peptide which also forms the lid to protect sterols, has also been identified as a membrane curvature sensor [2]. This work examines the binding mechanism of the peptide with bilayers containing different lipid types. A previous study showed ALPS peptides bind to membranes with surface-packing defects [3]. Unsaturated lipids and increasing values of γ were implemented to increase the surface packing defects of our membrane models. The simplest model had only phosphatidylcholine (PC) lipids; phosphatidylserine (PS) and ergosterol (ERG) were added to model yeast membranes more closely. Simulations using pure DOPC bilayers, a lipid with one double bond per tail, were carried out at different values of surface tension (γ). Additional systems were simulated to look at binding events with charged bilayers, and bilayers containing ergosterol. These systems include DOPC-DOPS, 60:40 and 70:30 mixtures; and DOPC-ERG, 50:50 and 70:30 mixtures. Molecular dynamics were carried out for at least 100ns using the CHARMM36 force field and the NγPT ensemble. Binding events were characterized through hydrogen bonding and binding free energy calculations. Since binding events are stochastic, replicate simulations were carried out for each system.

Keywords. Molecular dynamics, peripheral proteins, ALPS-like peptides, free binding energy.

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Hybrid potential methods for the simulation of condensed phase reaction processes

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Abstract. Hybrid quantum mechanical/molecular mechanical potentials are powerful tools for the simulation of reactions and other processes in condensed phase systems. This presentation will concentrate on the types of hybrid potentials that are used in the author's group, detail their implementation in the molecular simulation package, pDynamo, and highlight recent methodological developments aimed at increasing their efficiency and precision. A number of pertinent case studies will be described that illustrate the use of the presented methods.

Keywords. Enzyme catalysis, hybrid quantum mechanical/molecular mechanical potentials, molecular simulation, condensed phase reaction processes.

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Complex physical chemical properties of water in nanospaces

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Abstract. Water molecules can take complex behaviour under extreme conditions at nanoscale level [1]. Biomimetic ice forms can be formed at low temperature and pressure exciting the surface with electric fields, such as, microscopic palm leaves or icy microworms [2]. In salty sea water, macroscopic tubes of ice are formed due to interactions at microscopic level. These forms have been detected recently in nature [3]. Mixtures of water with hydrophobic molecules, like methane and CO_2, can form clathrates as gas hydrates. Gas hydrates are crystalline compounds consisting of gas molecules encaged in cavities of a hydrogen-bonded network of water molecules. Methane hydrates are found in permafrost regions and sediments of the ocean floor. Phyllosilicates are major constituents of ocean sediments and their interactions with hydrates on seafloor can determine variations on hydrate stability. Characterization and better understanding of those deposits are necessary to develop CO_2 storage as hydrates by methane replacement, and to explore these clathrates in other planets. Molecular Dynamics simulations of these clathrates within the interlayer nanospace show that the CO_2 and methane hydrate structures are more stable in the smectitehydrate complex [4]. First principles calculations show clathrates of alkylammonium with water in the interlayer nanospace of vermiculite. *Ab initio* molecular dynamics can explain the water behaviour in pyrophyllite dehydroxylation.

Keywords. Ice, interlayer space, phyllosilicates, clathrates, gas hydrates, molecular dynamics.

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Nanostructured clay minerals: A SCC-DFTB Study

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Abstract. We have applied the SCC-DFTB method for investigating the clay mineral nanotubes (NTs) such as halloysites, imogolites and chrysotiles. The SCC-DFTB method requires the so-called Slater-Koster files and the parameterization of the atomic pairs. A set of parameters are available elsewhere (www.dftb.org). However, for some of the systems studied the SCC-DFTB parameterization was necessary. The parameterization normally involves intensive manipulation of files, chemical models and programs in order to set up the correct parameters that describe reasonably the target system. In order to avoid human error in handling files and other data and increase the quality of the parameters, we developed the FASP (Framework for Automatization of SLAKO Parameterization) program. FASP is a framework that automates the procedure of finding the best polynomial fit (based on statistical criteria) that describes the E_{rep} of atomic pairs for a set of interception points of the band (E_{bnd}) and reference (E_{ref}) energy. The quality of the parameters is evaluated based on the description of the structural properties of desired molecules, clusters and solids (obtained from experiment or any quantum chemistry method) set in a database. The new parameters were used to investigate NTs with well defined structure such as imogolite-like NTs[1]. These NTs are monodisperse with well-defined diameter, length and chirality, which has been observed experimentally and predicted by theory. We have shown that the Ge-imogolite derivative can form double-walled tubes with the strongest stabilization found for tube indexes with nine units of difference around the circumference. The minimum structure is found for the (12,0)@(21,0) tube. In this presentation we intend to show the strategy used to develop the FASP program and the SCC-DFTB parameterization. The results obtained for the Geimogolite NTs will be also presented and discussed.

Keywords. Clay minerals, imogolites, SCC-DFTB, parameterization, nanotubes.

Acknowledgements. This work has been supported by the Brazilian agencies INCT-ACQUA, CAPES, FAPEMIG, CNPq.

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MRI contrast agents interacting with water molecules: Hierarchical clustering method for molecular dynamics data analysis

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Abstract. A revised method to compute mean residence time (MRT) from molecular dynamics (MD) simulations is reported. Our methodology is based on hierarchical clustering analysis, and it is proposed as a step for the computational design of novel contrast agents for MRI taking into consideration that MRT of water interacting with a given contrast agent directly affects the quality of the MRI images. It is shown that the presented method is applicable in a wider range of scenarios in MD data analysis.

Keywords. Hierarchical clustering method, magnetic resonance imaging, mean residence time, molecular dynamics data analysis, contrast agents.

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Vibrationally induced dissociation of H_2SO_4

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Abstract. Vibrationally induced dissociation of H_2SO_4 to H_2O and SO_3 is one of the important reactive steps in the Earth's atmosphere. Although this reaction has great significance in atmospheric chemistry, the exact mechanism whereby the reaction happens is still unknown. It has been postulated that the photodissociation of H_2SO_4 to form sulfur trioxide and water, can explain the anomalous enhancement of the polar stratospheric sulfate aerosol layer in the springtime. Because the electronic absorption spectrum of H_2SO_4 up to 140 nm could not be found experimentally, alternative mechanisms, including vibrationally induced dissociation, were proposed [1, 2]. In order to perform the simulation of the photodissociation process Multi State Adiabatic reactive MD (MS–ARMD) was developed.[3] MS–ARMD is a surface–crossing algorithm for modelling chemical reactions in classical MD simulations scheme. With a refined and physically meaningful PES which allows to follow both, intramolecular H-transfer and water elimination within the same framework, it is shown through explicit atomistic simulation that by exciting the υ_9 OH-stretching mode, photodissociation can occur on the ps time scale [4]. Our results suggest that $\upsilon_9 = 4$ is sufficient for the water elimination reaction to occur. Because MS–ARMD simulations allow multiple and long–time simulations, both nonstatistical, impulsive H–transfer and statistical, intramolecular vibration energy redistribution (IVR) regimes of the decomposition can be characterized [4, 5]. The typical rates for H–transfer and water elimination to occur, are on the ps to ns time scale depending on the level of excitation [5].

Keywords. Reactive force fields, H_2SO_4 photodissociation, MS–ARMD.

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Intense laser induced ultrafast molecular processes: Imaging and control

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Abstract. Intense laser fields produce strong internal distorsions in molecules that can be exploited in designing control strategies. These strategies rest on some resonances and their underlying basic mechanisms. In the high frequency visible-UV 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* [1]. More unexpectedly, the dissociation may 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 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 [2]. 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 processes. Here we report a theory versus experiment comparison on the dissociative ionization of H_2 in a two-color (attopulse XUV pump+intense IR probe) field, where the variation of the IR pulse duration 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 [3, 4].

Keywords. Attosecond spectroscopy, dissociation, ionization, resonances, basic mechanisms.

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DF-vdW vs. GGA functionals in methane adsorption on Ni surfaces

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Abstract. Although methane on metallic surface, for instance Ni, is a typical case of a weak interaction, this molecular adsorption on Ni has been studied by means DFT using GGA functionals (PW91, PBE) with several works reported in the literature [1-3]. However, there is strong evidence that these functionals do not provide accurate enough information about the physisorption of this molecule on Ni, and on other less catalytically active, surfaces. In this work a systematic study of the adsorption energy and the vibrational frequencies of CH_4 on perfect and stepped Ni surface is presented. Calculations are carried out using PW91 and PBE (GGA) functionals and the approach proposed by Klimeš that includes the PBE functional and the van der Waals (vdW) contribution [4, 5]. In all cases, the surfaces are represented by a periodic supercell model and several sites and molecular orientations have been explored with one, two and three H atoms pointing towards the surface. The results indicate that use of the vdW-functional largely improves the description of this interaction, and allows one to discuss the effect of the surface structure in the adsorption of methane on nickel. The possible implications in the breaking of C-H bonds of this molecule are discussed.

Keywords. DF-vdW, DFT, methane, nickel, adsorption.

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A Hopf bifurcation in a closed system under constant irradiation and the onset of chemical oscillations

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Abstract. A closed system with sustained oscillations of some of its components under illumination may have the ability to transform the energy of light into mechanical energy. However, sustained oscillations were anticipated only for open systems – i.e., exchanging mass with an infinite external reservoir – because a closed chemical system at constant temperature and pressure should attain equilibrium. We designed a closed set of chemical reactions that are at most bimolecular, respect mass conservation, contain three composition variables (x, y, z) and two photochemical steps, that has all the terms required to obtain a Hopf bifurcation, including a bimolecular autocatalytic reaction. These are the necessary and sufficient conditions for oscillatory behavior. We name this system of ordinary differential equations the *Coimbrator*. An analytical study of the *Coimbrator* identifies the equilibrium points and the conditions for periodic orbits to occur. Numerical simulations illustrate the cyclic time-dependence of the composition variables. Interestingly, we found sharp variations in the concentrations of the intermediates x, y and z, followed by relatively long periods of low concentrations of these species. We use the *Coimbrator* to simulate the gross features of climate changes in the absence of astronomical forcing, namely, the CO_2 concentration changes over the last 420,000 years reliably recorded in the Vostok ice core [1]. Additionally, we show how the *Coimbrator* may inspire the transformation a continuous polychromatic light source into thermal pulses amenable to pyroelectrical conversion. Alternatively, thermoelastic expansion in a confined material will produce a pressure pulse, and piezoelectric conversion may convert the pressure pulse in a voltage peak [2]. The transformation of the energy of light into mechanical energy using oscillatory reactions establishes for the first time the foundations for a "solar engine". The thermodynamic and kinetic restrictions of the "solar engine" are discussed.

Keywords. Oscillatory reactions, climate changes, solar engine.

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How reliable is the hard-soft acid-base principle?

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Abstract. By computing the reaction energy for over two million of *actual* double acid–base exchange reactions and the electron-transfer reaction energy of several millions of simulated reactions, we assess the reliability of the global hard–soft acid–base (HSAB) principle. We find that the HSAB principle is often thwarted by the tendency of strong acids to prefer strong bases. We define the strong–weak and hard–soft driving forces to characterize the strength of these two competing effects, and assess the reliability of the HSAB principle for different strengths and directions of the hard–soft and strong–weak driving forces. We also provide mathematical proof of situations where the HSAB principle always holds. A brief criticism to what we consider is a wrong but very common way to enunciate the HSAB principle it is addressed. This is the most comprehensive computational test ever done to the HSAB. Moreover, we also provide the most recent theoretical scrutiny of the HSAB. Finally, we provide a series of probability tables and histograms for making informed predictions about the preferred products of double acid–base exchange reactions.

Keywords. HSAB principle, chemical reactivity, acids and bases.

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Tracking quantum control of arbitrary N-level systems

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Abstract. We propose a tracking quantum control protocol for any observable in arbitrary N-level systems. It is numerically robust (free of divergences) and relatively fast since we need to solve only nonlinear algebraic equations to obtain proper piecewise time-independent potentials (as laser fields) for the control. Multiple solutions are systematically accessed, yielding a simple way to search for the best ones. The method can also test the necessary potential features (*e.g.*, beyond the dipole regime) resulting in easier implementation conditions. Illustrations for 3-, 4-, and 5-level problems are given [1-3].

Keywords. Quantum control, N-level systems, piecewise time-independent procedure.

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Magnetic exchange couplings parameters from density functional theory calculations

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Abstract. I will review our current efforts for the evaluation of magnetic exchange coupling parameters in transition metal complexes from density functional theory (DFT) calculations. I will focus on the performance of different DFT approximations and show that hybrid density functionals containing approximately 30% Hartree-Fock type exchange are in general among the best choice in terms of accuracy [1, 2]. I will also present a novel computational method to evaluate exchange coupling parameters using analytic self-consistent linear response theory. This method explicitly avoids the evaluation of energy differences, which can become cumbersome for large systems. The underlying idea behind this approach is based on the evaluation of the magnetic torque between two magnetic centers for a given spin configuration using explicit constraints of the local magnetization direction via Lagrange multipliers [3]. This method is applicable in combination with any modern density functional with a noncollinear spin generalization and can be utilized in a "black-box" fashion. I will show proof-of-concept calculations in small test systems, and an application to determine the ground state spin of frustrated Fe_7^{III} disk-shaped complexes [4].

Keywords. Magnetic exchange couplings, density functional theory, transition metal complexes.

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Studying positron binding with the any particle molecular orbital method

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Abstract. A number of theoretical methodologies developed within the any particle molecular orbital approach [1], APMO, have been applied to study positron bonding to atoms and molecules [2-3]. Our results show that the APMO approach is a reliable and affordable alternative to study the nature of the interaction of positrons with molecules.

Keywords. APMO, positrons.

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From Ps_2 to CH_4^+: A report on adiabatic vs non–adiabatic and normal–time vs extreme–time quantum regimes

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Abstract. This report starts with the dipositronium (Ps_2) molecule and other akin species made of two negative and two positive Fermions. Using simple Gaussian–type wave functions and the variational principle, it is shown that the Born–Oppenheimer approximation can yield accurate results provided that the mass of the positive Fermions exceeds ∼200 times the mass of the electron [1]. After a digression on potential energy surfaces (PES) and adiabatic atom+diatom quantum reactive scattering, we focus on *ab initio* quantum dynamics studies, including nonadiabatic coupling, of the photoelectron spectra of CH_4 and CD_4. Of particular interest is the observation that the rearrangement from the T_d structure of methane to the C_{2v} geometry of CH_4^+ upon ionization must be a very fast process as both structures lie far from each other. As Baker et al. [2] concluded from their experiments using the high-harmonic generation technique, the time-scale of such an event must be of the order of a few fs. Besides the good agreement obtained between the calculated and measured vibronic bands of CH_4^+ and CD_4^+, it is shown [3] that one can extract information on the subfemtosecond nuclear dynamics occurring at the triply-degenerate ground electronic manifold of CH_4^+ by simulating the ratio of the emitted high-harmonic signals. Simplified schemes are also examined where only a subset of the nuclear degrees of freedom are utilized. This suggests that a *5D* PES developed from the JT distorted bending vibrations of e and t_2 symmetry, rather than the full *9D* hypersurface, may suffice to explain the structural rearrangement of CH_4 upon ionization. Some prospective remarks conclude the talk.

Keywords. Dipositronium, Born–Oppenheimer approximation, photoelectron spectra of CH_4 and CD_4, high–harmonic generation, sub-femtosecond dynamics.

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Temperature and pressure effects on elastic and structural properties of minerals from *Ab-initio* simulations: The case of silicate garnets

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Abstract. Standard *ab-initio* quantum-chemical methods based on the Density Functional Theory (DFT) represent a powerful tool for the accurate determination of a variety of properties of materials, such as structural, electronic, spectroscopic, optical, elastic, magnetic, etc [1]. The increasing efficiency of the algorithms and the growing parallel computing resources are rapidly widening the range of applicability of such schemes which can now be routinely used for studying minerals of geophysical interest, defective materials for the electronics, adsorption of biomolecules on biomaterials, porous materials for hydrogen storage, etc. [2, 3]. Such methods describe the ground state of the system at zero temperature and pressure, which is a severe limitation to their general applicability. On the one hand, the effect of pressure, for instance, is particularly relevant to the study of minerals at geophysical conditions; on the other hand, temperature is affecting a large variety of properties (also simple ones such as equilibrium structure and electron charge distribution), even at ambient conditions. We have recently developed and implemented in the CRYSTAL14 public program [4] a variety of fully-automated, general-purpose, computationally-efficient algorithms for the calculation of elastic, piezoelectric and photoelastic tensors [3, 5, 6]. Related quantities such as bulk, shear and Young moduli, Poisson's ratio and directional seismic wave velocities can now be computed. The effect of pressure on computed elastic response properties can be computed as well [7]; the evolution under pressure of the elastic anisotropy of minerals can then be predicted from *ab-initio* simulations [8]. We have also recently developed an algorithm for computing the thermal lattice expansion of minerals by explicitly describing the lattice dynamics through the quasiharmonic approximation: the combined effect of temperature and pressure on structural properties of minerals can be evaluated within this approach. A family of silicate garnets (namely, pyrope, almandine, spessartine, uvarovite, grossular and andradite) has been considered which are major rock-forming minerals of the Earth's mantle. They are cubic crystals of space group Ia-3d, with 80 atoms in the primitive cell; their size represents a challenge for the *ab-initio* description of their elastic properties at geophysical conditions.

Keywords. Elastic properties, pressure, CRYSTAL program.

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Second derivatives and chemical descriptors: Advances and remarks

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The convex piece-wise linear dependence of the molecular energy with the number of particles and its based physico-chemical descriptors formulation [1] involves non integer electron number domains. The existence of descriptors defined as first derivatives of the energy and the electron density has been rigorously established from both, the conceptual DFT (Density Functional Theory) [2] and the recent Grand-canonical formulation [3, 4]. The further and natural consideration of the higher order descriptors, *i.e.*, those related to the second derivatives of the mentioned magnitudes, and the discontinuity of the first derivatives at the integer number of electrons induce a non linear dependence of these magnitudes even regarding the isolated piece-wise linear hypothesis for the electronic energy and then the onset of such dependence is due to the interaction with the environment [5]. The physical domains within a molecule thus considered may be regarded *sensu strictu*, as open quantum systems at equilibrium. So, the number of electrons is obtained by means of an average over the like GC ensemble configurations of integer **N** and **N+1** particles and the fractional population can be fixed at $\mathbf{N} + \boldsymbol{\nu}$; $0 < \nu < 1$ [2]. In this report we discuss the conditions for the attainability of the statistically mixed states description defining the system and the descriptors.

Keywords. Derivatives, energy, electronic density, chemical descriptors, open quantum systems.

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Intense field molecular photodissociation: The adiabatic views

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Abstract. The adiabatic approach has been designed to obtain approximate solutions of the time-dependent Schrödinger equation [1, 2]. This is usually done by introducing the instantaneous solutions of the wave equation. We examine the case of the photodissociation of a molecular system exposed to an intense laser pulse in the optical range. A method referred to as the adiabatic Floquet approach has been used in recent works [3, 4]. We show that it is not based on instantaneous solutions, despite the name given to it. Although the conditions for the applicability of the traditional adiabatic method are far from being fulfilled, it is instructive to introduce the instantaneous solutions of the wave equation. The photodissociation mechanism is then very inefficient. The adiabatic Floquet approach should be called, in fact, quasi-adiabatic. The physical description of the quasi-adiabatic method is to let the system to be exposed to a field with a frequency and an intensity corresponding to some point along the curve describing the laser pulse and to have the field oscillating with these laser parameters. This is repeated for the next point, and so on. For the example considered here (phodissociation of H_2^+)the direct solution of the time-dependent Schrödinger equation confirms the validity of the quasi-adiabatic Floquet approach.

Keywords. Adiabatic theory, Floquet formalism, intense-field photodissociation.

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Electronic structure of molecules in supercritical fluids

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Abstract. The combination of quantum mechanics with molecular modeling is a powerful tool for studies of biomolecules such as proteins and led to the Nobel Prize in Chemistry in 2013. This procedure can also be used to study simple and complex liquids. In addition, it may also be used to study the spectroscopic and reactivity of molecules in solution, a situation that is germane in chemical laboratories. The understanding of the solvent effects is thus a major concern in the rationalization of experimental results. In the last two decade theoretical treatments have been developed to incorporate solvent effects. There are two major lines of treatment. One follows the early ideas of Onsager and Kirkwood enclosing the solute molecule in a cavity and the medium effects are obtained from an interaction with a dielectric continuum. The other uses some sort of computer simulation to perform hybrid calculations. This is generally called QM/MM method, because both classical and quantum methodologies are employed. The drawback with the first procedure is that it reduces the liquid to a simple dielectric medium and can not, for instance, treat specific hydrogen bond interaction and solute-solvent (and vice-versa) charge transfer. The conventional QM/MM methodology, on the other hand, is so costly that normally only a small fraction of the system is indeed treated by quantum mechanics. A systematic procedure based on a sequential Monte Carlo (or Molecular Dynamics) quantum mechanics (S-QM/MM) methodology has been developed in our group that treats the solvent as an explicit liquid system. Applications in absorption spectroscopy and NMR chemical shieldings of organic molecules in supercritical fluids will be shown.

Keywords. QM/MM method, spectroscopy in solution, supercritical fluids.

