Applications **P281**

Theory of Chemical Bonds in Metalloenzymes IV: Hybrid-DFT study of Rieske-type [2Fe2S] clusters

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The Rieske-type [2Fe2S] cores of electron-transfer (ET) proteins in mitochondrial respiratory chain have unusual properties. Spectroscopy, EPR, Mössbauer, and X-ray crystallography had been extensively studied to elucidate their characteristic magnetic, electronic, and structural properties in mixed-valence states.

In this study, the inherent molecular structures and the electronic structures in Rieske-type [2Fe2S] clusters are investigated by using broken-symmetry hybrid density-functional theory (HDFT). The molecular structures of Rieske-type cluster (Fig) in their oxidation and reduced states are determined by BS-HDFT, and vibrational analyses at the optimized geometries are also carried out. Their characteristic Raman and IR spectrums are assigned and the Raman spectra changes in protonations are also discussed. The magnetic properties including their spin coupling J and valence delocalization B between Fe spin sites are also discussed by applying appropriate spin Hamiltonians. Their chemical bond natures are characterized by chemical indices from natural orbital analysis.

Figure Molecular structure of Rieske-type [2Fe2S] clusters ([Fe_2S_2](SCH_3)$_2$$Imi_2$).

Applications **P282**

Weak Hydrogen Bonding: Dimer of 2-pyridone and n-fluorobenzene n=1..3

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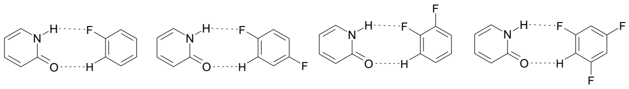
Recent research in modified DNA has shown that hydrophobic effects can be exploited to induce complementary nucleobase pairs involving phenyl and pentafluorophenyl moieties.[1] These synthetic basepairs involve C-F$\cdots$H hydrogen bonds. Here, we investigate analogous dimer complexes in supersonic jets that involve C-H$\cdots$O and C-F$\cdots$H hydrogen bond motifs.



The complexes of 2-pyridone (2PY) with 1-fluorobenzene, 1,2- and 1,4-difluorobenzene and 1,3,5-trifluorobenzene (nFB) were investigated by fluorescence and mass-selected $S_1 \leftarrow S_0$ vibronic spectroscopies. DFT studies (PW91 and B3LYP with the basis set 6-311++G(d,p)) play a key role to understand structural and vibrational behavior of these dimers in the ground state S_0.[2] With increasing fluoro substitution from fluorobenze to hexafluorobenzene the total binding energy of the dimers also increases from 6.1 to 6.7 kcal/mol. This are very weakly bound clusters, compared to (2PY)$_2$, which has as binding energy of 22 kcal/mol. The C-H$\cdots$O bond is five times stronger than the C-F$\cdots$H hydrogen bond. Assignment of the intermoleculare vibrations were based on DFT calculations. These are in very good agreement with the experimental data.

[1] Gerald Mathis and Jürg Hunziker , *Angew. Chem. Int. Ed.*, **2002**, *41*, 17, 3203
[2] Andreas Müller, Martin Losada, and Samuel Leutwyler, *J. Phys. Chem. A.*, **2004**, *108*, 157.

Applications **P283**

The self electron transfer rate of large TPA based compounds by means of DFT calculations and electrochemistry

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Molecular modelling can help to design molecules with suitable properties to fabricate organic light emitting diodes (OLEDs), once the correlation of the molecular structures with the ionisation potential (IP), the electron affinity, and the self electron transfer rate is established.

The electron-transfer mechanism of triarylamine (TPA) derivatives, used as hole transporting materials, is related to their reorganisation energies (λ) associated with this process[1]. The relaxation processes taking place in TPA and TPD model systems have already been investigated by means of density functional theory[2,3].

We extend the investigation of these compounds considering those having up to four TPA units combining the information obtained by B3LYP/6-31G* method of Gaussian 03 with those obtained by cyclic voltammetry. Measured ΔE_p are correlated with the calculated λs, elucidating the trend followed by the self electron transfer rate (k_{ET}) of these compounds. Besides a direct dependency upon the dimension of the cationic fragment contributing to the hole stabilisation, the λs are tuned by the symmetry local to the TPA units, as evidenced by the structural relaxation of the cations. TAPC turns out to be the most effective compound with respect to the self electron transfer process, while MDTAB shows the interesting combination of low IP and high k_{ET}. This can make these compounds interesting for practical applications in OLED devices, due to the direct correlation of the IP and k_{ET} with the hole transfer efficiency to the anode, along with the hole mobility.

[1] C. Lambert et al., *N*at. Mater., **2**002, *1*, 69.
[2] K. Sakanoue et al., *J.* Phys. Chem. A, **1**999, *1*03, 5551.
[3] M. Malagoli et al., *C*hem. Phys. Lett., **2**000, *3*27, 13.

Applications **P284**

Determination of Topology of Mixed Ammonia-Water Solvent Wire Clusters by DFT and TD-DFT Calculations

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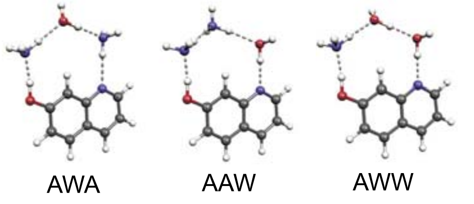
Mass-selected $S_1 \leftarrow S_0$ two-color resonant two-photon ionization spectra were measured for the 7-hydroxyquinoline·$(NH_3)_n$·$(H_2O)_m$, $n + m = 3$ series. 18 possible minimum structures of these mixed clusters were obtained at the B3LYP/6-311++G(d,p) level. The most stable structures correspond to the solvent wires bridging the two functional groups of the aromatic chromophore with three molecules.



The assignment of the three isomers observed in the 2C-R2PI spectra was based on both calculated binding energies and time-dependent DFT calculations of the electronic origin. The total binding energy increases with substitution of ammonia by water molecules, consistent with the stabilites of 7HQ·$(NH_3)_3$ and 7HQ·$(H_2O)_3$.[1,2] Due to the high acceptor characteristic of ammonia, the O-H···N hydrogen bond is most stable intermolecular bond of the cluster. Consequently, the common feature of mixed ammonia-water solvent wire clusters is the hydrogen bond from the OH group to the ammonia as first wire molecule.

[1] C. Tanner, C. Manca, S. Leutwyler, *Science*, **2003**, *302*, 1736.
[2] A. Bach, S. Coussan, A. Müller, S. Leutwyler, *J. Chem. Phys*, **2000**, *113*, 9032.

Applications **P285**

Density functional calculations of the optical properties of rare earth compounds

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The optical properties of rare earth compounds are of fundamental as well as practical importance. For example, alkali-doped cerium sesquisulfides, γ-$Ce_{2-x}A_{3x}S_3$ (A = alkali metal), are inorganic pigments of red to orange hue and are currently at the stage of industrial production. Earlier band structure calculations within the local density approximation (LDA) provided qualitative insight into the electronic structure of these compounds and pointed to the importance of f-electrons in the optical transitions. However, these earlier calculations were unable to provide quantitative predictions of optical gaps[1,2]. The present work aims at a clearer understanding of the absorption mechanism and at quantitative predictions of the absorption energies in this class of compounds. As a first step, density functional (DF) methods extended with a Hubbard-U term are performed. As prototypical compounds we have chosen pure γ-Ce_2S_3 and the alkali-doped compounds $Na_{0.5}Ce_{2.5}S_4$. The results confirm the involvement of f-electrons in the optical transitions and offer better quantitative predictions.

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[2] Zhukov, et al., *J. Solid State Chem.* **1997**, *128*, 197.

Applications **P286**

Linear and non-linear optical properties of ruthenium-polypyridyl complexes by Time-Dependent DFT calculations

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The optical properties of Ru-polypyridyl complexes have attracted considerable interest due to their potential applications in the field of solar cells,[1] photoactive polymers,[2] DNA-intercalating agents [3] and materials for non-linear optics.[4] The research in these fields has been fostered by the recently developed time-dependent extension of density functional theory (TDDFT), which allows the accurate calculation of excited states properties (absorption energies, oscillator strengths, dipole moments and solvatochromic-shifts) and of static and frequency dependent hyperpolarizabilities of complex inorganic molecular systems of nanometric dimensions.[2] Examples of the interpretative and predictive power of TDDFT calculations applied to the investigation of the linear and non-linear optical properties of several Ru-polypyridyl complexes will be presented.

[1] S. Fantacci, F. De Angelis, A. Selloni *J. Am. Chem. Soc.* **2003**; 125, 4381; b) F. De Angelis, S. Fantacci, A. Selloni *Chem.Phys. Lett.* **2004**, *389*, 204.
[2] S. Fantacci, F. De Angelis, J. Wang, S. Bernhard, A. Selloni *J. Am. Chem. Soc.* **2004**, 126, 9715.
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Applications **P287**

Searching the Gibbs free energy surface for the P-IV phase by the first-principles metadynamics simulation

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To explore global structure of the free energy surface (FES) is challenging but an important problem for the computational materials science. When local mimima separated by large barriers are explored, metadynamics [1] is the effective method. Since the well of the FES is gradually filled with the artifitial potential energy, and then the neighboring local minimum is automatically visited, we can correctly explore metastable states in a short computational time.

