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Representing continuum wave functions with complex Gaussian functions

Abdallah Ammar ^{*} ¹, Arnaud Leclerc ^{*}

¹, Ugo Ancarani ^{*}

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¹ LPCT, UMR 7019 – CNRS – Université de Lorraine – France

The advantage of Gaussian functions in simplifying multi-center integrals is known since the work of Boys [1]. Their use has become pivotal in molecular calculations of bound states functions (see for example ref. [2]). The representation of continuum wave functions with Gaussians, on the other hand, has been much less studied. In 1990 Nestmann and Peyerimhoff [3] applied a nonlinear least square approach in an attempt to fit Bessel functions with Gaussians. While this approach is robust for low energy functions, the accuracy is poor when the functions are oscillating fast, especially at large distances. This drawback is related to the nodeless nature of real Gaussians. On the contrary complex Gaussians, i.e. Gaussians with complex exponents, have an intrinsic oscillating behavior which renders them more appropriate to represent oscillating functions.

In this work we generalized the approach of Nestmann and Peyerimhoff to complex Gaussians using a quadratic approximation method [4] to perform the optimization. An illustration of the representation, with both real and complex Gaussians, is shown in the figure for the case of a pure Coulomb continuum function. As a physical application we have considered the ionization of Hydrogen by a photon or an electron, and performed cross section calculations comparing to benchmark values.

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Mots-Clés: complex Gaussians, nonlinear optimizations, continuum wavefunctions

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Dynamics of electrons and nuclei in molecules: Beyond the Born-Oppenheimer approximation

Federica Agostini * ¹

¹ Laboratoire de Chimie Physique, UMR 8000 CNRS/University Paris-Sud, University Paris-Saclay (LCP) – University Paris-Sud – 15, rue Georges Clémenceau 91405 Orsay, France

Excited-state dynamics is at the heart of Photophysics and Photochemistry. Nonadiabatic transitions are induced by the strong coupling between electronic dynamics and the ultrafast motion of the nuclei, and are observed in phenomena such as photosynthesis, photovoltaics, and exciton transport in pi-conjugated complexes. An essential part of the research efforts in these fields is directed towards developing theoretical and computational approaches to describe conformational changes, energy dissipation, or quantum decoherence, i.e., the signature aspects of excited-state processes. In this context, among the most successful frameworks for molecular dynamics simulations of excited-state processes stand trajectory-based quantum-classical methods, as they give access to the study of complex molecular systems. Trajectory-based approaches combine a classical description of nuclear dynamics with a quantum-mechanical description of electronic dynamics. However, the approximations underlying quantum-classical methods are sometimes severe, and are at the origin of controversies as well as of continuous developments.

In this talk I will introduce the problem in general, and I will present a recently-developed trajectory-based approach to nonadiabatic dynamics [1,2]. The actual numerical scheme has been derived from the exact factorization of the electron-nuclear wavefunction [3], a new framework proposed to investigate, interpret and approximate the coupled dynamics of electrons and nuclei beyond the Born-Oppenheimer approximation. The exact factorization provides a new perspective to analyze nonadiabatic processes: (i) it proposes an alternative [4] to the standard Born-Oppenheimer framework, that pictures excited-state processes in terms of wavepackets moving on and transferring between static potential energy surfaces; (ii) it suggests new interpretations [5] of molecular geometric-phase effects, related to conical intersections; (iii) it provides guidelines for developing simulation algorithms in different [6] nonadiabatic regimes.

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Mots-Clés: excited, state dynamics, electron, nuclear entanglement, nonadiabatic processes

IONIZATION PROCESSES OF ATOMS AND MOLECULES: A STURMIAN APPROACH

Ugo Ancarani * ¹

¹ Laboratoire de Physique et Chimie Théoriques – Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique : UMR7019 – France

The ionization of atoms and molecules by photon or charged particle impact is a N-body Coulomb problem. Its quantum mechanical study requires, amongst other things, an adequate description of continuum states. In practical calculations one needs accurate wave functions, on large radial domains, corresponding to one or two active electrons escaping in the field of the ionized target.

In the last ten years a Sturmian approach, using Generalized Sturmian Functions (GSF), has been developed and applied successfully both for structure calculations [1,2,3] and for the study of several ionization processes with atomic (by impact of electrons [4], protons [5] or photons [6]) and, more recently, with molecular (by impact of photons [7] or electrons [8]) targets.

GSF are two-body functions that solve a Sturm-Liouville problem. They can be used as a numerically efficient orthogonal and complete basis set to solve correlated Coulomb three-body bound or scattering problems. 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. This property makes the GSF method particularly adapted when applied to describe charged particles in their long-range Coulomb interaction.

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

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On the Road to the Modeling of Resonance UV/vis Spectroscopic Properties

Éric BrÉmond * ¹, Philippe Laine ¹, François Maurel ¹

¹ Université de Paris – Université de Paris, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013
Paris, France – France

Upon a resonant excitation by a specific wavelength, the collectively oscillating electrons in the conduction band of a noble metal nanoparticle, *i.e.* localized surface plasmon resonance (LSPR), prompt a strong light absorption in the UV/vis region. The wavelength coincidence of a chromophore with LSPR leads to an enhanced optical response of the system and could facilitate its study at low concentrations [1].

The state-of-the-art modeling of the resonance UV/vis spectroscopic properties relies on a specific hybrid discrete interaction/quantum model (QM/DIM) which describes the chromophore at TDDFT level, in presence of an electrodynamical treatment of the nanoparticle, including electrostatics and polarization of the atoms [2]. However, prior to applying such a complex model, the nanosystem under investigation has to be carefully chosen. Indeed, a resonant coupling between a large inorganic nanoparticle and a small organic chromophore can only occur in specific conditions, thereby necessitating the design of both nanosized systems. We propose here to investigate the optical properties of a new class of versatile chromophores [3] whose first singlet-singlet absorption energy can be tuned to be in resonance with the surface plasmon of a noble metal nanoparticle. At lower size scale, we further show that the coupling between an organic chromophore and an inorganic metal cluster is a methodological challenge. We thus demonstrate how our last developments in DFT can provide some answers to that specific issue [4].