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Molecular spectroscopy as a probe for quantum water potentials

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Abstract. All of existing liquid water potentials are intrinsically classical as they were obtained by fitting a simple functional form to some experimental properties of the bulk, using Molecular Dynamics simulations. True quantum potentials, *i.e.* independent of any experimental input, and capable of describing both water aggregates in the gas phase and liquid water, are presently under development. This approach consists in a many-body expansion performed at the ab initio level

$$V(M_1, M_2 ... M_N) = \sum_a V^{(1)}(M_a) + \sum_{a<b} V^{(2)}(M_a, M_b) + \sum_{a<b<c} V^{(3)}(M_a, M_b, M_c) + V_{pol}$$

truncated at third order, but augmented from the overall polarization term $V_{pol}(M_1 \ldots M_N)$. While the 1-body term $V^{(1)}$, essential to describe the monomers' flexibility, has been known at spectroscopic accuracy for two decades [1], high quality 2- and 3-body terms are still under development [2-4] based on high quality calculations performed at the CCSD(T) and MP2 levels respectively. One approach to test these terms is to compare, for the lower clusters $(H_2O)_n$ (n=2,3...), the predicted observable values to their experimental counterparts obtained from high resolution molecular spectroscopy, such as THz spectra and infrared shifts. We will show that the specificity of these clusters, which undergo Large Amplitude Motions between the multiple equivalent minima of their potential energy surfaces (8 for the dimer, 48 for the trimer...), has to be explicitly considered to achieve a meaningful comparison.

Keywords. Water potential, molecular spectroscopy.

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Study of the antihypertensive capacity of bioactive peptides using the QSAR computer model

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Abstract. In this study, a QSAR methodology employed to establish the structure-activity relationship of di- and tri-peptide bioactive, with their capacity to inhibit the Angiotensin Converting Enzyme (ACE), and obtain a classification model that permits the prediction of activity of other peptides obtained from other food products. The data-base of 262 molecules of di- and tri-peptides used in the study was obtained from the Peptide Database of the Central Food Technological Research Institute, India [1]. The capacity of peptides to inhibit ACE is expressed in values of IC50, which were previously auto scaled. Three real classes were assigned by utilizing the K-means algorithm: class 1, low capacity to inhibit ACE, class 2, medium capacity to inhibit ACE and class 3, high capacity to inhibit ACE. The selection of variables was made using genetic algorithms and the model was developed using KNN. The model obtained had a NER of 0.9728, with 8 variables (molecular descriptor), and the validation NER value of the model was 0.9359. The analysis of the centroids of the samples in each class showed that for class 1, high values of Eig15_EA(bo)y R3s+, and low values of ATS7s, RDF085u and P_VSA_s_6. For class 2, mid values of ATS7s, RDF085u P_VSA_s_6 and R3+, and low values of Eig15_EA(bo). For class 3, high values of ATS7s, RDF085u and P_VSA_s_6, with low values of R3+ and mid values of Eig15_EA(bo).

Keywords. QSAR, antihypertensive capacity, KNN, bioactive peptides.

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Electromagnetic study of the chlorosome antenna complex of Chlorobium tepidum

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Abstract. Green sulfur bacterium is an iconic example of nature's adaptation: thriving in environments of extremely low photon density, the bacterium ranks itself amongst the most efficient natural light-harvesting organisms existing. The photosynthetic antenna complex of this bacterium is a self-assembled nanostructure ∼60 x 150 nm, made of bacteriochlorophyll molecules. I will present our study [1] of this system from a computational nanoscience perspective by using electrodynamic modeling with the goal of understanding its role as a nanoantenna. Three different nanostructures, built from two molecular packing moieties are considered: a structure built of concentric cylinders of aggregated bacteriochlorophyll-d monomers, a cylinder of bacteriochlorophyll-c monomers and a model for the entire chlorosome containing over 70000 molecules. The theoretical model employed captures both coherent and incoherent components of exciton transfer. The model is used to extract optical spectra, concentration and depolarization of electromagnetic fields within the chlorosome and fluxes of energy transfer for the structures. The second model structure shows the largest field enhancement. Further, field enhancement is found to be more sensitive to dynamic noise rather than structural disorder. Field depolarization is similar for all structures. This indicates that the directionality of transfer is robust to structural variations while on the other hand the intensity of transfer can be tuned by structural variations.

Keywords. Exciton dynamics, photosynthesis, antenna, electrodynamics.

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Interactions between precursors underlying the deposition of lucrative semiconductor materials: insights from theoretical calculations

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Abstract. Hexagonal boron nitride (h-BN) and aluminum nitride (AlN) is being established as semiconductor materials of direct wide-band-gap properties giving rise to deep-ultraviolet emission [1, 2], and of importance for the development of various heteroepitaxial structures, which constitute emerging deep-ultraviolet light-emitting diodes with continuously increasing efficiency to be implemented in portable units for water/surface/air disinfection. Most importantly, the achievement of these materials has been approached by metal-organic-chemical-vapor-deposition (MOCVD), which is the paramount deposition technology for the fabrication of device structures. The overall chemistry in the deposition process of any material system, including reactions between precursors taking place in the gas-phase and near the hot deposition surface, can dominate the chemical and electrical properties of the material. This general material issue is addressed here by considering aspects of the gas-phase interactions between precursors underlying the MOCVD of BN, and AlN doped by silicon, for which there is no previous deliberation. The pertinent gas-phase chemistry involving respective metal alkyls and hydrides is investigated by the approach of DFT-based modeling combined with saddle point finding methods (*e.g.*, nudged elastic band code), which permits identification of the lowest energy path from reactants and products [*e.g.*, 3]. A better understanding is built for the actual mechanisms underlying the deposition of modern-technology-important group of materials.

Keywords. *Ab-initio* calculations, nudged elastic band code, organometallics, III-nitrides

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Assessment of exchange–correlation functionals for calculating NMR coupling contants

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Abstract. One of the most important parameter derived from NMR spectra is the indirect nuclear spin-spin coupling constant (SSCC). The importance of this parameter lies in its close relationship with the electronic structure and therefore with the molecular structure. Calculated SSCCs can be formulated within the Ramsey nonrelativistic theory as originating in four different terms, Fermi Contact (FC), spin-dipolar (SD), paramagnetic spin-orbit (PSO) and diamagnetic spin-orbit (DSO). The FC term is the most important for several types of SSCCS, however, the remaining terms are important when coupling pathway involves multiple bonds or nuclei with lone pair electrons. In last years, DFT has been successfully applied to the prediction of NMR SSCC [1]. A detailed analysis about more useful SSCCs have carried out, showing the best compromise between accuracy and computational cost [2, 3]. However, a comprehensive study of the effect of exchange and correlation functionals on this molecular property is lacking. We present an exhaustive study of different types of SSCCs calculated with most of the exchange and correlation functionals included within DFT methods. All possible combination of ten exchange functional with thirteen correlation functional are used and compared within SSCCs computed at the MCSCF level [3]. We conclude that the variation of computed SSCCs with the exchange functional is small (less than 10 Hz) and the effect of the correlation functional is larger. Best results are obtained using a percentage of the exact (HF) exchange to the local Slater exchange functional and LYP correlation functional, giving values similar to the SOPPA method.

Keywords. NMR coupling constants, Exchange functional, Correlation functional.

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New catalysts for CO_2 activation and hydrogenation based on Au/TiC and Cu/TiC: Theoretical modeling and experiments

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Abstract. Small, two dimensional, Au and Cu nanoparticles in close contact with TiC(001) undergo a charge polarization which makes them very active for H_2 dissociation and CO_2 activation. Theoretical studies suggest that these systems are suitable candidates for the catalytic synthesis of methanol; which is confirmed by experiments under controlled conditions. These experiments show that the major product over these model catalysts is CO which is produced by the reverse water-gas shift reaction (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O$) whereas the secondary product is methanol ($CO_2 + 3H_2 \rightarrow CH)OH + H_2O$). These experimental finding are rationalized by means of density functional theory (DFT) based calculations on large supercells. The DFT calculations show that for both Au/TiC and Cu/TiC, the combination of the small size of the particle and of the polarization induced by the underlying carbide facilitates the dissociation of the hydrogen molecule with respect to the case of the extended surfaces. Moreover, DFT calculations show that these systems strongly activate CO_2 and point to HOCO as a key intermediate for the generation of CO through the RWGS, with the production of methanol probably involving the hydrogenation of a HCOO intermediate or the CO generated by the RWGS. The interesting and appealing features described here for Cu and Au deposition on TiC may not be unique since it has been proven that other metal carbides are also able to induce charge polarization in admetals.

Keywords. CO_2 activation, theoretical heterogeneous catalysis, Au, Cu, TiC.

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QCT studies on the dynamics of the F+CH_4 system performed on a new potential energy surface

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Abstract. Unraveling the microscopic details of gas phase reactions has always been a central aim of physical chemistry. For several three and four atom reactions this aim has been fulfilled, thanks to the combined effort of both, theoretical and experimental investigations [1]. Full-dimensional quantum-dynamical computations, performed on high-level *ab initio* potential energy surfaces (PES), have been able to reproduce and explain the results of detailed experimental studies [2]. In this regard, outstanding examples are provided by H+H_2 → H_2+H and F+H_2 → HF+H [1-3]. Unfortunately, to extend those achievements to larger systems has proved to be quite challenging. However, some steps forward have been done in studies of X+CH_4 systems, with X=H and F [4, 5]. Experiments performed during the last ten year on the F+CH_4 system and its isotopic variants, revealed interesting and unexpected details about its dynamics [6]. Also, numerous computational analysis were performed to rationalize those findings. However, because of the aforementioned difficulties, most of the theoretical studies relied on approximated methods, mainly on QCT calculations [7, 8]. Recently the first full-dimensional quantum-dynamical studies on this system were presented [5, 9]. They simulated the photodetachment spectra of $FCH_4(-)$, describing the dynamics around the transition state and the van der Waals complexes at the entrance channel of the reaction. The first of those studies simulated the low resolution spectra, but some inaccuracies were detected on the PES employed to carry out the computations [5]. Because of that a new surface was developed by Manthe and co-workers [10]. The new surface was then used to simulate the high resolution spectra [9]. The good comparison between these calculations and the experimental results of Neumark and co-workers lends credit to the quality of the new PES. In our presentation we will show the results of QCT computations for the F + CH_4 → HF + CH_3 reaction, performed on the PES recently developed by Manthe and co-workers. The results are compared with the experimental evidence, as well as with the previous QCT studies that employed different potential energy surfaces. Also, we will show how classical trajectories can assist to the interpretation of photodetachment spectra by detecting quasi-periodic orbits.

Keywords. Reaction dynamics, quasi-classical trajectories, F+CH_4 → HF+CH_3.

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Novel methyl-silyl-metal $(H_3C)_nX(SiH_3)_{3-n}$ (X = B, Al, Ga, In) precursor molecules: Structure, reactivity, synthesis routes and identification by first-principles calculations

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Abstract. We employ *ab-initio* calculations to predict the geometry, stability, and reactivity of sixteen different methyl-silyl-metal $(H_3C)_nX(SiH_3)_{3-n}$ (X = B, Al, Ga, In) [1]. Only the pure methyl-metal $(H_3C)_3X$ members of this family, namely the TMB (X = B), TMA (X = Al), TMG (X = Ga), and TMI (X = In) are currently well-studied and commercially available. All of them are widely used as precursors, together with ammonia, in a metallorganic chemical vapor deposition (MOCVD) processes for epitaxial growth of AlN, GaN, InN, as well as mixed phases such as AlGaInN [2, 3]. The remaining twelve molecules proposed by us open up a two-dimensional array of new possibilities as precursors for MOCVD processes for III-Nitride growth. In addition, they are expected to be of interest for diversified applications in chemical synthesis. For addressing the structural and energetic features of the metallorganics considered in this work, and for assessing the corresponding transition states relevant to reaction paths for molecule formation, we employ both the DFT/PW91 and the Møller-Plesset (MP2) methods as implemented in the Gaussian 09 code. From all $(H_3C)_nX(SiH_3)_{3-n}$ considered, those molecules containing less silyl groups and more methyl groups are less reactive and, at equal conditions, generally more stable. This tendency is corroborated by our results comprising the cohesive energies per atom data as well as and by the Gibbs free energies of formation. We propose sequential reaction routes (including the optimization of corresponding Transition States (TS) and calculation of related reaction barriers) for synthesis of $(H_3C)_nX(SiH_3)_{3-n}$ by substitution of methyl by silyl groups where the Si source is silane gas. The reaction barriers for these chemical transformations remain in the usual energy range typical for MOCVD processes. We also report the Raman spectra of the newly proposed $(H_3C)_nX(SiH_3)_{3-n}$ molecules thus providing useful information for their identification and separation.

Keywords. New organic substances, *ab-initio* calculations, metal-organics, MOCVD, III-Nitrides, Raman spectroscopy.

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Chiral discrimination via anapole magnetizabilities

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Abstract. The orbital anapole induced in the electron cloud of a molecule in the presence of a static and spatially uniform magnetic field **B**, and a non uniform magnetic field **B**' with uniform curl **C**=$\nabla \times$ **B**' is rationalized via anapole magnetizabilities, $a_{\alpha\beta}$ defined as minus second derivative of the second-order interaction energy W^{BC} with respect to the components C_α and B_β Induced magnetic dipole, quadrupole and anapole moments are expressed via multipole magnetic magnetizabilities. Dependence of response properties on the origin of the coordinate system with respect to which they are defined is investigated. Relationships describing the change of multipole and anapole magnetizabilities in a translation of the reference system are reported. For a single molecule, and more generally in an ordered medium, two invariant properties, which are, in principle, experimentally measurable, have been defined, *i.e.*, the average anapole magnetizability $\bar{a} = (1/3)a_{\alpha\alpha}$ and the diagonal components of the $a_{\alpha\beta}$ tensor, provided that they are referred to the principal axis system of the second rank magnetizability $\chi_{\alpha\beta}$. The trace of a second-rank anapole magnetizability is related to a pseudoscalar obtained by spatial averaging of the dipole-quadrupole magnetizability. It has different sign for D and L enantiomeric systems. Therefore, in an isotropic chiral medium, a homogeneous magnetic field induces an electronic anapole, having the same magnitude but opposite sign for two enantiomorphs. Calculations have been carried out for $C_4H_4X_2$ cyclic molecules, with X= O, S, Se, Te, characterized by the presence of magnetic-field induced toroidal electron currents.

Keywords. Anapole moments, anapole magnetizability.

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How DFT computations can help in the design of new photosensitizers active in photodynamic therapy

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Abstract. The possibility to design new photosensitizers active in photodynamic therapy starting from computed chemical physics electronic and geometrical properties by using density functional theory should be presented. In particular, we will show as the main photophysical properties that a drug active in photodynamic therapy must possess (absorption wavelengths shifted in the Near Infrared Region, singlet–triplet energy gaps and spin–orbit matrix elements large enough to allow an efficient intersystem spin crossing) can be reliably predicted by modern density functional methods. The studied systems include isoindole BODIPY, squaraine, porphycene, non-porphyrin, bar and metallated porphyrin– like systems able to activate singlet O_2 excited state (Type II reactions) [1-15].

Keywords. Density Functional Theory, photodynamic therapy, spin-orbit couplings, photosensitizers.

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Some theoretical contributions concerning the physical chemistry properties of atmospheric media

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Abstract It is now well known that many processes involving molecules and radicals in gas–phase and heterogeneous media take place in atmosphere. A precise knowledge of these processes is then necessary if we want to monitor efficiently and reduce the pollution of the environment. In this line of actions, soot particles released by diesel engines and plane reactors are the subject of numerous experimental and theoretical works. In this presentation, I plan to present several aspects of the role played by soot particles on the environment, like i) their hydrophilic power leading to the formation of artificial clouds (contrails), ii) their catalytic or inhibiting action on the oxidation of organic compounds adsorbed on soot particles and iii) their role on the absorption and diffusion of the solar light (albedo). Theoretical chemistry is now able to give reliable arguments to describe qualitatively and even semi–quantitatively these effects and provide provisional laws for a realistic modelling of the atmospheric media.

Keywords. Heterogeneous chemistry, soot particles, modelling, hydrophilicity, optical properties.

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Experimental/theory coupling characterize transient species, understand and predict the behavior of molecules

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Abstract. The experimental/theory coupling is extremely powerful in characterization of intermediate species, understanding of reaction mechanisms and can also contribute to anticipate the behavior of new molecules. These are the major concerns of chemists. Results from our group will illustrate the contribution of quanto-chemistry in these fields – coupled with experiment - with particular emphasis on the use of a novel apparatus developed to Pau, UV photoelectron spectroscopy in gas phase (UV-PES). I'll describe this technique for a start, and show you the efficiency of the UV-PES/theory tandem a) when applied to the characterization of reactive species of transition metal complex by their ionization potentials- characterization requesting specific experimental conditions [1] – but also b) when applied to stable species in the field of conjugated organic compounds such as phenylene-thiophene oligomers to determine their electronic properties, essential to explain their optoelectronics behavior [2].

Keywords. UV-Photoelectron spectroscopy, transition metal complex, oligomers, reactivity.

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Understanding the influence of terminal ligands on the electronic structure and bonding nature in $[Re_6(\mu_3\text{-}Q_8)]^{2+}$ clusters

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Abstract. Since the synthesis of the first molecular cluster $[Re_6(\mu_3\text{-}S_8)Br_6]^{4-}$ [1] and the substitutional lability of the terminal ligands prompted new developments in their chemistry, that makes these molecular clusters a reasonable point of departure for building new materials. The development of novel inorganic materials of technological interest certainly requires an understanding of the electronic structure, bonding, spectroscopy, photophysical[2,3] and structural properties of these clusters. Taking into account the potential applications on material science, and the lack of systematization on the study of these kind of clusters, the proposal of the present work is to perform a detailed theoretical study of the $[Re_6(\mu_3\text{-}Q_8)X_6]^{4-}$(Q = S^{2-} , Se^{2-}, Te^{2-}, X = F^-, Cl^-, Br^-, I^-, CN^-, NC^-, SCN^-, NCS^-, OCN^-, NCO^-) clusters based on the deeply description of the electronic structure of these complexes and the bonding nature between the $[Re_6(\mu_3\text{-}Q_8)]^{2+}$ core and several peripheral ligands. All this work was developed on the framework of the relativistic density functional theory (R-DFT) by using the Amsterdam Density Functional (ADF) code, where relativistic effects were incorporated by means of a two-component Hamiltonian with the zeroth-order regular approximation (ZORA). To describe the relative stability of these complexes, we employed the global descriptors of chemical hardness (η) and softness (S) introduced by Pearson. Moreover, an analysis of bonding energetics were performed by combining a fragment approach to the molecular structure with the decomposition of the total bonding energy (EBE), according to the Morokuma-Ziegler energy partitioning scheme. After an analysis of these results we found in all cases an extensive ionic character in the bonding between the core an each peripheral ligand. The interaction between the halide ligand and the core gives about 75% ionic character while the other ligands shows a more covalent interaction due to an effective synergic donation and back-donation mechanism.

Keywords. Rhenium cluster, bonding energetic, relativistic effect.

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Electronic quenching in nitrogen atom-diatom collisions: Surface hopping dynamics and relevance for the atmosphere

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Abstract. The reaction of $N(^2D)$ with O_2 produces the NO species, which is vital for the cooling mechanism of the atmosphere. The amount of $N(^2D)$ available is in turn regulated by the deactivation to its ground state $N(^4S)$, which may occur through collisions with other atmospheric species such as:

$$N(^2D)+O \rightarrow N(^4S) + O \ (1)$$
$$N(^2D)+N_2 \rightarrow N(^4S) + N_2 \ (2)$$

Given its importance, reaction (2) has been the subject of several experiments [1], but the disagreement among the results is such that no recommended values are available. In this work the first theoretical predictions for this reaction are presented. For this purpose we have obtained [2–3] accurate and multi-sheeted potential energy surfaces for the 1^4A", $1,2^2A$' and $1,2^2A$" states of the N_3 system, calibrated to accurate multireference configuration interaction energies including the Davidson correction. Quasiclassical trajectories were integrated over the temperature range of $240 \leq T/K \leq 1000$, while the electronic transitions induced by spin-orbit coupling [4] were incorporated using the surface–hopping method. The theoretical results at room temperature agree remarkably well with the experiments, while the temperature dependence is now clarified by theoretical arguments. Using the results achieved [5] and atmospheric models for the concentrations of each species, it is argued that the reaction under study will be important for the altitude range of 120 to 500 km. Further details of the analyzed reaction, such as state-to-state cross sections and opacity functions, are also given [6].

Keywords. Reaction dynamics, electronic transitions, potential energy surfaces.

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First principles based study of the surfaces and interfaces in lithium batteries: structure, electronic properties and thermodynamic stability

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Abstract. Although computational approaches are widely used in material science, interface studies are still challenging issues because of the computational cost, the difficulty to build relevant models or to merge different formalisms. Nevertheless, interfacial effects play a dominant role in numerous systems or applications and computational investigations coupled to experimental approaches can bring new insights in these fields. We developed new strategies based on a coupling experiment (XPS, Auger, AFM, STM) and theory (periodic DFT or DFT+U calculations) approach has led us to develop to investigate the properties of electrode/electrolyte interfaces in Li-ion batteries and microbatteries. The first example is devoted to the study of the $LiCoO_2$, Al-based coated $LiCoO_2$ or mixed Li-Ni-Mn-Co-O oxides (NMC) electrodes surface reactivity. Although it is admitted that the coating acts as a protection for the electrode against cobalt dissolution in the electrolyte at high potential, the exact mechanisms are not totally understood. Moreover NMC electrodes exhibit higher capacity, and apparently better chemical stability compared to $LiCoO_2$ electrodes. To identify the active sites at the surface of these electrodes, adsorption experiments of gaseous probes (SO_2) followed by XPS analyses evidence that either the Al or Mn and Ni substitutions not only decrease the surface reactivity of $LiCoO_2$, but also modifies the nature of the adsorbed species. Indeed, only sulfate species are identified for $LiCoO_2$ whereas both sulfate and sulfite species are characterized for $LiCo_{1-x}Al_xO_2$ and $LiCo_{1-x-y}Ni_x\ Mn_yO_2$ compounds. The adsorption of sulfur dioxide (SO_2) on $LiCoO_2$ and $LiMO_2$ surfaces (M=Al, Ni and Mn) is theoretically investigated within the periodic DFT method developed in the VASP code. It appears that only sulfite species adsorb on α-$LiAlO_2$, without any electronic transfer between adsorbate and surface, whereas both sulfate and sulfite species clearly appear on $LiCoO_2$with important electronic transfer from adsorbate to the surface [1]. The same result is obtained for $LiMnO_2$ while the adsorption of sulfate type species is thermodynamically favored at the surface of $LiNiO_2$. In the another example [2], we consider copper oxide (CuO), a promising positive electrode, which displays a high theoretical capacity correlated to the complete conversion of the metal oxide into a composite electrode consisting in metallic nano-sized particles embedded into a Li_xO matrix [3]. We investigate the formation of all the interfaces susceptible to be generated during the conversion/reconversion cycles of CuO [4]. They are first characterized from a chemical point of view with interface bonding descriptors (charge transfer and bond reorganization). Then, thermodynamic quantities (stress, cleavage, adhesion and interface formation energies) are computed and a comparison of the respective stability of the interfaces is done to investigate the electrode morphology (nanostructuration) at different stages of the cycling [5].

