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# Réunion générale du GdR-CORREL

## Corrélation Électronique

### Marseille – 8-10 Juillet 2015

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Campus St-Charles  
Amphi de Sciences Naturelles

## Résumés des communications orales



**GDR CORREL**  
méthodes corrélées pour la structure électronique



## Programme

### MERCREDI, 8 JUILLET

8:30	Accueil des participants (Amphi Sc.Nat.)	
8:55	Ouverture	
		<i>Y. Carissan</i>
9:00 - 10:30	<b>Pr. Willem Klopper</b> <i>Overview on explicitly correlated methods</i>	
10:30 - 11:00	Pause café – Installation des posters (salles C1 et C2)	<i>J.-P. Malrieu</i>
11:00 - 11:20	<b>Denis Hagebaum-Reignier</b> <i>Stability and bonding in the ground and excited states of lithium fluoride <math>Li_nF</math> clusters</i>	
11:20 - 11:40	<b>Anthony Scemama</b> <i>A convenient issue to the multiple parentage problem: test of a MRCC method and prospects</i>	
11:40 - 12:00	<b>Emmanuel Giner</b> <i>Spin density and metal-ligand delocalization: some insight from wave function theory</i>	
12:00 - 14:00	Pause déjeuner (salles C1 et C2)	
		<i>M. Caffarel</i>
14:00 - 15:30	<b>Pr. Cyrus Umrigar</b> <i>Overview on QMC methods</i>	
15:30 - 16:30	Pause café – Session posters (salles C1 et C2)	<i>P. Nava</i>
16:30 - 16:50	<b>Roland Assaraf</b> <i>Computing physical properties in quantum Monte Carlo with statistical fluctuations independent of system size</i>	
16:50 - 17:10	<b>Félix Mouhat</b> <i>Fully quantum dynamics of proton transfer in aqueous systems: the case study of the Zundel ion</i>	
17:10 - 17:30	<b>Ayadi Sameh</b> <i>Etude théorique de réactions d'oxydation des monoterpènes: myrcène et ocimène</i>	

## JEUDI, 9 JUILLET

8:30	Accueil des participants	
9:00 - 10:30	<b>Pr. Trygve Helgaker</b> <i>Fundamentals of DFT</i>	<i>J. Toulouse</i>
10:30 - 11:00	Pause café	<i>E. Fromager</i>
11:00 - 11:20	<b>Elisa Rebolini</b> <i>Time-independent range-separated density functional theory for molecular excitation energies</i>	
11:20 - 11:40	<b>Emanuele Coccia</b> <i>Time-dependent configuration interaction for high-harmonic generation</i>	
11:40 - 12:00	<b>Bastien Mussard</b> <i>Range-Separated Random Phase Approximations</i>	
12:00 - 14:00	Pause déjeuner	
14:00 - 15:30	<b>Dr. Xavier Blase</b> <i>Green functions and beyond</i>	<i>M. Casula</i>
15:30 - 16:30	Pause café – Session posters	
16:30 - 16:50	<b>Saber Guedidha</b> <i>Un algorithme GW de complexité <math>O(N^3 N_{Brillouin})</math> pour les cristaux organiques</i>	<i>P. Reinhardt</i>
16:50 - 17:10	<b>Claudio Attaccalite</b> <i>Nonlinear reponse of solids within the GW plus Bethe Salpeter approximation: application to second- and third-harmonic generation</i>	
17:10 - 17:30	<b>Patrick Cassam-Chenaï</b> <i>Electron correlation versus electron-nucleus correlation</i>	
20:00	Dîner : Restaurant "Les Arcenaulx" 25 Cours Honoré d'Estienne d'Orves, 13001 Marseille	

## VENDREDI, 10 JUILLET

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8:30	Accueil des participants
	<i>D. Hagebaum-Regnier</i>
9:00 - 9:20	<b>Arjan Berger</b> <i>Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional</i>
9:20 - 9:40	<b>Nathaniel Rimbault</b> <i>Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from Current Density</i>
9:40 - 10:00	<b>Odile Franck</b> <i>Convergence en base de la théorie de la fonctionnelle de la densité avec séparation de portée</i>
10:00 - 10:30	Pause café – Retrait des posters
	<i>S. Humbel</i>
10:30 - 11:00	<b>Michel Caffarel</b> <i>Bilan des activités du GdR-CORREL et perspectives</i>
11:00 - 11:20	<b>Lorenzo Ugo Ancarani</b> <i>A Sturmian Approach to Structure and Ionization Processes of Atoms and Molecules</i>
11:20 - 11:40	<b>Patricia Guevara</b> <i>Étude des vibrations intermoléculaires et intramoléculaires de l'indène et de ses analogues hétérocyclés</i>
11:40 - 12:00	<b>Roberto A. Boto</b> <i>On the topology of the reduced density gradient</i>
12:00	Clôture