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Mots-Clés: resonance UV/vis spectroscopy, carbenium chromophore, surface, enhanced absorption,

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range, separated exchange density functionals

The Quantum Many-Body Problem from a Dynamical Mean Field Perspective

Silke Biermann * ¹

¹ Centre de Physique Théorique [Palaiseau] (CPHT) – Polytechnique - X, Centre National de la Recherche Scientifique : UMR7644 – Ecole Polytechnique 91128 Palaiseau cedex, France

Dynamical mean field techniques (DMFT), in conjunction with electronic structure methods, have led to tremendous progress in the description of spectral properties of materials with strong electronic Coulomb correlations. In this talk, we will provide an overview and review some highlights. Finally, we will comment on current construction sites in the field and future perspectives.

Mots-Clés: Correlated Materials, Dynamical Mean Field Theory

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Unitary Group Adapted Iterative Configuration Expansion(ICE): Implementation and Applications

Vijay Gopal Chilkuri * ¹, Frank Neese ²

¹ Max-Planck-Institut für Kohlenforschung (coal research) – Allemagne

² Max Planck Institut für Kohlenforschung – Allemagne

We present a novel implementation of selected CI (ICE) including non-abelian SU(2) symmetry with an emphasis on efficiency. A detailed comparison of the SU(2) adapted selected CI with the usual determinant based CI and DMRG is performed in order to access the efficiency and accuracy of the ICE method. Finally, we present a few case studies which demonstrate the power of the SU(2) adaptation as opposed to the determinant representation. Our method seems especially effective for describing the wavefunction of molecules containing a number of transition metal atoms interacting via a strong anti-ferromagnetic coupling.

Mots-Clés: selected CI, non-abelian symmetry, SU(2), magnetic molecules

*Intervenant

Le problème quantique à N-corps en chimie théorique

Michel Caffarel * ¹

¹ Lab. Chimie et Physique Quantiques – CNRS : UMR5626 – Université Paul Sabatier, Toulouse,
France

Dans cet exposé de nature essentiellement pédagogique, je présente un rapide survol des principales méthodes utilisées en chimie théorique pour traiter le problème quantique à N-corps.

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La boîte à outils de l'algèbre extérieure pour le problème à N-corps fermionique

Patrick Cassam-Chenai * ¹

¹ Université Côte d'Azur – CNRS : UMR7351 – France

It has been argued by Valatin in 1951 that the exterior algebra is the natural mathematical framework for the N-body problem of identical Fermionic particles [1]. However, the tools developed in this mathematical field [2] have remained little exploited up to now in quantum physics. It is the purpose of this talk to review some of the key exterior algebra concepts and techniques that we find particularly relevant for physicists and chemists.

We will focus on the concept of p-internal space and the derived one of p-orthogonality [3], which generalizes that of strong-orthogonality and can be viewed as a graded indistinguishability measure for electronic states. p-orthogonality has been applied in the past to constrain geminal models [4], and work in progress shows that computational cost can be drastically reduced by using new geminal ansätze based on such algebraic constraints.

Time permitting, we will show the connection between the concept of "cancelator space" and Configuration Interactions with arbitrary reference wave functions.

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Mots-Clés: algèbre extérieure

*Intervenant

Nuclear quantum effects in protonated water clusters

Michele Casula * ¹, Félix Mouhat ², Sandro Sorella ³, Rodolphe Vuilleumier ⁴, Antonino Marco Saitta ⁵

¹ Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC) – Museum National d’Histoire Naturelle, Université Pierre et Marie Curie - Paris 6 : UM120, Institut de recherche pour le développement [IRD] : UR206, Centre National de la Recherche Scientifique : UMR7590 – Tour 23 - Barre 22-23 - 4e étage - BC 115 4 place Jussieu 75252 PARIS, France

² École Normale Supérieure, 24 Rue Lhomond, 75005 Paris, France – Ecole Normale Supérieure de Paris - ENS Paris – France

³ SISSA, via Bonomea 265, 34136 Trieste, Italie – Italie

⁴ École Normale Supérieure, 24 Rue Lhomond, 75005 Paris, France – École normale supérieure [ENS] - Paris – France

⁵ IMPMC, Sorbonne Université, 4 Place Jussieu, Paris – Sorbonne Université UPMC Paris VI – France

Water is a key ingredient for life and plays a central role as solvent in many biochemical reactions. However, the intrinsically quantum nature of the hydrogen nucleus, revealing itself in a large variety of physical manifestations, including proton transport, is still elusive. Here we study, by an unprecedented combination of state-of-the-art quantum Monte Carlo methods and path-integral molecular dynamics, the structure and hydrogen-bond dynamics of the protonated water hexamer, the fundamental unit for the hydrated proton. We show that nuclear quantum effects and thermal ones cooperate to produce an unexpected non-monotonic behavior of the hydrogen-bond length as a function of temperature. This behavior can be explained by an inverse Ubbelohde effect, as it results from quantum delocalization of the hydrated proton across two water molecules upon temperature rise. The corresponding hydrogen bond is the shortest precisely around 250-300 K. As a consequence, room temperature is revealed to be the “sweet spot” for proton transport and diffusion, and thus for many phenomena depending on proton transport, including life.