Keywords. DFT+U calculations, surface reactivity, adsorption, Li-ion batteries, $LiMO_2$ oxides.

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A theoretical study of formation routes and dimerization of methanimine and implications for the aerosols presence in the upper atmosphere of Titan

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Abstract. Methanimine is an important molecule in prebiotic chemistry since it is considered a possible precursor of the simplest amino acid, glycine, via its reactions with HCN (and then H_2O) or with formic acid (HCOOH). According to this suggestion, the simplest amino acid can be formed 'abiotically' starting from simple molecules relatively abundant in extraterrestrial environments and primitive Earth. Interestingly, methanimine has been observed in the upper atmosphere of Titan, which is believed to be somewhat reminiscent of the primeval atmosphere of Earth. Methanimine can be produced in the atmosphere of Titan by the reactions of N (^{2}D) with both methane and ethane, or by other simple processes, including the reaction between NH and CH_3 or reactions involving ionic species [1]. Recent models derived a larger quantity of methanimine than that inferred by the analysis of the ion spectra recorded by Cassini Ion Neutral Mass Spectrometer. Growing evidence suggests that nitrogen chemistry contributes to the formation of the haze aerosols in the Titan upper atmosphere. In this respect, since imines are well-known for their capability of polymerizing, CH_2NH is an excellent candidate to account for the nitrogen-rich aerosols of Titan through polymerization and copolymerization with other unsaturated nitriles or unsaturated hydrocarbons. Polymerization of methanimine provides an important contribution to the formation of the nitrogen-rich aerosols, but a quantitative inclusion of this process in the model could not be obtained as there is no information (either experimental or theoretical) on methanimine polymerization. Since the first step of polymerization is dimerization, in this contribution we report on a theoretical characterization of methanimine dimerization. Electronic structure calculations of the potential energy surfaces representing the reactions of electronically excited atomic nitrogen, N(^{2}D), with methane and ethane are also presented, as they are possible formation routes of methanimine under the conditions of the upper atmosphere of Titan.

Keywords. *Ab initio* calculations, atmospheric chemistry, potential energy surface.

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Quantum chemical approach to modeling binuclear metallohydrolase catalyzed reactions: The case of binuclear Co^{2+} *Opd*A enzyme

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Abstract. Organophosphate degrading enzyme from Agrobacterium radiobacter (OpdA), is a promiscuous binuclear metalloenzyme able to hydrolyze a large number of phosphotriesters, including highly toxic pesticides and nerve agents, with a modest disterase activity. Despite its promiscuous nature make it possible for OpdA to have different metals in the active site, *in vitro* studies showed that the binuclear di-Co^{2+} derivative possesses a catalytic activity higher than the native Fe^{2+}-Zn^{2+} form. Herein, the diesterase and triesterase activities of di-Co(II) OpdA have been compared investigating the hydrolysis of trimethylphosphate and dimethylphosphate at density functional level of theory in the framework of the cluster model approach. The reaction mechanisms have been fully elucidated also confirming the crucial role played by a water molecule and some residues in the outer coordination sphere. Three exchange-correlation functionals have been used to derive the potential energy profiles, in gas phase and protein environments. Moreover, to correctly describe the electronic configuration of the d shell of the binuclear center, high- and low- spin arrangement jointly with the occurrence of antiferromagnetic (AFM) coupling, have been considered [1]. Similarities with the working mechanism of other bimetallic hydrolases have been found and will be discussed [2-5]. The outcomes of these theoretical investigations allow us to show how computational methodologies can be helpful in elucidating catalytic reactions of such enzymes.

Keywords. DFT, cluster model approach, binuclear metalloenzymes, phosphatases.

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Diffusion coefficients and intrinsic viscosity of PAMAM dendrimers

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Abstract. Dendrimers are synthetic polymers with very low polydispersity and highly branched [1]. Due to its unique structural features dendrimers have been used for various applications. Several experimental and computational simulation techniques have been used to characterize and understand the behavior of these polymers in aqueous solution. Techniques such as molecular dynamics and Monte Carlo methods have been used to characterize the structure and form of dendrimers, particularly the polyamidoamine (PAMAM) dendrimer. However, the transport properties of dendrimers have not been subject to detailed studies. Only a few reports, at Monte Carlo level have dealt with the intrinsic viscosity of these species [2]. On the other hand Determinations of the diffusion coefficients of PAMAM dendrimers have been carried out by atomistic Molecular Dynamics. However, in these studies effects of water box size have not been considered, although previous studies have established a strong dependence between the size box and the values of the diffusion coefficients calculated from Molecular Dynamics simulations [3, 4]. In this work determinations of intrinsic viscosity and the diffusion coefficient of PAMAM dendrimers and their acetylated derivatives will be discussed. Our efforts are doomed to determine the size and the force field effects on the intrinsic viscosity and diffusion coefficients of these species. Molecular Dynamics Simulations contemplate the use of water box of different sizes and two force fields CHARMM and AMBER.

Keywords. Dendrimers, molecular dynamics, transport properties.

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DFT study of catalysis dissociation of sodium nitrate ($NaNO_3$) on (533) and (577) irregular Cu, Pd and Rh surfaces

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Abstract. Nowadays, the use of the technologies for reduce the pollution of natural water sources continually is updated, for instances, for eliminated excessive amounts of nitrates and nitrites on water. Since years ago, the bimetallic catalysts, as PdCu, RhCu among others have been used for remove these substances, but the molecular mechanism of the catalyzed reaction is unknown, yet [1, 2]. In this work, a DFT study of catalytic dissociation of $NaNO_3$ on irregular (533) and (577) surfaces of Cu, Pd and Rh, is showed. The periodic approach is used for this end. The active sites for the dissociation of the $NaNO_3$ –molecule have been found, between all possible sites, *i.e.* edges, terraces and steps of the irregular surfaces. A conclusion of this research is that the steps are the most active sites. The results indicate that these surfaces are highly active for N-O bond breaking. However, the complete dissociation of this molecule toward N_2 or O_2 had not been found. It seems that the models of these surfaces are in agreement with the experimental data [3], which indicate that these metals are good catalyst for N-O bonds breaking, an important step for the complete dissociation of this molecule.

Keywords. Nitrate, nitrite, DFT, catalytic, irregular surfaces, dissociation.

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Comparison of the reaction electronic flux and ETS-NOCV picture of the HCN→CNH isomerization reaction

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Abstract. The HCN→CNH isomerization reaction, and the corresponding reaction assisted by water, have been extensively studied by many theoretical methods. Changes in the electronic structure during the reaction were described using various theoretical concepts, *e.g.*, bond orders, charge distribution as well as frontier orbitals analysis. The main goal of this study was to analyze and compare the changes in the electronic structure along the IRC for the HCN → CNH isomerization reaction assisted by water. Emerging from two, relatively new theoretical approaches: the reaction electronic flux (REF) [1, 2], and ETS-NOCV method [3]. The REF provides information about the electronic activity that can be decomposed into the polarization and charge transfer components. The ETS-NOCV allows to analyze the changes in the bond-energy components along the reaction path, and in particular, to rationalize the changes in the orbital-interaction contribution in terms of the deformation-density components. The results show the complementarity of both methods.

Keywords. HCN, CNH, REF, ETS-NOCV.

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Theoretical predictions of physicochemical properties of ionic liquids based-on bis(trifluoromethylsulfonyl)imide anion

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Abstract. Ionic liquids (ILs) are organic salts composed of organic cations and mostly inorganic anions with low melting points, usually below 100°C. ILs have been recognized as "green solvents" [1, 2] due to their negligible vapor pressure, low flammability, high ionic conductivity and good thermal stability, and are currently considered as an environmentally friendly alternative to organic solvents [3]. We have selected several cations like pyridinium, pyrrolidinium and imidazolium, in combination with one anion: bis(trifluoromethylsulfonyl)imide ($[NTf2]^-$) to investigate the influence of cation on the physicochemical properties on this series of ILs at room temperature using COSMO-RS method, and molecular dynamics (MD) for changes in temperature. Molecular structures of corresponding to low-lying stable conformers are computed, and properties such as density, viscosity and conductivity are predicted using COSMO-RS with the ion-pair model [4]. Moreover, its dependence on temperature is simulated using classical MD in the isobaric-isothermal ensemble and in the canonical ensemble. The simulations were carried out using the GROMACS 4.6 package, which enables to modelize the time dependence of the behavior of IL molecular system, providing detailed information on the fluctuations and conformational changes of ILs. Finally, MD results are compared with those estimated using COSMO-RS method.

Keywords. Ionic liquids, physicochemical properties, COSMO-RS, molecular dynamics.

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Compactness of full configuration interaction wave functions: A seniority number approach

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Abstract. The concept of seniority number, widely used to classify Slater determinants, is extended to N-electron wave functions of spin S, as well as to N-electron spin-adapted Hilbert spaces. A spin-free formulation of the seniority number operator allows us to determine the invariant character of the expectation value of this operator for spaces of N electrons and spin S and its non-invariant character under unitary transformations for a determined wave function. We study the convergence of the full configuration interaction wave function expansions in terms of Slater determinants, using three types of basis sets, *i.e.* i) the canonical molecular orbitals, ii) the natural orbitals for the corresponding wave function and iii) the orbitals which minimize the expectation value of the seniority number operator for that wave function. The results found show that the last expansions exhibit a superior convergence and that the expectation value of the seniority number operator provides a quantitative procedure to evaluate the compactness of the wave functions [1].

Keywords. Seniority number, FCI/CI expansions, convergence of wave functions, unpaired electrons.

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Misfolding, metals and neurodegenerative diseases: XAS experiments and *ab-initio* simulations

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Abstract. Metal ions are essential cell components and are required in many biochemical reactions (metal proteins represent about one third of all proteins). It is therefore not surprising that an unbalanced concentration of metals, either too high or too low, can result in severe threats to the organism. In the brain, metals like Cu, Zn, and Fe, are normally present at fairly high concentration and there are evidences that a breakdown in metal trafficking regulation has a significant impact in the development of several neurodegenerative pathologies such as Alzheimer's disease (AD), Parkinson's disease (PD), amyotrophic lateral sclerosis (ALS) and Creutzfeld-Jakob's (CJ) disease. Despite the intrinsic heterogeneity, important common features have been suggested and identified among these diseases, namely the presence of intra- or extracellular proteinaceous deposits associated to changes in protein folding and to a loss of bio-metal homeostasis. We have used [1-3] a combination of experimental and numerical techniques to study the effect of the presence of metal ions on the folding of the peptides involved in some of these pathologies, namely AD and CJ. In particular, we performed X-ray absorption spectroscopy measurements on several fragments of the amyloid-beta peptide and on the tetra-octarepeat region of the prion protein in the presence of Cu and Zn ions. We then compared experimental data with the results of first principle molecular dynamics simulations of the Car-Parrinello type that are especially well suited to describe the local binding of the metal to these peptides.

Keywords. Neurodegenerative diseases, metal ions, *ab-initio* simulations, XAS spectroscopy.

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Revisiting the role of nucleophile, leaving group and solvent in *backside* S_N2 reactions ($Y^- + CH_3X \rightarrow YCH_3+X^-$; X,Y= F, Cl, Br, I): An atomic contribution study

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Abstract. Bimolecular nucleophilic substitution (S_N2) is one of the simplest and most extensively studied reactions in organic chemistry. In addition to being widely used in organic synthesis, it also plays a central role in many biological systems and natural processes [1]. Several experimental and computational studies have pointed out that the two major factors defining the kinetics and thermodynamics of S_N2 reactions are 1) the solvent effects and 2) the nature of nucleophile and leaving-group [1, 2]. From a computational point of view the first aspect has been considered by studying the differences of the reaction paths in gas and condensed phases. On the other hand, the interpretation of *nucleophilicity* and *leaving-group* ability has been limited to the study of changes in activation and reaction energies with different substitutions and the prediction of nucleophilicity and leaving-group ability indices [1]. Although these indices serves as qualitative indicators to evaluate trends in reaction barriers, a truly understanding of the role of nucleophile and leaving-group requires a quantitative estimation of their contribution to the energy changes along the reaction paths. In the present study, we propose to evaluate the individual contribution of each atom to the activation and reaction energies of a series of S_N2 reactions with halomethanes ($Y^- + CH_3X \rightarrow YCH_3+X^-$; X,Y= F, Cl, Br, I) employing the Reaction Force and Atomic Contributions analysis proposed by Toro-Labbé [3, 4]. We calculated the energy barriers in aqueous solution and both values and trends are in agreement with experimental data. Accordingly, we establish relationships between the atomic contributions to the activation energy of nucleophile and leaving groups with nucleophilicity and leaving-group ability properties. Our analysis allow us to conclude that the best nucleophile has the largest atomic contribution to the activation energy and performs the largest work to overcome the energetic barrier. In contrast, the best leaving groups perform the smallest work to overcome the energetic barrier.

Keywords. Bimolecular nucleophilic substitution (S_N2), reaction force, atomic contributions, solvent effects, nucleophilicity and leaving-group ability.

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Predicting reactivity of 5–trifluoromethyluracil in gas and aqueous solution phases

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Abstract. As part of our investigations on compounds with interest pharmacologic and biological [1], in the present work, selected descriptors such as, chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S), global electrophilicity index (ω) [2] and the local and global Fukui functions [3, 4] were used to predict reactivities and sites selectivity of the three stable conformers of 5–trifluoromethyluracil (TFMU) derivative in gas and aqueous solution phases and, to explain the nature of the interactions with electrophiles and/or nucleophiles. The solvent effects were simulated by means of the self-consistent reaction field (SCRF) method employing the integral equation formalism variant (IEFPCM). All the calculations were performed by using the hybrid B3LYP/6–31G* method. The comparison show that in gas phase the presence of the CF_3 group increase the HOMO–LUMO gap while in aqueous solution, the results changes notably because uracil increases the band gap and, as consequence, it is few reactive probably because it is linked to the water molecules by H bonds formation. On the other hand, comparing the calculated η, μ and ω values with those obtained for uracil in gas phase we observed that the three conformers of TFMU are more stable in gas phase (larger η) than uracil, but it has better capability to accept electrons (bigger electrophilicity index) while, on the contrary, the conformers of TFMU are better electrons donor than uracil. Besides, the variations in the atomic charges, bond orders, dipole moments and molecular electrostatic potentials with the solvent, much smaller for the conformers of TFMU than uracil, are attributed as a result of replacing in the 5 position the proton by the CF_3 group. The effects due to polarization of the medium for those three conformers are well represented at local and global level.

Keywords. 5–Trifluoromethyluracil, descriptors, DFT calculations, HOMO–LUMO.

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Hydrated ethanol dissociation mechanisms

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Abstract. Ethanol is currently one of the most important renewable energy sources. Both ethoxy (CH_3CH_2O) and 1-hydroxyethyl (CH_3CHOH) radicals are major intermediates in the thermal decomposition and oxidation of ethanol which play an important role in the chainpropagation step their decomposition reactions produce primarily H atoms which are the key chain carrier in the thermal decomposition process [1, 2]. The reactions of these radicals with H atoms generate small, more reactive radicals such as CH_3 and OH_3 resulting in chainbranching. The potential energy surfaces of $(H_2O)_n$ reactions with CH_3CH_2OH, have been studied at the CCSD/6-31+G** level of theory with geometric optimization carried out at the M06L/6-31+G level. The reaction rate has been calculated using transition state theory and Wigner, Eckart and CVT tunneling correction factor and writing down in the Ahrreniuns form for temperature range of 200-4000K [3], $k(T)=1.02\times10^{42}$ $T^{1.79\times10^{-2}}$ $\exp(-1.87\times10^{4}/RT)$. One reaction path goes through complex reactant and product, while the other one has only the reactant complex. The barrier varies from 55.8 to 68.5 kcal/mol.

Keywords. Hydrated ethanol dissociation mechanisms, H_2O, CH_3CH_2OH transition state theory, rate constants.

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Study of resonance-assisted hydrogen bonds via magnetically induced currents

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Abstract. The assessment of hydrogen bond strengths is a difficult task for computational chemists for it is necessary to evaluate accurately bond energies. Energies involved in hydrogen bonds can range from 1 kcal/mol (very weak) to about 40 kcal/mol (very strong) [1]. In this work we will focus on the resonance-assisted hydrogen bond (RAHB). An interesting work of RAHB has been done by Elguero *et al.* [2]. They have studied a series of 40 different enols of ß-diketones using density functional theory (DFT) and have found a correlation between the hydrogen bond length and the electron density at the corresponding bond critical point. Another alternative has been suggested by Sundholm *et al.* [2] They have found that the strength of a chemical bond correlates with the mobility of electrons within the bond. This mobility is associated with the concept of aromaticity that can be evaluated via external magnetic fields that can induce currents in a ring. In this sense, the strongest the hydrogen bond, the higher the value of the induced current. We will take part of the set of enols of β-diketones of reference 1 and will calculate the strength of the ring current flowing around the molecular ring formed by the RAHB. In addition we will plot the current density maps which allow us to visualize the current density streamlines. The calculations will be performed with the DIRAC code [3] using DFT. In DIRAC, the magnetically induced currents can be obtained, accurately, using LONDON orbitals (synonym of gauge-including atomic orbitals) which allow to use relatively small basis sets. Preliminary results show the expected trend reported in reference [1].

Keywords. RAHB, current density, aromaticity.

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Monte Carlo Adsorption affinity studio of modified nano-montmorillonite for the removal of chromate ions

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Abstract. Industries discharge large quantities of pollutants to the hydric sources, with primary and secondary treatments it is possible to reduce the indexes of chemical oxygen demand and biological oxygen demand but the higher cost treatments are the tertiary treatments that remove the ions presents in water. In addition there are not a lot of renewable tertiary treatments. Nano-montmorillonite is a clay with a T:O:T structure (this is two tetrahedral and one octahedral layers). It also has interchangeable ions that can get exchanged with the contaminant ions (*i.e.* Silver [1], Cd [2], Zn [3]). Montmorillonite's cation exchange capacity (CEC) is 0.82 a 1.2 meq/g. [4] Montomorillonite has a behavior like a weak acid , it also has the biggest specific surface area from clays. In this work we studied the montmorillonite structure using computational methods (molecular dynamics and montecarlo methods) and we simulated the crystal's interaction with the cations in the case of lead, and with chromates for the case of chromium. The main purpose is to evaluate the capacity of montmorillonite for decontaminating industrial water sources and capture some ions that could not be removed without a tertiary treatment to the polluted water. To build the crystal we used a model with Al O Si and Ca, a model derived from powder X-ray data. We modified this unit cell adding OH, optimizing it using DMol3 (DFT) and adding to it an alkyl polyglucoside (n-hexadecyl-1-beta-D-maltopyranoside) using adsorption locator. In some of configurations generated with Monte Carlo method, a chromate or a lead was added and later also their interaction with a surfactant using Monte Carlo was studied. The obtained configurations were optimized with DMol3. An experimental research which used HDMA-modified montmorillonite [5] was used as reference to prepare our control model.

Keywords. Clay, montmorillonite, tertiary treatment, computer simulation.

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Recombination dynamics between bipolarons and excitons in conjugated polymers

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Abstract. The temperature influence over the intrachain recombination process between a positive charge carrier (polaron or bipolaron) and an exciton is theoretically investigated by using the Su-Schrieffer-Heeger (SSH) model modified to include temperature, external electric field and Coulomb interactions. Through a Time-Dependent Hartree-Fock approximation, we observed that the recombination process is spin independent whenever thermal effects are taken into account. Considering the interaction between a polaron and an exciton, the charge carrier may be dissociated when subjected to temperature higher than a critical value or, alternatively, if a lower temperature regime is considered, it is observed that the quasiparticles pass through one another, maintaining their consistencies. Regarding the recombination process between a bipolaron and an exciton, it is observed that the latter can be annihilated whereas the former dissociates into two trions or into a conventional polaron and one trion. It is important to emphasize that these mechanism depend on a suitable balance between the critical temperature and the external electric field applied. These results can extend the knowledge about electroluminescence process in conjugated polymers, thus being of potential use to improve internal quantum efficiency in Polymer Light Emitting Diodes.

Keywords. Conjugated polymers, molecular dynamics, time-dependent hartree-fock.

