Poster session and flash presentations - ISTPC 2017

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BOOK OF ABSTRACTS

Flash presentations

Tackling strong non-dynamic correlation effects with PNOF7

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Abstract

Natural Orbital Functional Theory[1] is based on the approximation of the second order density matrix $\left({}^2D\right)$ in terms of the occupancies $\left(\{n_i\}_{i=1}^{M}\right.$ where *M* is the size of a basis formed by the natural orbitals $\left.\{\chi_i\}_{i=1}^{M}\right)$ obtained from the diagonal representation of the first order density matrix. The ${}^2D$ is therefore a functional of the occupancies ${}^2D[n]$ within NOFT. The purpose of NOFT is to avoid the computation of the usually expensive exact ${}^2D$ (the one obtained from a partial summation of an *N* electron wave function) which is required for the evaluation of the electronic energy:

$$E[{}^2D]=T[{}^1D]+V_{ext}[{}^1D]+V_{ee}[{}^2D] \qquad (1)$$

Upon replacing the exact ${}^2D$ in Eq. 1 with the aproximated ${}^2D[n]$ we obtain a NOFT functional [2]. The recently developed PNOF7 functional[3] is put to the test in the present work; Specially in the strong non-dynamic correlation regime. The systems studied are the two-sites and the six-sites ring Hubbard models. The Hubbard model has been widely used for developing and benchmarking functionals[4] but it also serves as a practical model to study systems of physical interest (e.g. fermions trapped in optical lattices, Mott insulators, etc.) [4].

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Extending the AP1roG model

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My current research is situated in the realm of the antisymmetric product of interacting geminals (APIGs) [1]. In second quantization, we would write this wave function model as

$$|\text{APIG}\rangle = \prod_{p}^{N_P} \left(\sum_{i}^{K} C_p^i \hat{a}_{i\alpha}^\dagger \hat{a}_{i\beta}^\dagger \right) |\text{vac}\rangle \ , \tag{1}$$

where N_P is the number of electron pairs (i.e. half of the number of electrons in the system), K is the number of spatial orbitals and C_p^i is the coefficient of the i-th spatial orbital in the p-th geminal. The APIG model is an approximation of doubly occupied configuration interaction (DOCI [2]), in a way that the expansion coefficients of the DOCI wave function are written as permanents of geminal coefficients, leading to intractability. Recently, however, a computationally tractable form of APIG, called AP1roG (antisymmetric product of 1-reference-orbital geminals),

$$|\text{AP1roG}\rangle = \prod_{p}^{N_P} \left(\hat{a}_{p\alpha}^\dagger \hat{a}_{p\beta}^\dagger + \sum_{a=N_P+1}^{K} C_p^a \hat{a}_{a\alpha}^\dagger \hat{a}_{a\beta}^\dagger \right) |\text{vac}\rangle \ , \tag{2}$$

with a labeling virtual orbitals, has shown to lead to energies in strong agreement with DOCI, but with only a fraction of the computational cost, using a projected Schrödinger equation approach. [3] The AP1roG wave function is equivalent to pair coupled cluster coubles [3, 4], and performs well for strongly correlated systems. [3]

Currently, I am working on the optimization of the underlying spatial orbital basis, which is needed to ensure size-consistency [3]. Orbital optimization in AP1roG has already been formulated using a variational [5] and projected [6] approach, but since the DOCI energy landscape is riddled with local minima, some research effort should be devoted to making sure that we end up in a global minimum rather than a local one.

Further topics of interest concerning the AP1roG wave function include open-shell systems, magnetic field effects, relativistic effects for rare earth elements, and excited states.

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Basis set effects on multiphoton processes in H_2^+

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Abstract

New theoretical approaches are demanded to correctly describe multiphoton processes that occur when a multi-electron system (e.g. an atom or a molecule) interacts with a strong laser field. The quantum-chemistry methods based on Gaussian functions demonstrated to be successful in the description of bound and excited states of a multi-electron system in a time-independent framework. The extension of these methods to the time-dependent domain give a new perspective to investigate electron correlation of large molecular systems in multiphoton processes. However, the main problem of these methods lies in the difficulty to accurately represent the continuum part of the system eigenstate spectrum. To explore this issue we explicitly solved the time-dependent Schrödinger equation (TDSE) for H_2^+ under the action of an intense electric field, by using three different ways of representing the system wave function: with a Gaussian basis set (Gaussians), with a B-splines basis set (B-splines) and in a discretized real-space grid (Grid). This study compares the efficiency of a Gaussian basis set, optimally designed for the continuum [1-2], with B-splines [3] and grid calculations, which demonstrated to be suitable to describe processes involving continuum states. Above-Threshold Ionization (ATI) and High-order Harmonic Generation (HHG) spectra have been obtained for different laser parameters and intermolecular distances. The two-center interferences, expected in molecular HHG [4], have been observed, see Figure 1.