Mots-Clés: quantum Monte Carlo, nuclear quantum effects, water clusters

*Intervenant

Stochastic treatment of electronic dissipation on top of a mean-field approach.

Phuong Mai Dinh ^{*} ¹, Eric Suraud ², Paul-Gerhard Reinhard ³, Jordan Héraud ¹, Marc Vincendon ¹

¹ Laboratoire de Physique Théorique de Toulouse – Université Toulouse III - Paul Sabatier, Centre National de la Recherche Scientifique – France

² Laboratoire de Physique Théorique - IRSAMC (LPT) – Université Paul Sabatier - Toulouse 3, Centre National de la Recherche Scientifique : UMR5152 – 118 route de Narbonne, 31062 Toulouse Cedex 4, France

³ University of Nuremberg-Erlangen – Allemagne

The quantum description of dissipative mechanisms in finite quantum systems is a long standing question in physics. It was originally addressed in nuclear physics, in particular a few decades ago, with the development of classical and semiclassical approaches. Meanwhile, a strong experimental motivation, now in the case of nanostructures and molecules irradiated by intense lasers, has shown up. This has motivated an increasing number of theoretical investigations in finite electronic systems, mostly on the basis of the well developed Time Dependent Density Functional Theory (TDDFT) that provides a robust effective mean field description of many low energy dynamical scenarios. Still, these TDDFT approaches fail to account for dissipative effects leading to observed electronic patterns. There is thus a crucial need for a formal and practical route to account for dissipative/thermalization features on top of quantum mean field.

We propose here a formalism allowing to describe the collisional correlations responsible for thermalization effects in finite quantum electronic systems. The approach is built as a stochastic extension of TDDFT, coined Stochastic Time-Dependent Hartree-Fock (STDHF). Dynamical correlations are treated in time-dependent perturbation theory and stochastic loss of coherence is assumed at some time intervals. This theory was formulated long ago for density matrices but never applied in practical cases because of its computational involvement. With a recent reformulation of the theory, applications are now conceivable. We obtained results in a 1D model and a full 3D sodium cluster that satisfactory led to dissipative features in the electronic response of the system after an initial excitation.

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^{*}Intervenant

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Mots-Clés: TDDFT, mean, field, stochastic TDHF, electronic dissipation

Le problème quantique à N-corps en physique nucléaire

Thomas Duguet * ¹

¹ cea saclay Irfu/DPHN – CEA – France

After an introduction about low-energy nuclear physics, I will briefly introduce the modern modelling of inter-nucleon interactions within the frame of chiral effective field theory and discuss the recent progress of the subsequent solving of the many-body Schroedinger equation for the "ab initio" description of always heavier nuclei.

*Intervenant

Theoretical approach for simulating single photon double core ionization of small molecules

Anthony Ferté * ¹, Richard Taïeb ¹, Stéphane Carniato ¹

¹ Laboratoire de Chimie Physique - Matière et Rayonnement – Sorbonne Université, Centre National de la Recherche Scientifique : UMR7614 – France

We present a theoretical approach for simulating single photon double core ionization of small molecules in the dipolar approximation. Our method couple a selected CI computation of wave functions to reduce the number of Slater determinants needed to converge the peak relative energies and the use of non-orthogonal molecular orbital basis set for the neutral and the ionised system in order to speed up the convergence of the peak intensities.

Mots-Clés: Applied quantum chemistry, Spectroscopy, Core electrons, Chemical physics, Non orthogonal basis sets

*Intervenant

N-centered ensemble density-functional theory for open systems

Bruno Senjean ¹, Emmanuel Fromager ^{* 2}

¹ Instituut-Lorentz, Universiteit Leiden and Division of Theoretical Chemistry, Vrije Universiteit
Amsterdam – Pays-Bas

² Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg – université de Strasbourg –
France

Two (so-called left and right) variants of N-centered ensemble density-functional theory (DFT) [Senjean and Fromager, Phys. Rev. A 98, 022513 (2018)] will be presented. Unlike the original formulation of the theory, these variants allow for the description of systems with a fractional electron number. While conventional DFT for open systems uses only the true electron density as basic variable, left/right N-centered ensemble DFT relies instead on (i) a fictitious ensemble density that integrates to a central (integral) number N of electrons, and (ii) a grand canonical ensemble weight which is equal to the deviation of the true electron number from N. Within such a formalism, the infamous derivative discontinuity that appears when crossing an integral number of electrons is described exactly through the dependence in the ensemble weight of the left and right N-centered ensemble Hartree-exchange-correlation density functionals. Incorporating N-centered ensembles into existing density-functional embedding theories is expected to pave the way towards the in-principle-exact description of an open fragment by means of a pure-state N-electron many-body wavefunction.

Mots-Clés: ensemble density functional theory, open systems, embedding

*Intervenant

New Hohenberg-Kohn theorems

Louis Garrigue * ¹

¹ Centre de REcherches en MATHématiques de la DEcision – Université Paris-Dauphine, Centre National de la Recherche Scientifique : UMR7534 – France

The Hohenberg-Kohn theorem (1964) states that at equilibrium, the ground state one-body density contains the information of the external electric potential. This implies that all physical quantities are functionals of this simple and measurable density, and justifies Density functional theory. We will explore its extensions to other kinds of external fields : which ground state reduced quantities contain the information of the interactions, of the magnetic field, of the temperature, and of non-local potentials ?

Mots-Clés: HohenbergKohn theorems, Density functional theory

*Intervenant

Embedding nuclear physics inside the unitary-limit window

Mario Gattobigio * ¹

¹ Institut de Physique de Nice, CNRS, Université Côte d'Azur – CNRS, Université Côte d'Azur – France

The two-body scattering lengths in nuclear physics are (much) larger than the typical interaction length which is given by the inverse of the pion mass; this natural fine-tuning places nuclear physics inside the universality window of Efimov physics. In this talk, I'll give a brief introduction to Efimov physics and I'll show to which extent it is a good spot to observe and to understand the nature of the spectrum of light nuclei.