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Theoretical study of the geometric and electronic properties of theobromine

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Abstract. The theobromine (3,7–dimethylxantine or 3,7dimethyl–1H–purine–2,6–dione) is a major compound present in cacao, and is a metabolite of caffeine. These compounds are methylxanthines derivatives and are classified as alkaloids. It stimulates the central nervous system, cardiac muscle and recent studies have also shown that theobromine as a potent antitosse, by exerting influence on the respiratory system [1, 2]. In order to contribute to the consolidation of scientific knowledge about this molecule, we propose to study the geometric and electronic properties of theobromine with and without solvent. Equilibrium geometries for isolated theobromine, radial pair distribution function and residence time of the interactions in aqueous solution were calculated via Car-Parrinello Molecular Dynamics (CPMD) through Quantun Espresso software. The Car-Parrinello method performs *ab-initio* simulations using classical mechanics to describe the ionic motion, obtained from the solutions of the equations of Newton, and the Born-Oppenheimer approximation to separate the nuclear and electronic coordinates. The connection between classical and quantum treatment for the ions and for the electrons, respectively, is done by solution of Lagrange's equations through extended Lagrangian of Car-Parrinello [3]. The theobromine electronic properties with and without aqueous solution were determined using the Gaussian computer package at M06L/6–31G(d,p) level.

Keywords. Theobromine, car-parrinello, electronic properties.

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The total position spread tensor in a molecular context

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Abstract. The localization tensor was introduced in the context of Kohn's theory of the insulator state [1]. He showed that the isolator state was related to the localization of the wave function rather than to the band gap. Later, Resta and collaborators [2-4] introduced the Localization Tensor (LT) to provide a measure of this delocalization. This tensor, which is defined as $\Lambda = 1/N(\langle R^2 \rangle - \langle R \rangle^2)$ diverges in the thermodynamic limit for a conductor and converges to a finite value for isolators. We recently implemented the Total Position Spread (TPS) tensor in molecular quantum chemistry codes at the Full Configuration Interaction (FCI in Neptunus) [5] and Complete Active Space Self Consistent Field (CASSCF in MOLPRO) [6] level. Contrary to the "per electron" quantity, LT, which is usually considered for extended systems like chains, graphene islands, the TPS may be chosen instead as the correct descriptor in molecular case. Indeed, the TPS is size-consistent and, for instance, in the case of diatomic molecules it converges to the sum of the atomic values at dissociation. We present here some calculations for neutral and ionic diatomic molecules at FCI level and show the different behavior of the TPS depending on the bond nature. We also show why the TPS may be a valuable tool to localize transition state for mixed-valence systems through some results at the CASSCF level for spiro-like molecules.

Keywords. Total position spread tensor, CASSCF, FCI.

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Relativistic theoretical study of the C–F bond activation mediated by lanthanide ions

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Abstract. Reactions involving lanthanide metals exhibit special trends on their reactivity behavior when we move through the period. This unique character is probably due to the singular features of the *4f*-shell. Although these are in the valence region, they are less involved in the bond formation; moreover the participation of the outer *5d*- and *6s*-shells needs to be clarified for the entire understanding of the bonding nature and the reactivity in activation reactions of this kind. It is well-known that the C–F bond in inorganic compounds is significantly stronger than the corresponding C–H and C–C bonds and that the C–F bond activations is a formidable task in organometallic chemistry [1]. In recent years, C–F bond activation by metal centers has attracted a great deal of interest, and many theoretical and experimental studies have shown that bare metal monocations are able to activate the C–F bond selectively [2]. Previous experimental results [3] allowed a re-examination of the mechanism of F-atom transfer with a particular view to the insertion and the "harpoon"–like mechanism that have been advanced previously. In the present work we provided a relativistic theoretical study of the electronic structure, stability and reaction mechanism of La^+, Ce^+, and Pr^+ with fluoromethane, with the aim to give a qualitative model that explains how the lanthanide monocations Ln^+ activate the C–F bond in fluorohydrocarbons. Due to the importance of a correct description of the electronic structure and the consideration of relativistic effects, we performed this study using a 4–C Dirac-Coulomb Hamiltonian implemented in DIRAC13 program. Geometry optimizations and frequency analysis calculations were done for the identification of minima and saddle points. We used the uncontracted Dyall's Triple-ζ basis set for heavy-atoms and the aug-cc-pVTZ Dunning basis set for light atoms. Preliminary results show that La^+ and Ce^+ shares a different reaction mechanism than Pr^+ that is mainly due to the 2 non–f electrons that formers monocations have in their ground state. In this sense, La^+ and Ce^+ atoms predominantly proceed through an insertion mechanisms and Pr^+ through a "harpoon"–like mechanism.

Keywords. Bond activation, fluoromethane, lanthanide monocations.

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Representation of potential energy surfaces and role of chirality in weakly bound complexes: The hydrogen-peroxide-noble-gas interactions revisited

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Abstract. Hydrogen peroxide (H_2O_2) is arguably the simplest molecule showing chirality at its equilibrium geometry. Over the past years the understanding of its structural and dynamical properties, and of its interaction with atoms, ions and molecules have been the goal of several studies. Because of the diversity of applications, a basic point of general interest concerns the role that non-covalent forces and hydrogen bonding play on the thermodynamics of H_2O_2 and of its structural analogues. Another important point concerns the influence that non-covalent forces can exert on the spatial distributions of approaching partners and when/how such influence may lead to the selective formation of intermediate states, therefore, favoring or hindering the successive evolution of the system towards a hydrogen bound, a weakly bound complex formation, or even a chemical reaction. Complexes with noble gases (Ng) are specially relevant as reference systems for isolate the importance of the vdW plus induction contributions, particularly, permitting to focus on the rule of the Ng polarizabilities. In this work we study the exemplary cases defined by the H_2O_2−Ng (Ng=He, Ne, Ar, Kr and Xe) complexes in order to determine the radial and the angular dependence of PES on the relative position of the Ng atom, particularly, the symmetries and the barriers separating the chiral equilibrium geometries. The analysis of our PES sheds light on several interesting features of these systems: the role that the enantiomeric forms and symmetry of the H_2O_2 molecule play on the resulting chiral geometries of these weakly bound complexes; the presence of a local minimum geometry between the two global (chiral) ones; and finally, the lower radial limits for the correct representation of the *ab initio* energies indicates the region where charges transfer effects begin to be important.

Keywords. Hydrogen peroxide, noble gases, PES.

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Study of some simple approximations to the non-interacting kinetic energy functional

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Abstract. Within the framework of density functional theory, we present a study of approximations to the non-interacting kinetic energy functional $T_s[\rho]$. For this purpose, we employ the model of Liu and Parr [1] based on a series expansion of $T_s[\rho]$ involving powers of the density. We use this functional to determine the non-interacting kinetic energy enhancement factor expressed as a function of the density. Applications to 34 atoms, at the Hartree-Fock level showed that the enhancement factors present peaks that are in excellent agreement with those of the exact ones. Also, these factors give an excellent description of the shell structure of these atoms. The application of Z-dependent expansions to represent some of the terms of these approximation, which allows $T_s[\rho]$ to be cast in a very simple form, is also explored.

Keywords. Density functional theory, enhancement factor, Kohn-Sham, Hartree-Fock, kinetic energy functional.

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Molecular mechanics study of quercetin dimers in different conformations

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Abstract. Quercetin (Q) is one of the most abundant flavonoids in the human diet, which has antioxidant and anti–inflammatory properties [1]. An experimental study [2] has shown that the presence of quercetin activates IRE1–RNAse (the protein responsible for triggering the autophagy action) and enhances the activation of the IRE1-RNAse by ADP, its natural ligand. The X–ray structure of the complex *IRE1-RNAse:ADP:Q* has been obtained showing the active form of IRE1–RNAse as a dimer, which is bound and stabilized by two molecules of Q. Dimerization was shown as a prerequisite for RNase activity [3]. A theoretical study of the *Q–dimer:IRE1–RNAse* interactions will allow assessing the contribution of Q in the stability of IRE1–RNAse dimer quantitatively. The general features of the Q–dimer geometry can be obtained from the X–ray structure [2], however, the orientation of the B–ring (*syn* or *anti* respect to the atoms O3 and O3' mutual alignment) and the hydroxyl groups' orientations (other than those involved into the hydrogen bonds formation) could not be determined with experimental resolution. In this work we used Molecular Mechanics method to investigate possible mutual positions of the dimers formed by Q molecules in the *syn* and *anti* orientations of the B–ring. Different arrangements of the hydroxyl groups were considered also. It was found that certain orientations of O3 and O3' hydroxyl groups can result in significant changes (up to 6 kcal/mol) of the interaction energy. The positions that were found to be close to the experimental one [2] were used to construct the interaction energy profiles. Local energy minima in these profiles are proposed as the candidates for future calculations of their interactions with IRE1–RNAse using docking and molecular dynamics.

Keywords. Quercetin dimer, molecular mechanics, IRE1-RNase.

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Oxidation and spin states in the cyclopropanation of alkenes catalyzed by Fe-porphirin catalysts

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Abstract. The mechanisms of the cyclopropanation of alkenes with diazocompounds catalyzed by Fe^{II}–porphyrin and Fe^{III}–porphyrin complexes [1, 2] have been investigated using DFT methods [3]. Among the different mechanistic possibilities, it is found that the only kinetically viable mechanistic route involves Fe^{II}–porphyrin species. Catalytic cycles through Fe^{III}–porphyrin intermediates exhibit too large activation energies. Within the Fe^{II} oxidation state, the catalytic cycle involves triplet, quintet, and singlet spin states [3]. Reaction of triplet Fe^{II}–porphyrin complexes with diazocompounds leads to axial and bridged Fe^{II}–carbene complexes. The former type is favored at the singlet state and the latter is the most stable one at higher spin states. The second key step of the reaction consists of the [2+1] cycloaddition of the axial Fe^{II}–carbene complex to yield the corresponding cyclopropane. Both formation of the Fe^{II}–carbene complex and the [2+1] cycloaddition occur on the singlet state hypersurface. Several minimum energy crossing points (MECP) [4] ensure the kinetic and thermodynamic feasibility of the reaction. The proposed mechanism is compatible with the *trans* selectivity observed in the reaction between diazocompounds and olefins.

Keywords. DFT, MECP, porphirins, carbene ligands, cycloadditions.

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Reliable computational model for nitrogen isotropic hyperfine coupling constants

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Abstract. The availability of a theoretical model to reproduce the hyperfine coupling constants (HFCCS) constitutes an essential tool for a correct interpretation of the EPR spectroscopic data. The DFT methodology has resulted to compute HFCCS of different nuclei of organic radicals on a very reliable way, by using a combination of B3LYP functional and TZVP or EPR-III basis sets [1–3]. However, the accurate prediction of theoretical isotropic HFCCS of ^{14}N nuclei is not trivial [4, 5], being the selection of the basis set is of fundamental importance, specially the number of components of d functions. A wide study of the ^{14}N hfcc in aromatic neutral radicals [5] showed that the combination of PBE0 functional with the N07D basis set with 6 components of d functions, specially developed for the calculation of HFCCS [6] presented, in general, the best predictive power but, notoriously, underestimated the values of ^{14}N HFCCS in nitroxide-type radicals. The well-established sensitivity of the ^{14}N to the computational scheme, in contrast with that observed for ^{1}H HFCCS, and the necessity to an available methodology to obtain the best possible for nitrogen nuclei of neutral and charged radicals has prompted out to carry out a deep study of nitrogen containing radicals with special attention to nitroxide radicals. The solvent and dynamic effects on the HFCCS values, very important in these radicals [4, 7], are also being considered.

Keywords. Isotropic hyperfine coupling constant, DFT, organic radical.

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Ripping silicene: A theoretical study

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Abstract. Recently, graphene cracking propagation have attracted attention due the possibility to understand the process [1]. The understanding of crack formation due to applied stress is key to predicting the mechanical behavior of many solids. Here we present theoretical studies on cracks in silicene monolayer using reactive molecular dynamics. We observe effect for preferred tear directions when we take into account different stress orientations. Our study provides some insights into breakdown mechanisms of silicene in the presence of defective structures such as cracks.

Keywords. Silicene, crack, tear, crack propagation, silicene edge, grain boundary.

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Highly reactive intermediates: Reaction mechanisms between substituted nitrenium ions and water

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Abstract. A nitrenium ion $[X\text{-}N\text{-}Y]^+$ is a molecular species characterized by an electron-deficient nitrogen atom having a positive formal charge and two covalent bonds [1]. Nitrenium ions are isoelectronic analogues to carbene radicals, and like carbenes they can behave as nucleophiles and as electrophiles, a feature that allows them to participate in a variety of chemical reactions. Nitrenium ions have been suggested as intermediates in reactions leading to DNA damage: nitrenium ions are thought to be generated in the degradation of aromatic amines which subsequently react with purines or pyrimidines [2]. In the singlet state, nitrenium ions are often involved, among others, in reactions associated with rearrangements, nucleophilic addition to water and alcohols, electrophilic addition to arenes and hydride transfer, etc [1]. The strong tendency of carbenes and nitrenium ions to be inserted into OH bonds has been a matter of research in recent decades, especially regarding the details of the mechanism [3]. The reaction between chlorocarbene with one and two water molecules to produce chloromethanol, has been well described theoretically [4]. In this work, aiming at a comprehensive analysis of how nitrenium ions react in microsolvated environments, we use a variety of theoretical techniques including chemical reactivity descriptors within the framework of density functional theory (DFT), the properties of bond critical points in the electron density in the context of Atoms in Molecules (AIM) and quantities derived from natural bond orbitals (NBO) calculated along the Intrinsic Reaction Coordinate (IRC). In addition, the concepts of reaction force [5], reaction force constant and an approach to the reaction electronic flux are applied, to determine the mechanistic preferences for such reactions.

Keywords. Nitrenium, reaction force, reaction electronic flux, reaction mechanisms.

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QSAR study of antioxidant activity of curcuminoids and analysis of their chemical reactivity under DFT

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Abstract. Curcuminoids (curcumin, demethoxycurcumin and didemethoxycurcumin) are diarylheptanoids compounds which are major constituents of the rhizomes of Curcuma Longa. Curcuminoids have been used for a long time in the pharmaceutical, cosmetic and food industries. Nowadays there is great interest in curcuminoids because of their therapeutic capacity, which is associated with their antioxidant properties [1]. Experimental studies have examined the antioxidant capacity of curcumin, but there are still issues about structural and physicochemical properties, including the identification of the active tautomer, which influences pharmacological activities [2]. Curcumin crystals [2] and curcumin in solution [3] exist as enol tautomers, having three ionizable protons: one from the enol group and two from the phenolic groups. It has been reported that the antioxidant mechanism of curcumin enol starts with enol proton abstraction due to the lower ionization energy. In contrast, increased stability has been reported for the gaseous diketo tautomer [1], which has two ionizable protons (phenolic groups), suggesting proton abstraction of the phenolic group [3]. Due to these differences there is an interest in analyzing the antioxidant capacity of curcuminoids using computational tools such as QSAR studies or reactivity indices [5] in the context of DFT to describe the possible reactive sites of these molecules in different solvents. It is important to notice that theoretical studies of this type have not been conducted for systems consisting of curcuminoids. Our QSAR results for the keto form of curcuminoids in the gas phase using the HAT (H-atom transfer) and SET (Single electron transfer) methodologies duplicate the same trends as those found in experimental studies.

Keywords. Curcuminoids, DFT, QSAR, antioxidant capacity.

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Identification of binding mode of the epothilone-tubulin complex by molecular dynamics

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Abstract. Tubulin is a protein that acts as an important target for anticancer drugs, among them are the epothilones. These are macrocyclic compounds of natural origin with promising pharmacological properties [1]. Even though, the chemical synthesis of a wide variety of epothilones analogues has been possible, only some have emerged as effective antitumor agents. Furthermore, the differences in antitumor activity of active and inactive epothilones are still unknown. It is certainly a drawback for the development of new drugs from epothilones structures [2, 3]. Due these facts, the identification of factors associated with biological activity of epothilones represents the greatest challenge. In the present work was performed a study of the binding mode of the epothilone-tubulin complex, considering 20 epothilones bound to the tubulin protein by Molecular Dynamics (MD). The initial structures of epothilones were obtained from semiempirical calculations at PM3 level using the Gaussian 03 software. MD simulations were performed with the NAMD [4] software and the all-atom CHARMM27 force field. The topology and parameters of epothilones were generated by SwissParam [5]. Finally, the results showed that there is a direct relationship between the tubulin-bound conformation of epothilone and its biological activity, because was found that the biologically active epothilone adopts a characteristic binding conformation to tubulin in contrast to the inactive epothilones that are not capable of acquiring it. Furthermore, the most important interactions of epothilone-tubulin complexes were identified and binding models studied of the protein-ligand complexes were obtained.

Keywords. Epothilone, tubulin, molecular dynamics.

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DFT and TD-DFT study of Lutetium bis-phthalocyanines: Electronic structure and spectroscopic properties

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Abstract. Since its first appearance in 1930's, phthalocyanines (Pc's) have been commonly used to develop technological devices because of their remarkable physicochemical properties, especially in areas like catalysis, electrochemistry and optics [1-3]. In the last years, the double-decker bisphthalocyanato lanthanide ($LnPc_2$) complexes have attracted significant attention because they show electrochromic properties, a high intrinsic semiconductivity and a particular absorption spectra in the visible and near-infrared (NIR) region.[4-7] The aim of the present work is to study deeply the ground and excited state properties of the $LuPc_2$ in three different oxidation states ($[LuPc_2\cdot]$, $[LuPc_2]^-$, $[LuPc_2]^+$). This study was carried out on the framework of the density functional theory (DFT) and the time-dependent DFT (TD-DFT) as implemented on TURBOMOLE V6.5 code [8]. Ground and excited states as well as excitation energies were performed using the PBE0 hybrid functional with a def-TZVP quality basis-set for all atoms and using effective core potentials (ECP's) for the Lutetium atom. The calculated bond distances, angles and excitations energies are in good agreement with the experimental data previously reported. Excitation energies were characterized as $\pi - \pi^*$ type electronic transitions with non-significant contribution of the Lutetium ion and are located mainly on the visible and NIR region of the spectrum. The electronic localization function (ELF) analysis and the spin density on the $[LuPc_2\cdot]$ system suggest a strong delocalization between the rings through possibly unoccupied "*d*" empty orbitals of the lanthanide center.

Keywords. TD-DFT, electronic structure, optical properties.

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Study of the effect of saponin Dioscin on the water–oil interface as a surfactant for enhanced oil recovery

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Abstract. Surfactants play an important role in Enhanced Oil Recovery (EOR) methods which are based on the use of chemical compounds, since they increase the miscibility between oil and water. Chemically synthesized surfactants have been widely used for this purpose with good results but their use have also brought environmental problems related to the chemical residues left on water and soil. The present work focuses on the study of the saponin Dioscin and its possible use as a surfactant for EOR in Ecuador. Due to the fact that saponins are substances produced by plants, they are biodegradable and for this reason, they could be a friendlier option to apply in oil recovery. The effect of Dioscin saponin over water-oil interfase was determined using Molecular Dynamic Simulation; the property calculated for analysis was Interfacial tension (IFT) between water and oil as first step, and then, after the addition of a monolayer of Dioscin molecules between both fluids. The simulation boxes were constituted by a volume of water beside to a volume of hydrocarbon mixture in representation of crude oil. The surfactant monolayer was build varying the number of saponin molecules included, in order to achieve the minimum interfacial tension value between oil and water. Based on this result, the next step was to calculate the binding energy among Dioscin molecules in the monolayer and also the area per molecule. Experimental results show that a saponin extracted from leaves of a plant called *Zizyphus spina christi*, which is grown in the Middle East, can low this interfacial tension from 48 to 9 dyn/cm [1]. This investigation is a theoretical study that evaluates whether Dioscin can reduce interfacial tension too and up which value. The method was also selected because it allows the visualization of molecules (water, oil and saponin) when interact among them. Dioscin can be extracted from plants belonging to *Dioscorea* species, since this saponin is their main constituent [2]. One plant of this kind is Ñame which is a tuber grown in Ecuador, and because of that, it might be the natural source of this chemical compound for a future production.

Keywords. Dioscin, interfacial tension, molecular dynamic simulation.

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Water-methanol mixtures: Simulations of excess properties over the entire range of mole fractions

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Abstract. Numerous experimental and theoretical investigations have been devoted to studies of the hydrogen bond in pure liquids and mixtures. Among the different approaches, infrared and Raman spectroscopies are particularly well suited due to their sensitivity to the frequency shift of the OH stretching vibration induced by the presence of a hydrogen bond. Molecular Dynamics simulations are one method of choice to obtain information, at the molecular level, on the structure and dynamics of the fluids. Applied to mixtures such as water-methanol, we expect that the combination of these techniques [1] will lead to an improved qualitative and quantitative understanding of the peculiar properties of these systems. An important first step is to check whether a classical potential model is able to reproduce the known excess properties of this system sufficiently well. We have used the available BJH [2] and PHH flexible models [3] for water and methanol, respectively, since these models are mutually compatible and well suited to study spectroscopic properties. In this poster we show that these models, after a slight reparametrization for use in NpT-simulations, allow to reproduce the excess mixing and molar properties of water-methanol mixtures [4-5]. Some preliminary results on the evolution of the state of aggregation in term of hydrogen bonds are also presented.

Keywords. Classical MD simulations, excess properties, hydrogen bonding.

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Theoretical study of the reactivity of ionic hydrocarbons in gas phase

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Abstract. Hydrocarbons ions are important species in flames, petroleum industry and interstellar medium; the literature presents a huge discussion about carbocations structure and their reactivity [1-3]. However, they geometry, electronic structure and reactivity are difficult to assess. The present study aims to give a contribution on the related knowledge presenting a quantum mechanics description of the methane cation dissociation by multiconfigurational methods. The geometrical and electronic parameters of the minimum structure were searched and determined for three main reaction paths: the dissociation $CH_4^+ \rightarrow CH_2^+ + H_2$ and the dissociation/recombination processes $CH_4^+ \leftrightarrow CH_3^+ + H$ The electronic and energetic effects on these the reactions were analyzed and it was found that each reaction path has a strong dependence on the applied methodology as well as a strong multiconfigurational character during the dissociation. The first duplet excited states are inner shell excited states and may represent those of the expected ions formed after electron detachment. The rate coefficient for each reaction path was evaluated by variational Transition State Theory and RRKM/Master equation study at MRCISD(7,8)/6-311G(d,p)//NEVPT2(7,8)/6- 311G(2df,2pd) level. The major dissociation paths are CH_4^+ ($\tilde{X}\ ^2B_1$) $\rightarrow CH_3^+$ ($A^2\ A_1^{'}$) + H(^{2}S) (k(T)=1.42x10^{+14} exp(-37.12/RT)) and CH_4^+ ($\tilde{X}\ ^2B_1$) $\rightarrow$ CH_2^+ ($A^2\ A_1$) H($^2\sum_g^+$) (k(T)= 9.18$\times$10^{+14} exp(-55.77/RT)). The findings of present work may help the understanding of abundance of some ions in the interstellar medium and build models of chemical evolution. The work was extended to formation of cationic ethane, ethene and others hydrocarbons in gas phase.