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## **Liste des Communications Orales**

1. Denis Hagebaum-Reignier
2. Anthony Scemama
3. Emmanuel Giner
4. Roland Assaraf
5. Félix Mouhat
6. Ayadi Sameh
7. Elisa Rebolini
8. Emanuele Coccia
9. Bastien Mussard
10. Saber Guédidda
11. Claudio Attaccalite
12. Patrick Cassam-Chenaï
13. Arjan Berger
14. Nathaniel Rimbault
15. Odile Franck
16. Lorenzo Ugo Ancarani
17. Patricia Guevara
18. Roberto A. Boto

# Stability and bonding in the ground and excited states of lithium fluoride $\text{Li}_n\text{F}$ clusters

Somnath Bhowmick, *Denis Hagebaum-Reignier*<sup>\*</sup>, Gwang-Hi Jeung  
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Hyperlithiated fluorine clusters  $\text{Li}_n\text{F}$  belong to the class of superalkali compounds. These are characterized by lower ionisation potentials (I.P) than the ones of the free alkali-metal atoms (5.39 – 3.89 eV) [1]. These heterogeneous alkali clusters are stable in the gas phase and have been experimentally detected using mass spectrometry techniques [2]. They can be considered as potential building blocks for the design of novel nanomaterials with unique properties that can be tailored through selection of size and composition. The smallest cluster, the  $\text{Li}_2\text{F}$  radical, has recently received particular attention, as its formation in the ultracold temperature regime could be accessible [2].

Because of the small difference between the I.P of the lithium atom and the large electron affinity of the fluorine atom, the electronic states of these compounds are expected to show ionic-covalent interactions in their dissociation potential energy surfaces in the  $\text{Li}_n + \text{F}$  channel. Thus, the correct description of these states along the dissociation paths, where electron correlation is of central importance, is challenging and requires the use of high-level ab initio methods.

In this talk, I will present potential energy surfaces of the ground and excited states of the  $\text{Li}_2\text{F}$  radical and its anion  $\text{Li}_2\text{F}^-$ , calculated with explicitly correlated ab initio methods (MRCI-F12, CCSD(T)-F12) [4]. We found that the first two  $^2\text{A}_1$  states of  $\text{Li}_2\text{F}$  show a strong avoided crossing at large  $\text{Li}_2+\text{F}$  distances, which is characteristic of a harpoon reaction, whereas no such interaction is present in the dissociation curves of the anion. The singlet ground state of  $\text{Li}_2\text{F}^-$  shows a clear multi-configurational character and its bonding displays the features of a 3c/4e  $\sigma$ -type “long-bonding”, recently introduced by Landis and Weinhold [5].

Finally, the dissociation curves of bigger clusters,  $\text{Li}_4\text{F}$ ,  $\text{Li}_6\text{F}$  and  $\text{Li}_8\text{F}$  will also be discussed.

## References

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# A convenient issue to the multiple parentage problem: test of a MRCC method and prospects

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The main difficulty of state specific Multi-Reference non-perturbative methods concerns a parentage problem: how to fix the amplitudes of the excitations sending from different references to the same excited determinant? The problem already appears when one wants to construct an effective Hamiltonian in the reference space which takes into account the effect of the outer space (for instance a valence Hamiltonian dressed under the effect of the dynamical correlation). We have tested a simple solution (1) scaling the amplitudes of the excitation operators on the amplitudes of the interactions between the references and the excited determinants. We have produced a MRCC method which proceeds through an iterative dressing of the MRSDCI matrix. The methods happens to be numerically efficient, it is parallelizable and very flexible. Some possible simplifications will be proposed, in particular a MR-CEPA type solution. This work illustrates the intimate relation between the modelization (extraction of effective interactions) and the conception of computational tools.