Mots-Clés: Efimov Physics, Universality. Few Body physics

*Intervenant

Overview of selected configuration interaction and its coupling with DFT

Emmanuel Giner * ¹

¹ Laboratoire de Chimie Théorique – CNRS : UMR7616 – France

The purpose of this talk is to give a brief (and non exhaustive) introduction and overview of the concept of selected CI and its application in modern quantum chemistry. More specifically, I will present the algorithm available in the open-source software Quantum Package and show some of the applications already performed.

Eventually, I will discuss about the basis set which consists in one of the major the limitations of wave function theory, and briefly introduce a very recently introduced approach based on DFT aiming at curing this problem.

Mots-Clés: wave function, DFT, selected CI

*Intervenant

Excitations of correlated nucleons within the second random-phase approximation

Marcella Grasso * ¹

¹ IPN Orsay – Institut National de Physique Nucléaire et de Physique des Particules du CNRS – France

The second random-phase approximation (SRPA) is an extension of the standard random-phase approximation (RPA) where two particle-two hole (2p2h) configurations are included together with the RPA one particle-one hole (1p1h) configurations. This beyond mean-field model allows for reliable quantitative predictions to describe the widths and the fragmentation of excited states, due to the coupling between 1p1h and 2p2h elementary configurations.

I will present the formal developments and the practical applications that we have realized in the last years. One important achievement was the development of a substantial implementation of the SRPA model, based on a subtraction procedure. This subtraction method was tailored to cure double-counting problems encountered when effective interactions are used in beyond mean-field models, within energy-density functional theories. At the same time, this procedure cures all the instabilities and divergences present in the standard SRPA and produces renormalized single-particle excitation energies. The subtracted SRPA (SSRPA) provides a well-defined theoretical framework for quantitative predictions on nuclear excitation spectra.

Several recent applications will be shown, for instance, a systematic study on collective axial compression modes in medium-mass and heavy nuclei. A related topic will be discussed, namely the modification (enhancement) of the effective masses induced by beyond-meanfield SSRPA effects. Low-lying compression excitations will also be described and a link with the incompressibility modulus of asymmetric nuclear matter will be illustrated. Finally, beyond-mean-field effects on the symmetry energy of infinite matter and its density dependence will be deduced from the low-energy dipole response of the nucleus ^{68}Ni .

*Intervenant

Exploration of the Core Valence Separation approximation to obtain the ionization potentials of the core electrons by the EOM-CCSD method according to a 4-component relativistic approach

Loïc Halbert ^{*} ¹, Marta Lopez Vidal ², Avijit Shee ³, Sonia Coriani ², André Severo Pereira Gomes ¹

¹ Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique : UMR8523 – France

² Department of Chemistry, Technical University of Denmark – Danemark

³ Department of Chemistry, University of Michigan – États-Unis

Advances in X-ray spectroscopy, both in high-energy and in resolution, now allow us to reach the ionization potentials (IP) of the core electrons of many systems [3, 5]. In quantum chemistry, these electrons must be treated using relativistic Hamiltonians (Dirac-Coulomb, Dirac-Coulomb-Gaunt), as well as for electrons belonging to molecular orbitals (MO) having a strong Spin-Orbit coupling. In addition, the Ionization Potential - Equation of motion Coupled-Cluster (IP-EOM-CCSD) method has many advantages both by the precision of the results [6] and by its explanatory and predictive nature [2]. However, its computational cost in N^6 quickly makes it inapplicable.

We then explore the Core Valence Separation approximation (CVS-EOM-CCSD) [4] based on the flexible separation between core and valence MO to be taken into account in the EOM calculation. In parallel, we were interested in the Frozen Core (FC) approximation whose role is to make certain MO inactive during the preliminary Coupled-Cluster (CC) calculation. These different technics, recently implemented by our team in Dirac [1], have been applied to X- and HX systems (X : Cl, Br, I, At) and a systematic examination shows the advantage of using these different methods to obtain the IP of the core electrons.

DIRAC, a relativistic ab initio electronic structure program (available at <http://dx.doi.org/10.5281/zenodo.3572>) see also <http://www.diracprogram.org>)

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Mots-Clés: Core, valence separation, ionization energies, halogens, equation of motion coupled cluster, relativistic electronic structure

DFT-based exchange vertex for the correlation energy and excited states

Maria Hellgren * ¹

¹ Institut de minéralogie, de physique des matériaux et de cosmochimie – Museum National d’Histoire Naturelle, Institut de recherche pour le développement [IRD] : UR206, Sorbonne Université : UM120, Centre National de la Recherche Scientifique : UMR7590 – France

In order to systematically go beyond the GW and random phase approximation (RPA) we introduce an approximate Hartree-Fock vertex based on the local exact-exchange (EXX) potential of time-dependent density functional theory (TDDFT). In certain limits this vertex is shown to exactly reproduce approximations from many body perturbation theory such as e.g. the SOSEX approximation [1]. It will be demonstrated that this vertex solves fundamental problems of the RPA such as the reliance of error cancellation and the underestimation of the van der Waals forces. The static approximation is for most cases sufficient to obtain good total energies but to a much lower computational cost. Excited states require, however, the inclusion of a dynamical discontinuity also captured by EXX TDDFT [2].