Keywords. Multiconfigurational methods, dissociation/recombination, Arrhenius parameters.

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Study of the mechanism of carbocationic triple shift rearrangement

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Abstract. The formation of carbocation is important in reactions that take place in the active sites of enzymes. Recently, Tantillo and collaborators have studied the mechanism of carbocationic triple shift rearrangement [1] and in this work we revisit the mechanism in an alkane group (2–methyl–3–isopropyl–pentane) using the conceptual framework of the reaction force [2]. All systems were characterized computationally using DFT at the B3LYP/6–31+G(d,p) level. A complete description of the electronic activity taking place during the reaction emerged through the use of the reaction electronic flux (REF) [3] that together with NBO Wiberg bond order produces a complete picture of the reaction mechanism in terms of chemical events that drive the reaction during the different stages of the process.

Keywords. Carbocationic triple shift, reaction force, reaction electronic flux.

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Quantum chemical approach to modeling binuclear metallohydrolase catalyzed reactions: The case of binuclear Co^{2+} *Opd*A enzyme

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Abstract. Organophosphate degrading enzyme from Agrobacterium radiobacter (OpdA), is a promiscuous binuclear metalloenzyme able to hydrolyze a large number of phosphotriesters, including highly toxic pesticides and nerve agents, with a modest disterase activity. Despite its promiscuous nature make it possible for OpdA to have different metals in the active site, *in vitro* studies showed that the binuclear di-Co^{2+} derivative possesses a catalytic activity higher than the native Fe^{2+}-Zn^{2+} form. Herein, the diesterase and triesterase activities of di-Co(II) OpdA have been compared investigating the hydrolysis of trimethylphosphate and dimethylphosphate at density functional level of theory in the framework of the cluster model approach. The reaction mechanisms have been fully elucidated also confirming the crucial role played by a water molecule and some residues in the outer coordination sphere. Three exchange-correlation functionals have been used to derive the potential energy profiles, in gas phase and protein environments. Moreover, to correctly describe the electronic configuration of the d shell of the binuclear center, high- and low- spin arrangement jointly with the occurrence of antiferromagnetic (AFM) coupling, have been considered [1]. Similarities with the working mechanism of other bimetallic hydrolases have been found and will be discussed [2-5]. The outcomes of these theoretical investigations allow us to show how computational methodologies can be helpful in elucidating catalytic reactions of such enzymes.

Keywords. DFT, cluster model approach, binuclear metalloenzymes, phosphatases.

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DFG-out kinase inhibitors: Understanding their binding mechanism

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Abstract. C-Abl tyrosine kinase and B-Raf are both promising anti-cancer targets. C-Abl is being targeted in Chronic Myelogenous Leukemia (CML) treatment [1] while B-Raf is with the ^{V600E}B-Raf inhibitor Sorafenib (Nexavar), which has been approved by the FDA for use in the treatment of advanced renal cell carcinoma (RCC) and hepatocellular carcinoma (HCC) [2]. Molecular Dynamics simulations, free energy calculations and other techniques have been used to investigate the interactions of different DFG-out allosteric kinase inhibitors to human B-Raf and c-Abl kinases. The analysis of the components in binding free energy [3] suggests that the major contribution to the binding of both proteins with their inhibitors is the van der Waals energy component, which explains the differences of binding affinity among the inhibitors. The pairwise energy decomposition [4] demonstrates that the favorable interactions of individual residues and the relative values of the predicted binding affinities are in good agreement with the experimental results. This work provides a better structural understanding of allosteric inhibition targeting the DFG-out form of c-Abl and B-Raf protein kinases and will allow a further rational design of new potent inhibitors of these proteins.

Keywords. B-Raf, c-Abl, molecular dynamics, drug design.

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Ab-initio calculations of the thermodynamic properties of disubstituted diperoxides

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Abstract. The past several years has seen a increased interest in diperoxides and triperoxides prompted by the proliferation of terrorist attacks using peroxide based explosives [1]. In the current literature there have appear a number of investigations involving the decomposition pathways of peroxides, with particular emphasis on di- and trialkyl derivatives [2]. Many of these reports involve experimental studies on solvent mediated decompositions, whereas there are few theoretical investigations in the gas phase [3]. Considering the latter, we have ventured into studying the energetics of the gas phase decomposition reactions not only of known diperoxides, but also of hypothetical derivatives to determine what substituents are likely to produce more energy in their decomposition reactions, and also which compounds are thermodynamically feasible. In this study, we have determined that alkyl substituted peroxides are more stable than their aryl counterparts; therefore, it is possible to state that the former systems give rise to more exothermic reactions. Also, electron withdrawing groups give rise to decompositions that are more energetically favorable possibly because of a lengthening of the O–O peroxide bonds compared to their proteo counterparts. These results, a discussion of steric factors, as well as a comparison to the decomposition of some triperoxides derivatives will be presented.

Keywords. Explosive, decomposition reaction, peroxides, thermodynamics.

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Theoretical study of amino disaccharides

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Abstract. The aim of this study is to determine the characteristic structures of three types amin-disaccharides. The examined disaccharides were, the 2-amino-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl (β-D-GlcpN-(1→4)-β-D-GlcpNAc), the β-D-GlcpN-(1→4)-β-D-GlcpN and the β-D-GlcpNAc-(1→4)-β-D-GlcpNAc, where both were modeled by the Car-Parrinello approach [1]. These computations have been done using Vanderbilt ultrasoft pseudopotentials [2] and PBE functional. These disaccharides are the fundamental blocks of two polymers, chitin and chitosan. Dynamically we found the most stable conformers of each disaccharide. The conformational analysis of the mainly dihedral angles ψ (glycosidic torsional angle O-C-O-C), Φ (glycosidic torsional angle C-O-C-C), ω (nonreducing ring O-C-C-O) and ω' (reducing ring O-C-C-O) reveals similar average values for the three disaccharides, except by the dihedral angle ω, which was found 121.4° (13.9°), 107.8° (12.5°), 81.2° (18.7°), for the β-D-GlcpNAc-(1→4)-β-D-GlcpNAc, β-D-GlcpN-(1→4)-β-D-GlcpN and the β-D-GlcpN-(1→4)-β-D-GlcpNAc, respectively. The occurrences of intramolecular hydrogen bonds [3] (H-bonds) during the simulations are observed. The highest occurrence of a H-bond (nearly 50%) involve a hydrogen donor from the reducing ring and the oxygen (acceptor) of the glycosidic linkage. This result is similar to that found for cellobiose (Glcβ(1→4)Glcβ) [4], that is the building block of cellulose. In other study [4-5], it was observed that this H-bond persist with the aqueous solvation, therefore very important to understand physico-chemical and mechanical properties of the polymers, such as rigidity, stability, and insolubility in water.

Keywords. Disaccharide, amino, dynamic, Car-Parrinello.

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Curie temperature in double perovskites systems

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Abstract. The half-metallic ferromagnetic double perovskite compound Sr_2FeMoO_6 is considered as an important material in view of its potential spintronic applications [1] due to its high Curie temperature T_C=420K, complete spin polarization and substantial low-field magnetoresistance at room temperature [2]. It appears to be fundamental to understand the role of electronic parameters controlling the half-metallic ground state and high Curie temperature in this system. We present an electronic approach to study the Curie temperature behavior in double perovskites systems, this approach is based on a correlated electron picture with localized Fe-spins and conduction Mo-electrons interacting with the local spins via a double-exchange-type mechanism [3]. The Curie temperature behavior is shown.

Keywords. Spintronics, double perovskites, curie temperature.

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Damage to DNA/RNA nucleobases by UV radiation and reactive oxygen species. II. OH radical addition and photochemistry of the hydroxylated products

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Abstract. Reactive oxygen species (ROSs) may cause damage in the cell in distinct manners. One of the target biomolecules of ROS attack is the DNA/RNA and, in particular, the pyrimidine nucleobases [1]. The oxidation of these systems by the OH radical is a well-known reaction in the field [2]. As it is observed in the experiments [2], the ·OH is attached to the carbon atoms of the C5-C6 double bond of the pyrimidine nucleobases. The regioselectivity of the reaction is however not well understood and, additionally, the photochemistry of the C5OH· and C6OH· adducts produced is unknown. By means of multiconfigurational second-order perturbation theory (CASPT2//CASSCF) computations, we have i) characterized the mechanisms for the production of the C5OH and C6OH adducts, ii) determined the absorption properties of the products and iii) studied the photochemistry of these hydroxylated species [3,4]. Great efforts have been dedicated to explore energy decay paths which might release the OH radical. The findings allow us to shed light on possible strategies to regenerate the pyrimidine nucleobases.

Keywords. DNA/RNA damage and repair, CASPT2//CASSCF, hydroxylation reactions.

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Determination of geometric and electronic parameters of hydrazone using Car-Parrinello molecular dynamic

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Abstract. Azines or di–imines are compounds containing R_1R_2C=N-N=CR_3R_4 fragment in its structure. These compounds have received special attention due to their importance as intermediates in the synthesis of drugs and substances with diverse pharmacological activities [1-2]. Its known biological applications include, among others, anticonvulsant, antibacterial, antiparasitic, insecticidal, anti-inflammatory, antioxidant and anti–tumor [3]. In this work, we performed dynamics calculations for a specific hydrazona, Ethanone,1–(4–nitrophenyl)–,hydrazone, and we have determined the geometric parameters and electronic properties using Car–Parrinello Molecular Dynamics (CPMD) [4] and we use density functional theory (DFT) method, implemented in the gaussian package, to compare. The basic idea behind of the CPMD procedure is to solve simultaneously the equations of motions for both the nuclear coordinates as for the Kohn–Sham orbitals which describe the electronic states of the system. In practice, the computational procedure starts with an initial standard minimization of the Khon–Sham orbitals and, after the orbital convergences, the fictitious dynamics of the orbitals keeps the wavefunction of the system close to the Born–Oppenheymer surface for each new ionic configuration. The *ab initio* molecular dynamics simulation were carried out using the Car–Parrinello code implemented in the Quantum ESPRESSO package. The electronic structure was treated within the generalized gradient approximation to DFT, through the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [5]. Vanderbilt ultrasoft pseudopotentials were employed to represent core-valence electron interactions [6]. In this context, we compare our results with experimental crystallographic data and we verify very good agreement.

Keywords. Hydrazone, Car-Parrinello, molecular dynamic.

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Cluster origin of solvent features of C nanostructures

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Abstract. The existence of nanographene (GR) [1, 2] and GR–fullerene bud (GR-BUD) [3] in cluster form is discussed in organic solvents. Theories are developed based on *columnlet, bundlet* [4, 7] and *droplet* models describing size-distribution functions. The phenomena present a unified explanation in *columnlet* model, in which free energy of GR involved in cluster comes from its volume, proportional to number of molecules n in cluster. *Columnlet* model enables describing distribution function of GR stacks by size. From purely geometrical considerations, *columnlet* (GR/GR-BUD), *bundlet* single–wall carbon nanotube (SWNT) (CNT) (NT) and NT–fullerene bud (NT-BUD) [8] and *droplet* (fullerene) models predict dissimilar behaviours. Interaction-energy parameters of GR/GR–BUD are taken from C_{60}. An NT–BUD behaviour or further is expected. Solubility decays with temperature result smaller for GR/GR–BUD than SWNT/NT-BUD than C_{60}, in agreement with lesser numbers of units in clusters. Discrepancy between experimental data of the heat of solution of fullerenes, CNT/NT–BUDs and GR/GR–BUDs is ascribed to sharp concentration dependence of the heat of solution. Diffusion coefficient drops with temperature result greater for GR/GR–BUD than SWNT/NT-BUD than C_{60}, corresponding to lesser number of units in clusters. Aggregates $(C_{60})_{13}$, SWNT/NT-BUD$_7$ and GR/GR-BUD$_3$ are representative of *droplet*, *bundlet* and *columnlet* models.

Keywords. Solubility of graphene-fullerene bud, *columnlet* cluster model, *bundlet* cluster model, *droplet* cluster model, nanobud, fullerene.

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Design targeted drug carriers for potential use in cancer treatments

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Abstract. Different software and algorithms have contributed to improve the modeling of chemical interactions and molecular models. On this way the structure-based models provides an efficient pathway to obtain thermodynamics properties which allow identify novel lead compounds in drug discovery and calculate protein-ligand binding free energies [1, 2]. In this work, targeted drug carriers capable to recognize and binding at E-selectin were designed. The design focuses on the surface modification of PAMAM dendrimers [3] with small molecules that present highly affinity to E-selectin [4]. A molecular Docking study with Grid-Based Ligand Docking Energetics (GLIDE) software on fifteen millions of compounds using three sampling protocols (HTVS to SP to XP) was performed [5]. Furthermore, we evaluated the absolute protein-ligand binding free energy of hit molecules by means of Molecular Mechanics Poisson-Boltzmann/Surface Area (MM/PBSA) and Thermodynamic Integration (TI), as implemented in software Amber12 [6, 7]. Moreover, Enzyme-Linked Immunosorbent Assay (ELISA) was used for measuring the in vivo affinity binding of the molecules to the target E-selectin [8]. Finally, the results show that GLIDE is an efficient tool for the research and selections of molecules targeted between a large database of compounds. However the absolute binding free energy provided by this methodology is not correlated with more accurate methods like TI.

Keywords. Targeted drug delivery, docking, binding affinity, MM/PBSA, TI, Molecular dynamics.

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Structural properties of a reverse inhibitor against the HIV virus, dideoxynucleoside zalcitabine in gas and aqueous solution phases

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Abstract. Zalcitabine is a synthetic nucleoside analogue, whose chemical name is Dideoxycytidine (DDC). It compound is used in combination with other antiretroviral drug for the therapy of the Acquired Immunodeficiency Syndrome (AIDS) [1]. The antiviral mechanism of action of this drug is the inhibition of HIV nucleic acid synthesis. The structural studies of these types of compounds are of great importance to the design of new and better drugs for the treatment of the causative agent of AIDS. Consequently, the structural modifications on these molecules are evidenced by the different structure-activity relationship (SAR), hence, the importance to study that compound from this point of view. In the present work, we have theoretically studied DDC by using the hybrid B3LYP method together with the 6-31G* basis set. Two stable conformers for DDC were determined in both media. The structural properties of both conformers in aqueous solution were performed taking into account the solvent effects by means of the self-consistent reaction field (SCRF) method employing the integral equation formalism variant (IEFPCM). The magnitude of the intramolecular interactions of both sugar deoxyribose and pyrimidine rings of DDC in the two media were studied at the same level of theory by using natural bond orbital (NBO) [2] calculations and the atoms and molecules theory (AIM) [3]. Thus, the atomic charges, molecular electrostatic potentials, bond orders, and the frontier molecular HOMO and LUMO orbitals for the two conformers of DDC were calculated and compared with those results obtained of the literature for other antiviral agent, thymidine [4].

Keywords. Zalcitabine, molecular structure, descriptors, DFT calculations, HOMO-LUMO.

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DFT study of rutile and anatase materials doped with vanadium

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Abstract. Titanium dioxide (TiO_2) exists in form of rutile and anatase crystals. In the present study, we have considered investigation of both materials doped with vanadium impurity. The study was considered due to huge amount of applications which have TiO_2. It is a key material for clean energy production by photocatalytic water splitting. TiO_2 also has applications in coatings and sensors and is gaining more interest as a material for novel electronic memory devices, such as memristors. Nanostructured TiO_2 electrodes are essential in solar energy applications [1, 2]. The principle objectives of the investigation were to obtain structural changes due to the impurity incorporation, find out energetic bands using density of states (DOS) as well as obtain the information on magnetic properties of doped materials. Supercell model consisting of 96 and 108 atoms for rutile and anatase crystals, respectively, were used in our calculations. Vienna *ab initio* Simulation Package (VASP) [3] software was our main tool; the code is based on the density functional theory (DFT) [4]. The main results obtained imply that there are structural changes in the defect vicinity. Defect–closest oxygens move towards the impurity whereas the titaniums located in the defective region find themselves displacing outwards with respect to vanadium. These particular atomic shifts might originate from the fact that the chemical bonding becomes more ionic as obtained from the analysis of Bader charges. Impurity introduction produces local magnetic moments in both materials.

Keywords. DFT, TiO_2, impurity doping, crystal structure, magnetism.

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Synthetic growth concept: A theoretical approach for designing novel nano-structured materials and low-dimensional phases

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Abstract. Tailored nanostructured materials find a rapidly expanding role in materials science, nano-opto-electro-mechanical systems and graphene-based electronics. In this context, we have developed the Synthetic Growth Concept (SGC) based on the Density Functional Theory. SCG is understood as structural evolution by sequential steps of atomic rearrangement where each step is assigned according to the previous relaxed states. Bonding issues, precursors, quantum size effects, chemical aspects of structural patterns are significant aspects of SGC. SGC has been successful in designing/guiding the synthesis in laboratory for several classes of nanostructured materials: 1) The SGC is literally the tool behind the discovery of a new class of carbon-based materials: Fullerene-Like (FL) C:N:P:S::F ... solids. FL-CN$_{.x}$ is industrially applied under the trade name of rubber diamond exhibiting outstanding mechanical properties. By using SGC, the FL-CN$_{.x}$ structure evolution was understood [1], the FL Phospho-carbide (FL-CP$_{.x}$) [2] was predicted and deposited by magnetron sputtering [3], the solid Carbon Fluoride (CF$_{.x}$) was discovered and synthesized at our lab [4]. CF$_{.x}$ is especially attractive since it may lead to a material as significant as Teflon. 2) Low-dimensional III-Nitrides. We introduce a two-dimensional graphene analogue based on the technologically highly prospective wide-band gap semiconductor Aluminum Nitride (AlN) [5]. Ill emphasize our encouraging theoretical findings on 2D h-AlN in the context of the vast competence and experience on growth of III-Nitrides available in our group [6]. 3) Metal-Silicide cluster-assembled materials are prospective compounds for achieving integrated nano-opto-electro-mechanical devices. The endohedral silicon-metal clusters (M@Si$_{.x}$) provide diversity of building blocks for synthesizing cluster-assembled materials [7], and low-dimensional phases, *e.g.*, M@Si$_{.x}$ nano-wires [8] emerging as stable Si-based analogues of carbon nano-tubes. The purpose of this presentation will be to advertise our original SGC as a transferable atomistic modelling concept with predictive power for a wide range of nano-structured materials.

Keywords. Nanostructured materials, chemistry of growth, bonding, carbon-based materials, nitrides.

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Functionalizing carbon nanotubes to hold chemical reactions: A DFT study

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Abstract. Chemical species, under spatial and chemical confinement, may show dramatic changes in their physical and chemical properties when compared to gas phase conditions. This work aims to characterize the structural features and energetics of simple chemical reactions when confined inside different single walled carbon nanotubes (SWCNTs). We hope it can contribute to plan new and cleaner chemical processes with interesting applications in scientific research, drug design and industrial processes. Using the known and relatively simple S_N2 Menshutkin reaction ($H_3N + H_3CCl \rightarrow H_3NCH_3^+ + Cl^-$), where reactants are neutral and products are charged, we are able to study the effects caused by the SWCNT confinement medium over the reaction path. The electronic properties of SWCNT are known to be fully determined by their (n,m) chiral indices, which essentially define the role-up direction of a graphene sheet [1]. In this work, (8,0), (9,0) and (5,5) SWCNTs, with and without some halogen functionalization, are considered to host the referred chemical reaction. Quantum mechanical calculations based on Density Functional Theory (DFT) are used to characterize different stages of the chemical reaction. The results presented here were obtained with functionals B3PW91, B3LYP and M062X, and with 6–31++G(d,p)/3–21G function basis set for the reaction/SWNT system. The typical endothermicity of the reaction in gas-phase is greatly reduced when it occurs inside SWCNTs, and the corresponding activation barrier is lowered significantly, which is in accordance with previously published results for this particular reaction [2, 3].

Keywords. Carbon nanotubes, catalysis, DFT, S_N2 reaction.

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Enthalpies of formation and acidities of thio- and selenobarbituric acids. A G3 and G4 study

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Abstract. Selenium is an essential element in the human body and is present in what is commonly known as the 21st natural amino acid, selenocysteine. However, the number of publications devoted to study selenium-containing compounds is very much smaller than that devoted to study compounds containing oxygen or sulfur. The chemistry and intrinsic properties of compounds with selenium is little known [1]. A computational study on the thermochemistry and the gas-phase acidities of barbituric acids containing one, two or three atoms of sulfur and/or selenium attached to the carbons in positions 2, 4, and/or 6 of the ring, has been carried out at the G3 [2] and G4 [3] levels. Tautomerism has been studied not only in neutral forms but also in deprotonated species. The most stable tautomers for neutral and deprotonated species are equivalent to those obtained by different authors for barbituric and 2-thiobarbituric acids [4]. Enthalpies of formation have been calculated through atomization and bond separation isodesmic reactions, using in this case as reference the calculated enthalpy of formation of selenoformaldehyde, which is not available in the literature. The influence of the number and position of sulfur or selenium atoms on the acidity will be discussed. The calculated acidities show that selenobarbituric acids are very strong Brønsted acids in the gas phase.