- 1) JCP 104, 4068 (1996)

# **Spin density and metal-ligand delocalization : some insight from wave function theory**

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The delocalization of the unpaired electrons in molecules containing transition metal atoms is still a subject of debate in non organic chemistry. This quantity can be determined experimentally through the spin density, that can be directly confronted by the various computational methods of quantum chemistry. As the spin density reveals the level of covalency of the metal-ligand bond, its correct determination by theoretical approaches is crucial to reproduce the expectation values of the main one body operators involved in the analysis of the such systems. The DFT and wave function (WF) methods give qualitative different results as it has been pointed by recent studies [1-5] : DFT tends to overestimate the covalency of the metal ligand bond, whereas the WF methods overestimate the ionicity of such bond.

In this talk, I will present some very recent results obtained for the CuCl<sub>2</sub> and (CuCl<sub>4</sub>)<sub>2</sub>-molecules, which investigate the Cu-Cl delocalization effect using a widespread type of WF methods. It will be shown that the main issue encountered by most of the post mean field approaches comes from the orbitals obtained in the mean field method, whether mono or multi reference. The reasons explaining the systematic failure of the mean field method will be discussed, highlighting the difficulties of the post mean field methods. The rôle of the size consistency error the and dynamic polarization will be highlighted, leading to a minimal configuration interaction (CI) space giving accurate results for the spin density. Then, the future application of such strategy on a variety of metal transition complexes will be pointed out.

## **Références**

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# Computing physical properties in quantum Monte Carlo with statistical fluctuations independent of system size

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(Dated: June 8, 2015)

Many important quantities of chemical or physical interest are localized in space, that is, they do not depend on distant degrees of freedoms. Standard Quantum Monte Carlo estimators of such properties are local in space, but the statistical uncertainty increases with the system size. We discuss a method which consists in simulating a stochastic process along its derivative with respect to some parameter: the so-called correlated sampling without reweighting. We show that this procedure extends the locality of the estimator to its statistical uncertainty. A proof is given for a large collection of non-interacting systems . Calculations on hydrogen chains suggest that this behavior holds not only for systems displaying short-range correlations, but also for systems with long-range correlations

# Fully quantum dynamics of proton transfer in aqueous systems: the case study of the Zundel ion

*Félix Mouhat*<sup>\*</sup>, Michele Casula, Rodolphe Vuilleumier, Antonino Marco Saitta,  
and Sandro Sorella

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In this project, we develop and implement a new method which combines accurate Quantum Monte Carlo (QMC) calculations of the electronic contributions, with a Path Integral Langevin Dynamics (PILD) approach for the ionic part, in order to take into account thermal and quantum effects affecting the dynamics of hydrogen in water. While the QMC framework based on a many-body wavefunction, guarantees the necessary accuracy to describe the dispersive intermolecular forces, the PILD is able to provide a fully quantum treatment of protons by efficiently dealing with the intrinsic noise present in the QMC forces. The combination of the two approaches, i.e. QMC and PILD, represents an original and powerful tool to overcome the numerical and theoretical bottlenecks of proton dynamics simulations in water and aqueous systems. The first test case tackled in this project is the hydrogenated water dimer (Zundel ion), whose energy surface has been accurately resolved at the QMC level of theory [1]. Moreover, this system represents an ideal benchmark for our new method since it has been widely studied both theoretically and experimentally in the last fifty years. We have confirmed that, in this system, quantum nuclear effects (NQE) are important even at room temperature. The natural extension of this project is to apply our method to larger model ions and water clusters and to study the proton transfer in water and aqueous systems.

## Reference

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# ETUDE THEORIQUE DES REACTIONS D'EPOXYDATION DES MONOTERPENES : MYRCENE ET OCIMENE

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Les terpènes possèdent des rôles importants à la formation des aérosols organiques secondaires (AOS). Ces (AOS) influent sur le climat et les conditions de vie sur terre. Dans le but de comprendre l'impact de ces polluants atmosphériques, plusieurs travaux de recherche ont étudié les mécanismes d'oxydation des terpènes [1-5]. En effet, ces (AOS) sont formés à partir de la réaction de COV avec l'ozone, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>, NO<sub>3</sub> et peracide ...[5].

Dans ce travail, nous avons étudié de point de vue thermodynamique et orbitalaire la possibilité et la stéréoselectivité des réactions d'époxydation des monoterpènes par l'acide métachloroperbenzoïque **2** (Figure 1). En utilisant la méthode de calcul DFT avec la fonctionnelle B3LYP et la base standard 6-311G\*\*, nous avons discuté la réactivité de ces réactions.