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*Intervenant

Using the density-functional toolkit (DFTK) to investigate floating-point error and improve SCF convergence in density-functional theory

Michael Herbst ^{*} ¹, Antoine Levitt ¹, Eric Cancès ¹

¹ CERMICS – Ecole des Ponts ParisTech, L’Institut National de Recherche en Informatique et en Automatique (INRIA) – France

Progress in density-functional theory is often the outcome of efforts involving physically sound approximate models, performant numerical schemes and optimal use of available computational hardware. In such an interdisciplinary field the lack of flexibility of many state-of-the-art codes poses an obstacle for multiple fields to join forces in one code. To close this gap, we have recently developed the density-functional toolkit, DFTK (<https://dftk.org>). In less than 3000 lines of Julia code, DFTK is capable of performing basic ground-state DFT simulations at a level of accuracy and performance comparable to well-established packages. At the same time one may conduct calculations using toy Hamiltonians with potentials ranging from a 1D harmonic oscillator to standard GGA functionals.

Two aspects of DFT simulations we currently investigate with DFTK are (a) the influence of floating-point precision and (b) mixing techniques for metal/insulator mixed systems. For the former aspect we exploit that DFTK is completely generic in the floating-point type, which allows to switch to elevated or reduced precision in parts or the complete code at runtime. In combination with interval arithmetic bounds on the floating-point error of a calculation may be computed. Traditionally in plane-wave DFT mixing of SCF iterations is used to improve SCF convergence. For systems with both metallic and insulating regions commonly used approaches are difficult to be made compatible. We investigate the use of the local density of states to construct a mixing scheme, which locally differs in insulating and metallic regions.

Mots-Clés: density, functional theory, plane, wave, self, consistent field, mixed precision, floating, point error

^{*}Intervenant

Progress in time-dependent density functional theory for excited states

Miquel Huix-Rotllant * ¹

¹ Institut de Chimie Radicalaire, CNRS - Aix-Marseille Université – Centre National de la Recherche Scientifique - CNRS, Aix-Marseille Université - AMU – France

The Runge-Gross extension of the Hohenberg-Kohn theorems to time-dependent external potentials opened a route to extract in principle exact excited state properties from the time-dependent density. The equivalent Kohn-Sham formulation for time-dependent problems stuffs all the complexity of the N-body problem into a time-dependent exchange-correlation (td-xc) functional, which is unknown as the ground-state counterpart. The td-xc functional depends on the densities at all times (memory), introducing thus a "time-dependence" of the exchange-correlation effects. The popular "adiabatic approximation" to the td-xc functional, which avoids whatsoever memory effects, is known to fail even qualitatively for representing strong correlation in excited states. Several memory td-xc functionals derived using many-body perturbation theory can describe excited-state correlation better. However, is the memory in the td-xc functional unavoidable or an artifact of the formulation? In this talk, I will discuss the meaning of "memory" from the perspective of time-dependent density response.

Mots-Clés: density functional theory, time, dependent density functional theory, excited states, linear response

*Intervenant

Molecular Density Functional Theory and its coupling with the N body quantum problem

Guillaume Jeanmairat * 1,2

¹ PHysicochimie des Electrolytes et Nanosystèmes Interfaciaux – Sorbonne Université, Centre National de la Recherche Scientifique : UMR8234 – France

² Réseau sur le stockage électrochimique de l'énergie (RS2E) – CNRS : FR3459 – France

The computational cost of the most advanced quantum methods used to study chemical systems tends to become rapidly prohibitive when the number of electrons increase. This is even worse when the solvation effects need to be taken into account. First, a large number of solvent molecules (i.e. a very large number of electrons) have to be considered. Second, it becomes necessary to sample the configuration space of the solvent since the meaningful quantity is free energy and not energy. Almost only one "ab-initio" method is used to study such problems: DFT-based Molecular Dynamics. Because of the computational cost, its usage remains limited to a few hundreds of atoms for a few ps.

To overcome this computational bottleneck, a natural choice is to adopt a more coarse description of the solvent. One common approach is to keep the explicit description of solvent molecules, but to describe their interaction with a classical force field, this is the so-called QM/MM technique. Another popular approach is to describe the solvent by a dielectric continuum. The latter has the advantage of keeping the computational cost comparable to a vacuum quantum calculation but it lacks molecular description of the solvent. In the former, it is still necessary to sample the phase space of solvent degrees of freedom and the computational cost is still several orders of magnitude larger than the in-vacuum calculation.

The purpose of this presentation is to introduce a liquid theory technique that might be a good alternative to tackle this problem: the molecular DFT. I will introduce the classical DFT framework [1, 2] and the approximations made to derive the MDFT formalism [3, 4]. I will illustrate its relevance to study classical solvation problems. Finally, I will present some preliminary work on the coupling between MDFT and QM techniques.

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Mots-Clés: Molecular DFT, Solvation, QM/MM

Direct nonadiabatic quantum dynamics in the moving crude adiabatic representation

Loic Joubert-Doriol * ¹

¹ Université Paris-Est Marne-la-Vallée – Université Paris-Est Marne-la-Vallée (UPEMLV), Université Paris-Est Créteil Val-de-Marne (UPEC), CNRS : UMR8208 – France

Conical intersections (CIs) play a central role in photochemistry by allowing radiationless electronic transitions. Unfortunately, CIs are synonymous of the Born-Oppenheimer approximation breakdown. Indeed, in the adiabatic representation, the Hamiltonian exhibits singularities at CIs prevent a straightforward numerical treatment of dynamical processes involving CIs. Furthermore, a Berry phase appears in the corresponding electronic states, which imposes additional non-trivial boundary conditions. These difficulties are in fact a failure of the adiabatic representation. Transforming the representation to diabatic is key to solve this problem. However, such a transformation is not known and is necessarily approximate. Therefore, we shall follow a different path.