Our aim is to explore the structure of the unknown high pressure phase of phosphorus (the P-IV phase) which was observed by Akahama *et al.* [2] by the metadynamics simulation combined with the first-principles calculation. Its structure has been investigated by both the Rietveld analysis and a theoretical calculation but unknown due to the low symmetrical structure. Thus, in order to explore its structure by the different approach from the early studies, we applied the first-principles metadynamics simulation using a system having 8 atoms in a simulation cell.

As a result, We succeeded in estimating a candidate for the P-IV phase. It has 98° about one internal angle of the simulation cell, and the atoms in the simulation cell are located in a zigzag. Comparing the structure of the P-IV phase and our obtained structure with respect to the x-ray diffraction pattern, they showed the good agreement in spite of the small system size. We consider the dependence of this structure on the size of the simulation cell.

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[2] Y. Akahama *et al.*, *Phys. Rev. B*, **1999**, *59*, 8520.

Applications **P288**

First-principles calculation of the ground-state and excited-state absorption spectra of ruby and alexandrite considering lattice relaxation

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The *d-d* transitions of transition-metal (TM) ions in ionic crystals have been utilized as solid state lasers such as ruby (chromium doped alumina) and alexandrite (chromium doped chrysoberyl). In order to establish a nonempirical computational approach for the optical spectra for impurity transition-metal ions or also rare-earth ions, we have developed a first-principles configuration-interaction (CI) calculation program, in which many-electron wave functions are obtained as linear combination of Slater determinants by direct diagonalization of the many-electron Hamiltonian. The transition probabilities between the eigenstates are calculated directly using the explicit many-electron wave functions[1].

For the analysis of optical spectra of impurity ions, it is also important to consider the effects of structural relaxation around them. Therefore, in this work, we have investigated the effects of structural relaxation around the chromium ions on the absorption spectra of ruby and alexandrite by combining the structural optimization using CASTEP code and first-principles CI calculations using model clusters composed of 63 atoms (ruby) or 60 atoms (alexandrite). The ground-state absorption (GSA) spectra and excited-state absorption (ESA) spectra for ruby and alexandrite have been calculated by this approach and the theoretical spectra quantitatively reproduced the peak positions, the peak intensities and their polarization dependence in the experimental spectra.

[1] K. Ogasawara *et al.*, Phys. Rev B **61**, 143 (2000).

Applications **P289**

A Hyrid-density-functional Study of Charge-transfer and Magnetic Properties of BDTA·Ni(mnt)$_2$

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BDTA·Ni(mnt)$_2$ (BDTA: benzo-1,3,2-diathizolyl, mnt: maleonitriledithiolate) is one of the donor-acctepter (DA) complex dicovered recently by Awaga and his co-workers. This complex has the intermolecular charge-transfer (CT) between BDTA and Ni(mnt)$_2$. Moreover, it forms two-dimentional S-S and S-N contacts network along the a- and b-axes, showing interesting magnetic properties.

In this work, CT ratio and magnetic interactions between the DA-pairs along axes were evaluated by the spin-polarized hybrid DFT method for DA-pairs extracted from the X-ray crystallographic strucuture. The basis sets used were 6-31G* for C, N, and H atoms, 6-31+G* for S, and MIDI+P for Ni. The magnetic properity has been discussed in terms of effective exchange integrals (J) of the Heisenberg model.

First, CT ratio was calculated by UB3LYP to be 0.75 in two-dimentional structure on an avarage, which reproduced experimental result (0.6). Spin densities distributed between the molecules as 30 % for BDTA and 70 % for Ni(mnt)$_2$. Next, the intermolecular J was calculated to be –240 cm^{-1} for pairs along the b-axis; 5 cm^{-1} for ones along the a-axis. The quantum Monte Carlo method simulated magnetic susceptibility with the J-values for this complex, which will be shown in detail at the conference.

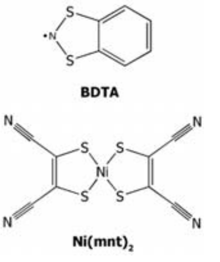

Figure Molecular structures

Applications **P291**

Nonlinear optical properties of azobenzene dyes by time-dependent density-functional theory

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Azobenzene dyes have attracted much interest in recent years due to their unusual optical and photochemical properties which make them interesting candidates for applications in fields such as high-density optical data storage or fast telecommunication technologies. By irradiation with visible or ultraviolet light, azobenzene dyes can be switched reversibly between two distinct states with largely different structural and optical properties. The light wavelength necessary for the switching process as well as other properties can be tuned to a considerable extent by rather simple modifications in the chemical structures of the dyes.

The effect of such changes on the linear an nonlinear optical properties of substituted azobenzene dyes is studied using time-dependent density-functional theory as implemented into the ADF program package. [1] Various exchange-correlation potentials are employed in combination with a kernel due to the adiabatic local density approximation. A focus of the contribution is on the identification of structure-property relationships that may allow for the prediction of new azobenzene and related dyes with improved properties.

[1] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comp. Chem.*, **2001**, *22*, 931.

Applications **P290**

Molecular Dynamics simulations of H$_2$O and NH$_3$ with Cu-FAU

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Transition metal ions exchanged in zeolites constitute a class of very efficient catalysts for the selective catalytic reduction (SCR) of NOx by NH$_3$ or hydrocarbons [1]. Among them, Cu-faujasite (Cu-FAU) is recently operating in industrial processes for stationary sources applications. Detailed knowledge of the dynamics of ligand interactions during the catalytic process is of particular interest. A Born Oppenheimer molecular dynamic approach of the reaction was chosen to study the interaction of water molecules and ammonia with Cu-FAU. The aim of this study is to investigate the behaviour of Cu(I) and Cu(II) in presence of these ligands, since the knowledge of the sitting and coordination of copper is of particular interest. Several model clusters were chosen to represent Cu in the supercage of the FAU. The results obtained using the deMon code will be presented. For instance,it will be shown that after a time of equilibration, Cu(I) remains always two-coordinated with one bond involving the zeolite and one bond involving a water molecule. In contrast, the coordination of Cu^{2+} is at least 3. In this case, the strong metal-zeolite interaction is not substantially modified by the addition of a few water molecules, although two of them enter into the Cu^{II} coordination shell.

[1] G. Delahay, D. Berthomieu, A. Goursot, B. Coq, in *Interfacial Applications in Environmental Engineering. Surfact. Sci. Series*, Vol.108, **2003**, 1.
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Applications **P292**

Combined experimental and theoretical studies of solid state proton migration.

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Hydrogen bonds are of great interest, due to their importance in structural, functional and dynamical properties of chemical systems, ranging from inorganic to biological chemistry [1]. The very strong hydrogen bonds are of current interest because they enable charge and energy to be transferred between molecules in the solid state.

Recent work has focused on urea-acid complexes, which contain a rich variety of short, strong hydrogen bonds in a relatively simple framework. It has been demonstrated that the combination of cutting edge computational techniques (MD/PW-DFT) with variable temperature neutron diffraction results was successful in showing the migration of the proton with increasing temperature and a plausible explanation for the effect has been presented [2].

A collaborative project with the aim of continuing this work has now begun. A series of hydrogen-bonded adducts have been prepared in a systematic manner, by substituting the hydrogen atoms on urea with methyl groups, raging from N-methyl urea to tetramethyl urea with various compositional mixtures, for experimental and theoretical investigation.

In particular, the effect of temperature on proton migration and disorder in these adducts are being explored to shed light on the factors that influence proton migration. In this poster presentation we will describe some of our most recent results.

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[2] Morrison, C. A., Siddick, M. M., Camp, P. J. and Wilson, C. C. *J. Am. Chem. Soc.*, **2005**, *127*, 4042

Applications **P293**

Anharmonic calculation of vibrational spectra in solution. Hybrid approach : *Ab initio* - DFT

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With the development of linear scaling procedure rooted in the framework of density functional theory (DFT), reliable computations of vibrational frequencies for medium-sized molecules in vacuum are becoming a routine [1].

Nevertheless, most of experimental data of this kind of molecules are recorded in solution which means that effects induced by the complex chemical environment such as the solvent, must be taken into account to further improve the results. To this end, explicit and implicit solvent models have been used to calculate the vibrational spectra of a test molecule : H_2CO in several solvent. This molecule and its surroundings have been chosen for the richness of available experimental informations.

While the work is in progress, the main results show that anharmonic CCSD(T)/cc-pVQZ computations with SCIPCM [2] model followed by a variational approach of the vibrational problem are in perfect agreement with experimental data and constitutes a reference approach.

As observed in gas phase, an alternative of this costly approach comes from the use of a hybrid potential (CCSD(T)/cc-pVQZ//B3LYP/6-31+G**)/SCIPCM were reliable results are obtained. Concerning the use of the cheap B3LYP/6-31+G** level of theory, a very good estimation of the shift on fundamental frequencies induced from solvent effects was observed.

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Applications **P294**

A DFT coordination chemistry study of the bonding in f-element complexes containing N-heterocyclic ligands

P. Maldivi[1], L. Petit[1,2], A. Pieyre[1], C. Adamo[2], C. Risch[1]

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A good knowledge of the electronic structure of molecular complexes containing f-elements is essential for the understanding of their chemical and physical properties, for instance in the area of the selective complexation of actinides and lanthanides, in relation with the nuclear waste disposal. The challenge is to design ligands able to give some selectivity for minor trivalent actinides americium and curium, compared to trivalent lanthanides, in solution.