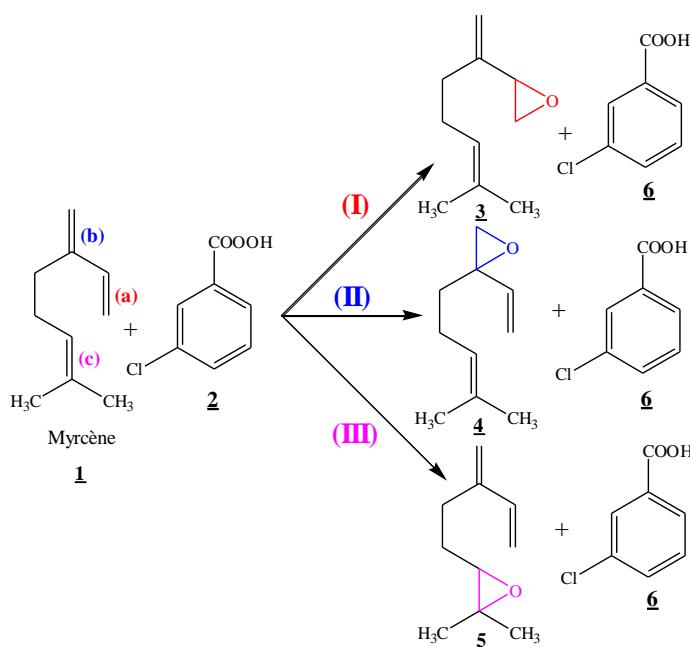


Figure 1

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# Time-independent range-separated density-functional theory for molecular excitation energies

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Linear-response time-dependent density-functional theory (TDDFT) [1] is nowadays one of the most wisely used method to compute molecular excitation energies thanks to its good cost versus accuracy ratio. The key object in TDDFT is the Hartree-exchange-correlation kernel which must describe the effects of the electron-electron interaction on the excitation energies of the system. Unfortunately the form of this kernel is unknown and the design of approximations remains a major challenge. Within the usual adiabatic semi-local approximations, although it reproduces correctly valence excitations, TDDFT is not able to describe properly Rydberg, charge-transfer or multiple excitations.

Range separation of the electron-electron interaction [2] allows one to mix rigorously density-functional methods at short range and wave-function or Green's function methods at long range. When applied to the exchange kernel, the inclusion of the long-range Hartree-Fock exchange kernel already corrects most of TDDFT deficiencies [3] as in particular the correct asymptotic behavior of the potential at long range is recovered. However the amount of different approximations that are made in this context makes difficult to assess their individual effects and to design a way of correcting them.

In this talk, I will present several developments in range-separated time-independent density-functional theory to improve the treatment of excitations energies. The effects of range separation are first assessed on the excitation energies of a partially-interacting system in an analytic and numerical study in order to provide guidelines for future developments of range-separated methods for excitation energy calculations [4]. Extrapolation and perturbation methods are then used to improve on the description of the physical energies of the system [5, 6]. Finally usual approximations are then reintroduced to assess their effects.

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# Time-dependent configuration interaction for high-harmonic generation

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The advent of attosecond ( $10^{-18}$  s) laser pulse generation allowed the scientific community to study with unprecedented accuracy atomic and molecular phenomena in intense ultrashort laser fields. The high-harmonic generation (HHG) is a nonlinear process where attosecond pulses of extreme ultraviolet and soft X-ray radiation can be obtained.

The basic features of the HHG process can be explained in terms of semiclassical models<sup>1,2</sup>, in which the single-active electron escapes from the nuclei by tunneling, it is accelerated away by the interaction with the laser field and it is reaccelerated back when the field changes sign, emitting a photon (harmonic of the laser field) as it relaxes to the ground state.

On the other hand, a fully quantum treatment of the electron dynamics<sup>3,4</sup> is mandatory to verify the reliability of such models and to rationalize all the properties of the HHG spectra. In the present work we apply the time-dependent configuration interaction for the real time propagation of the electron of the hydrogen atom. A systematic analysis of the crucial role played by a proper characterization of the above-ionization states and of the effect of using finite and localized basis sets is reported<sup>5</sup>, with specific attention to the application of Gaussian functions for the representation of the continuum.

## Références

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## Range-Separated Random Phase Approximations.