The recently introduced moving crude adiabatic representation circumvents this difficulty by introducing time-dependent crude adiabatic states. This representation is a formally exact diabatic basis, and thus, the aforementioned difficulties do not occur. This approach is combined with the use of local Gaussian basis functions to design an exact method for simulating molecular processes involving few intersecting potential energy surfaces. Another major advantage of the method comes from the fact that expressions of the Hamiltonian terms in this representation can all be evaluated exactly without resorting to any approximations or model.

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Mots-Clés: Nonadiabatic, Conical intersection, Direct quantum dynamics

*Intervenant

Analysis of self-consistent field and direct minimization algorithms for electronic structure

Gaspard Kemlin * ¹, Eric Cancès ¹, Antoine Levitt ¹

¹ CERMICS – Ecole des Ponts ParisTech, L’Institut National de Recherche en Informatique et en Automatique (INRIA) – France

Numerous algorithms exist to solve the Kohn-Sham equations of electronic structure. They are either based on the direct minimization of the energy under constraints or based on fixed point iterations to solve a self-consistent formulation of the problem. It is not clearly understood which class of algorithms is more efficient and robust in which situation. We propose in this poster a first approach to the understanding of the intrinsic differences between two simple algorithms of each class: a damped self-consistent field algorithm and a projected gradient descent. We perform a local analysis and derive explicit convergence rates, confirmed by numerical experiments.

*Intervenant

Problème quantique à N-corps en mathématiques

Mathieu Lewin * ¹

¹ Centre de REcherches en MATHématiques de la DEcision – Université Paris-Dauphine, Centre National de la Recherche Scientifique : UMR7534 – France

Dans cet exposé je présenterai quelques aspects mathématiques du problème quantique à N-corps en insistant sur ce qui est connu et ce qui est ouvert, et les diverses pistes qui sont actuellement explorées.

*Intervenant

Convergence of Brillouin zone sampling methods

Antoine Levitt ^{*} ¹

¹ CERMICS – Ecole des Ponts ParisTech, L’Institut National de Recherche en Informatique et en Automatique (INRIA) – France

As a consequence of Bloch’s theorem, the numerical computation of the fermionic ground state density matrices and energies of periodic Schrödinger operators involves integrals over the Brillouin zone. These integrals are difficult to compute numerically in metals due to discontinuities in the integrand. We perform an error analysis of several widely-used quadrature rules and smearing methods for Brillouin zone integration. We precisely identify the assumptions implicit in these methods and rigorously prove error bounds. Our results shed light on the properties of these numerical schemes, and provide guidance as to the appropriate choice of numerical parameters.

^{*}Intervenant

New theoretical approaches to describe single- and multi-photon processes in atoms and molecules

Eleonora Luppi * ¹

¹ Sorbonne Université – Sorbonne Université, CNRS, Laboratoire de Chimie Théorique – France

The optical response of atoms and molecules induced by an intense ultra-short laser field is a subject of increasing interest since the advent of attosecond (10–18 s) laser pulses. In the last decades, impressive advances in laser technology have introduced new time resolved spectroscopies, offering the opportunity to investigate electron dynamics in atoms and molecules with an unprecedented time resolution.

However, the mechanism that control electron dynamics of complex systems in strong fields is still a challenge that requires to be interpreted by advanced theory. Development of accurate theoretical and computational methods, able to provide a precise treatment of the fundamental processes generated in the strong field regime, such as above-threshold ionization (ATI) or high-harmonic generation (HHG), is therefore crucial. In general, the accuracy in describing single- or multi-photon processes is strictly related to two aspects : the representation of the continuum energy spectrum and the description of the correlation effects.

In this seminar, these two aspects are explored in simple atomic and molecular systems. We are going to analyze the numerical performance of three different basis sets (Gaussian/Grid/Bsplines) in order to reproduce a good continuum spectrum in molecules [1], and, in a second step, we present a new linear-response range-separated time-dependent density functional theory to study photoexcitation and photoionization processes in atomic systems [2].

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*Intervenant

ANALYTICITY AND hp DISCONTINUOUS GALERKIN APPROXIMATION OF NONLINEAR SCHRÖDINGER EIGENPROBLEMS

Yvon Maday * ^{1,2}, Carlo Marcati ³

¹ Institut Universitaire de France (IUF) – Institut universitaire de France, Institut universitaire de France – France

² Laboratoire Jacques-Louis Lions (LJLL) – Université Pierre et Marie Curie - Paris 6, Université Paris Diderot - Paris 7, Centre National de la Recherche Scientifique : UMR7598 – Université Pierre et Marie Curie, Boîte courrier 187 - 75252 Paris Cedex 05, France

³ Seminar for Applied Mathematics [Zürich] – Suisse

We study a class of nonlinear eigenvalue problems of Schrödinger type, where the potential is singular on a set of points. Such problems are widely present in physics and chemistry, and their analysis is of both theoretical and practical interest. In particular, we study the regularity of the eigenfunctions of the operators considered, and we propose and analyze the approximation of the solution via an isotropically refined hp discontinuous Galerkin (dG) method.

We show that, for weighted analytic potentials and for up-to-quartic nonlinearities, the eigenfunctions belong to analytic-type non homogeneous weighted Sobolev spaces. We also prove quasi optimal a priori estimates on the error of the dG finite element method; when using an isotropically refined hp space the numerical solution is shown to converge with exponential rate towards the exact eigenfunction. In addition, we investigate the role of pointwise convergence in the doubling of the convergence rate for the eigenvalues with respect to the convergence rate of eigenfunctions. We conclude with a series of numerical tests to validate the theoretical results.