We thus describe here a systematic theoretical study of the bonding between a series of polyazines and a f-element ion: lanthanides (III), U(III) and Am(III). This choice was made because many experimental studies have been published on these ligands or on ligands made up of these "building blocks". The study involves computed structural data, compared to experimental trends, and a detailed metal-N bond description. The whole study was performed by a quasi-relativistic one component method based on the use of the ZORA Hamiltonian [1], which as we have shown earlier, are able to reproduce bonding properties for these heavy elements [2, 3].

[1] ADF 2000. SCM, Vrije Universiteit. G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders, T. Ziegler. *J. Comp. Chem.* **2001**, *22*, 931-967.
[2] V. Vetere, P. Maldivi, C. Adamo. *J. Comp. Chem.* 24 **2003,** *24*, 850-58.
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Applications **P295**

The new class of silicon-carbonyl compounds: a DFT approach

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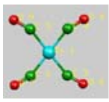
In view of its large applications in the chemical (silicones) and electronic (single crystalline silicon) industries, silicon has been the matter of extended experimental and theoretical investigations. In spite of that, many remarkable specific chemical behaviors have remained partially unexplained and are still matter of discussion. In last years we have been attracted by the chemical behavior of atomic-like silicon. Silicon may be produced in such a state by sputtering but also via its injection into SiO_2 during thermal oxidation. Our first investigation, dedicated to the interaction of atomic-like silicon with siloxanic network, has shown that silicon behaves as a weak bifunctional Lewis acid forming $((-O)_3Si)_2O \rightarrow Si \leftarrow O(Si(O-)_3)_2$ adducts [1,2].
Theoretical investigations by DFT are currently in progress to study which extent this property extends to other bases (H_2O, H_2O, NH_3, CO) (see Figure, the $Si(CO)_4$ molecule).



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Applications **P296**

A Density Fuctional Study on the Interaction of π-Conjugated Organic Molecules on the Silicon (100) Surface

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There is a rapidly growing interest in the functionalization of silicon surfaces with organic compounds in view of the development of new microelectronics devices. In particular, one of the most attractive target is the attachment of organic molecules containing π-conjugated electron systems, some of which are known to behave as semiconductors and may therefore function as active components in microelectronics devices. The successful realization of such devices requires the capability of analyze and control the geometrical and electronic properties at the organic-inorganic interfaces. It is especially critical to control how the interface formation affects the π conjugation within the molecule, in order to preserve the electronic properties of the organic material as semiconductors.

The 2×1 reconstructed Si(100) surface consists of rows of tilted silicon dimers with zwitterionic character, that provide an ordered and reactive template for surface chemistry. The zwitterionic character allows the attachment not only of molecules with unsaturated C-C bonds, but also with electrophilic and nucleophilic groups, such as alcohols and amines.

Taking into account the intrinsic limits and the gaps in the experimental characterization of the interface between organic molecules and silicon surfaces, theoretical investigations have been carried out by employing the Density Functional Theory to understand the mechanisms of the adsorption on the Si(100) surface of some promising organic molecules, as for instance polycyclic aromatic hydrocarbons.

Applications **P297**

Excitation energies of selected aromats in DFT, AOSOPPA and Coupled Cluster Theory

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The CC2 and CCSD total energies are both of second-order in the Møller-Plesset perpurbation theory (MP2). As is atomic orbital second-order polarization propergator approach AOSOPPA. Singlet excitation energies have been calculated using CC2, CCSD, AOSOPPA and are compared to the fast DFT and the noniterative triples model CCR(3). Calculations on Benzene, Napthalene, Anthracene, Phenanthrene, Azulene and Biphenylene have been performed.

Applications **P298**

Modelling of the Cation-Olefin Cyclizations in Solution by Density Functional Methods

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Cation-olefin cyclizations are very useful, albeit complex, carbon-carbon bond forming reactions. For such cyclizations a very high degree of stereocontrol is often achieved by cyclases in biogenesis of natural products. In the laboratory the cation-olefin cyclizations are accomplished by solvolysis of an appropriate substrate albeit with lesser stereocontrol. We here describe a modelling of cation-olefin reactions aimed at elucidating the solvolytic reaction mechanism in solution.

The electronic structures, energies, and equilibrium geometries of reaction intermediates involved in the cation-olefin cyclizations were studied by density functional theory methods. Several hybrid functional methods have been used together with moderate and large basis sets. The cyclization step was investigated by means of minimum energy reaction paths. The transition states were located and characterized, and subsequently the intrinsic reaction paths were computed. In order to achieve successfully the computational simulation of cation-olefin cyclizations in solvolytic conditions, it was necessary to improve the model by also taking into account the media effects. Based on these computations, the mechanisms and the pathways by which the reactive intermediates are formed and by which they rearrange on their potential energy surfaces will be presented. The results of several substitution patterns will be provided.

Applications **P299**

Computational Study of Protonated Cyclopropane Species and Related Carbocations in Solution Using the Explicit Solvent Model

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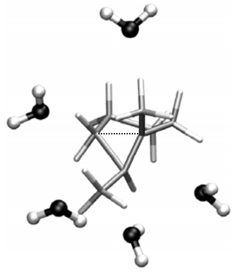
Computational studies *in vacuo* on potential energy surfaces relating to substituted cyclohexyl carbocations revealed the presence of several conformers where the cationic moiety adopts the form of a protonated cyclopropane.[1,2] These species are stabilized by the high degree of charge delocalization and in addition incorporate the pentavalent carbon.



To determine whether these carbocations are also stabilized in solution, we investigate in the present contribution the behavior of these species in the presence of explicit solvent molecules in order to study the media effects. In the cation-water supermolecules thus generated, the solvent molecules are hydrogen-bonded to the central cationic moiety of the cluster, thus mimicking the first solvation shell. This methodology was further improved by combining the fully optimized cation-water cluster geometry with the reaction field model (PCM method) where a continuous dielectric field was used to simulate the bulk of the solvent. Several density functional methods were used for these investigations and their results will be compared with the post-Hartree Fock computations. The structure, properties and relative stabilities of reaction intermediates that revealed extended charge delocalisations and sometimes-unusual bonding properties will also be discussed.

[1] J.K. Lee, K.N. Houk, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1003.
[2] C. Fouillet, J. Mareda, *J. Mol. Struct. Theochem*, **2002**, *589*, 7.

Applications **P300**

On the aromaticity of small boron and gold clusters

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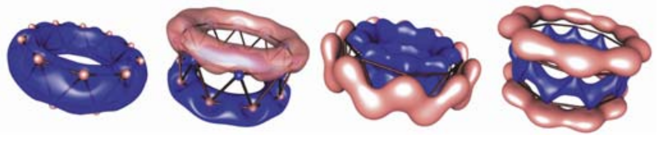
Small clusters of both boron and gold are planar, in contrast to most other inorganic clusters. Here, employing the ring current model for aromaticity as modelled by both the Aromatic Ring Current Shielding (ARCS) [1] and the Gauge Including Magnetically Induced Currents (GIMIC) [2] methodologies, we investigate the possible aromaticity of a selected subset of these planar species. The highly symmetric three-dimensional B_{20} [3] and Au_{32} [4] are also considered. We find that many of the clusters support strong induced ring, or sphere [5], currents. The character of the current is highly dependent on the charge state of the species. Additionally, for gold, the currents are significantly altered by relativity.



[1] J. Jusélius, D. Sundholm, *Phys. Chem. Chem. Phys.* **1999**, *1*, 3429.
[2] J. Jusélius, D. Sundholm, J. Gauss, *J. Chem. Phys.* **2004**, *121*, 3952.
[3] B. Kiran *et al.*, *Proc. Nat. Acad. Sci.* **2005**, *102*, 961.
[4] M.P. Johansson, D. Sundholm, J. Vaara, *Angew. Chem. Int. Ed.* **2004**, *43*, 2678; *Angew. Chem.* **2004**, *116*, 2732.
[5] M.P. Johansson, J. Jusélius, D. Sundholm, *Angew. Chem. Int. Ed.* **2005**, *44*, 1843; *Angew. Chem.* **2005**, *117*, 1877.

Applications **P301**

Absorption spectra in solution : combining Quantum Monte Carlo with QM/MM Car-Parrinello Dynamics

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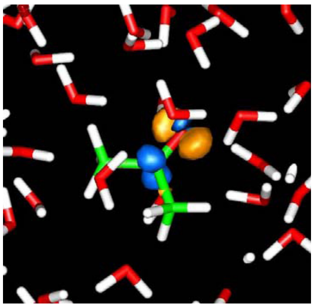
Accurate calculations of molecular excitations in solution and in condensed complex environments like proteins are still a challenge for both Density Functional Theory and other quantum chemistry methods. Recently, it has been shown that Quantum Monte Carlo (QMC) can accurately estimate excitation energies even in delicate cases like conjugated systems [1].

In the present contribution we extend the use of QMC to mixed quantum - classical models to allow a many-body study of electronic excitations for biological chromophores in situ.