Keywords. Barbituric acids, thiobarbituric acids, selenobarbituric acids, G3 and G4 calculations, enthalpy of formation, gas-phase acidity.

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Diffusion of atoms and ions in solid state matrices

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Abstract. Diffusion of atoms and ions in solid state matrices is studied for two systems. The first concerns the incorporation of hydrogen atoms in molybdenum carbide. This material has proved to be efficient in the hydrogenation of benzene [1] and the evolution of hydrogen from the bulk seems to play a part in the process, especially in what concerns the catalysts poisoning. It is shown that the diffusion of hydrogen in molybdenum carbide is an activated process [2] and can explain some peculiar features of thermal-programmed desorption of this material. The second problem studied was the diffusion of silver ion in silver and lead sulfides. The motivation to this study was to verify the viability of the mechanism proposed [3] to explain the electrochemical impedance response of a lead-sensitive electrode formed by those sulfides. In both cases, calculations were done at DFT level with periodic boundary conditions, plane wave basis set and pseudopotentials. The diffusion profiles were calculated by the nudged elastic band in supercells.

Keywords. Diffusion, solid state, DFT, catalysis, electrochemistry.

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Geometrical functionalization of carbon nanotubes

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Abstract. Due to the importance of phenomena associated to carbon dioxide, this gas has since long ago attracted the attention of the scientific community and the consequent technological effort developed in the investigation of its properties allowed the understanding of the CO_2 production as a result from coal and hydrocarbons combustion. As a consequence, CO_2 concentration in the atmosphere became an important problem in terms of global warming. In order to solve this CO_2 related environmental problems an accurate and reliable detection of this gas in a scale that allows mapping its concentration in any media is highly desirable. An efficient method to do so is the nanostructural arrestment of carbon dioxide [1]. In this sense, carbon nanotubes stands (SWNT) up as a promising structure. Provided an important adsorption energy is observed between the gas molecule and the nanotube lattice, the other physical and chemical features of this system are favorable to this nanotechnology application. In a previous study, we observed that, whereas pristine SWNT present low reactivity, the effect of doping this system with transition metals yielded excellent results [2]. In the present work, we propose a new route to functionalize SWNT in order to arrest carbon dioxide. By means of electronic structures calculations in the scope of the Density Functional Theory, we applied structural deformations to the lattice and conducted an analysis on whether or not the originated system was suitable to CO_2 detection. The feasibility of this system to the actual application is measured in terms of the interaction energy, energies levels profiles and spectroscopic constants. By means of this procedure we observed a reasonable adsorption energy, of about an order of magnitude higher than that of the pristine nanotube. This indicate that the conformational functionalization is an reasonable choice to obtain efficient gas sensors.

Keywords. Carbon nanotubes, adsorption energy, CO_2.

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Structure of cetyltrimethylammonium bromide surfactant micelles from dissipative particle dynamics simulations

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Abstract. We present the results of dissipative particle dynamics (DPD) simulations of cetyltrimethylammonium bromide (CTAB) in aqueous solution. A realistic model was employed to let the hydrophobic tails to entangle, bend, rotate and move away from straight alignment used in other models. Therefore we used five beads to represent the 16-alkyl carbon chain and the trimethylammonium head group. We considered the bromide dissociation factor using two types of hydrophilic heads: one including the bromide ion and the other one without it. In the same manner water was modelled by two types of beads, with and without bromide ion. Electrostatic long range forces were accounted for through an extension of Ewald summation method to DPD.

Keywords. Dissipative particle dynamics, micellar structure, CTAB.

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Evaluation of the CHARMM27 parameters by the topological study of G-Quadruplex

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Abstract. G-quadruplex DNA nanostructures have being explored because its possible applications as biosensors [1]. These molecules are present in biological systems and their physical and chemical properties makes them a useful tool for the assembly of nanostructures that could perform complex and specialized functions. For example, there are structures based on these materials named aptamers capable of specific attachment to a substrate. These molecules are generated using artificial selection in which from a set of initial random structures, those with the greatest affinity and selectivity are selected and later enriched by PCR. This process could however be improved if an engineering of the structures for the initial set results from a computer aided design. A possible way to accomplish this could be based on results derived from molecular dynamics simulation [2, 3]. To this end, this paper studies the reliability of simulating these structures with one of the most widely used force fields for nucleic acids, CHARMM 27 force field as implemented in NAMD. For this work the preparation of the models and data analysis was performed with VMD visualization package. Here, we report first the validation of the topology for the simulations as well as certain key indicators of convergence for the minimization phases and the correct equilibration for the molecular dynamics part. Comparison with suitable experimental values derived mainly from NMR and Crystallography were used as reference.

Keywords. G-quadruplex, CHARMM27, molecular dynamics.

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Solution vs. gas phase relative stability of the choline/acetylcholine 3iPO cavitand complexes: Mass spectrometry and theoretical studies

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Abstract. Selective host-guest recognition is fundamental in biological processes. The present study reports our investigation on the preferential capture of acetylcholine (ACh^+) (with respect to choline Ch^+) by the 3iPO triphosphonate cavitand **1**. We demonstrate that the substitution by ACh^+ must arise within the $Ch^+-Pic^--\mathbf{1}$ complex formed in solution, the picrate anion (Pic^-) being the counterion. This information, obtained by a combination of experimental techniques in the gas phase (mass spectrometry and collision induced dissociation) and DFT calculations, can be potentially helpful for instance in the tailoring of supramolecules for the selective recognition of substrates of biological interest.

Keywords. Mass spectroscopy, collision induced dissociation, DFT, cavitand, choline.

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A novel class of polymers containing boron-boron triple bonds

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Abstract. Since the discovery and isolation of an ambient–temperature stable compound containing a boron-boron triple bond [1], several studies have been performed to investigate and explore the chemistry of N–heterocyclic carbenes (NHCs) with boron atoms [2-5]. These novel studies focus mainly on the synthesis and reactivity of (NHC)–stabilized diborynes [2-4] and the formation of boron aromatic rings and clusters [5]. In a recent review, Braunschweig *et al.* pointed out that triply bonded diboryne compounds promise rich further chemistry and evidenced that a lot of progress has been made at the experimental level in the use of carbenes to stabilize boron-boron multiple–bonding [4]. Based on this astonishing progress, herein we propose a viable synthetic route – supported by theoretical calculations – for the formation of polymers containing several units of boron-boron multiple bonds, by making use of Janus-type biscarbenes [6] as ligands. To the best of our knowledge, the use of this type of compound has never been applied to the boron chemistry. Moreover, we show that, by replacing biscarbene spacer groups with carbonyl (CO) or dinitrogen (N_2) as end-on bridging ligands, it is possible to modify the linear arrangement bonding profile from alternating single and triple bonds to a cumulene–like structure. Finally, Generalized Valence Bond (GVB) diagrams are used to elucidate the chemical structure of the mentioned chemical species.

Keywords. Boron chemistry, N-heterocyclic carbenes, Density Functional Theory, polymers.

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Theoretical study of the proton transfer in formamide and the role of the water molecule in the reaction

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Abstract. The mechanism of the intramolecular proton transfer in the formamide molecule ($NH_2CHO \rightarrow NHCHOH$) and the role of the water molecule in the same reaction have been studied. These reactions are established as a basic model to understand and characterize complex systems, along with determining the role of the water molecule in the proton transfer process [1, 2]. To determine the mechanisms of each reaction, tools of the Density Functional Theory, concepts are used as a general theoretical framework, these are the chemical potential and hardness, along with descriptors developed by our research group as the Reaction Force and Reaction Electronic Flux [3, 4], to obtain information about the reaction mechanism of the proton transfer and the catalytic effect of a single water molecule in the system. It has been found that water molecule reduces the energy barrier by 45%. The reaction works W_1 and W_2 associated to structural and electronic reordering respectively, are higher in iPT than wPT; however, the percentage contribution to the energy barrier is similar. The electron activity occurs mainly in the transition state region, it is attributable to the strengthening of the C–N bond and the weakening of the C–O bond. The reactants and products regions involve structural arrangements.

Keywords. Proton transfer, formamide, water.

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A DFT study of complexes with two hyperjovinol a molecules binding to a Cu(II) ion

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Abstract. Hyperjovinol A (2–methyl–1–(2,4,6–trihydroxy–3–(3–hydroxy–3,7–dimethyloct–6–enyl)phenyl) propan–1–one) is an acylated phloroglucinol of natural origin exhibiting interesting antioxidant properties [1]. The interest in antioxidant compounds is continuously increasing because of their importance in preventing neurodegenerative diseases. Compounds of natural origin are particularly interesting because of their proven ability to exert an action within a living organism. The study of the molecular properties of biologically active compounds is important for a better understanding of their activity and, therefore, also for the design of more potent derivatives [2]. An approach to modeling antioxidant activity considers the molecule's ability to bind to a Cu^{2+} ion and reduce it to Cu^{+} [3]. A study of this type on hyperjovinol A has highlighted the molecule's ability to bind and reduce Cu^{2+}, and the roles played by the phenol OHs and the OH and the C=C π bond in the geranyl chain [4]. In a medium containing metal ions (including media in living organisms), an ion might bind to more than one molecule. This study considers complexes in which Cu^{2+} binds two hyperjovinol A molecules, investigating their possible geometries in relation to possible combinations of the different conformers of hyperjovinol A and their mutual steric suitability in the complex. Molecule-ion interaction energies are evaluated. The computational approach is the same as in [4] to enable comparisons: DFT calculations with the B3LYP functional, using the 6–31+G(d,p) basis set for the C, O and H atoms and the LANL2DZ pseudopotential for the Cu^{2+} ion. The results confirm the molecule's ability to reduce the ion, as the combined effects of the two ligands completely reduces its charge.

Keywords. Acylphloroglucinols, antioxidants, $(\text{hyperjovinol A})_2$ - Cu^{2+} complexes, polyphenolic compounds.

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Structure and electronic properties of few-layer Pd films deposited on Re(0001) surface

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Abstract. One of the major challenges in surface science is being able to control the electronic properties of surfaces in a precise manner. Such control may be used to enhance functional properties of materials, such as conductivity, reactivity, and catalytic performance. In the case of metal surfaces, one way to tune the electronic behavior is through the deposition of a very thin film (a few atomic layers) of a different metal. Bennett *et al.* have experimentally investigated the structure and properties of 1-4 monolayer Pd films on the Re (0001) surface, employing low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and electron microscopy techniques [1]. The LEED experiment clearly identified the stacking sequence of the Pd layers: if the Re stacking of (0001) planes is denoted as ABAB (the *hcp* sequence), then the first layer of Pd continues the *hcp* sequence, so the deposited monolayer (1ML) can be denoted as ABABa. However, consecutive layers of Pd stack follow the fcc sequence, leading to the ABABac structure for 2ML, ABABacb for 3ML, and ABABacba for 4ML. We have used density functional theory (DFT) calculations to compare the stabilities of different stacking sequences for each surface composition, and found that in each case the experimentally observed configuration is the lowest-energy one. We therefore conclude that the stacking sequence of the Pd films is thermodynamically controlled. The DFT values of the interlayer distances are also in excellent agreement with the LEED measurements. Our DFT calculations predict that the minimum interface formation energy is achieved for 2ML Pd. From the variation of the formation energy with the number of deposited layers we also conclude that the homogeneous 3ML composition is thermodynamically unstable with respect to separation in islands of 2ML and 4ML, although this separation is not observed in the experiment. A Bader charge decomposition analysis from the DFT results shows that electrons are transferred from the Re substrate to the deposited Pd atoms, but most of the transferred charge is localized on the first Pd layer, near the Re/Pd interface. We found that the properties of the surface, as characterized by the position of the *d*-band centre with respect to the Fermi level and by the surface workfunction, saturate after 2ML, in agreement with the experimental conclusion based on XPS measurements.

Keywords. Re (0001), Pd adlayers, density functional theory, *d*-band centre.

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Molecular interactions between anionic dimethylphosphate and water

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Abstract. The study of the molecular interactions between polar heads in phospholipids constituting of cell membranes and surrounding water molecules is of special interest because of implications in transport and exchange processes to the interior and exterior of cellular environments. In particular, microsolvation of phospholipids dictate conformational preferences that severely influence the ability of the membranes to interact with exogenous substances. Aiming at accurate quantum mechanical calculations, previous reports have succesfully used anionic dimethylphosphate (DMP^-), as a reduced model to simulate the polar head in phosphatidylcholine, the major component of eucaryotic cell membranes [1-3]. In this work, we use a combined QTAIM (Quantum Theory of Atoms in Molecules) [4] and NBO (Natural Bond Orbitals) [5] approach to characterize the molecular interactions responsible for bonding and stability in $[DMP\ (H_2O)_n]^-$, (n = 1, 2, 3) clusters. Our results suggest that besides $HOH\cdots OH_2$ hydrogen bonds among the solvating water molecules, significant contributions to stability arise from three types of charge assisted DMP-/water hydrogen bonds: $PO_2^-\cdots HOH$, $CH_3O\cdots HOH$ and $H_2CH\cdots OH_2$. The formal charge drives structural preferences and alters the covalent/closed shell nature of the interactions.

Keywords. Microsolvation, phospholipids, cell membranes, interactions with water.

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Configuration interaction wave functions based on the seniority number

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Abstract. This work deals with the N-electron wave functions arising from the configuration interaction method when an N-electron Hamiltonian is projected on Slater determinants classified according to their seniority number [1]. The spin properties (spin contamination) of the wave functions provided by this method are analyzed and compared with those resulting from the traditional configuration interaction procedure, based on Slater determinant classifications according to excitations from a determined reference state. The computational expense required in the seniority-number-based treatment has been calculated in terms of the size of the matrices utilized to formulate the states of any spin symmetry within this framework. In order to know the performance of this configuration interaction method, we have determined correlation energies, at identical level of seniority number in several basis sets. The results show that the basis set in which the expectation value of the seniority number operator is minimum yields energy values closer to those provided by the full configuration level.

Keywords. Seniority number, FCI/CI expansions, convergence of wave functions, unpaired electrons.

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Theoretical investigation of the potential of metal-functionalized pyrogallol[4]arenes as molecular hydrogen storage materials

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Abstract. In the present study, a theoretical investigation of the potential of various metal-functionalized R-substituted (i.e., M-R-Pyg[4]arene; M = Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}; R = methyl and fluorethyl) as media for molecular hydrogen (H_2) storage is reported. In a first stage of the study, the structural features of the metal-functionalized systems are obtained at the B97D/6-311G(d,p) level of theory. Subsequently, the interaction of a H_2 molecule with the cations embedded in the cavity of the macrocyclic molecules is described with the same B97D functional together with two basis sets of different flexibility, namely BSA:6–311G(d,p) and BSB:aug-cc-pVDZ. Notably large binding energy values were obtained at the B97D/BSB for the different H_2/M-R-Pyg[4]arene complexes spanning the 12.6–46.5 kJ/mol. Binding energy values refined at the MP2 level by means of an ONIOM-like approach for the H_2/Be-Methyl-Pyg[4]arene complex result in an increment of about 42.63 kJ/mol, showing that these materials are promising candidates for molecular H_2 storage.

Keywords. Pyrogallol[4]arene, hydrogen storage, metal-functionalized.

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Analysis of key structural properties for a study group of intermolecular parallel G-quadruplexes X-ray and NMR structures simulated with molecular dynamics

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Abstract. The simulation of biomolecules with molecular dynamics is very important field to help the understanding, at the atomic level, the function and properties of complex systems. DNA based structures are of the special interest because they regulate many key biological processes [1]. DNA G-quadruplexes can exist as structures with one, two or four different strands in various combination of parallel or antiparallel orientations. Furthermore, all of them show a quartet of four guanines in the same plane stabilized by hydrogen bonds and interactions with cations [2]. Although it may seem that the structures are simple but this is not so in reality because several topological variances can be created depending on conditions such as temperature, solvent, ions and other molecules present. There are several intramolecular and intermolecular forces that determine which structure is the most stable under particular conditions this makes that the systems are very challenging to model. Here we report an analysis of parallel DNA-G quadruplex denominated 1NP9, which structure is based on human telomeric DNA sequence d(TTAGGGT)4 and taken of the Protein Data Bank. In addition, this contains structural parameters that directly relate to several of the energy terms (bonding interactions, non bonding interactions as electrostatic and Van Der Waals contributions) that determine if the system is partially or correctly modeled using MD with a force field called CHARMM 27 as it is present in NAMD a very important software for biological modeling. Specifically from the trajectory data using python we extracted information such as distance between hydrogen bridge and base pair at different G-quartet planes. Moreover, bond length changes for instance in torsional glucosidic bond angles and the position of key cations and solvation interactions. These will capture the main characteristics of this system letting us compare the stability of the structures along the trajectory when the total time increases to hundred of nanoseconds as well as the transferability of the parameters to simulate parallel G-quadruplex structures and others related structures.

Keywords. CHARMM 27, force field, molecular dynamics, van der Waals contributions.

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Adsorption of polycyclic aromatic pollutants on graphene, and effect of the structural defects and doping

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) constitute an important class of environmental pollutants commonly emitted from natural and anthropogenic sources, which have carcinogenic and mutagenic characteristics [1]. Regarding this, graphene based materials offer an improved alternative to adsorption and removal of PAHs by solid phase extraction, enhancing the surface area for adsorption and extraction efficiencies, and having the quality to be reusable materials by several cycles [2]. Density functional theory (DFT) calculations were carried out to study the physisorption on graphene of PAHs type pollutants; B97(D) [3] functional was used with the atom pairwise method (DFT-D3) [4] and the density dependent dispersion correction (DFT-NL) [5-6] for description of van der Waals interactions. The DFT-NL method was capable to predict the cohesive energy of graphite (∼52 meV), while DFT-D3 overestimate that value. The results show that the adsorption energies of PAHs on graphene are dependent of the number of aromatic rings and molar mass, with values between 0.88 (naphthalene) and 1.83 eV (dibenz[a,h]anthracene), even being strong in a water environment. All intermolecular distances ranges between 3.2–3.3 Å, with a parallel displaced π–π stacking, slightly stabilized by charge transfer toward graphene of the order of until 5×10^{-2} electrons. Moreover, it was found that boron doping, Stone-Wales defects and mono vacancies at the adsorbent surface have a minimal effect on the adsorption energies, decreasing them in average 0.6, 0.4 and 1.6%, respectively. However, doping with nitrogen atoms decreases the adsorption energies in ∼10%.

Keywords. PAHs, pollution, graphene particles.

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Using nanoinformatic methods to automatically identify optimum polymerosomes for drug delivery applications

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Abstract. In the last decades, there has been an increasing interest in the use of nanoparticles for drug delivery applications. Of special interest are polymeric devices, such as polymersomes and micelles [1]. The ability to encapsulate broad range of drugs and molecules, tunability and biocompatibility are some of the advantages that make these systems appealing as promising drug carriers. Many efforts to obtain nanoparticles with the desired characteristics have been done and a vast amount of empirical data of nanoparticle properties is now available, but very little is known about how to apply *in silico* approaches, commonly used in small molecule drug development, to improve the de *novo* design of these nanoparticles. The physical and chemical properties of these polymeric devices depend on several factors. In polymersomes, it has been shown that properties such as geometry, mechanical stability and permeability depend on the membrane properties, which are directly related with its chemical composition. Since these polymeric devices are intended to be used as drug delivery vectors, other important factors to be considered are the payload and the target, which are typically drugs and pathological cells, respectively. Due to the lack of well curated data bases on polymersomes physico chemical and bioactivity a prerequisite to develop quantitative predictive model of structure-function relationships is to efficiently obtain this data from the original literature. This task cannot be accomplished manually due to the large and complex literature volume. The work presented here show our efforts to develop methods to automatically extract information about chemical compositions (polymers), payloads (drugs) and targets (cells) by means of NLP (Natural Language Processing) techniques. For this task, a corpus of selected abstracts from PubMed has been prepared and each term associated with each category (polymer, drug, cell) is manually annotated. The annotated corpus is processed with the adequate NLP techniques to measure the performance and accuracy of this method [2].

Keywords. NLP, nanomedical iformatics, polymersomes, structural-function relationships.

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Theoretical study of $N_2O \rightarrow N_2 + O$ reaction catalyzed by O-doped Pt_8 nanoparticles

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Abstract. The main nitrogen oxides, NO_x, present in the atmosphere are: NO, NO_2 and N_2O. Among them, N_2O is considered an air pollutant because it contributes to the destruction of the ozone layer and the greenhouse effect. Its global-warming potential is 300 times greater than that of CO_2 [1-2]. The reduction of these oxides is not a simple process, because they are more easily reduced to N_2O than to N_2. To prevent the formation of N_2O, it is necessary to determine the conditions under which the reduction reaction is completed, which leads to the formation of N_2. This paper studies theoretically the dissociation of N_2O molecule catalyzed by O-doped platinum nanoparticles by means of Density Functional Theory (DFT) incorporated into the ADF2013.01 program [3]. Generalized gradient approximation (GGA) was used with exchange-correlation functional proposed by Perdew-Burke-Ernzerhof (PBE) [4] and with ZORA approximation [5] in order to include relativistic effects of platinum. The N_2O interaction with OPt_8 nanoparticle in its most reactive sites gives rise to complete dissociation of the molecule in O and N_2, being these products further adsorbed by cumulus. On doping the platinum nanoparticle with O, the yield of dissociation reaction improves due to the increased number of reactive sites where spontaneous dissociation takes place. The results are also affected by the geometry of interaction and spin multiplicity.

Keywords. Nanoparticles, platinum, N_2O, DFT, ZORA.