Mots-Clés: Analyse numérique, méthode des éléments finis, adaptativité, problème aux valeurs propres non linéaire, problèmes de type Schrödinger

*Intervenant

Quantum motion of small molecular hydrogen clusters confined by carbon nanostructures

Alexander Mitrushchenkov ^{*} ¹, María Pilar De Lara-Castells ²

¹ Laboratoire MSME – UPEM - Université Paris-Est Marne-la-Vallée – France

² Institute of Fundamental Physics, Consejo Superior de Investigaciones Científicas (CSIC) – C/Serrano 123 28029 Madrid, Espagne

We use symmetry-adapted perturbation theory based on density functional theory (SAPT-DFT) to derive accurate interaction potentials of molecular hydrogen with carbon nanostructures (graphene/graphite and single-wall carbon nanotubes, SWCNTs) [1-3]. Small hydrogen-saturated carbon clusters are used to obtain and fit dispersion- and dispersionless-interaction parameters. These parameters are then used in a pairwise model to obtain the full interaction of H₂ with extended nanostructures. The resulting potentials are also used to assess the accuracy of different DFT van der Waals-corrected functionals [1].

The interaction potentials are further applied to study the quantum motion of up to four H₂ molecules confined to different nanostructures [2]. For a single molecule, the molecular rotation is explicitly taken into account. The calculated vibrational levels of H₂ on graphite [1] (which is a simple assembly of graphene sheets) are in extremely good agreement with the experiment, see Fig.1. The rotational splitting ($m=0,1$) of ($j=1$) ortho-hydrogen [3] is of the correct order of magnitude, but somewhat larger than available experimental data obtained for an assembly of SWCNTs. This difference might be due to the orientational damping and requires further investigation.

For clusters of hydrogen molecules [2], the structure-less ($j=0$) boson model is used, that is justified due to the higher rotation energy ($2B=120$ meV) of H₂ as compared to the H₂-nanostructure interaction (about 10 meV). We have shown that three H₂ molecules form a triangular structure inside (11,4) SWCNT subject to a very large amplitude motion, see Fig.2. To obtain the corresponding wave functions and energies, we used the discrete-variable-representation (DVR) numerical approach in internal coordinates. The obtained arrangements are in line with very recent experimental data, indicating the stability of HCP structure of hydrogen stored inside SWCNTs and pointing out their very strong quantum nature. Work is in progress to treat larger molecular clusters at *ab initio* quantum level.

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^{*}Intervenant

Mots-Clés: hydrogen molecules, carbon nanotubes, graphene

Molecule-fixed axes in many-body Hamiltonians

Mirjana Mladenovic * ¹

¹ Laboratoire de Modélisation et Simulation Multi Echelle (MSME) – Université Paris-Est Marne-la-Vallée (UPEMLV), CNRS : UMR8208, Université Paris-Est Créteil Val-de-Marne (UPEC) – Université Paris-Est, 5 Bd Descartes, 77454 Marne-la-Vallée, Cedex 2, France

The separation of the dynamics of the quantum many-body systems into the overall rotation and internal motions leads to their quantization in rotating frames. Whereas the rotating body frame is unique for a rigid body, there is a great degree of freedom for choosing a body frame for a general rotating and vibrating N-particle system. This, in turn, implies the need to study many-body systems for a class of body frames.

The concept of vibrational coordinates and of rotational coordinates is particularly clear for the case of a triatomic molecule: three particles form a single plane, in which the molecule vibrates, and at the same time the molecular plane rotates in the space-fixed frame of reference. The overall molecular rotation is made explicit by means of an orthogonal transformation, which brings the space-fixed into the body-fixed axes. The direction perpendicular to the molecular plane uniquely determines one of the three axes of the frame. Rotation about this direction will change the position of the axes in the molecular plane, in fact the axis system. It is already intuitively clear that this axis transformation will not affect the vibrational portion of the kinetic energy operator. The other parts of the kinetic energy, the rotational part and the rotation-vibration coupling part, will then need to adjust themselves to the new definition of the body frame. In this fashion, we may address the problem of the interaction of rotations and vibrations, which is one of the most important problems in molecular studies.

The variation of the rovibrational kinetic energy operator following a change of orientation of the axis system is investigated in the present work from the physical and mathematical points of view. Various types of axis embedding are analyzed in a systematic fashion for triatomic molecules of arbitrary structure, including the bisector, principal axis, and Eckart frames. We also consider the bisector axis embedding for tetratomic molecules and the local axis embedding for pentatomic molecules. Different axis conventions lead sometimes to a complex entanglement of rotational and vibrational motions, which may pose serious obstacles to numerically exact approaches.

Mots-Clés: kinetic energy operators, rotating frames

*Intervenant

From pseudopotentials for the chemical environment to challenges in the computational treatment of catalysis

Paola Nava * ¹, Alexander Punter , Yannick Carissan

¹ Institut des Sciences Moléculaires de Marseille, UMR7313 (iSm2) – Aix-Marseille Université - AMU – Campus St. Jérôme, 13397 Marseille cedex 20, France

We have recently developed pseudopotentials for reproducing properties of chemical fragments based on sp² and sp³ carbon atoms. The pseudofragments retain only one or two explicit protons and electrons and use non-atom-centered potentials, which are however very close to the position of the carbon atom, so that the whole pseudofragment can be considered as an atomic building block. The pseudopotentials were extracted at the Hartree-Fock level, but they can be employed in the framework of DFT or multireference calculations. We have used the pseudopotentials to reproduce the molecular absorption spectra for large organic molecules and carbon allotropes, and are found to recreate both absorption and ECD spectra to a good accuracy. Besides that, we are interested in the computational description of metal complex catalytic activities. The comprehension of the reactivity of first-row transition metal catalyst has become crucial in the last decades, as these elements are more available than second- and third-row transition metals. Their computational treatment is challenging, especially if several spin states are involved in a reaction mechanism. We shall see an example on a cobalt intermediate, where the singlet-triplet energy gap is not trivial to obtain accurately for computational methods.