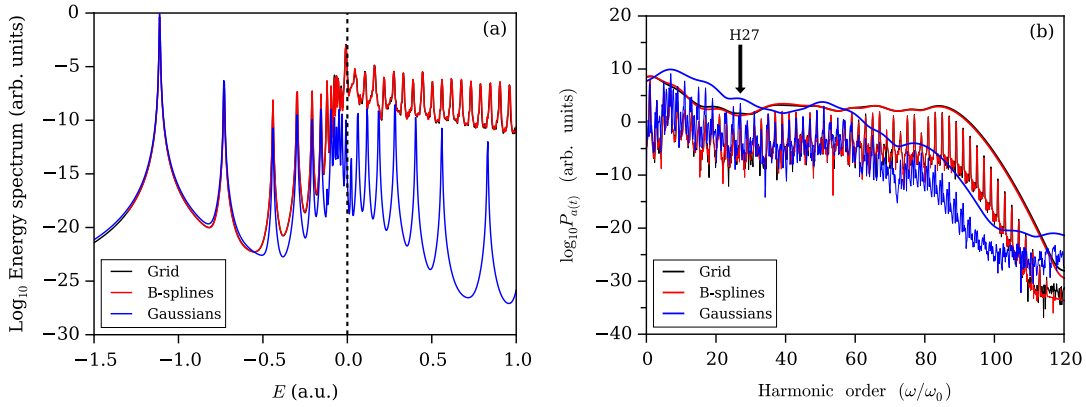

Figure 1: Comparison of ATI **(a)** and HHG **(b)** spectra for H_2^+ at its equilibrium distance in one dimension. Calculations have been performed with a Ti:Sapphire(800nm) trapezoidal shaped laser pulse with a total duration of 10 optical cycles and a maximal intensity of $I_0 = 5 \cdot 10^{14}\mathrm{W/cm}^2$.

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Posters

Relativistic correlated calculations of the thermodynamics properties of gaseous plutonium oxides

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The PUREX process has been designed for the reprocessing of spent nuclear fuel to separate uranium and plutonium from the fission products. Following the dissolution of the irradiated fuel in aqueous nitric acid, uranium and plutonium are transferred to an organic phase by intensive mixing with an organic solvent extraction (tributyl phosphate in kerosene), while fission products remain in the aqueous nitric phase. The degradation products of TBP by hydrolysis can react with nitric acid through very exothermic chemical reactions that can lead to a rapid increase of temperature in the reprocessing vessels. In the worse cases, the in-cell solvent fire is considered to be an important postulated accident even if its probability is low. In such cases plutonium is released in volatile forms such as PuO_2, PuO_3 or $PuO_2(OH)_2$. Our theoretical study focusses on the thermodynamics properties of those molecules, in particular the former two species for which large experimental uncertainties remain.

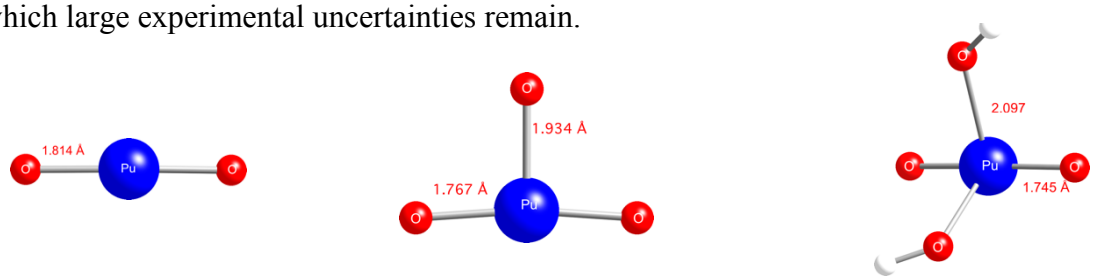

Figure 1: PuO_2, PuO_3 and $PuO_2(OH)_2$ molecules in C_{2v}, D_{2h} and C_2 respectively

However, to assess the desired accuracy, highly accurate calculations are required including static and dynamic correlation effects as well as relativistic effects. In particular, the clear multi-reference character of the wave-function of those compounds requires that the energies of formation to be computed with multi-configurational quantum chemical methods like CASSCF and CASPT2. Spin-orbit interaction is treated *a posteriori* with the state-interaction RASSI method. Our results illustrate the complex multi-configurational character of PuO_3 and $PuO_2(OH)_2$. The computed thermodynamics quantities reach a high accuracy allowing us to predict the composition of the released volatile products.

This work has been supported by grants funded by the French national agency for research under the contract ANR-11-LABX-0005 chemical and physical properties of the atmosphere (CaPPA).

The Effect of Ions on the Clustering of Organic Acids and Sulfuric Acid

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Introduction

According to current knowledge, new-particle formation is believed to involve sulfuric acid coupled with a stabilizing component such as ions, bases, or oxidized organic compounds. We have previously studied the cluster formation between sulfuric acid and pinic acid or MBTCA, and found a favorable interaction between them. However, by cluster kinetics calculations we showed that the growth of the clusters is essentially limited by a weak binding of the largest clusters, suggesting that pinic acid and MBTCA cannot contribute the cluster growth when clustering occurs via neutral pathways (Elm *et al.* 2017). Here we have investigated the ability of bisulfate anion, ammonium cation, and ammonia to enhance the formation and growth of sulfuric acid and pinic acid or MBTCA clusters.

Methods

Cluster structures have sampled using semi-empirical technique. Geometries are optimized and frequencies are calculated using three density functionals M06-2X, PW91, and ωB97X-D with the 6-31++G** basis set. Electronic energy corrections were performed using DLPNO-CCSD(T)/def2-QZVPP level of theory. Obtained Gibbs free energies are subsequently used to further investigate cluster kinetics.

Conclusions

The interaction with ions and sulfuric acid or carboxylic acid group is strong, and thereby small two-component ionic clusters are found to be very stable against evaporation. Figure 1 shows the molecular structure of $(MBTCA)_2(H_2SO_4)_3(NH_4^+)$ cluster. Ammonium ion is in the core of cluster and it forms hydrogen bonds with carboxylic acid groups and sulfuric acid which stabilize the cluster structure.