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Synergism between surfactants through mesoscopic dynamics to produce low interfacial tension at the hydrocarbon-water interface

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Abstract. Petroleum has hydrophobic high molecular weight chemical compounds that contribute to the formation of interfaces with high interfacial tension between hydrocarbon and water layers. It has been demonstrated through the use of surfactants whose interfacial tension might decrease as much as three orders of magnitude, the effectiveness of this will depend mainly in hydrocarbon's composition, as well as environment and its porous medium. It is currently being studied the combined use of surfactants to enhance their effectiveness, as a selection criterion its synergistic behavior is used [1]. The present work makes use of mesoscopic models in DPD (*Dissipative Particles Dynamic*) simulation to study the hydrocarbon-water interface [2] with the help of Material Studio® software. For this models an anionic and other non-ionic surfactant were considered. We extend our study taking as anionic surfactant a series of isomers in the family of Alkyl Benzene Sulfonates (ABS) that range from hexyl to nonyl in its hydrophilic group and as non-ionic surfactant the Lauryl Alcohol Polyoxyethylene Ether (LAP-9) was studied. We found that the energy of formation of interface is lower when an stable assembly was formed where these molecules were aligned and compacted forming a monolayer. The monolayer's thickness is affected by difference between hydrophilic-lipophilic ability [3] of each surfactant involved in mixing. It shows a maximum thickness when a surfactant is very lipophilic and the other is very hydrophilic. The layer's thickness in some cases can reach four thirds the length of the larger molecule, which indicates that the molecules have a lipophilic linker effect [4]. It was found that the interfacial tension increased with decreasing the thickness of the interface as a function of benzene sulfonate's position. The lipophilic linker effect and the benzene sulfonate's position are related in terms of alkyl tail's miscibility in the surfactant. The synergism between surfactants was studied by a semi-empirical way measuring the interfacial tension against a series of alkanes, which range from hexane to tetradecane, process known as alkane scanning curve [4]. The synergism originate changes of hydrophilic-lipophilic ability of individual surfactants included in the mix, which allows to obtain a very low interfacial tension (<0.01mN/m) [5].

Keywords. DPD, molecular dynamics simulations, surfactants.

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Application of an orbital localization technique based on the topological analysis of the electron localization function

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Abstract. In this work we present a new molecular orbital localization procedure [1, 2]. The approach is based on the decomposition of the overlap matrix in accordance with the partitioning of the three–dimensional physical space into basins with clear chemical meaning arising from the topological analysis of the electron localization function (ELF). Studies on benchmark molecules have shown excellent results in agreement with the genuine chemical expectations of the classical bonding paradigms exhibited by these systems. Applications on atomic clusters, including a family of planar boron clusters, and comparative analyses with adaptive natural density partitioning (AdNDP) are presented. Furthermore, in order to complement these studies, magnetically induced current-densities are analyzed to examine aromaticity and antiaromaticity of these systems.

Keywords. Orbital localization criterion, ELF, AdNDP.

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Simulations of the absorption spectrum of crysteine modified gold nanoparticles in presence of TNT

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Abstract. In this work, we use the program ADF 2010 [1] with ZORA-DFT [2–5] for the optimization of the structures and for the spectroscopic calculations. The experimentals absorption spectrum of the Meisenheimer complex between cysteine modified gold nanoparticles and TNT [8–10] are compared to the theoreticals spectrum and will be shown with the structures studied during the poster session. The Time Dependent Density Functional theory (DFT/TDDFT) [2, 6, 7] was employed to calculate the excited states of the absorption spectrum (100 or 200 excitations). The DFT method with exchange and correlation functional (XC), the Generalized Gradient Approximation (GGA) and the LDA VWN BP86 functionals were used. The Slater type basis set (19 valence electrons) 4f(TZ.4f) with a frozen core 4f [5s2-5p6-5d10-6s1] was used for Au atom (denoted (TZ.4f)) and the zeroth-order regular approximation (ZORA) [4, 5] was employed in these calculations for the optimization and the spectroscopic calculations to take into account the relativistic effect.

Keywords. Gold clusters, gold nanoparticles, molecular interaction, absorption spectroscopy, ADF, DFT, TDDFT, ZORA.

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Study of models for the structure of ecuadorian crude oil

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Abstract. The Ecuadorian reserves of oil have a high content of heavy crude oil, this suppose several challenges starting from the recovery from the production wells, to the transport and to oil refining. Therefore to understand the behavior of this oil specially the forces that lead to their aggregation is critical to decide the strategies to overcome the difficulties in their handling. For this we are studying via molecular dynamics several test models for heavy crude oil. The simulations were realized using GROnigen MAchine for Chemical Simulations (GROMACS), in a set of NVT and NPT. Important interfaces to study include the water-surfactant-oil-soil. For our study we analyze the relationship oil–soil in order to elucidate the different structures of the chemical components and be able to select which is more feasible and a sufficiently realistic model interface for the interaction with the soil. The construction of suitable soil models, made up of crystal structures of zeolites and mormorillonites, which are usually present in the highest percentage in soils, has been studied in order to find the equilibrium in each phase, and predict the interfacial energy. The theoretical model corresponding to the phase of oil is made up entirely by asphaltenes. For our analysis, asphaltenes are modeled by two types of stoichiometric conformations: the continental and the archipelago seeking to identify that the physic-chemical properties obtained by molecular dynamics are close enough with available experimental data.

Keywords. Ecuadorian crude oil, GROMACS, asphaltenes.

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Two-electron three-center (2e-3c) interactions in CH_4-Me^+ systems and simple X_4H^+ clusters

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Two-electron three-center (2e-3c) interactions are typical patterns in electron deficient systems as for instance, boron hydrids [1], closo-boranes [2], and even some organic ions [3]. In this report, as continuation of previous works we apply the topological formalism of the density decomposition into paired and unpaired contributions, to the detailed description of the electron distribution to two group of systems which are considered as candidates of possessing such (2e-3c) patterns in order to conclude about the existence of the mentioned pattern. The first group is composed by stable gaseous structures of methane and metallic cations of alkaline and alkaline earth atoms CH_4-Me^+ (Me=Li,Na,K,Be,Mg,Ca) [4] and the second one by simple clusters X_4H^+ (X=P,As) [5-7]. It is shown that such patterns are not present in the first group while they arise within the second group distributions.

Keywords. 2e-3c interactions, topology, paired density, unpaired density.

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Docking studies of eugenyl acetate derivatives as new insect repellents

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Abstract. Worldwide, approximately 700 million people are infected each year with diseases transmitted by mosquitoes, which are responsible for killing one among 17 infected individuals. [1] In Brazil malaria and dengue are the diseases transmitted by mosquitoes of greatest relevance. [2] In view of the cost and complexity of the treatment of these diseases, the development of insect repellents for protection against the mosquito vector becomes an interesting alternative. [1] Today, the main marketed formulations of repellents have the synthetic N, N–dimethyl–m–toluamide (DEET) as the active ingredient. However, molecules of natural origin could be more interesting as repellents due to its faster degradation andlow to moderate toxicity, in addition to a lower cost compared to synthetic molecules. [1, 2] Based on these data, Affonso *et al.* [2] proposed the eugenyl acetate, a component of the ethanolic extract from indian clove (*Syzygium aromaticum*), as an alternative to DEET, based on results recently obtained from a molecular modeling study on the ability of this compound to bind to the odorant binding protein from *Anopheles Gambiae* (*Agam*OBP_1), an important receptor of the olfactory perception system of the malaria's vector. [2] Here we proposed 09 analogues of eugenyl acetate and performed docking studies of them on *Agam*OBP_1 in a search for new and more efficient repellents. Our results showed that these compounds presented better interactions with *Agam*OBP_1, reaching a 88% increase in the values of the energy of interaction. This reinforces the idea of using eugenyl acetate as an additive to commercial repellents and also propose effective synthetic molecules using it as a precursor.

Keywords. Eugenyl acetate, *Agam*OBP_1, repellency, anopheles, malaria.

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β-Carotene encapsulation into single-walled Boron-nitride nanotubes: A theoretical study

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Abstract. Recently, the encapsulation of β-carotene molecules into carbon nanotubes has been achieved [1,2]. In this work, we report molecular dynamics simulations and tight-binding density functional-based results for a theoretical study of the encapsulation processes in Boron-Nitride nanotubes. Our results show that the molecules undergo geometrical deformations when encapsulated with significant changes in their electronic structure. Besides this, we report how the charge transfer between β -carotene and boron-nitride nanotube occurs, what changes occur in density of states (DOS) after the encapsulation process, and compare it with previous results for carbon nanotube [3].

Keywords. β-carotene molecule, molecular dynamics, tight-binding density functional, electronic structure, Boron-nitride nanotubes.

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Reaction force and reaction flux analysis of proton transfers on DNA bases

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Abstract. The reaction force and the reaction electronic flux [1] are very useful tools to fully analyze a particular reaction in order to understand the structural and electronic rearrangements that take place along the reaction coordinate. In this work we have applied these concepts with NBO electronic population analysis [2], in order to characterize the intramolecular proton transfer on the DNA basis, Adenine, Citosine, Guanine and Thymine, along the *intrinsic reaction coordinate* (IRC), implemented at Gaussian 09 [3], using B3LYP/6–311g(d,p). Our results indicate that although all the electronic rearrangements occur at the transition state, there is a different behavior of the electron transfer due to the differences of donor and acceptor atoms.

Keywords. Reaction force, reaction electronic flux, proton transfers.

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Anisotropic and chemical agent effects on Fe-S bond stability of mechanically stressed rubredoxin

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Abstract. The function of iron-sulfur proteins, such as rubredoxin, depends in large part on the stability of their Fe-S bonds. Recent atomic force microscopy experiments unexpectedly showed that Fe-S dissociation in rubredoxin single molecules under mechanical stress occurred at relatively low forces [1-2]. In order to probe the detailed mechanism of forced rubredoxin unfolding, we develop here an approximate molecular dynamics scheme to simulate unfolding trajectories with bond dissociation and employ a hybrid quantum chemical molecular mechanical (QC/MM) potential to describe in detail the mechanism of Fe-S rupture in stretched rubredoxin in the presence of competing chemical agents such as SCN^- and H^+. In opposition to results previously observed in the absence of such agents [3], a heterolytic bond cleavage mechanism is obtained here with a ferric–thiolate dissociation product. Analysis of hundreds of unfolding trajectories also explains the anisotropic response of stretched rubredoxin [1-2] when force is applied at different points along the protein primary sequence.

Keywords. Hybrid QM/MM potentials, density functional theory, atomic force microscopy, single-molecule spectroscopy.

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Ab initio and DFT study of chinesins I and II

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Abstract. Chinesin I and chinesin II are prenylated acylphloroglucinols of natural origin, differing only by their acyl chains [1, 2]. They exhibit antimicrobial and antiviral activities, including inhibitory effects on the replication of the vesicular stomatitis and herpes simplex viruses [1, 2]. Their structures are different from those of the acylphloroglucinols so far investigated computationally [3-5] and are particularly interesting because of the combination of different factors which influence conformational preferences: the presence of a keto O replacing one of the phenol OH ortho to the acyl chain; the presence of an additional OH attached to a pentagonal ring and capable of forming a second intramolecular hydrogen bond with a neighboring phenol OH (besides the first intramolecular hydrogen bond between the *sp2* O of the acyl chain and an ortho OH, characterizing all acylphloroglucinols); and the presence of a prenyl chain. The compounds were studied at the Hartree Fock (HF/6–31G(d,p)) and Density Functional Theory (DFT/B3LYP/6–31+G(d,p)) levels, selected to enable comparisons with the results of a general study of acylphloroglucinols and the patterns therein identified [3-5]. Calculations in vacuo were carried out with fully relaxed geometries. Calculations in solution were carried out as single point calculations on the in-vacuo optimized geometries, considering chloroform, acetonitrile and water solutions and utilizing the Polarizable Continuum Model (PCM). Adducts with explicit water molecules were calculated because of their interest in relation to the presence of several hydrogen bond donor or acceptor sites in the componds. The results show fair correspondence with the patterns identified for acylphloroglucinols, including the close similarities in the conformational preferences of the two compounds, scarcely influenced by the difference in the acyl chains.

Keywords. Acylphloroglucinols, antiviral compounds, intramolecular hydrogen bonding, polyphenols, solute-solvent interactions.

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Comparison of methallyl nickel complexes and their boron adducts in activation of ethylene: An explanation using dual descriptor of chemical reactivity

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Abstract. In this work, the global and local descriptors [1] of chemical reactivity and selectivity are used for explaining the reactivities of methallyl nickel complexes **1**-**4**/[Ni(η^3-methallyl)] and their boron adducts formed with **1**-**4**/$B(C_6F_5)_3$, **4**/BF_3 toward ethylene [2]. It is shown that chemical potential, hardness, electrophilicity, dual descriptor [3] of chemical reactivity and selectivity as well as molecular electrostatic potential (MEP) surfaces can fairly well describe the reactivity of these organometallic systems toward ethylene. Computational studies are in a good agreement with experimental results showing that adding a borane molecule to a nickel complex increases the probability of electron transfer, lowers its hardness, enhances the electrophilicity power improving the reactivity of these systems with ethylene.

Keywords. Nickel complexes, chemical reactivity, dual descriptor.

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A theoretical study of formation routes and dimerization of methanimine and implications for the aerosols presence in the upper atmosphere of Titan

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Abstract. Methanimine is an important molecule in prebiotic chemistry since it is considered a possible precursor of the simplest amino acid, glycine, via its reactions with HCN (and then H_2O) or with formic acid (HCOOH). According to this suggestion, the simplest amino acid can be formed 'abiotically' starting from simple molecules relatively abundant in extraterrestrial environments and primitive Earth. Interestingly, methanimine has been observed in the upper atmosphere of Titan, which is believed to be somewhat reminiscent of the primeval atmosphere of Earth. Methanimine can be produced in the atmosphere of Titan by the reactions of N (^{2}D) with both methane and ethane, or by other simple processes, including the reaction between NH and CH_3 or reactions involving ionic species [1]. Recent models derived a larger quantity of methanimine than that inferred by the analysis of the ion spectra recorded by Cassini Ion Neutral Mass Spectrometer. Growing evidence suggests that nitrogen chemistry contributes to the formation of the haze aerosols in the Titan upper atmosphere. In this respect, since imines are well-known for their capability of polymerizing, CH_2NH is an excellent candidate to account for the nitrogen-rich aerosols of Titan through polymerization and copolymerization with other unsaturated nitriles or unsaturated hydrocarbons. Polymerization of methanimine provides an important contribution to the formation of the nitrogen-rich aerosols, but a quantitative inclusion of this process in the model could not be obtained as there is no information (either experimental or theoretical) on methanimine polymerization. Since the first step of polymerization is dimerization, in this contribution we report on a theoretical characterization of methanimine dimerization. Electronic structure calculations of the potential energy surfaces representing the reactions of electronically excited atomic nitrogen, N(^{2}D), with methane and ethane are also presented, as they are possible formation routes of methanimine under the conditions of the upper atmosphere of Titan.

Keywords. *Ab initio* calculations, atmospheric chemistry, potential energy surface.

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Deciphering the effect of fluorination of benzene in the chemical bond and its impact on the induced current densities and NICS

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Abstract. In this work, the recently proposed free of in-plane component NICS (FiPC-NICS) strategy [1] has been applied to assess aromaticity in fluorinated benzenes ($C_6FnH_{(6-n)}$, n=1–6). The results suggest that the aromatic character of the investigated systems is weakened by the fluorination, which has a linear correspondence with explicitly integrated current strengths. In contrast, other NICS computations (NICS(0), $NICS(0)_{zz}$ and NICS(1)) predicts that fluorination increases the aromaticity in these systems, which is attributed to effects that do not arise from the π-electron delocalization in the C_6 ring. A rigorous chemical bonding analysis using different electronic density partitioning schemes based on scalar fields: the electron localizability indicator (ELI-D) [2] and based on natural orbital localization: natural bond orbitals (NBO) [3] and adaptive natural density partitioning (AdNDP) [4], supports that fluorination should decrease aromaticity in this series of molecules.

Keywords. Aromaticity, NICS, FiPC-NICS, NBO, AdNDP.

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Spectroscopy, binding energy and properties calculations on silver and gold nanorods clusters: Staggered pentagonal (Ag_n for n=12 to 121) staggered cigare (Ag_n for n=12 to 120 and Au_n for n=12 to 120) and staggered hexagonal (Au_n n=14 to 74)

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Abstract. In this work, we use the program ADF 2010 [1] with ZORA-DFT [2–5] for the optimization of the structures and for the spectroscopic calculations. The experimentals absorption spectrums [6–7] are compared to the theoreticals spectrums and will be shown with the structures studied during the poster session. Metal-metal distances, binding energies per atom, ionization potentials, and electron affinities were determined and their trends with cluster size were examined. The TDDFT calculated excitation energies and oscillator strengths were fit by a Lorentz line-shape modification, which gives rise to the simulated absorption spectra. The significant features of the experimental spectra for actual silver and gold nanorod particles are well reproduced by the calculations on the clusters. The Time Dependent Density Functional theory (DFT/TDDFT) [2–5] was employed to calculate the excited states of the absorption spectrum (100 or 200 excitations). The DFT method with exchange and correlation functional (XC), the Generalized Gradient Approximation (GGA) and the LDA VWN BP86 functionals were used. The Slater type basis set (19 valence electrons) 4f(TZ.4f) with a frozen core 4f [5s2-5p6-5d10-6s1] was used for Au atom (denoted (TZ.4f)) and Double-z (DZ) Slater type basis set with a [1s2-4p6] frozen core for Ag atom (denoted DZ.4p) and the zeroth-order regular approximation (ZORA) [4–5] was employed in these calculations for the optimization and the spectroscopic calculations to take into account the relativistic effect.

Keywords. Gold clusters, gold nanoparticles, absorption spectroscopy, nanorods, TEM, ADF, TDFT, DDFT, ZORA.

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Docking studies of DEET derivatives as new mosquitoes repellents

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Abstract. Malaria and leishmaniasis together infect about 217 million people worldwide and take about 700,000 deaths annually. In view of the cost and complexity of the treatment of these diseases, the development of insect repellents for protection against the mosquito vector becomes an interesting alternative [1]. Today, the main marketed formulations of repellents have N, N-dimethyl-m-toluamide (DEET) as the active ingredient. However there are reports in literature of insect's resistance and cases of allergy in human [1, 2]. In this context, Affonso *et al.*, (2013) [2], have performed docking and molecular dynamics (MD), studies of DEET and alternative ligands on the odorant binding protein from *Anopheles Gambiae* (*Agam*OBP1), an important receptor of the olfactory perception system of the malaria's vector. Their results suggest a mechanism of interaction between DEET and *Agam*OBP1, due to its strong interaction compared to the molecules that usually attract the mosquitoes (indole, lactic acid and octen-3-ol). In the present work, we proposed 13 analogues of DEET and performed docking studies of them on *Agam*OBP1 in a search for new and more efficient repellents. Our results showed that the analogues of DEET, which are more hydrophobic, presented better interactions with *Agam*OBP1, reaching a 150% increase in the values of the energy of interaction.

Keywords. DEET, *Agam*OBP1, repellency, anopheles, malaria.

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Damage to DNA/RNA nucleobases by UV radiation and reactive oxygen species. I. Dissociation mechanisms caused by low energy electrons (0-3 eV)

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Abstract. The indirect damage of UV radiation to the genetic material is defined as the harmful effects that secondary species, generated after the exposure to UV radiation, can do to the DNA macromolecules. A wide variety of reactive oxygen species (ROS), such as ·OH, ·OOH, etc., as well as secondary ballistic electrons, are formed after the irradiation of biological systems [1]. Those electrons have attracted the attention of the scientific community since the discovery that, even with low kinetic energies (0-3 eV), they are able to break the DNA/RNA strands [2]. When the electron is attached to the nucleobase, a transient anion is formed which loses almost exclusively one hydrogen atom from the N–H positions [3]. Such reactions are known as dissociative electron attachment (DEA) processes. In order to determine the mechanism for these dissociative reactions in the four DNA nucleobases and to interpret the DEA spectra recorded in the experiments [4], minimum energy path (MEP) and linear interpolation of internal coordinates (LIIC) computations along the N–H fragmentation channels have been systematically performed with the multiconfigurational CASPT2//CASSCF methodology. Four theoretical magnitudes have been determined: a) the vertical electron affinities (VEA) of the low-lying anion states of the systems, b) the energy thresholds of the dehydrogenation channels, c) the potential energy surfaces (PECs) along the N–H coordinates and d) the energy thresholds for the population of the π_2^- states. The findings allow us to determine the relevance of two types of anions [dipole-bound (DB) and valence-bound (VB)] in the DEA mechanisms; the areas of the spectra related to each N–H bond breaking; and the participation of the ground and excited states of the anion in the dissociation processes.

Keywords. DNA/RNA damage, CASPT2//CASSCF, ballistic electrons.

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The mechanism of menshutkin reaction in gas and solvent phases from the perspective of the reaction electronic flux

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Abstract. The mechanism of Menshutkin reaction [1, 2], NH_3 + CH_3Cl = $[CH_3–NH_3]^+$ + Cl^- has been thoroughly studied in both gas and solvent (H_2O and cyclohexane) phase. It has been found that solvents favor the reaction, both thermodynamically and kinetically. The electronic activity that drives the mechanism of the reaction was identified, fully characterized and associated to specific chemical events, bond forming/breaking processes, by means of the reaction electronic flux [3, 4]. This led to a complete picture of the reaction mechanism that was independently confirmed by natural bond order analysis and the dual descriptor [5] for chemical reactivity and selectivity along the reaction path.

Keywords. Menshutkin reaction, density functional theory, reaction electronic flux.