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The Random Phase Approximation (RPA) can be derived in different variants (depending on how the exchange interactions are handled) and in different formulations (depending on how the integrations involved in the equations are carried out)[1].

The past explorations of the performances of these versions of RPA to calculate ground-state correlation energies of closed-shell electronic systems, in particular systems where long-range electron-electron interaction play an important role and in the context on range-separation[2-5], have provided a first understanding of the quality and drawbacks of these different RPAs.

The key equations of range-separated RPAs are given, and some new results on basis set convergence[6], open-shell systems (atomization energies and barrier heights energies)[7] and fractional occupation number calculations are presented.

### Références

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# Un algorithme GW de complexité $O(N^3 N_{\text{Brillouin}})$ pour les cristaux organiques

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La théorie de la fonctionnelle de la densité (DFT) a été reconnue en chimie quantique pour son aptitude théorique pour décrire les propriétés de l'état fondamental de nombreux matériaux (des molécules et des solides). En revanche, les prédictions de la DFT pour les états excités ne s'accordent pas avec l'expérience. Par exemple, la structure de bande et la bande interdite du plus part des semi conducteurs sont souvent sous-estimées. Cependant, l'approximation GW proposée par Hedin donne une bonne estimation de la bande interdite de ces matériaux et montre un bon accord avec l'expérience. Mais, les calculs GW sont très lourds de point de vue numérique, car le temps de calcul CPU augmente en  $N^4$  ( $N$  est le nombre d'atome dans la cellule unitaire).

Le but de notre travail est de réduire la complexité de la résolution des équations GW pour les cristaux organiques. Cet algorithme est une extension d'un algorithme GW  $O(N^3)$  pour des systèmes finis, développé en 2007[1]. Notre algorithme a donné des bons résultats pour la densité d'états, l'énergie d'ionisation et l'affinité électronique des systèmes de grande taille, en accord avec ceux de Xavier Blase [2].

Nous sommes motivés par les cellules solaires de Heeger *et al.* [3] de type « bulk hetero junction » qui intéressent par leur faible coût de fabrication. En utilisant une approche d'espace-temps réel et des fonctions atomiques centrées, nous trouvons que le temps CPU de l'approximation GW évolue comme  $(N^3 N_{\text{Brillouin}})$  pour des cristaux organiques. Par conséquent, notre algorithme permet de prédire les propriétés de ces matériaux dans un temps raisonnable avant leur synthèse.

Nos résultats devraient améliorer et optimiser les cellules solaires organiques.

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# **Nonlinear reponse of solids within the GW plus Bethe Salpeter approximaion: application to second- and third-harmonic generation**

*Claudio Attaccalite\**

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We present a real-time approach to study nonlinear optical properties in Condensed Matter systems that is especially suitable for crystalline solids[1]. The equation of motions and the coupling of the electrons with the external electric field are derived from the Berry phase formulation of the dynamical polarization. Many-body effects are introduced by adding single-particle operators to the independent-particle Hamiltonian. Specifically we include crystal local field effects, renormalization of the energy levels and excitonic effects. The approach is validated by calculating the second and third harmonic generation of bulk semiconductors. Finally we present second-harmonic generation spectrum of h-BN or MoS<sub>2</sub> monolayers and we show that correlation effects double the signal intensity at the excitonic resonances with respect to the contribution from independent electronic transitions.[2]

## **Références**

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## **Electron correlation versus electron-nucleus correlation**

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We define electron-nucleus correlation energy by analogy with the quantum chemical definition of electron correlation, as the difference between the exact energy of a molecular state and its best approximate corresponding to a direct product wave function :  $\Phi_{nucleus}(R) \otimes \Phi_{electron}(r)$  . Both electron and nucleus wave functions are general wave functions of full configuration interaction (CI) type, that is to say, they include electronic correlation and nuclear motion correlation respectively. However, in contrast to the Born-Oppenheimer or adiabatic approaches, the electronic wave function does not depend parametrically upon nuclear variables, so that there is no built-in electron-nucleus correlation already accounted for in the ansatz.

We will present the electron-nucleus mean field configuration interaction method [1], which encompasses as particular cases the best electron-nucleus direct product wave function and the exact full CI electron-nucleus wave function for a given finite basis set. Then, electron-nucleus and electronic correlation energies will be compared quantitatively on dihydrogen isotopologues. It will come out that in the molecular ground state, electronic correlation is more important than the electron-nucleus one, i.e. the correlated motion of the electrons dominates their tendency to “follow” the nuclei.