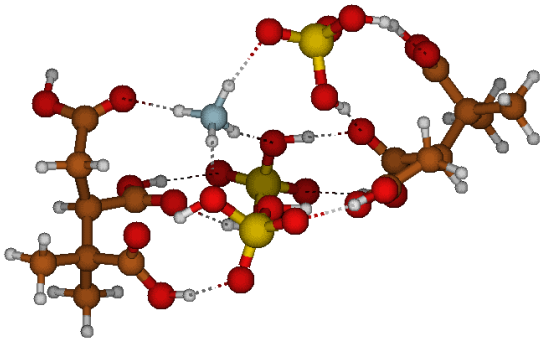

Figure 1. The molecular structure of $(MBTCA)_2(H_2SO_4)_3(NH_4^+)$ cluster.

The presence of bisulfate stimulates the cluster formation by addition of sulfuric acid, whereas the presence of ammonium favors the addition of organic acids. Bisulfate and ammonium enhance the first steps of cluster formation (see Figure 2); however, at atmospheric conditions cluster growth is limited due to the weak interaction of the larger three-component clusters which results in fast evaporation. (Myllys *et al.* 2017). Therefore, it is unlikely that organic acids and sulfuric acid, even together with bisulfate, ammonia, or ammonium can drive new-particle formation via clustering mechanisms, suggesting that perhaps chemical reactions are needed to explain observed atmospheric new-particle formation events in the presence of oxidized organic compounds.

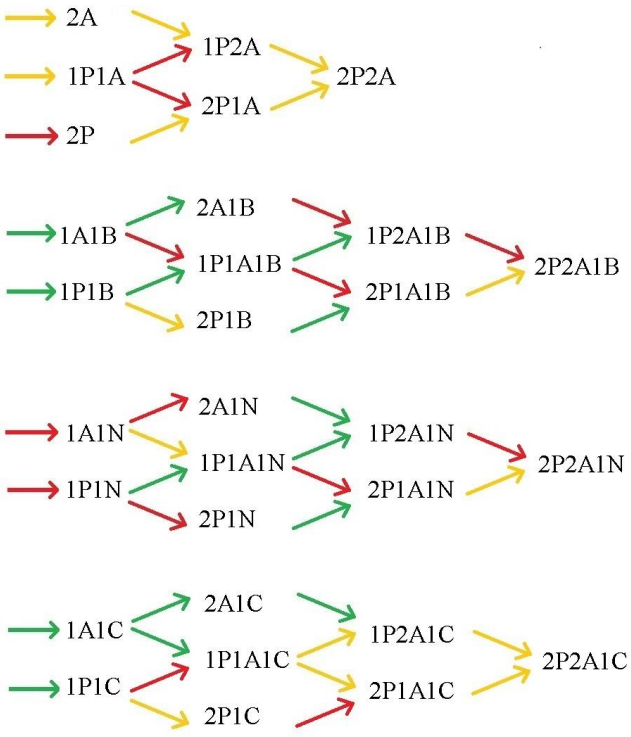

Figure 2. Gibbs free reaction energy diagram for pinic acid clusters at 298 K and 1 at. Red > -5 kcal/mol, yellow -5to -10 kcal/mol green <-10 kcal/mol. P=pinic acid, A=sulfuric acid, B=bisulfate, N=ammonia, and C=ammonium.

Elm, J., Myllys, N., Olenius, T. *et al.* (2017), *Phys. Chem. Chem. Phys.* 19, 4877-4886.

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Spin-reversal energy barriers of 305 K for Fe^{2+} d^6 ions with linear ligand coordination

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The notion of single-molecule magnet (SMM) came into the field of quantum magnetism with recognizing that certain molecules may display, as individual entities, the behavior of a tiny magnet. Their essential characteristic is a slow relaxation of their magnetization if no external field is applied. SMM physics was first pointed out by Sessoli *et al*. for a Mn_{12} complex, in 1993 [1]. Since then the field advanced dramatically, with dozens of new SMM's being reported, either *d*-metal or *f*-metal based. As concerns their specific magnetic properties, the most remarkable are nowadays the Tb^{3+} and Dy^{3+} SMM's with N_2^{3-} ligand bridges [2,3], some lanthanide single-ion magnets with high-symmetry environment [4], the fullerene-encapsulated *f*-electron SMM's [5], and the linear Fe^{1+} complexes [6]. Interestingly, SMM-like behavior has been also identified recently for linearly coordinated Fe-ion substitutes within the solid-state matrix of Li_3N [7]. Here we provide *ab initio* quantum chemistry results for both Fe^{1+} d^7 and Fe^{2+} d^6 species at Li lattice sites in Li_3N. A remarkably large magnetic anisotropy energy of 305 K is computed for divalent Fe^{2+} d^6 substitutes with D_{6h} environment. This is similar to values calculated by the same approach and confirmed experimentally for linearly coordinated monovalent Fe^{1+} d^7 species, among the largest so far in the research area of single-molecule magnets. By breaking D_{6h} symmetry through creation of an additional Li-ion vacancy in the immediate neighborhood, the magnetic anisotropy is reduced to 14 meV, in agreement with experimental data for very low concentration of Fe species in Li_3N.Our *ab initio* results therefore mark a new exciting exploration path in the search for superior single-molecule magnets, rooted in the $d_{xy}^{1.5}d_{x^2-y^2}^{1.5}d_{z^2}^1d_{yz}^1d_{zx}^1$ configuration of d^6 transition-metal ions with linear or quasilinear nearest-neighbor coordination. This d^6 axial anisotropy may be kept robust even for symmetries lower than D_{6h}, provided the ligand and farther-neighbor environment is engineered such that the $d_{xy}^{1.5}d_{x^2-y^2}^{1.5}d_{z^2}^1d_{yz}^1d_{zx}^1 - d_{xy}^1d_{x^2-y^2}^1d_{z^2}^2d_{yz}^1d_{zx}^1$ splitting remains large enough.