Using a Jastrow-Slater trial wave function we calculate the QMC absorption spectra of small molecules in solution using snapshots of Car-Parrinello QM/MM trajectories [2,3]. The effect on the excitation energy of the solvent environment, of the basis set, and of the trial wave function will be also discussed.



n-π^* excitation of acetone in water solution calculated by Quantum Monte Carlo OM/MM simulation

[1] Schautz, Buda, Filippi, *J. Chem. Phys.* **2004**, *120,* 10931.
[2] Laio, VandeVondele, Rothlisberger, *J. Chem. Phys.* **2002**, *116,* 6941.
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Applications **P302**

Theoretical study of the structural, electronic, and optical properties of thieno[3,4-*b*]pyrazine and derivatives

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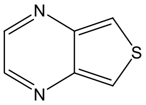
The use of fused-ring systems has become a successful strategy to obtain low band gap oligo/polythiophenes. For instance, thieno[3,4-*b*]pyrazines lower the gap dramatically when incorporated into a polymer backbone,[1] leading to materials with novel optoelectronic properties.[2-3] The understanding of the relationships between the chemical structure of this type of molecules and their electronic and optical features is of fundamental concern in order to design new compounds with enhanced characteristics.



In this contribution, we present a theoretical study of the geometric and electronic structures of thieno[3,4-*b*]pyrazine and several derivatives, carried out by employing density functional theory (DFT) procedures. With the aim of rationalizing their UV-vis absorption and emission spectra, the electronic excited states have been calculated by means of a time-dependent (TD-DFT) method. The performance of the theoretical approaches employed, as well as the effect that different modifications have on the π-conjugated structure and on the nature, position, and intensity of the spectral bands, have been analyzed in detail.

[1] D.D. Kenning, S.C. Rasmussen, *Macromolecules*, **2003**, *36*, 6298.
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Applications **P303**

A dft reactivity analysis of the species involved in the keto-enol tautomeric equilibrium

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The keto-enol tautomeric equilibrum involves an intramolecular hydrogen shift. The molecular structure and a density functional theory (dft) reactivity analysis of the reactant, product and transition state is presented for a set of molecules that exhibit this chemical behavior. A study on the performance of dft methods was made on three small molecules with (1,2)- and (1,3)-hydrogen shifts.

Molecular basic sites are characterized with the Fukui function and the molecular electrostatic potential. It is found that both quantities provide similar results. The evolution of basic sites along the reaction path is presented and, in some cases, the electronic reactivity indices can be used as qualitative criterion of similarity. Substituent effects on the reactivity of these species and the corresponding enolate ions are also analyzed.

Applications **P304**

A First Principles Study of Asymmetries in the Tautomerization Potentials of Benzoic Acid Derivatives

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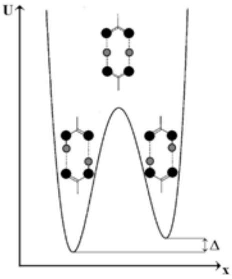
Dimers of benzoic acid (BA) and derived materials (specifically, the halobenzoic and trimethylbenzoic acids) are now well known as hosts for proton disorder, and have been extensively studied by X-ray and neutron diffraction [1], and NMR relaxometry [2] techniques. In the crystalline state, the two dimer configurations shown below are inequivalent, and a small energy difference, or asymmetry, separates them, of the order of 0.5 – 2 kJ mol^{-1} depending upon the material. NMR relaxometry and neutron refined site occupancy factors at varying temperature provide estimates of this asymmetry parameter which are found to be of comparable accuracy. Plane wave pseudopotential calculations have been used to investigate whether the asymmetries emerging from theory in the proper crystal field are comparable to experimental values, and whether weak intermolecular interactions, normally poorly represented by DFT, play an important role.



[1] C. Wilson, N. Shankland and A. Florence, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 5051; C. Wilson and A. Goeta, *Angew. Chem.* **2004**, *43*, 2095
[2] A. Horsewill, C. McGloin, H. Trommsdorff and M. Johnson, *Chem. Phys.* **2003**, *291*, 41

Applications **P305**

The Formation of Neutral Copper Clusters From Experimental Binding Energies and Reactivity Descriptors.

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In this work we study and rationalize the formation of neutral copper clusters from dimer to nonamer using the available experimental data of binding energies and electronic properties [1]. A complete and consistent picture of the formation of copper clusters in term of the changes in chemical potential and hardness emerges indicating that the one–atom growth reactions are mainly driven by changes in hardness. An analytic expression for the binding energy as a function of the cluster size is proposed and used to predict the growth pattern of copper clusters.

[1] P. Jaque, A. Toro–Labbé, *J. Phys. Chem. B*, **2004**, 108, 2568.

Applications **P306**

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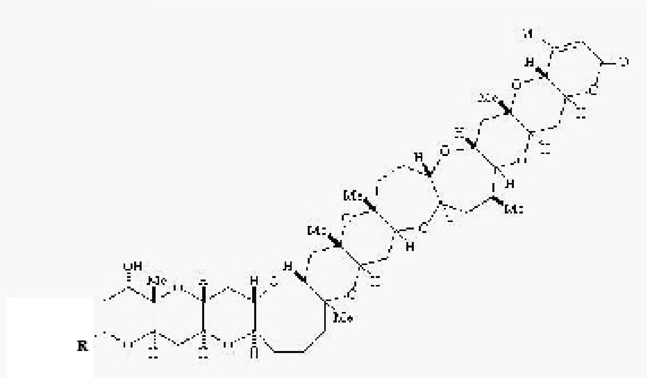

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Applications **P307**

Calculation of the hydration energies of lanthanides(III) and actinides(III) using QM/MM and continuum solvent methods

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The hydration energies of 3+ cations of actinides and lanthanides have been carried out using a mixed solvent approach in which the ion together with its first and second shell is immersed in a continuum. The effect of the first shell is computed within full QM model by means of the density functional theory; the second shell is added in a MM fashion with a fixed number of 19 water molecules. The first shell can have different coordination numbers (CN=8,9,10) depending on the ion involved. An extensive analysis of the geometry and the electronic structure is presented. A comparison of the hydration energies with the experimental data for the lanthanide shows an agreement within 5% on the absolute values, whereas this error is decreased to 1-2% if we compare the trend in the change of the hydration energies along the lanthanide series. We also initiated a study of the hydration energies of the 3+ cation of the actinide series, for which no experimental data are available.

Applications **P308**

Ab initio HF and DFT investigation of crystalline urea

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In the present work, we aim to assess the perfomance of different DFT functionals in dealing with hydrogen bonded (HB) molecular crystals. Crystalline urea was adopted as a case study due to its relevance in biological processes, industrial chemistry, and non-linear optical properties, and because accurate experimental data are available [1,2].

Structural, cohesive and vibrational properties were computed with local, gradient-corrected and hybrid functionals (i.e. SVWN, PW91, PBE, B3LYP and PBE0) and the results compared to the HF ones. The basis set dependence was also investigated at B3LYP level. All calculations were carried out by using a development version of the periodic ab initio code CRYSTAL03 [3] which performes full geometry optimization and vibrational frequency calculation at the Γ point [4].

Structural features are well reproduced by hybrid methods and GGA. LDA gives too short lattice parameters and hydrogen bond distances while at HF level the opposite trend is observed. When BSSE and ZPE are taken into account, all methods, but LDA, give computed cohesive energies that are underestimated with respect to the experimental sublimation enthalpy. Dispersion energy, not properly taken into account by DFT methods, seems to be mandatory. A good agreement with the experiment is observed for the vibration frequencies computed at the B3LYP level. Results show that hybrid methods are more accurate than HF and both LDA and GGA functionals, with a trend in the computed properties similar to that of HB molecular complexes [5].

[1] S. Swaminathan, *et al.*, *Acta Cryst. B*, **1984**, *40*, 300.
[2] R. Keeulers, *et al.*, *J. Phys. Chem. A*, **1999**, *103*, 4621.
[3] V. R. Saunders, *et al.*, *CRYSTAL03*, `www.crystal.unito.it`.
[4] F. Pascale, *et al.*, *J. Comput. Chem.* **2004**, *25*, 888.
[5] C. Tuma, *et al.*, *PCCP*, **1999**, *1*, 3939.

Applications **P309**

How electronic correlation effects influence structure and magnetism of Fe and Fe-Ni clusters

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While certain energetic properties of small Fe clusters have been measured to good accuracy, from experimental side practically nothing is known about their geometries and electronic structure. Therefore, the major part of information comes from computational studies, up to day mainly based on density functional theory (DFT). In these calculations, it is found that ground state geometries of Fe clusters show pronounced Jahn-Teller distortions, while corresponding magnetic moments are collinear and ferromagnetic. But there is evidence both from experimental side as well as from high-level quantum chemical calulations that structural and magnetic properties of these clusteres are not reproduced correctly in the framework of conventional DFT.
Our calculations show that this can be overcome when a Hubbard-like term is incorporated into the density functional to describe the strong Coulomb repulsion between the localized Fe $3d$ electrons (DFT + U method [1]). It turns out that the magnetic moments of nearly all Fe clusters we have investigated are enhanced, while distortions of the clusters are decresaed, which can be related to changes in the electronic structure of the clusters. Adding Ni to form mixed clusters greatly increases the complexity of the systems. But the trends we find when considering on-site Coulomb repulsion explicitly are similar to those of the pure clusters.

[1] S.L. Dudarev *et al.*, *Phys. Rev. B*, **1998**, *57*, 1505.

Applications **P310**

Adsorption of Carbon Monoxide and Carbon Dioxide onto the Alkali-Metal-Exchanged ZSM-5 Zeolite: A Critical Test for Methodologies

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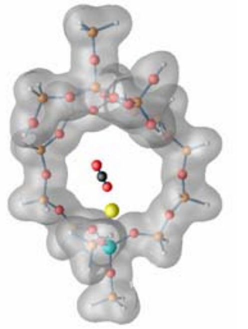
The interaction between a probe molecule and alkali cations in ZSM-5 zeolite can provide useful indications for understanding adsorption. The interaction of the probe molecule with the zeolite is characterized by changes in vibrational frequencies and intensities[1].