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A single-wall ZnO nanotube molecular modeling of β-Carotene encapsulation

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Abstract. It is well known that single-wall carbon nanotubes (SWCNTs) have been considered as attractive nanoscale electronic components and the encapsulation of β-carotene molecules into carbon nanotubes has been revealed as an elegant strategy of nanotube functionalization [1, 2]. In this work, we investigate the encapsulation process in ZnO nanotube based on molecular dynamics simulations and tight-binding density functional-based. The results revealed significant changes in the electronic structure and density of states, geometrical deformations during the process of encapsulation, and charge transfer between β-carotene and ZnO nanotube. Finally, in comparison with the previous results for SWCNT [3] we have confirmed some expected predictions.

Keywords. β-carotene molecule, molecular dynamics, tight-binding density functional, electronic structure, ZnO nanotubes.

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Theoretical study of the formation of acetyl intermediates over a cluster model of ZSM-5 zeolite

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Abstract. The adsorption on Brønsted acid sites of typical acylating agents with formula CH_3CO–G (G = –OH for acetic acid, $–OCOCH_3$ for acetic anhydride, –Cl for acetyl chloride and $–OCHCH_2$ for vinyl chloride), has been theoretical studied by applying QM calculations at DFT level on a 3T-cluster model of ZSM-5, one of the most important zeolite with many important uses in heterogeneous catalysis. We investigated how the adsorption energies and the energetics of the acyl intermediate formation from different acylating agents vary in the 3T model. The geometries of the reactants, products, 3T-cluster, complexes and transition states have been optimized by using the B3LYP/6–311+G(d) level. The stationary points have been characterized by the vibrational frequency analysis. All the stationary points have been positively identified for minimum (number of imaginary frequencies, NIMAG=0) and transition states (NIMAG=1). Intrinsic reaction coordinates (IRC) were reconstructed by following the steepest descent path toward reactants at one side and products at the other side, starting form reoptimized transition structures at the AM1 level. The results indicate that the adsorption follows a concerted mechanism where the OH of the zeolite protonates the O–G group of the acylating agent. Simultaneously, the carboxylic Carbon interacts covalently with the Oxygen atom of the same OH group from the zeolite. Adsorption energies of the substrates were calculated by taking the difference in energy between the zeolite-substrate complex, the isolated zeolite and the isolated substrate. The calculated activation energies for the formation of the acylium-ion-like acetyl-zeolite intermediate of acetic acid, acetic anhydride, acetyl chloride and vinyl acetate were 57.5, 41.0, 36.9 and 41.5 kcal/mol, respectively. The acetyl-zeolite intermediate is likely the most important in acylation reactions carried out over zeolite catalysts, these results are in agreement with those informed in previous reports [1]. Similarly, the acylium-ion-like acetyl-zeolite intermediate that these molecules generate is completely analogous to the carbenium-ion-like alkoxide intermediate found by dehydration of alcohols or protonation of small olefins over Brønsted acid sites [2].

Keywords. Acylation, zeolite, heterogeneous catalysis, 3T-cluster.

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Computational and experimental studies on β-Sheet breakers targeting Aβ_{1-40} fibrils

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Abstract. We present and compare with experiments the results of extensive molecular dynamics simulations of model systems comprising an Aβ_{1-40} peptide in water in interaction with short peptides (β-sheet breakers) mimicking the 17-21 region of the Aβ_{1-40} sequence. Various systems differing in the customized β-sheet breaker structure have been studied [1]. Specifically we have considered three kinds of β-sheet breakers, namely Ac-LPFFD-NH_2 and two variants thereof, one obtained by substituting the acetyl group with the sulfonic amino acid taurine (Tau-LPFFD-NH_2) and a second novel one in which the aspartic acid is substituted by an asparagine (Ac-LPFFN-NH_2). Thioflavin T fluorescence, circular dichroism, and mass spectrometry experiments [2] have been performed indicating that β-sheet breakers are able to inhibit in vitro fibril formation and prevent the β-sheet folding of portions of the Aβ_{1-40} peptide. We show that molecular dynamics simulations and far UV circular dichroism provide consistent evidence that the new Ac-LPFFN-NH_2 β-sheet breaker is more effective than the other two in stabilizing the native β-helix structure of Aβ_{1-40}. In agreement with these results thioflavin T fluorescence experiments confirm its higher efficiency in inhibiting Aβ_{1-40} aggregation. Furthermore, mass spectrometry data and molecular dynamics simulations consistently identified the 17-21 Aβ_{1-40} portion as the location of the interaction region between peptide and the Ac-LPFFN-NH2 β sheet breaker.

Keywords. Neurodegenerative diseases, molecular dynamics simulations, thioflavin T fluorescence, circular dichroism, and mass spectrometry experiments.

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A multiconfigurational approach for inner-shell states of liquid water

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Abstract. Electronic transitions concerning inner-shell electrons represent an important type of microscopic process and are at the heart of important spectroscopic techniques used to probe the electronic structure of gases, liquids and solids. Particularly related to the liquid phase, the development of photoemission methods based in liquid micro jets in vacuum studies have expanded the understanding of the behavior of compounds, especially in aqueous phase [1]. In the present study, we will try to rationalize the main features of the spectrum of liquid water in the O 1s edge. When referred to the corresponding gas phase spectrum, the liquid water core-hole states are shifted to higher energies when the final state is discrete (pre-ionization-edge) and to lower energy when the final state is in the continuum (post-ionization-edge). Transition energies for the first three excited states and the first ionization potential in the oxygen 1s edge were first calculated for an isolated water molecule and then to the liquid model. The liquid phase was approximated by five-molecule cluster. Although simple, this approach has proved to be quite suitable to describe the main features of the spectrum summarized above. Reasons to that will be discussed. Geometry optimization at DFT/CAM-B3LYP and PCM model, done using Gaussian 09, gives the cluster structure. All excited states calculations were done by using MOLPRO package, with aug-cc-pCVTZ basis set. Results show that a single geometry approach to the structure of liquid water is insufficient to describe all features of the experimental spectra. We consider interactions among the excited molecule and solvation molecules for several values of intramolecular distances and angles, by fixed scan calculations.

Keywords. Inner-shell states, theoretical spectroscopy, liquid phase.

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Hypertension therapy coming from computational enzymology

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Abstract. Hypertension is a major risk factor in cardiovascular and kidney diseases. Currently, the development of novel therapeutic approaches has targeted the renin-angiotensin-aldosterone system (RAAS) that is crucial to reduce the healthcare impact of these illnesses [1]. An overview of computational approaches will be presented for two essential enzymes of the RAAS [2-4]. We will focus in enzymatic catalysis and drug discovery studies. The reaction mechanisms of renin and angiotensin-converting enzyme (ACE) were assessed with atomistic detail to identify efficient ways of inhibiting their activities and subsequently design Transition-State (TS) analogue molecules with potential clinical use. The computational hybrid ONIOM method (DFT:AMBER calculations) was used, and the whole enzymatic systems were subdivided in the two regions, QM and MM [2]. Furthermore, Molecular Dynamics simulations and mutagenesis studies were performed to characterize the binding mode of the substrate and well-known inhibitors of renin [3-4]. Our calculations have identified some flexible regions and specific residues that are crucial to an efficient renin activity. Virtual screening studies using databases of natural compounds are currently under assessment in order to identify new lead compounds that efficiently inhibit both renin and ACE targets. Altogether, our results are preeminent to future development of a new class of anti-hypertensive drugs.

Keywords. Hypertension, drug discovery, QM/MM, DFT, molecular dynamics simulations, molecular docking, CompASM.

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Probing the ground and excited states of the HIO_2 isomers

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Abstract. HXO_2 (X = Cl, Br, and I) species can have fundamental importance in ozone depletion [1]. While the chlorine containing compounds play a well-known role in the referred process, the analogous bromine and iodine compounds may (most likely) also play critical roles. The reason is related to the potential for ozone depletion which is 40 and 100 times larger than that of chlorine for bromine and iodine, respectively [2]. Although the chlorine and bromine containing compounds have received considerable attention in both theoretical and experimental studies [3-5], to our knowledge, there is only one incomplete theoretical [6] and no one experimental study on the iodine containing ones. In order to provide more information on this species we performed the present work. In this work we present a computational study on the ground and excited states of the HIO_2 isomers. Structures, relative energetics, and vibrational frequencies beyond the harmonic limit of HOOI, HOIO, and HIOO were obtained at the CCSD(T)/aug-cc-pVTZ level of theory. Vertical excitation energies were determined at the EOM-CCSD approach. All the computations were performed using the CFOUR [7] package.

Keywords. Electronic structure, HIO_2, CCSD(T), EOM-CCSD.

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Rh_6, Rh_6^+ and Rh_6^- high reactivity to N_2O dissociation

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Abstract. Nitrogen oxides (NO_x) are a very important and interesting family of chemical air contaminants compounds. These oxides are partially reduced to a mixture of nitrogen (N_2) and nitrous oxide (N_2O). It is necessary to determine the complete reduction conditions because the nitrous oxide is an important factor in ozone (O_3) biosphere production and simultaneously, the main ozone layer destroyer in the stratosphere [1]. The N_2O dissociation catalysed by Rh_6^0 and $Rh_6^\pm$ clusters was theoretically studied using the density functional theory [2], with PBE/ZORA method to consider scalar relativistic corrections [3]. The ground state geometries of Rh_6^0 and $Rh_6^\pm$ clusters obtained were octahedral. A septuplet was the Rh_6^0 spin multiplicity of the ground state. The ion ground states are different. Rh_6^- with different spin multiplicities was the most active particle to obtain N_2O dissociation. On the contrary, Rh_6^+ presented a lesser dissociation capacity, whereas Rh_6, Rh_6^+ and Rh_6^- spontaneously activated the N_2–O and the reaction was highly exothermic. The N_2–O bond was only broken in parallel approaches to an Rh–Rh bond or to an Rh_3 face. Approaching N_2O to an Rh_6 vertex only results in adsorptions. In conclusion, the principal factors to obtain the N–O rupture are approaches between the reactors and the spin multiplicity.

Keywords. N_2O dissociation, transition metal particles, excited states, PBE/ZORA method.

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B_{18}^{2-}: The non-planar member of the Wankel Motor Family

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Abstract. In 2010, Boldyrev *et. al* published the experimental and theoretical work about the B_{19}^- [1]. This mono-anionic boron cluster is a planar double-concentric ring, with one boron atom enclosed by a pentagonal core that is surrounded itself by thirteen atoms placed in the outer ring. Each ring satisfied the Hückel rule of (4n+2) π electrons for aromatic systems with two and ten electrons. In the same year, some of us discovered the negligible rotational barriers of B_{19}^-, allowing a free movement of the internal pentagon respect to the external ring.[2] This free-rotational behavior has been found in other planar boron clusters, as such B_{13}^+ and B_{20}^- [3]. In the current work we performance the search of the global minimum of other possible boron clusters. Particularly, B_{18}^{2-} more stable isomer is a bowl-shaped structure with a central six boron pentagon core surrounded by a twelve-membered outer ring. The non-planar symmetry presents a 0.1 kcal mol^{-1} rotational barrier, which it is a hint of a fluxional behavior. BOMD calculations confirm the Wankel Motor character of this system. The rotation of the B_6 unit is found accompanied by the simultaneous bond braking and bond making between the six-boron pentagon unit with the twelve-membered external ring.

Keywords. Boron cluster, global minimum, internal rotation, Wankel motor.

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Mechanisms of retro-Diels Alder reaction of bicyclic organic compounds in the gas phase: Density functional Theory calculations

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Abstract. The mechanisms of the gas-phase thermal decomposition of bicyclo[2.2.1]heptadiene (**BCH**) and 3,7,7-trimethylbicyclo[2.2.1]hept-2-ene (**TMBCH**) were examined by Density Functional Theory (DFT) calculations with the hybrid functionals: B3LYP, MPW1PW91, and PBEPBE by using GAUSSIAN 09 package [1]. Reasonable agreement was found between theoretical and experimental values [2, 3] with the B3LYP. For bicyclo[2.2.1]heptadiene (**BCH**) three molecular concerted pathways are proposed. The retro Diels-Alder (retro-**DA**) pathway yields cyclopentadiene and acetylene through a nearly synchronous transition state in nature (Sy=0.97). The others two reaction channels are stepwise with a common step; that is, the formation of the intermediate bicyclo[4.1.0] heptadiene dominated by the breaking of the C–C bond conducing to the methylene migration by an early transition state in the reaction coordinate and the reaction is less synchronous (Sy=0.91) than the retro- **DA**. The rearrangements of the latter intermediate to produce toluene were also studied. The retro-**DA** elimination of 3,7,7-trimethylbicyclo[2.2.1]hept-2-ene (**TMBCH**) gives 1,5,5-trimethylcyclopenta-1,3-diene across a less synchronous process, compared to BCH (Sy=0.77), due to the electronic effects of the methyl substituents. This product is unstable and undergoes several methyl migrations to give a more stable isomer 1,2,3-trimethylcyclopenta-1,3-diene.

Keywords. Gas phase elimination, Gaussian, density functional theory, bicyclic organic compounds.

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Predicting the electronic structure and magnetic properties of UO^{2+}, $[UO_2(CO)_5]^+$ and $[UO_2(Ar)_5]^+$ using wavefunction based methods

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Abstract. The electronic structure and magnetic properties of UO_2^+, and two complexes, $[UO_2(CO)_5]^+$ and $[UO_2(Ar)_5]^+$ in D_5h symmetry are studied with a combination of relativistic theoretical methods: *Ab-initio* wavefunction calculations, density functional theory (DFT), and crystal–field (CF) models with parameters extracted from the *ab-initio* calculations. The model Hamiltonian techniques are employed to describe theoretically the state interaction and the competition between crystal- feld (CF) and spin-orbit coupling (SO), this is important besides for a correct description of the sign of the g-factors using also a symmetry criteria.

Keywords. Actinide, magnetic properties.

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Steered molecular dynamics and umbrella sampling approaches to the binding mechanism of DFG-out p38α kinase inhibitors

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Abstract. The inhibition of protein kinases is one major goal in pharmaceutical research [1]. Most of currently known kinase inhibitors (Type I inhibitors) target the ATP binding pocket, which is highly conserved among the majority of kinases, thus making these inhibitors not very selective [2]. Type II inhibitors however target a less conserved pocket that becomes available due to the rotation of a highly conserved DFG motif. The inhibitor blocks this motif in the so-called DFG-out position, in which the Phe side chain occupies the ATP binding site, thus blocking it [3]. As this binding site is not as conserved as is the ATP one, these new inhibitors represent new opportunities for the selective inhibition of protein kinases, but in order to guarantee their selectivity and effectiveness, not only the bound state interactions, but also the binding mechanism must be known. This work focuses on p38α MAP kinase and some Type II inhibitors for which their binding modes are well characterized [4-6]. We have used Steered Molecular Dynamics and Umbrella Sampling approaches to gain insight into their binding mechanism. This work will improve the understanding of allosteric inhibition of p38α protein kinase and will allow a further rational design of new potent inhibitors of this protein.

Keywords. Steered molecular dynamics, umbrella sampling, DFG-out inhibitors, kinase inhibitors.

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Resorcenarene cavitands as gas storage devices: A theoretical computational study

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Abstract. Like calyxarenes, resorcenarenes are a group of molecules that have attracted considerable attention in the past few decades because of their cup-like structure, which makes them suitable to act as hosts for a variety of small molecules [1]. Regarding resorcen[4]arenes, the OH functionalities in the upper rim have shown to be quite important when these molecules self-assemble in solution, for they generate a number of H-bonds with solvents and among neighboring resorcenarene molecules[2]. These OH groups have also been essential in trapping organic molecules and metal ions[1-3], which has prompted some investigators to propose resorcenarene and similar derivatives as molecular devices for environmental remediation [3]. Unlike resorcen[4]arenes, resorcenarene cavitands do not have OH groups in their upper rim for the latter are used as bridges between adjacent resorcinol groups by the introduction of a methylene moiety or larger aromatic groups [4, 5]. These creates a cup-like structure with limited fluxionality and without OH groups, which may prevent small molecules from entering the cavity. Thus, we have studied the thermodynamic properties of C-Methyl-resocen[4]arene cavitands as host molecules for molecular hydrogen, methane, carbon monoxide and molecular nitrogen. It was determined that all of these guest molecules form stable complexes deep inside the cavitand bowl, and the binding energies increase in the order $H_2 < CO < N_2 < CH_4$. Furthermore, we found that more than one of these guests can be accommodated inside and about the upper rim of the cavitand. To our surprise, CO_2 (i.e., a typical probe molecule) was not a suitable guest molecule for, and it was pushed out of the cavitant well regardless of its alignment or position. It was also determined that the proximity of opposite phenyl rings is paramount to give better binging energies. This implies that the aromatic π systems and the electrostatic potential that forms at the bottom of the well are important in determining which molecules are fitting guests [7]. These findings are important because they corroborate[6] and will encourage experimental investigations to test resorcenarene cavitands as gas storage molecular devices and also because they suggest that cavitands can be molecular platforms for catalytic reactions.

Keywords. Resorcen[4]arenes, guest-host, H-bond, adsorption.

Acknowledgements. This study was carried out with the computer resources of USFQ's High Performance Computing System (HPC-USFQ).

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Polar molecules engaged in pendular states captured by molecular beam scattering experiments

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Abstract. We demonstrate that when two polar molecules as those of water, ammonia and hydrogen sulfide encounter each other at a distance much larger than their dimensions they engage a synchronous motion that promotes the transformation of free rotations into coupled pendular states. This discovery has been prompted by high resolution molecular beam scattering experiments presented here, addressed to the measure of the total integral cross section changes as a consequence of molecular rotation couplings. The experimental observations and the theoretical treatment developed to shed light on the details of the phenomenon suggest that the interplay among free rotations and pendular states depends on the relative velocity, on the rotational levels and on the dipole moments of the interacting molecules. The features of this intriguing phenomenon may be crucial for the interpretation and the control of basic chemical and biological processes.

Keywords. Polar molecules, long-range interaction, pendular states.

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Assessing the importance of electron correlation: Study of trimethylamine – hydrogen halide pairs using Hartree-Fock and post Hartree-Fock methods

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Abstract. Despite accounting for less than one percent of the total energy of a given molecular system, electron correlation energy is crucial for the accurate evaluation of molecular energies and the description of bond breaking and bond formation [1]. In this work, the $(CH_3)_3N$–HX dimers (X = F, Cl, Br) have been theoretically studied with Hartree-Fock Self Consistent Field (SCF) and Second-Order Möller-Plesset Theory (MP2) [2, 3]. The potential energy surfaces along the proton-transfer pathway of the systems were calculated at both SCF/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory to illustrate the importance of incorporating electron correlation in their description. From the results it is observed that SCF calculations, which do not include electron correlation, predict that all three dimers under study behave as hydrogen-bonded complexes. On the other hand, the MP2 calculations which include electron correlation, predict that the $(CH_3)_3N$–HF system is a hydrogen-bonded complex but the other two dimers, $(CH_3)_3N$–HCl and $(CH_3)_3N$–HBr, show a significant extent of ion pair character. Therefore, when electron correlation is taken into account, it is found that an increasing extent of proton transfer is observed along the series of dimers under study.

Keywords. Electron correlation, Möller-Plesset theory, ion pairs.

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Computational modelling of copper complexes relevant to alzheimer disease

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Abstract. Metal cations, such as Cu^{2+}, have been shown to induce amyloid aggregation and formation of reactive oxygen species. Elucidation of the structural features of $Cu^{2+}-A\beta$ is thus, essential to understand their role in the aggregation of $A\beta$, formation of reactive oxygen species and to rationally design new chelators with potential therapeutic applications. Present contribution reviews our computational studies in this field. First, computational strategies used to determine three dimensional structures for $Cu^{2+}-A\beta$ and the redox properties of these complexes will be discussed. Second, we will summarize our recent studies on Cu^{2+} chelators and finally our recent advances on markers to identify $A\beta$(1-40) fibrils [1-4].

Keywords. Alzheimer disease, β-amyloid, metal chelation, Standard Reduction Potential, DFT, homology modelling, virtual screening.

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Molecular engineering methods applied to the efficient development of catalysts

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Abstract. Ecuador is a country with important oil reserves; thus, its economy is mainly based on oil production, exportation, and internal use. Although significant experience has been gained in Ecuador during the last 40 years, the oil derivatives production are neither efficient nor optimal. Indeed, only the imports of high quality gasoline allows the ecuadorian government to supply the national demand of fossil fuels. One of the main problems of oil refination in Ecuador relies in the use of comercial catalysts that are not necessarily adequate for the composition of ecuadorian oil, which possesses important concentrations of heavy compounds (*i.e.,* asphalthenes) and sulfur. In the present work, a methodology based on DFT approaches and thermodynamical analysis is proposed for the computational design of catalysts with potential for asphaltene oxidation. This theoretical study is focused on magnetite (Fe_3O_4) as material for the catalysts design, because of the ability of this system to oxidize asphaltenes [1]. As the first stage of the study, models of the Fe_3O_4 [111] surface with different terminations are optimized by employing the PBE functional [2] as implemented in the VASP code [3]. Upon obtaining the equilibrium geometry of one to the considered models, a frequency calculation is performed to determine whether the computed structure represents a global minimum or a local minimum of the potential energy surface. The grand canonical potential [4] of each optimized model is then obtained. Typical temperature and pressure ranges of operation for asphaltene oxidation are considered. As a final step, the most efficient catalyst is suggested defining the most stable model according with the comparison of the computed thermodynamic functions.

Keywords. Ecuadorian oil, catalysts, Fe_3O_4, molecular engineering.

Acknowledgements. This work has been performed with the computational resources of USFQ's High Performance Computing System (HPC-USFQ).

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2014 will be remembered as a significant year for the Community of Theoretical Chemists of Latin Expression, because the QUITEL congress is held in Ecuador for the first time. In order to celebrate the incorporation of Ecuador to the QUITEL hystory, the ecuadorian Local Organizing Committee has chosen San Cristobal Island in the Galapagos Archipelago to host the XL Edition of the Congress. Universidad San Francisco de Quito