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Site-Occupation Embedding Theory

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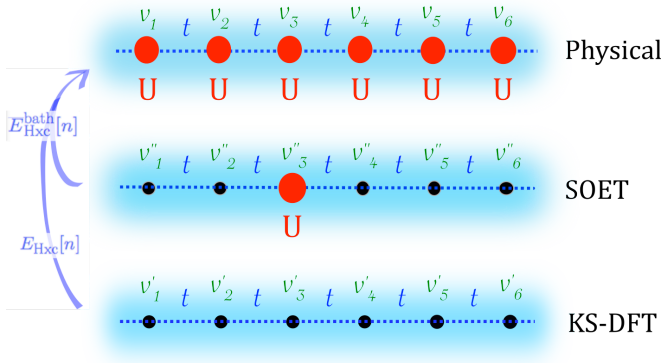

Modelling strongly correlated electronic systems is still challenging in both quantum chemistry and condensed matter physics. A system is said to be strongly correlated if its physical properties are governed by non-trivial electron-electron interactions. For instance, this is the case for transition metal oxides when the electrons are close to a metal-insulator transition. In this case, mean-field approaches such as the Hückel method or Hartree Fock give a wrong description of the properties of the system. To deal with such systems, we have to go beyond the mean-field approximation:

- On the one hand, the interaction can be computed thanks to an explicit treatment of the electronic wavefunction (Density Matrix Renormalization Group[1], post Hartree-Fock methods), which is computationally expensive.
- On the other hand, Kohn-Sham Density Functional Theory (KS-DFT)[2] is a computationally low cost method with a relatively good accuracy. However, standard approximations made for the density functionals often fail to describe strong correlation energies.

One strategy is to build a theory which makes the best compromise between computation time and accuracy. In this context, an embedding scheme in principle exact called *Site-Occupation Embedding Theory* (SOET)[3,4] treats the correlation explicitly on some sites (called impurities), while the rest of the system is noninteracting (called bath) and treated with a density functional. SOET is therefore a rigorous combination of wavefunction method (DMRG) and DFT. The Hubbard model (see Figure) will be our laboratory because of its simplicity as well as its physical richness. In this embedded context, approximate density functionals based on KS-DFT applied to model Hamiltonians[5] and on the standard Anderson impurity model[6] are studied.

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Modelling the electronic states of polyphenylene-ethynylenes

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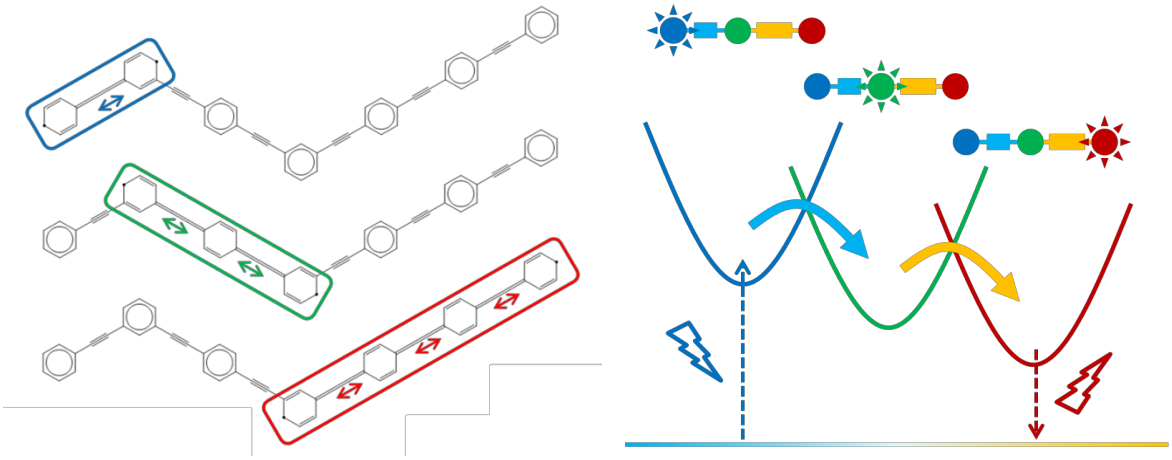
Hydrocarbon dendrimers are macromolecules experimentally well-known for their exceptional optoelectronic properties [1]. Polyphenylene-ethynylene (PPE) dendrimers behave as light-harvesting antennae in which unidirectional exciton transfer occurs along a series of linear, conjugated building blocks connected *via* the *meta*-substitution of phenylene rings. Thus, PPE dendrimers have received much interest as artificial photosynthetic systems. Recent theoretical investigations based on semi-classical dynamics simulations [2] have indicated that the unidirectional energy transfer involves a cascade of conical intersections between excited states localized on different linear fragments. Yet, the calculations of full-dimensional potential energy surfaces (PES) remains out of reach for any level higher than semi-empirical, due to the size of the systems.

Different types of calculations (TDDFT, extended Hückel) enlightened a strong hierarchy within the interactions governing the electronic structure of *meta*-PPEs; in particular, their first excited states result from weak couplings among the excited states of the corresponding *para*-PPEs. This allows us to build a new type of diabatic representation for the PES under the form of a Hubbard matrix, whose eigenvalues are expected to reproduce the adiabatic energies at a TDDFT level of theory. The dependence on the nuclear coordinates will be expressed through the Hubbard parameters that are involved in the energies of the diabatic states (diagonal) and their couplings (off-diagonal); as all are local, each will only depend on a few nuclear coordinates, thus simplifying drastically the potential energy functions. The explicit expression of the Hubbard matrix elements through their constituting parameters as functions of the nuclear coordinates will be based on a multiscale approach.