The purpose of this work was to study the adsorption of carbon monoxide and carbon dioxide by means of density functional theory calculations.
For the three alkali cations (Li^+, Na^+, K^+), calculations[2] were performed for CO and CO_2 in cluster models of the zeolite framework using the orbital-free embedding formalism[3] developed in our group. In order to attempt to identify the reasons of some mismatch between calculated frequency shifts and experimental data, a second series of calculations was carried out using the Kohn-Sham formalism on the same systems to allow the comparison.

[1] A. Zecchina, C.O. Areán., *Chem. Rev.*, **1996**, *25*, 187.
[2] T.A. Wesolwski, et al., *J. Chem. Phys.*, **2001**, *115*, 4791.
[3] T.A. Wesolowski, A. Warshel, *J. Phys. Chem.*, **1993**, *97*, 8050

Applications **P311**

Theoretical and Experimental Vibrational Circular Dichroïsm of TRISPHAT [Tris(tetrachlorobenzenediolato)phosphate(V)] Anion

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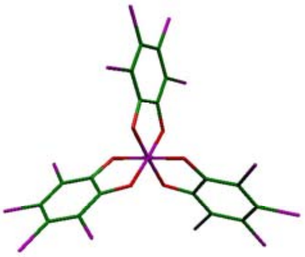
Density functional theory calculations were performed to study the structure and determine the absolute configuration of the TRIPSHAT anion[1] using vibrational circular dichroïsm.



This anion has been shown to be a valuable NMR chiral solvating, resolving, asymmetry-inducing and solubilizing reagent for organic, organometallic and polymer substances[2].
The absolute configuration Δ for the anion was previously established by X-ray structural analysis of the cinchonidinium salt.
Herein we report a theoretical study of the structural and vibrational properties of the TRISPHAT anion that confirm the absolute configuration in solution obtained by electronic CD[3].

[1] J. Lacour et al., *Angew. Chem. Int. Ed.*, **1997**, *36*, 608
[2] J. Lacour et al., *Chem. Soc. Rev.*, **2003**, *32*, 373.
[3] D. Bas et al., *Chirality*, **2005**, *17*, S143.

Applications **P312**

DFT investigation of the flavonoid degradation in radiolized solution

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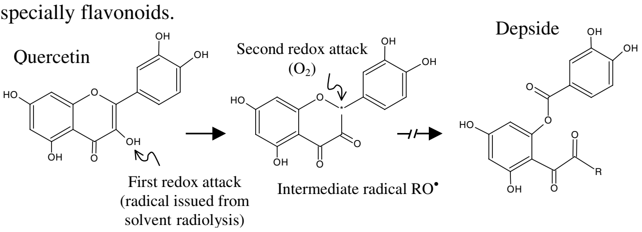
Food irradiation is a process approved as a good technique of food preservation without inducing major nutritional changes. Nevertheless little is known concerning changes in phenolic compound concentration, especially flavonoids.



Here theoretical investigations are described in order to confirm the mechanism of degradation of flavonols in radiolyzed solutions. We calculated BDE and IP with the DFT/B3P86/6-311+G(d,p) method for twelve flavonoids. We demonstrated the importance of both the 3-OH BDE and the IP values to explain the first redox attack (H abstraction from the 3-OH group of flavonols). The Mulliken spin density of the subsequent phenoxy radical was analyzed and allowed to identify the C-2 atom as the second redox site attacked by O_2. The following steps were also studied by calculating the stability of the peroxy radical and hydrogen peroxide formation. Then O-O BDE was computed and the electron distribution of the corresponding radical was calculated in order to explain the C-ring opening that led to the formation of depsides, the major radiolytic products.

Applications **P313**

Phosphorescence and Triplet State Energies of Oligothiophenes: Experimental and Density Functional Theory Approach

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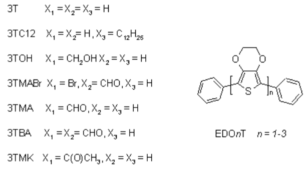
The phosphorescence spectra of a series of small oligothiophenes (*n*T, *n* = 1–3) incorporating a variety of substituents, end cappers, and functional groups has been recorded for the first time using gated detection in combination with nanosecond excitation in frozen solution at 80 K. The vibrationally resolved emission spectra provide accurate estimates of the T_1 and S_1 levels, and the singlet-triplet energy gap. The triplet energy E_T and the S_1–T_1 gap ΔE_{ST} are directly obtained from the emission spectra.



Apart from a small, but systematic underestimation of ~0.1 eV, the experimental energies and their variation with the changes in chemical structure of the oligomer are accurately reproduced by DFT (B3LYP/6-31G*) calculations when using optimized geometries for S_0 and T_1. The combined experimental and theoretical results demonstrate that there is a significant dispersion of both triplet and singlet excited-state energies with chain length and a decreasing S_1-T_1 gap with increasing *n*. In the triplet state, there is a significant change in the bond length alternation compared to the singlet ground state. The triplet exciton localizes at the center of the oligomer and an analysis of the spin density reveals that the “natural” size is circa 3-4 thiophene rings.

Applications **P315**

Structural, electronic, and phonon properties of $AuAl_2$ and $AuGa_2$

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We have investigated the structural, electronic and vibrational properties of $AuAl_2$ and $AuGa_2$ in the framework of the density functional theory. The calculated lattice constant and bulk modulus for these materials are found to be in good agreement with previous experimental results[1,2]. Theoretical results on the electronic properties of these materials are also presented. In particular, the calculated electronic band structure for $AuAl_2$ shows good agreement with angle-resolved photoemission results[2]. Although electronic properties of the inter-metallic compounds $AuAl_2$ and $AuGa_2$ have been widely studied by different groups, their vibrational properties are currently lacking from the literature. However, it is important to make through investigation of vibrational modes, as these play a significant role in determining various material properties such as phase transition, electron-phonon interactions, and transport coefficients. Thus, the phonon dispersion curves for these materials have been obtained from first principles using the linear response method[3]. The highest zone-center phonon mode is found to be 148 cm^{-1} for $AuGa_2$ and 268 cm^{-1} for $AuAl_2$. These values compare very well with the Raman scattering measurements[4] of 149 cm^{-1} and 267 cm^{-1}. In addition to their phonon dispersion curves, we have presented the phonon density of states for these materials. Finally, we have analyzed vibrational eigenvectors at the X and L points of the Brillouin zone for $AuAl_2$ and $AuGa_2$.

[1] L. Hsu, et al., *J. Phys. Chem. Solids*, **2001**, 62, 1047.
[2] S. Baroni, et al., *Phys. Rev. Lett.*, **1987**, 58, 1861.
[3] S. Baroni, et al., *Rev. Mod. Phys.*, **2001**, 73, 515.
[4] W. J. Brya, *Sol. State Commun.*, **1971**, 9, 2271.

Applications **P314**

Ground-state properties of zinc-blende and wurtzite phases of MgS

S. Duman[1], H. M. Tütüncü[1], S. Bağcı[1], F.Soyalp[2] and G. P. Srivastava[3]

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The structural and electronic properties of zinc-blende and wurtzite phases of MgS have been investigated using an *ab initio* pseudopotential method. The calculated lattice parameters, bulk modulus and the pressure derivative of bulk modulus for both phases of MgS are in good agreement with previous theoretical calculations[1,2]. The electronic structure of both phases is analyzed and compared with previous experimental and theoretical results[2,3]. In agreement with previous calculations[2,3], we have observed that both phases of MgS are characterized by a direct band gap which is found to be 3.10 eV for zinc-blende MgS and 3.15 eV for wurtzite phase. Althoguh considerable progress has been made in theoretical description of the structural and electronic properties of zinc-blende and wurtzite MgS, many of their vibrational properties have been entirely ignored in the literature. Thus, we have used a linear-response approach to density functional theory in order to derive Born effective charges, dielectric constants, phonon frequncies, and eigenvectors. Our calculated zone-center frequencies for zinc-blende MgS compare very well with the Raman scattering measurements reported by D. Wolverson *et al*[4]. For the wurtzite MgS, the zone-center frequencies are found to be 9.79 and 13.30 THz (E_1(TO), E_1(LO)), 9.72 and 12.08 THz (A_1(TO), A_1(LO)), 2.69 and 10.15 THz (E_2^1, E_2^2), 7.78 and 10.31 THz (B_1^1, B_1^2). We have also discussed the effect of the internal parameter u on the A_1(LO) and E_1(LO) modes.

[1] S. Lee, et al., *Phys. Rev. B.*, **1995**, 52, 1918.
[2] F.Drief, et al., *Catal. Tod.*, **2004**, 89, 343.
[3] M. Rabah, et al., *Mat. Sci. Eng. B.*, **2003**, 100, 163.
[4] D. Wolverson, et al., *Phys. Rev. B.*, **2001**, 64, 113203.