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# Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional

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The Bethe-Salpeter equation (BSE) has proved to be an accurate tool for the description of the optical spectra of solids [1]. Unfortunately the computational effort required to solve the BSE precludes its application to large systems. Therefore an approach based on the numerically more affordable density-functional theory giving optical spectra of similar quality as the BSE is much sought after.

In this work we present the first fully parameter-free density-functional approach for the accurate description of optical absorption spectra of insulators, semiconductors and metals [2]. We show that this can be achieved within time-dependent current-density-functional theory using a simple dynamical polarization functional. Our method is truly predictive because it gives results of BSE quality without using any parameters. In particular, we do not use an *ad hoc* material-dependent broadening parameter to compare theory to experiment as is usually done. Our approach describes the excitonic effects in insulators and semiconductors as well as the Drude tails in metals. It is also numerically efficient; the cost of a calculation equals that of a calculation within the random-phase approximation.

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# Gauge-Invariant Calculation of Static and Dynamical Magnetic Properties from the Current Density

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In this work we solve two problems related to the calculation of static and dynamical magnetic properties with density functional theory (DFT). First, we show that the dependence of the dynamical magnetic dipole moment on the reference point of the multipole expansion and on the gauge origin of the vector potential have a clear physical significance. They are due to a dynamical electric dipole moment and an electric field, respectively. Both are fully determined by the experimental setup and do not pose any fundamental problem, contrary to what is commonly assumed. Second, in the static case, any dependence on the gauge origin is an artifact of the computational method. We show that the artificial dependence on the gauge origin can be removed in an elegant way by the introduction of a sum rule that puts the diamagnetic and paramagnetic contributions on equal footing. Our approach can be applied to calculate any magnetic observable that can be derived from the current density. To illustrate our method we apply it here to time-dependent current-density-functional theory (TDCDFT) for the calculation of static and dynamical magnetizabilities of molecules [1]. We will also show that our approach is rigorous and efficient for the calculation of other magnetic properties and in particular the optical rotation tensor [2].

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# Convergence en base de la théorie de la fonctionnelle de la densité avec séparation de portée

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En DFT avec séparation de portée, l'interaction coulombienne est séparée en deux contributions. Une contribution de courte portée en DFT et une contribution de longue portée traitée par une méthode fonction d'onde [1]. En pratique on peut observer une convergence plus rapide de l'énergie de corrélation de longue portée. Dans notre étude nous nous sommes intéressés à ce phénomène. Nous avons dans un premier temps montré que la convergence était exponentielle par rapport au moment angulaire maximal  $L$  pour la fonction d'onde le longue portée [2] et polynomiale pour l'interaction coulombienne[3] . Nous avons ensuite étudié la convergence de l'énergie de correlation de longue portée obtenue par la théorie de perturbation de longue portée au second ordre Møller-Plesset [4] pour différents systèmes (He, Ne, N<sub>2</sub>, H<sub>2</sub>O) par rapport au nombre cardinal  $X$  des bases de Dunning (cc-p(C)VXZ) et montré que l'erreur sur l'énergie de correlation suivait un modèle exponentiel par rapport à  $X$  dans le cas de la longue portée, alors qu'elle était polynomiale pour l'interaction coulombienne [5]. Enfin en se basant sur ce comportement exponentiel, nous avons proposé une méthode d'extrapolation en base complète pour la DFT à séparation de portée.

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# A STURMIAN APPROACH TO STRUCTURE AND IONIZATION PROCESSES OF ATOMS AND MOLECULES

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The Sturmian approach, using Generalized Sturmian Functions (GSF), is a spectral method that has been applied successfully both for structure calculations [1,2] and for the study of several ionization processes [1,3,4] with atomic targets.

GSF are two-body functions that solve a Sturm-Liouville problem. They can be used as a basis set to solve correlated three-body bound or scattering problems. When compared with other basis functions, the GSF increase expansions convergence rates because they diagonalize the kinetic energy and the main (Coulomb) interactions. Moreover, the whole GSF set can be chosen to possess asymptotic conditions appropriate for the physical problem under consideration: bound-type behavior with a specific asymptotic charge are chosen for bound states, while – for example – outgoing behavior with a given adequate energy are taken for solving scattering processes.