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Ab initio study of dysprosium-based Single Molecule Magnets

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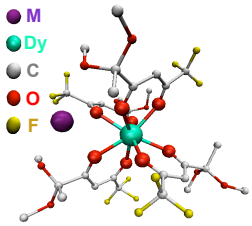
Since the beginning of the century, lanthanide-based Single Molecule Magnets (SMMs) have attracted the interest of the molecular magnetism community over their transition metal counterparts. [1-4] They exhibit strong magnetic anisotropy, slow magnetic relaxation and a large energy barrier to the reversal of the magnetization. These properties arise from the effect of both the crystal field created by the surrounding ligands and the spin-orbit coupling of the lanthanide centre.

Among the large family of lanthanide-based SMMs, dysprosium(III)-based molecular systems are, by far, the most studied class of compounds since they provide good SMM candidates. These systems are numerous in the literature due to the large Ising-type (axial) magnetic anisotropy coupled with the unique electronic structure of the dysprosium(III) ion (Kramers' ion) which allow a bistable ground state with a large magnetic moment $m_J = 15/2$.

On the computational point of view, the SA-CASSCF/(MS-CASPT2)/RASSI-SO approach is a powerful tool to obtain a good description and a good understanding of both the electronic and the magnetic properties of such systems.

In this work, we use such computational approach to investigate the effect of the counter-ion M on both the electronic and magnetic properties of a series of $[DyL_4]M$ compounds (where L = 6,6,6-trifluoro-5-hydroxy-2,2-dimethoxy-4-hexen-3-one and M = Li, Na, K, Cs).



Representation of a $[DyL_4]M$ system

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Optical property of buckled GaAs monolayer under transverse electric field

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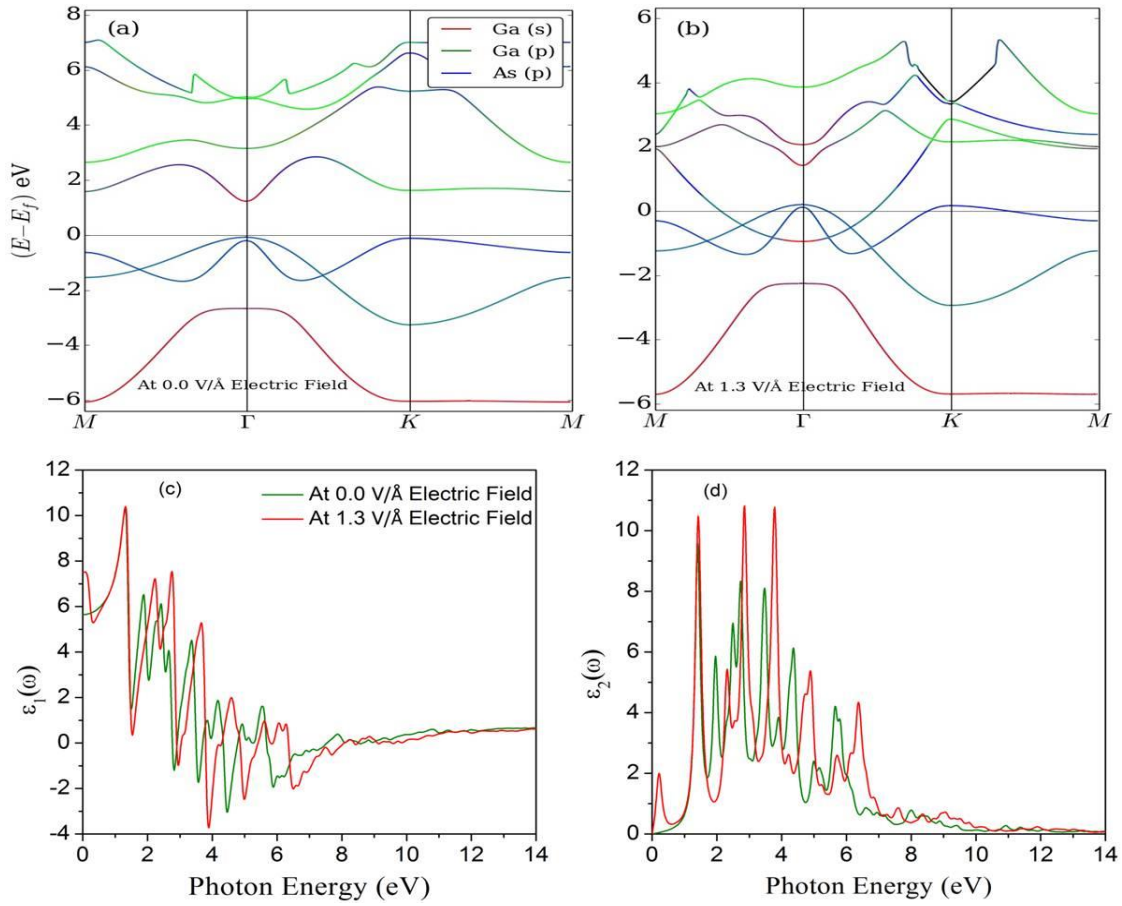
Buckled GaAs monolayer has a direct band gap semiconductor with energy gap of 1.31 eV in the absent of electric field. When we applied transverse electric field, the value of band gap decreases with increasing of electric field strength. In our previous work [1], it is observed that the Buckled GaAs monolayer becomes metallic at 1.3 V/A. We investigate the optical properties such as photon energy-dependent dielectric functions, refractive index, extinction coefficient, absorption spectrum and reflectivity of buckled GaAs monolayer in the semiconducting phase i.e. absence of external electric field and metallic phase i.e. presence of external electric field using density function theory.