Applications **P316**

First-principles calculations for vacancy formation and migration energies in nickel : comparison between local and non-local approaches

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Many theoretical and experimental works are available concerning the formation energy of vacancies in nickel. The range of the data is very large between nearly 1.3 and 1.85 eV.[1] The results depend strongly of both the theoretical approaches and the experimental techniques. In our study we perform DFT calculations on formation and migration energies of vacancies and divacancies in Ni. In a first step we show that the inclusion of non local effects improves significantly the determination of various well known experimental properties of the bulk (lattice parameter, magnetic moment, bulk modulus, cohesion energy, …). Thus, we conclude that the non local approach leads to a better estimation of both the vacancies (1.4 eV) and divacancies (2.75 eV) formation energies at 0 K. Furthermore, we show that the dilatation effects which take into account the anharmonic effects due to the temperature allow to understand the high formation energy (1.8 eV) determined experimentally by positron annihilation measurements.

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Applications **P317**

Revisiting the Regioselectivity of Some Organic Reactions Through the *Δf(r)* Descriptor.

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The ***Δf(r)*** descriptor [1] defined as the difference of the nucleophilic Fukui function $f^{+}(r)$ and the electrophilic Fukui function $f^{-}(r)$, characterizes the response of the absolute hardness of a molecule to a variation of the external potential.

$$\Delta f(r)=\left(f^{+}(r)-f^{-}(r)\right)_N\approx\left(\frac{\Delta\eta}{\Delta v(r)}\right)_N$$

The sign of the ***Δf(r)*** describes the electrophile ($\Delta f(r)>0$) and nucleophile($\Delta f(r)<0$) zones within a molecule. The aim of this work is to show how this index can be used to predict the regioselectivity of some classical organic reactions such as Diels Alder cycloaddition or the Aromatic Electrophilic Substitution. The calculation have been carried out at the HF and/or B3LYP level of accuracy using the 6-311G** basis set. The Fukui functions have been approximated by the spin density of either the N+1 system or the N-1 system, with N standing for the overall number of electrons, as it was suggested by Galvan, Gazquez and Vela [2].

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[2] Galvan, M.; Gazquez, J.L., Vela, A. *J.Chem.Phys.* **1986**, 64, 2337

Applications **P318**

DFT conformational analysis revealed 64 local minima on hypersurface of potential energy for 1′, 2′-deoxyribose, model sugar motif of 2′-deoxyribonucleosides

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We have firstly applied comprehensive conformational analysis for 1′, 2′-deoxyribose using density functional theory at the MP2/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory. In our opinion, such an approach is necessary for nucleosides conformational properties elucidation.

It was shown that 64 found conformations have a relative range of energies 0-7.3 kcal/mol. They consist of such conformational subfamilies: C1′- exo – 8; C1′- endo – 6; C2′- exo – 4; C2′- endo – 18; C3′- endo – 12; C4′- endo – 7 and C4′- exo – 9 conformers.

The intermolecular OH…O H-bonds were firstly found. It was shown that 16 conformers from the full conformational family have H-bonds of the type O5'H…O4', as well as 2 conformers – of the type O5'H…O3' and 2 conformers – of the type O3'H… O5'.

It is established that all H-bonds are characterized by O…O distance which has a range of values from 2.72 to 2.99 Å; in these cases OH…O average angle for O5'H…O4' type H-bonds is ~110.4° and ~136.4° for O5'H…O3' or O3'H… O5' type H-bonds. We observed the hydroxyl OH bond elongation in the range of values 0.003-0.005 Å. The hydroxyl groups involvement to the H-bond exerts influence on their characteristic vibrational values: torsional vibration frequencies $\nu_{\tau_{OH}}$ increase by ~170 cm^{-1} and stretching vibration frequencies ν_{OH} decrease by ~ 50 cm^{-1}, which is accompanied by growth in their intensities.

Applications **P319**

Ionisation effects on peptide bond: A DFT study for the simplest peptide N-Glycylglycine.

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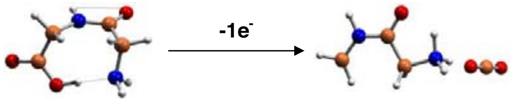
The ionisation effects on peptide bond were studied using the B3LYP density functional with the 6-31++G(d,p) basis set. The suitability of this functional to study ionised peptides was tested by comparing the relative energies with those obtained from single-point calculations at the MP2/6-31++G(d,p) and CCSD(T)/6-31++G(d,p) levels of theory.

Three major trends are observed upon ionization depending on the initial neutral conformations.

1.- There is a strengthening of the peptide bond for almost all conformations. Only few trans structures lengthen slightly the peptide bond distance. These structures present a OH···OC hydrogen bond in which the oxygen of the carbonyl group associated to the peptide bond is involved.

2.- CO_2 elimination is observed when the most stable cis structure is ionised, this conformation is the only one that contains a OH···NH_2 hydrogen bond.



3.- Ionisation of some cis conformers induces a strengthening of the NH_2^{+}···OC intramolecular hydrogen bond. These structures become more stable than most of ionised trans structures.

The reaction energy of the Gly + Gly → GlyGly + H_2O condensation reaction is more favourable for the ionised system (-14.3 kcal/mol) than for the neutral one (-5.8 kcal/mol). These trends have been rationalised from the spin distribution of the ionised systems.

Applications **P320**

INTRASTRAND BRIDGED DNA BASES : A DFT STUDY

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A new class of DNA damage, which is called the “tandem bound” has been recently experimentally detected.
These damages are produced by an initial attack of the Hydroxyl radical issued from the water radiolysis by UV rays. Following different radicalar paths, the reaction leads to the bond of two adjacent bases in a DNA strand.
Up to now some of these damages have been identified and measured, and mainly those involving the couple “adenine-thymine” bases.
The formation mechanisms of these damages are unknown. But the damages of A^T type outnumber the T^A type by 8 to 1.
It is for studying these two interesting points, mechanism and yield of formation why we have undertake this study.
This theoretical work was performed using DFT methods.
The results show that the chemical reaction paths are rather different, even if the reaction energies are similar. That will explain the great difference in the yields of production, and give a new light on the mechanisms of formation.

Applications **P321**

Geometry, energetics and optical properties of the Cobalt(II)tris(2,2'-bipyridine) complex in the low- and high-spin states: a Density Functional Study

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The spin-crossover phenomenon is observed in d^4 to d^8 transition metal complexes and involves the reversible switching of the complexes between their low-spin electronic ground state and their high-spin metastable electronic state characterised by magnetic and electronic properties which differ remarkably. $[Co(bpy)_3]^{2+}$(bpy: 2,2'-bipyridine) is a high-spin complex which can be turned into a spin-crossover system when incorporated into the cavities of zeolites or into three-dimensional oxalate networks [1]. We report the characterisation of the free complex in its low- ^2E $(t_{2g}^6e_g^1)$ and high- $^4T_1$ $(t_{2g}^5e_g^2)$ spin states using Density Functional Theory (DFT). This study allowed the determination of the high- and low-spin energy gap together with the associated structural differences. It also allowed the characterisation of the distortions in the Jahn-Teller active low-spin state along with the corresponding energetics. Moreover, several exchange-correlation functionals were used and their performance was assessed with regard to their ability to correctly predict the high-spin ground state and to reproduce the observed HS-LS structural changes. Further insight into the electronic properties of $[Co(bpy)_3]^{2+}$ is obtained through analysis of the absorption and circular dichroism spectra of the complex in the two spin states using the Time Dependent Density Functional Theory (TDDFT) approach.

[1] M. Zerara and A. Hauser, ChemPhysChem, **2004**, *5*, 394, and references therein.

Applications **P322**

Theoretical and experimental study of the photophysical properties of iron(II) and ruthenium(II) polypyridinyl complexes

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The $[Fe(bpy)_3]^{2+}$, $[Fe(tpy)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$ complexes, (bpy = 2,2'-bipyridine, tpy = 2,2':6,2"-terpyridine), exhibit a remarkable diversity in their photophysical properties which contrasts with their chemical similarity as polypyridinyl complexes of d^6 transition metal cations with a low-spin $^1A_1(t_{2g}^6)$ electronic ground state. The $3d^6$ iron(II) complexes differ by the dynamics of the relaxation following the photoinduced population of the high-spin $^5T_2(t_{2g}^4e_g^2)$ state. Due to high ligand-field strengths, they both are low-spin species: that is, the high-spin state lies too high in energy to be thermally populated. However, as in spin-crossover complexes, the low-spin → high-spin transition can be triggered by using laser excitations. The study of the low-temperature high-spin → low-spin relaxation dynamics provides a mean for indirectly characterising the complexes in the thermally inaccessible high-spin state [1]. While $[Fe(bpy)_3]^{2+}$ relaxes very fast as expected for a low-spin complex, the $[Fe(tpy)_2]^{2+}$ can be trapped in the high-spin state. By combining the density-functional characterisation of the iron(II) complexes in the two spin-states with the study using timed-resolved spectroscopy, we show that the two complexes have a similar high-spin/low-spin energetics, as expected, and that the difference in their relaxation dynamics originates from the manner in which their coordination spheres distort upon the change of spin-states. For the luminescent $4d^6$ $[Ru(bpy)_3]^{2+}$ complex, we similarly proceed to get new insight into the mechanism of its luminescence quenching.