Compared to the case of many-electron atoms several extra challenges occur for molecules: the scattering problem is generally multicenter and highly non-central, and the molecular orientation must also be taken into account. These features make the computational task much more cumbersome and expensive than for atomic targets. The extension and implementation of the Sturmian approach for scattering from molecular systems has been recently put forward [5].

In the presentation, I will briefly review the GSF method and show some applications in three-body correlated (bound and continuum) systems.

This work has been done in collaboration with: G. Gasaneo, D.M. Mitnik, J.M. Randazzo, F.D Colavecchia, M.J. Ambrosio, J.A. Del Punta and C.M. Granados-Castro. We would like to acknowledge the CNRS (PICS project N. 06304) and CONICET (project N. DI 158114) for funding our French-Argentinian collaboration.

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# Étude des vibrations intermoléculaires et intramoléculaires de l'indène et de ses analogues hétérocyclés

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L'étude des interactions non-covalentes occupe une place prépondérante dans les problématiques actuelles de recherche, celles-ci étant aujourd'hui considérées comme les pierres angulaires de disciplines telles que la chimie supramoléculaire, la science des matériaux ou la biochimie.<sup>1</sup> L'une des problématiques majeures des industries du pétrole et du gaz est le dépôt d'hydrocarbures aromatiques condensés et d'autres composés organiques lourds existant dans l'huile brute, ce type de dépôts étant directement lié aux interactions entre molécules aromatiques. Les asphaltènes, qui représentent la fraction lourde, sont constitués de composés liés sous forme d'agrégats de noyaux aromatiques condensés, substitués par des groupements aliphatiques et naphténiques et faisant intervenir des hétéroatomes (azote, soufre, oxygène) au sein d'arrangements de type hétérocycles.<sup>2</sup> Nous avons étudié les molécules d'indène, de benzothiophène, de benzofurane et d'indole, ainsi que leurs dimères et certains dérivés d'intérêt dans le but de comprendre leurs interactions et d'interpréter leur spectre vibrationnel. Nous avons réalisé des calculs DFT du type  $\omega$ B97X-D/6-311++G\*\* pour optimiser et calculer les champs de forces. Les énergies d'interaction des dimères ont été calculées en utilisant la méthode counterpoise<sup>3</sup>. Afin de tenir compte de l'erreur liée à la superposition de bases (BSSE) et juger la qualité de nos résultats, nous avons réalisé des calculs DFT-SAPT (théorie des perturbations à symétrie adaptée)<sup>4</sup>. Les énergies calculées par ces deux méthodes révèlent des différences inférieures à 1,5 kcal/mol. Nous avons utilisé le programme P\_Anhar.v2.0<sup>5</sup> pour étudier les bandes caractéristiques des structures aromatiques des spectres vibrationnels, qui apparaissent à des nombres d'onde inférieurs à 1000 cm<sup>-1</sup>. Dans le but de prendre en compte l'effet de l'environnement, constitué par les molécules à l'état cristallin, nous avons réalisé des calculs VASP en appliquant les corrections de l'énergie de dispersion disponibles.<sup>6</sup> Les résultats obtenus permettent d'illustrer l'influence de l'hétéroatome et du motif sur l'allure des spectres infrarouge et Raman et la possible identification de ces composés au sein de systèmes complexes.

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# On the topology of the reduced density gradient

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Non-covalent interactions (NCIs) play a key role in many areas of science, ranging from biochemistry to condensed matter. In this regard, the NCI index, as a new tool to identify and characterize weak interaction of various strengths as chemical intuitive reduced density gradient (RDG) isosurfaces that reveal both stabilizing (hydrogen-bonding and van der Waals interactions) and destabilizing interactions.[1] Beyond qualitative analysis, the integration of both volume and charge within NCI isosurfaces are in good agreement with the hydrogen-bonding potential-energy surfaces. [2] Recently Saleh *et al.* found a good linear correlation between stabilization energies and kinetic energies integrated on the main NCI isosurfaces. [3] These results connect the topology of the reduced density gradient with energetics.

In this work we present the latest version of the NCIPILOT code: NCIPILOT 4.0. This version is capable of performing topological analysis of the reduced density gradient isosurfaces: localization of critical points, computation of flux lines and integration of different quantum mechanical properties. As a proof of principle we apply our code to the analysis to characterize non-covalent interaction in a self-assembly monolayer (SAM) system such as octylamine/platinum. [4]

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