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Breathing mode of C_{60} using a quantum hydrodynamic model

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This work is a part of the project QHYDRO funded by European Commission under the action of Marie Skłodowska-Curie Individual Fellowships (H2020-MSCA-IF-2015-EF). The goal of the project is the development and implementation of a set of quantum hydrodynamic (QHD) models to investigate many open problems in the emerging field of nanoplasmonics. We are in the first quarter of the project. In this particular problem, we have studied the breathing mode of C60 by implementing QHD model by means of a variational approach. We have studied the ground state and the linear response frequency of the system. A further investigation to study the dipole mode in the nonlinear regime is under way. In the near future nonlinear, nonlocal, and quantum effects of several configurations of nano-objects (i.e., dimers and trimers of metallic nanoparticles, metal-dielectric multilayers, nanoparticles in the vicinity of a thin metal film, and arrays of nanoparticles interacting via the dipole force) will be studied.

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Ab initio study of inorganic perovskites: towards the prediction of $PbZr_{1-x}Ti_xO_3$ (PZT) IR spectrum

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Abstract

Physical and chemical properties of materials are dependent on its chemical composition, its thickness, the temperature, … . New applications of materials can be developed if we understand the link between these factors, their fabrication conditions and their phase transitions. $PbZr_{1-x}Ti_xO_3$ (PZT), for instance, is commonly used for its high piezoelectric effect at x=0.48 (morphotropic, tetragonal / rhombohedral, phase boundary) but is currently studied for its possible interest in the information storage (RAM). To do so, the AILES beamline team of SOLEIL chose IR spectroscopy[1].

However, to fully interpret the experimental spectra, theoretical modelling is necessary[2]. In order to model PZT, the first step was to correctly reproduce the previous experimental and theoretical results on $PbTiO_3$ (PT) and $PbZrO_3$ (PZ) with a same set of parameters. In this purpose, we used the Density Functional Theory (DFT) code CRYSTAL 2014 which allows the application of the Linear Combination of Atomic Orbitals (LCAO) method on periodic systems. Structure geometry optimisations and electronic structure calculations were performed first. Then, harmonic vibrational frequencies were determined for transverse optical (TO) phonons, as well as those for longitudinal optical (LO) phonons, by way of the density functional perturbative theory (DFPT). Comparison with previous experimental and theoretical results permitted to find a set of parameters well suited to correctly describe both PT, PZ and, hopefully, PZT.

Next step is the study of PZT. We started with the simplest case of x=0.75. As it is a solid solution, we cannot define a unique lattice. Thus, it was decided to use the supercell (2×2×2) technique and to consider the 5 independent configurations (*i.e.* the different ways to distribute Ti and Zr atoms inside the supercell). Each configuration has a different space group (Pm, Pmm2, Cm11, P1 and Cm11) that seem incompatible with the tetragonal geometry observed experimentally[3]. However, our geometry optimisation results show a good accordance with the experimental ones. Indeed, even though none of these configurations is of tetragonal space group, they have their geometrical characteristics (a=b≠c and α=β=γ=90°) with a small difference between the lattice parameters of each configuration. Moreover, the IR absorption spectrum of one of the configurations has been calculated and compared to the simulated spectra of PT and PZ (Figure 1). As we can see, PZT IR spectrum is similar to the PT one, with the appearance of some PZ features, confirmed by the comparison of wavevectors associated to the phonon modes.

Illustration

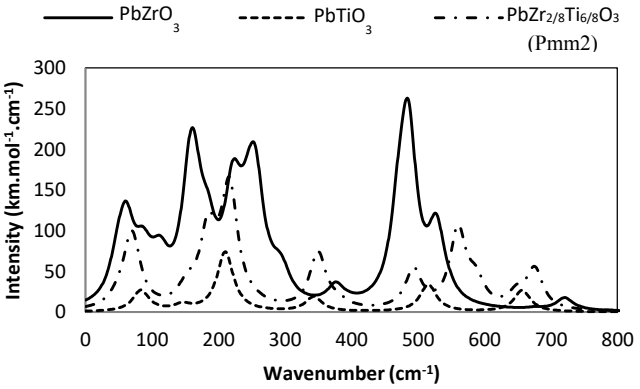

Figure 1. Calculated IR absorption spectra of $PbZrO_3$, $PbTiO_3$ and of one statistical configuration of $PbZr_{2/8}Ti_{6/8}O_3$.

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Making 2-electron response reduced density matrices N-representable

In quantum mechanics, any system can be described by the Schrödinger equation. However, this eigenvalue problem is only exactly solvable for a few very specific systems. This is due to the exponential scaling of the Hilbert space with the number of particles. Consequently, one has to rely on approximate methods. A great variety of approximations has been developed each with their own strengths and weaknesses. In recent years, the double occupied CI[1] [2](DOCI) method has gained a lot of interest because it was found to be an excellent model for describing static correlation in strongly correlated systems. Recently, several of us introduced a computationally tractable approximation to DOCI calles the anti-symmetric product of 1-reference orbital geminals[3] (AP1roG), also known as pair-coupled cluster doubles[4] (pCCD).
In methods like geminal-based approaches or coupled cluster that are solved using the projected Schrödinger equation, direct computation of the 2-electron reduced density matrix[5] (2-RDM) is impractical. Furthermore, the 2-RDMs from response theory are not N-representable[6]. That is, the response 2-RDM does not correspond to an actual physical N-electron system. The necessary and sufficient conditions for a 2-RDM to be N-representable are known, however they are of no practical use since it would require the knowledge of the ground state energy of every possible two-particle Hamiltonian. The most important necessary conditions for N-representability of the 2-RDM were originally proposed by Garrod and Percus[7] (PQG-conditions).
We present a new algorithm for making these non-N-representable 2-RDMs approximately N-representable. We aim to find the 2-RDM with the right properties that is the closest (w.r.t. the Frobenius norm) to the 2-RDM from the response method. This optimization problem can be formulated as a semidefinite programming problem[8]: the square norm of the difference between the response 2-RDMS and the targeted 2-RDM is minimized under the constraint that the trace is normalized and the 2-RDM, Q- and G-matrices are positive semi-definite, i.e. their eigenvalues are non-negative.