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Applications **P323**

Theoretical generation of chemical diversity applied to the design of highly luminescent Tb^{3+} complexes

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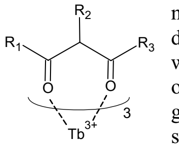
The relation between the structure and luminescent properties of Tb^{3+} complexes containing β-diketonate ligands has been investigated by means of combinatorial chemistry.[1] The groups at the R_1, R_2 and R_3 positions in the β-diketonate ligands (see Figure) have been varied in order to produce 108 new Tb^{3+} complexes. It has been chosen groups with different donor and acceptor powers, whose magnitudes were quantified by the sum of the atomic partial charges obtained from B3LYP/6-31G** calculations. The geometries of the complexes were optimized using the semiempirical Sparkle model[2] and the excited triplet states calculated by the INDO/S method implemented within the ZINDO program. The calculated triplet energies were then used to estimate the emission quantum yields of each complex by using the experimental curve proposed by Latva et al.[3]



The plot of the estimated emission quantum yields versus the total partial charges of each group has shown that the combination between a donor group at the R_1 position and an acceptor group in R_3 position (or vice-versa) should give luminescent complexes with higher emission quantum yields, mainly when the group at the R_2 position is CF_3. The results obtained may be used as a valuable tool for predicting luminescent properties of new Tb^{3+} complexes in a completely theoretical way.

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Applications **P324**

Hemilabile Ligand Induced Selectivity: a DFT Study on the Ethylene Trimerization Catalyzed by Ti-Complexes

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A DFT study has been undertaken in order to better understand the trimerization reaction in which ethylene is selectively transformed into 1-hexene with a $[(\eta^5\text{-}C_5H_4CMe_2C_6H_5)TiCl_3/MAO]$ type catalyst [1].

For the ring-opening reaction of the metallacycle distinction has been made between agostic assisted β-hydrogen transfer and hydride formation. Gibbs Free energies (298 K, 1 atm.) show that the reaction barrier to form 1-butene is substantially higher than the growth of the metallacycle to a 7-membered ring. However, the ring-opening reaction of the 7-membered metallacycle, to finally yield 1–hexene, is lower in energy than the coordination + insertion of the fourth ethylene molecule (9-membered ring). Therefore, our calculations predict the selective formation of 1-hexene, which is in agreement with the available experimental results [2].

The selectivity of the reaction appears to be the results of two effects: the ring size of the metallacycle and the stabilizing effect of the hemilabile phenyl ligand. Indeed, upon interchange of the phenyl group by the more labile methyl group, the calculations predict the formation of polyethylene, which is in agreement with the experimental data.

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Applications **P325**

Relationships between local topology and reactivity on the sidewall of defected carbon nanotubes: a DFT approach

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Despite their large popularity, gained during the last few years, the use of carbon nanotubes (CNTs) in real applications is often hindered by low solubilities in most common solvents. In this respect, covalent derivatization of CNTs represents an appealing possibility, opening new ways to their chemistry. However, both experimental and theoretical investigations evidence a low propensity to chemical interaction between functionalizing agents and the perfect hexagonal network of the CNT sidewall. On the other hand, the presence of topological and structural defects on the sidewall has been recently evidenced in particular growing conditions, leading to an enhanced reactivity towards functionalization. In this work, we perform a systematic investigation on the relationship between the local topology of the coordinating site on the sidewall, induced by the presence of different kinds of defects, and propensity to chemical functionalization. Hence, the definition of structural and electronic properties of the defect leading to an increase of the sidewall reactivity can be used in further studies on the functionalization process. Density functional theory calculations are carried out on model systems describing the interaction between the functionalizing agent and the defected sidewall of a CNT. Preliminary test calculations allowed us to assess a general computational strategy to adopt thourough the study in order to obtain reliable and comparable results for all model systems considered. Moreover, general relationships between local structure of the defect and its reactivity were derived by taking into account different topologies of the functionalization process, as in the case of the addition of radical species or the dissociative chemisorption of small molecules. In particular, the interaction between an amidogen radical ($NH_2\cdot$) and the defected sidewall was considered, thus analyzing the effect on the overall reactivity due to the change in the hybridization of a single carbon atom. The role of structural modifications of carbon atom pairs on the sidewall was then investigated by considering the functionalization with the methylene radical, leading to three-membered rings upon chemisorption. Finally, calculations on the dissociative chemisorption of ammonia or aliphatic amines on the sidewall provides the stepping stone for further investigations on the role of defects on the functionalization process in several cases of technological relevance.

Applications **P326**

Theoretical Study of Methyl Group Redistribution at Silicon Using Lewis Acid $AlCl_3$ as Catalyst

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Redistribution at silicon has been known for a long time and represents an important reaction in silane chemistry. This process is normally catalyzed by strong bases and strong acids or by transition metal complexes. From a mechanistic point of view, several proposals have been investigated experimentally by Russell[1] in the case of aluminum chloride as catalyst: carbonium or siliconium ion intermediates, organoaluminum intermediates, bimolecular reaction between a molecule of silane and a silane-aluminum chloride complex.

A DFT study of the redistribution reaction at silicon of SiH_3Me with aluminum chloride as catalyst has been carried out in order to identify the intermediates which lead to the formation of SiH_4.

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Applications **P327**

An ab initio study of iron wires interacting with BN nanotubes

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A systematic study of Fe wires interacting with zig-zag boron nitride (BN) nanotubes is presented. Spin-polarized total-energy ab initio calculations based on the density functional theory are used to describe the structural, electronic and magnetic properties of all studied systems. For the Fe wires, either outside or inside the nanotube, the most stable configuration is found to be over the centre of the hexagonal site. For all the investigated Fe structures adsorbed on the BN nanotubes, either high-spin or low-spin, the interactions between Fe atoms, between Fe and B and between Fe and N atoms become stronger as the Fe coordination number increases. The resulting magnetic moments for all adsorbed systems are found to be close to their original values for the corresponding free Fe structures. Some special magnetic properties resulting from the interaction between the Fe wires and zig-zag BN nanotubes are found. Our calculations suggest that for applications to spin transport devices, it is desirable to form magnetic nanostructures isolated by a non-magnetic material, i.e., BN walls, could be efficiently used for high-density data storage.

Applications **P328**

Selective bond activation in aromatic systems by transition metals

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Selective activation of hydrocarbon C-H and C-C bonds by metals under mild conditions is an important pursuit in the functionalization of organic substrates.

A theoretical study of the activation of the C-H bond in aromatic systems by transition metals has been carried out. The process analysed is an oxidation reaction catalyzed by mononuclear copper complexes. The aromatic systems are a rich source of carbon, but from an organic point of view they have the inconvenient of being very inert. It is for this reason that it is important to study different ways of breaking or selectively activating the C-H bond in these species. One way is through coordination of these C-H bonds to insaturated transition metals. In particular, a copper complex with a tridentate N ligand has been studied. For this complex we have investigated the effect of the metal changing the copper by a high variety of transition metals with the suitable oxidation state. Our study focuses in the nature of agostic C_{ar}-H_{ar}-Cu bond by an energy decomposition analysis. We have analyzed also the effect of solvents having different different affinities of coordination to the metal.

Finally, the study of the same complex with the exchange of the activated H atom by a methyl group leads to a clear activated C_{ar}-C bond. Our results can be applied to promote C-C bond breacking in hydrocarbons.

Applications **P329**

Elongation Cutoff Technique for Linear SCF Scaling

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The elongation method was designed as a device for routine electronic structure calculations for huge aperiodic polymers and biopolymers.[1,2] The method extends the polymer chain by stepwise adding a monomer unit or a slightly larger molecular fragment to a starting oligomer. Every elongation step is finished by molecular orbital (MO) localization. Huge part of the chemical information is preserved from step to step by freezing the shape of localized MOs (LMOs) that are far away from the chain propagation center. Such procedure effectively reduces the variational space that remains almost constant along the whole elongation process. Besides diminishing the space, LMO basis can also reduce the size of the Fock matrix (the cutoff procedure),[3] therefore the number of integrals computed in the SCF process is drastically reduced. Depending on the level of theory, the elongation method can be considered as an approximation to Hartree-Fock (HF) or Kohn-Sham (KS) method. In this presentation we describe the elongation method together with cut-off technique at KS level of theory. All calculations, illustrating its accuracy, are performed for model systems.

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Applications **P330**

Reliability and degradation of ultrathin gate oxides

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The essential limitations on gate insulator of CMOS devices are related to the exponentially increasing gate tunneling current as the thickness of the oxide is reduced (below 5 nm), and the effect of this current on both the functionality and reliability of devices and circuits. Quantum mechanical (ab-initio) calculation models can be used to simulate the formation of atomic defects of a realistic material structure. Density Functional Theory [1] has been used to model and study the degradation properties of alpha quartz and amorphous silica. The bulk of amorphous silica has been generated using classical molecular dynamics starting from a cubic unit cell matching the experimental density following the generation procedure of reference [2]. The system so generated has been relaxed by Car and Parrinello quantum mechanical simulated annealing [3].

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Applications **P331**

One-dimension metal molecules: DFT Investigation of delocalized interactions at the nanometer scale.

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Extended metal atom chains (EMACs), and more specifically those based upon the stabilization of linear metal backbones by polypyridylamide ligands have been synthesized and their properties characterized by the groups of F. A. Cotton and S.-M. Peng [1]. The unprecedented structural variability discovered for the trinuclear species of Co(II) and Cr(II), as well as the great interest presented by EMACs in the context of an emerging nanoscale technology, provide a powerful incentive toward a theoretical investigation of the family of trimetallics obtained to date with Co, Cr, Cu, Ni, Ru and Rh.. The sequence of metal orbitals obtained from DFT calculations for M3(dipyridylamide)4Cl2 has been used to delineate the general trend toward a delocalized, σ-type metal-metal bonding extending over the whole metal framework, except with M = Cu [2]. In the case of nickel, we will discuss the superexchange mechanism coupling the terminal atoms via the central nickel, and the electronic and structural changes occurring upon a one-electron oxidation of Ni3(dpa)4Cl2. Extrapolation to longer nickel chains is attempted [3]. For Cu3(dpa)4Cl2, no formal metal-metal bond is present, but antiferromagnetic interactions have been characterized for the neutral as for the oxidized, mono-cationic species [4]. DFT/B3LYP calculations explain the origin of these interactions and accurately reproduce the observed J constants. Finally, we will introduce the tetra- and hexanuclear chains of iridium atoms formed by concatenating two or three pyridonate-bridged iridium dimers by means of a two-electron oxidation. The metal-metal bonding is delocalized along the chain, and its intensity is expected to decrease with the length of the chain [5]. The thermodynamics of the reactions will be discussed.

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Applications **P332**

Modeling of the catalytic mechanism of urate oxidase.

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Urate oxidase, ou uricase (UOx), is responsible of the degradation of uric acid into allantoïn in most living organisms. This enzyme which is not naturally present in human body is often used as a drug to reduce hyperuricemic disorders resulting from the treatment of cancer by chemotherapy. Urate oxidase shows some very interesting properties: it does not need any co-factor nor any metal to catalyze its redox reaction, and no functional group seems to be directly involved in the catalytic mechanism. Today, the chemical reaction pathway of uricase is still largely unknown.

A theoretical study has been carried out in order to understand the catalytic mechanism of UOx. *i*) study of the physical and chemical properties of the uric acid and its anions; *ii*) determination of the intrinsic reactivity of the uric acid and its anions with dioxygen; *iii*) determination of the urate form bound by the enzyme and its reactivity in an active site model. All these studies were carried out at various levels of quantum mechanics, including semi-empirical, DFT and *ab initio* (HF and MP2) methods.

Our study highlights two significant peculiarities of the catalytic mechanism of urate oxidase: *i*) the substrate bound to the enzyme is the 3-7 urate dianion form, which is not the most stable dianion form in solution but the second most one; *ii*) the reaction pathway displays a "continuous" spin change from the reactive state, a triplet state, to the final state, a singlet state. This spin change occurs without any photon emission but through a degenerescency between the singlet and the triplet states along the first steps of the reaction.

CHIMIA **2005**, *59*, No. 7/8

Applications **P337**

Melamine derivatives antitumor drug: theoretical study for predicting their biological activity, I.R and Raman vibrational spectra

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The area of quantum chemistry has developed considerably over the last decades. Accurate computational techniques can now be applied to much larger molecular system than before. Accurate calculations on biologically active compounds are very important in the search of the correlation between the structure and physical chemical and biological properties of such system.

In this study we will present recent computational work on Triethylene Melamine and Hexamethyl Melamine drug. These drugs are an alkylating agent their antitumor action consist essentially in alkylating the N7 position of guanine base in DNA.

In the present investigation a detailed theoretical study of Triethylene Melamine and Hexamethyl Melamine drug by performing ab initio and density functional type calculations to obtain several descriptors of the electronic charge distribution such as dipole moment as well as electrostatic potential charge. A biological activity of Triethylene Melamine and Hexamethyl Melamine have been studied using the computed highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy value. The application of IR and Raman spectroscopy in structural studies of biologically active compounds is widely used. In this purpose, theoretical investigation have been made to develop an understanding of normal co-ordinates associated with the vibrational mode and to simulate IR and Raman spectra of Triethylene Melamine, Hexamethyl Melamine.

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Ab initio study of structural, electronic and dynamical properties of the cubic AlLiSi phase of MgAuSn

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Using the first-principles pseudopotential LDA approach, we have calculated structural and electronic properties of the cubic AlLiSi phase of MgAuSn. The lattice constant of this material is found to be 6.39 Å, which compares very well with the experimental value of 6.41 Å [1]. In addition to lattice constant, we have presented bulk modulus and the pressure derivative of bulk modulus of the cubic AlLiSi phase of MgAuSn. The electronic band structure of this material is also calculated along the high symmetry directions. Our calculated electronic structure is also compared with recent tight-binding linear muffin-tin orbital results in detail [1]. In contrast to the experimental and theoretical works [1] presented on the structural and electronic properties of this material, phonons in this material has not been studied experimentally and theoretically yet. However, vibrational properties are very important for specific heats, thermal expansion, heat conduction and electron-phonon interaction. Thus, linear response theory [2] is used in the calculations of the phonon dispersion curves and density of states of MgAuSn. The frequencies of zone-center phonon modes are found to be 143, 213 cm^{-1}. We have also presented atomic displacement patters of selected phonon modes at the Γ, X and L symmetry points. From these displacement patterns, we have observed that the highest optical phonon mode is characterized by the vibrations of Mg atoms due to large mass differences between Mg and Au(or Sn).

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Applications **P334**

First principle investigations of finite temperature behavior of small sodium clusters (Na$_n$, $8 \leq n \leq 55$)

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Thermodynamical studies of finite–sized systems have been a topic of great interest in last couple of decades. Usually, clusters melt at temperatures lower than bulk because of their high proportion of surface atoms, with the reduction in melting temperature being roughly proportional to 1/R, where R is the radius of the cluster. In a series of experiments on free sodium clusters in the size range of 55–350, Haberland and co–workers observed that the simple 1/R scaling is lost; instead they observed a large size–dependent fluctuations in the melting temperature. Our recent calculations reveal a rather subtle interplay between geometric and electronic shell effects. Interestingly, in very recent experiments Jarrold *et al.* also showed a remarkable size-sensitive features of the melting transition in gallium and aluminum clusters.

We have carried out a systematic and detailed *ab initio* investigations on small sodium clusters, Na$_n$ (n = 8–55), using density–functional molecular–dynamics within ultrasoft pseudopotentials. We compute specific–heat via multiple–histogram technique. using the data of 150 *ps* simulation time for each temperature. We find that the smallest sizes (n =8–10) do not show obvious melting–like transition. Clusters with n =13–25 show very broad melting transition. When the size of the system increases, the system starts showing a sharper peak in specific heat. In the range of Na$_{40}$ to Na$_{55}$, we observe size–sensitive features, which is very similar to experimental observations in the cases of sodium, gallium and aluminum. Specifically, while Na$_{40}$ and Na$_{55}$ shows a recognizable peak in the specific heat, Na$_{50}$ has very broad specific heat curve. We attribute this difference to their ground state geometry. We argue that if the ground state geometry is *ordered*, e.g. Na$_{40}$ and Na$_{55}$, it shows a well defined peak in the specific heat, whereas *disordered* clusters, like Na$_{50}$, would show a continuous transition.

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An Aromaticity Analysis of Lithium-Cation/π Complexes of Aromatic Systems

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In the last two decades, extensive experimental and theoretical investigations have been carried out for the alkali metal cation–π complexes involving aromatic rings to investigate the participation of these complexes in important processes related to chemical and biological recognition. Only few of them have concisely analyzed the change of aromaticity in aromatic rings upon complexation of alkali metal cations using nucleus-independent chemical shift (NICS) values as indicators of aromaticity.

In this work we have analyzed the changes of local aromaticity upon Li$^+$ association in a series of extended fused aromatic compounds. Our aim was to discuss whether the strength of the binding of the lithium cation to a given aromatic ring in a molecule is related to its aromatic character or to the change in aromaticity upon complexation. To take into account the multidimensional character of aromaticity, local aromaticity measures have been: the *para*-delocalization index (PDI), the aromatic fluctuation index (FLU), the harmonic oscillator model of aromaticity index (HOMA), and the nucleus-independent chemical shift (NICS).

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Thiotepa antitumor drug: DFT and ab initio study for predicting its biological activity

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In this study we will present recent computational work on thiotepa drug of general formula (C$_2$H$_4$N)$_3$PS. Thiotepa drug is an alkylating agent whose antitumor action consist essentially in alkylating the N7 position of guanine base in DNA. The alkylating drug thiotepa has been the subject of just few theoretical studies. The aim of the latter studies was to clarify the molecular structure of thiotepa.

Kosvich et al[1] have noted a discrepancy between molecular structure in solid state (X-ray study) and the MNDO optimized structure. Kosvich et al[1] did not specify molecular symmetry of thuiotepa. Igore Novak et al[2] reported the ab initio calculation with full geometry optimization suggesting that the molecular structures resemble a "windmill" shape corresponding to C$_{3v}$ symmetry with Nitrogen ion pairs (Nip) in the Trans conformation vs. PS bond. Another conformer with C$_3$ symmetry have a gauche arrangement of the Nitrogen ion pair were found higher in energy than C$_{3v}$. Igore Novak et al[2] have also carried out semi-empirical calculations (AM1, PM3, MNDO), all of them suggested C$_3$ symmetry as the conformation with minimum energy.

It is important to note that in the literature the crystal structure indicate the existence of distorted C$_3$ symmetry with each < (Nip) PS angle slightly different. In the present investigation a detailed theoretical study of thiotepa drug by performing ab initio and density functional type calculations utilizing 6-31G* basis set to obtain several descriptors of the electronic charge distribution such as dipole moment as well as electrostatic potential charge. A biological activity of thiotepa have been studied using the computed highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy value.

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