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Green's function-based site-occupation embedding theory: the example of the Hubbard dimer

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Abstract

In exact density-functional theory (DFT), the physical electronic density is recovered by using a fictitious non-interacting reference system known as the Kohn-Sham system. In practice, this approach is insufficient because approximate functionals and a single Slater determinant turn out to be a poor starting points, especially for strongly correlated systems. In order to improve DFT, one could start from another fictitious reference system, namely a partially interacting one, such as an embedded impurity.

In this work, the site-occupation embedding theory (SOET)[1,2] is applied to the one-dimensional Hubbard model in the context of Green's functions. The embedded impurity system is treated exactly by a high level method such as exact diagonalization or density matrix renormalization group (DMRG),[3] whereas the non-interacting bath is treated by a correlation functional which can be derived from the Green's function and the self-energy. The exact theory is illustrated by the analytically solvable two-site Hubbard model. In the case of the symmetric Hubbard dimer, the exact impurity and bath self-energy are calculated by using the Dyson equation. Thanks to the simplicity of this toy model, we gain more insight into the Green's function SOET formalism. The correlation functionals are derived via the adiabatic connection by integrating over the coupling constant,[4] and the embedding potentials, which restore the density of the physical system, are obtained by using the Sham-Schlüter equation.[5]

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Exact individual state energy expression from ensemble density-functional theory for excited states

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Abstract
Ensemble density functional theory (eDFT) is in principle an exact alternative to time dependent density functional theory (TD-DFT) for the calculation of excitation energies[1].In eDFT a calculation for an individual state is usually not possible due to the normalization constraint on weights (i.e.,they sum up to 1)[2]. Indeed, differentiating the ensemble energy with respect to the ensemble weights only gives access to excitation energies.[2, 3, 4, 5, 6] However this normalization can be removed and non-normalized weights are now used.
In this poster I explain how the eDFT in this new context gives the individual states. This formalism can be used, for example, for computing excited-state molecular gradients.[8] Subsequently, calculations are applied on the non-symmetrical Hubbard dimer where some results about eDFT have already been shown. [6, 7]

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Keywords: ensemble density-functional theory for excited states, individual excited states, Hubbard dimer, strong correlation.

Numerical investigation of the thermodynamic properties of aqueous species involved in the transfer of contamination of nuclear reactors

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The chemistry occurring in nuclear reactor circuits, especially due to the high radio toxicity and extreme conditions (currently around pressures of 150 bar and temperatures from 280 to 330 °C), is rich but also difficult to be characterized by standard experimental techniques. Even so, some experimental data have been obtained, but there remains large zones to be explored. Therefore, the aim of this study is to extract some thermodynamic quantities by the use of simulation, to compare them with the experimental data and to extrapolate the behavior on domains not yet explored. In particular, we will focus on the behavior of chemical species (Ni^{2+} and Co^{2+} ions), responsible agents of contamination (primary circuit) fouling and clogging (secondary circuit).

Our objective is to probe the local structure and explore the trends for Ni^{2+} and Co^{2+} ions in the bulk conditions with molecular dynamics (MD) simulations that allows us to monitor the dynamics of a hydrated ions in bulk conditions in a long-time scale ($>$ 10 ns). However, the reliability of the MD results entirely depends on the quality of the force-field (FF), i.e., the description of the interaction between the solute and the solvent (M/water molecule interaction), and also on the description of the solvent properties. We propose an innovative FF model that accounts, not only for the standard electrostatic and repulsion interactions, but also for polarization and dispersion or charge-transfer terms, many-body effects, and explicit hydrogen bonds in the water/water interactions.

The interactions are described by a consistent FF model adjusted to state-of-the-art *ab initio* calculations (multi-configurational methods, i.e CASPT2), i.e., without using any experimental input, for the Ni^{2+} and Co^{2+} ions. We present the associated preliminary results coming out from bulk molecular dynamics simulations, so far at room temperature and standard pressure. The results will be compared to existing X-ray and EXAFS data.

Theoretical study of deep-center defects in some semiconductors

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The prototypical example of a deep-center defect is the nitrogen-vacancy (NV) center in diamond. The spin states of this defect can be optically manipulated at room temperature which makes it attractive for quantum applications. However, the fabrication of devices from diamond is quite difficult. The prospective material which is believed to have similar properties as diamond is SiC. Moreover, SiC growth and device engineering technologies are well established. The aim of this work is to obtain a reference method to model the electronic properties of the NV-center in diamond (C), and to transfer it to various defects in silicon carbide (SiC), so as to understand the photoconversion process in this material.

We first study the point defect consisting of one carbon atom substituted by one nitrogen atom in diamond with the density functional theory in the local density (LDA) and generalized gradient (GGA) approximations. Despite much work has been done on N substitutional center in diamond, there is still disagreement in results obtained with different theoretical methods, and between theory and experiment, for instance for the symmetry of the atomic structure of the point defect, and for the ordering of the electronic energy level(s) that appear in the band structure, and in particular in the band gap, due to the presence of the defect. To obtain these quantities, some calculation issues have to be resolved.

Firstly, the knowledge of proper band gap edge is crucial in order to study defect levels. But one of the most common problems is the band-gap problem of semiconducting and insulating materials: it is well-known that the DFT systematically underestimate their electronic bandgap. To go beyond DFT, quasiparticle correction can be introduced with the GW method [1]. Recently, it has been reported that the use of with range-separated hybrid functional HSE06 within DFT can yield the band gap of diamond with an accuracy better than 0.1 eV [2]. To study the charge state of the defects defect levels, an empirical method has been introduced, with an empirical bulk polarization energy correction applied to large supercells [3].

Since defects we are going to study have charged state, the long-range interaction poses an important problem. The conventional method is to neutralize the net charge with the homogeneous background jellium density. An alternative approach is the local moment countercharge method (LMCC) [4]. Nonetheless, by introducing a defect in the supercell, both electric and elastic deformations arise which have hardly reached the equilibrium at the boundary of the cell. This creates interactions between neighboring cells which must be carefully studied. We plan to perform ab initio calculations within DFT and the HSF06 exchange and correlation functional, and eventually to study the effect of quasi-particle corrections. Group theory will be used to develop analytical impurity wavefunctions of the defects in their ground and excited states. Finally, the role of electron-phonon coupling will be studied to understand the spin-decoherence time.

Calculations are performed using the Quantum ESPRESSO package. Supports from the ANR-10-LABX-0039-PALM program (Femtonic project), from DGA (France) and from the CEA-CNRS NEEDS-Matériaux program (France) are gratefully acknowledged. Computer time is granted by École Polytechnique through the LLR-LSI project and by GENCI (Project No. 2210)

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Title: Sub-systems approaches to model molecules containing heavy elements in solids and surfaces.

Summary:

The accurate description of electronic structure of large systems requires a development of new quantum approaches that give us the best compromise between the accuracy and the calculation cost. In such cases embedding approaches, which are based on the division of a system into a number of smaller subsystems, are appealing since in many cases the property of interest is localized in a small part of the total system. Therefore, it is often not desirable to treat the whole system at the same level, but instead to apply methods in which different parts of the system are described using different approximation. Usually, one combines a high-level method for the important part of the system (the subsystem of interest) with a low-level method for the environment.

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Electronic excitations in the irradiation of materials:
from the stopping power to displacement cascades

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Irradiation damage in condensed matter is central to many technological fields: materials in nuclear plants of course, but also electronics in space which is subjected to the solar irradiation, and living matter treated by radiotherapy to eliminate tumors. For all these subjects, an accurate knowledge of the interaction between the irradiating projectile and the target is crucial. More precisely, this interaction can be split into two contributions: a classical collision part and a purely quantum mechanical part induced by the excitation of the electrons in the target material.

The present thesis is devoted to the latter contribution that is way more complex and far less studied. Employing numerical modeling within quantum mechanics for the excited electrons, we aim at predicting the energy transfer from a swift impinging ion and condensed matter, in order to understand its influence on damage in materials. The computer simulations will combine the precise quantum mechanical description of the interaction with classical molecular dynamics of the damage, with an overall multi-scale approach.

Previously it was seen that the linear response theory is in a good agreement with experiment for proton irradiation [3]. However, it predicts square dependence on charge of stopping power, which is wrong according to experiments. To extend simulations to any incident particle (in charge and mass) and for any material, one needs to use the Real-Time Time Dependent Density-Functional Theory (RT TD-DFT) calculations.

In order to calculate a time evolution of a system under an external excitation, we solve numerically the time-dependent Schrödinger equation. As a starting point, we use the ground state of the system, obtained from DFT within the *ab initio* program MOLGW (developed in the SRMP CEA Saclay [1]). We calculate the evolution of the system using the time propagator technique with a certain predictor-corrector scheme [2].

Despite the final goal to calculate an interaction between a projectile and material, we have first studied light excitation of model systems. With a short in time pulse of homogeneous electric field we excite the system and then calculate its time evolution. During the RT TD-DFT simulation we calculate the dipole moment of the system and then taking the Fourier transform of $\vec{d}(t)$ we can calculate absorption of the system. We have achieved a good agreement with similar RT TD-DFT calculations [4] as well as linear response theory results (in weak excitation regime).

For the moment we are developing the programming code in order to calculate projectile-matter interaction. We have accomplished first step of this part which was devoted to description of projectile as a “naked” nuclei without electronic states around it. Our prospective is to describe a projectile with electronic states and realize molecular dynamics to calculate movement of nuclei of material as well as real projectile trajectory during the RT TD-DFT simulation.

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Study of the Keto-Enol Tautomerism in Acetylacetone, in Gas Phase and in Solvent.

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Abstract

The keto-enol tautomerism constitutes a relevant process in organic and biological chemistry. For example, this reaction occurs in the DNA basis and can induce some mutation points. Hence, this isomerism has been, and is still, widely investigated. This process is a proton transfer which is influenced by many environmental factors as the solvent nature, the temperature and so on[1].

We studied this equilibrium involving acetylacetone (ACAC) molecule in vacuum[2] and in explicit water solvent. The role played by the water molecules on the reaction barrier and the origin of their catalytic effect were also investigated. We used the density functional theory (DFT) through the VASP (Vienna Ab-initio Simulation Package) code[3-4] and we applied the NEB (Nudged Elastic Band) method[5] to evaluate the activation energy. To understand the catalytic effect of the water molecules from the geometries of the activated complexes, we partitioned the different energy contributions in the solvent and in the ACAC basin according to the QTAIM theory[6].

This study was done at 0 Kelvin. However, the temperature was proved, in literature, to have a strong influence on the activation barrier[7]. Therefore, it will be interesting to investigate this process by molecular dynamics.

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TITLE
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Ab-initio studies of excited states in vacancy impurity complexes.

ABSTRACT
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Nitrogen Vacancy defects in diamond have become over the last years an important candidate for a bulk room temperature quantum information processing device. We investigate the feasibility of calculating properties such as inter-system crossings between triplet and singlet levels, spin-spin interaction parameters and deformation tensors using state-of-the-art ab-initio techniques.