Mots-Clés: pseudopotential, pseudofragment, first, row transition metal, catalysis

*Intervenant

Theoretical core spectroscopy of molecules interacting with ice surfaces

Richard Asamoah Opoku * ¹, André Severo Pereira Gomes ², Céline Toubin ³

¹ University of Lille – University of Lille, 59655 Villeneuve d’Ascq - France – France

² Physique des Lasers, Atomes et Molécules (PhLAM) – Université de Lille, Sciences et Technologies, Centre National de la Recherche Scientifique : UMR8523 – Bat. P5 - Université de Lille1 - 59655 Villeneuve d’Ascq - France, France

³ Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique : UMR8523 – France

Ice is everywhere in the environment and plays an essential role as a catalyst for reactions between atmospheric trace gases. The uptake of halogenated molecules to ice has been proposed to have a major impact on geo-chemical cycles, human health and ozone depletion in the stratosphere [1]. X-ray photoelectron spectroscopy (XPS) [2], serves as a powerful technique to delineate the elemental composition of interacting molecular systems due to its surface sensitivity. Given the existence of complex physico-chemical processes such as adsorption, desorption, and migration within the ice matrix, it is important to establish a theoretical framework to determine the structural and electronic properties (electron binding energies, chemical shifts, etc) of these molecules or species under different conditions such as temperature and concentration. The focus of this work is to construct an embedding framework employing DFT and WFT to model and interpret photoelectron spectra of adsorbed halogenated species on ice surfaces at the core level with the highest accuracy possible.

We utilize a theoretical approach to determine the electron binding energies of adsorbed halide (HCl) and its ion (X⁻, Cl⁻), which has been suggested to cause perturbation in the hydrogen bonding network of the liquid-like layer on ice [3]. We construct model systems consisting of the halide/halide ion adsorbed on different (H₂O)_n-clusters (n = 8, 50, 100, 150 and 200). The structure used is obtained through classical molecular dynamics (CMD) simulation with a force field. For the interpretation of XPS spectra, the core energy shift is of relevance and the interaction of molecules needs to be modeled in a relativistic manner [4]. In this respect, the core-electron binding energies of the adsorbed halide ion are explored through the exact 2-c SR/SO-X2CAMF CVS-EOM-IP-CCSD and approximate 2-c SR/SO-ZORA through the SAOP model.

We show that the use of fully quantum mechanical embedded method to treat solute-solvent systems is computationally efficient, yet accurate enough to determine the electronic properties of the solute system (halide ion) as well as the long-range effects of the solvent environment (polar ice). The results of our calculations add further information to the debate on the long-range effects of water molecules on ionic systems.

This project has been supported by the French Ministry of Higher Education, Research and

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Mots-Clés: core spectroscopy, CVS, EOM, IP, CCSD, embedding

Calculation of effective interaction among different electronic shell using cRPA in ABINIT

Robinson Outerovitch * ¹, Bernard Amadon ²

¹ CEA, DAM, DIF, F-91297 Arpajon, France – CEA DAM Bruyères le Châtel – France

² CEA – CEA – CEA, DAM, DIF, F-91297 Arpajon, France, France

The calculation of the Hubbard U and Hund J parameters used in DFT+U or DFT+DMFT has been implemented in ABINIT using the constrained Random Phase Approximation in 2014. This implementation only considers intra-shell correlation (f-f in Ce for example).

We present here a work on the generalization of this implementation that allows us to perform inter-shell interaction calculation. In general, inter-shell interactions can be computed on a single atom (e.g. f-d in Ce), or on different atom site (e.g. Ni-O in NiO).

This new implementation is based on the extension of Projected Localized Orbital Wannier functions to several atoms and orbitals, previously implemented in ABINIT.

The role of those inter-shell interactions has rarely been discussed in the literature, but has been proved to be non-negligible (1.8 eV in Ce). We hope that the ability to calculate those terms from first principle will allow us to quantitatively explain the difficulties that DFT+U or DFT+DMFT face when treating some correlated materials.

Mots-Clés: corrélations, DMFT, Wannier, cRPA

*Intervenant

Automatic computation of global intermolecular potential energy surfaces for non-covalently bound systems

Ramon Lorenzo Panades-Barrueta *¹, Emilio Martínez-NÚÑez², Daniel PelÁez-Ruiz¹

¹ Laboratoire de Physique des Lasers, Atomes et Molécules (PhLAM), Unité Mixte de Recherche (UMR) 8523, Université de Lille, Bât. P5, Villeneuve d'Ascq Cedex – Université de Lille - Sciences et Technologies – France

² Departamento De Quimica Física, Universidad de Santiago de Compostela, E-15706, Santiago de Compostela – Espagne

We aim at simulating full quantum mechanically (nuclei and electrons) the processes of adsorption and photoreactivity of NO₂ adsorbed on soot (modeled as large Polycyclic Aromatic Hydrocarbons, PAHs) in atmospheric conditions. A detailed description of these processes is necessary to understand the differential day-nighttime behavior of the production of HONO [1, 2], which is a precursor of the hydroxyl radical (OH) [3]. In particular, the specific mechanism of the soot-mediated interconversion between NO₂ and HONO is to date not fully understood. Due to its relevance, we have chosen the NO₂-Pyrene system [1].

The first stage in this study has consisted in the determination of the stable configurations (transition states and minima) of the NO₂-Pyrene system. To this end, we have used the van der Waals Transition State Search Using Chemical Dynamics (vdW-TSSCDS) method [4], the non-covalent version of the TSSCDS algorithm [5]. Starting from a single input geometry, vdW-TSSCDS permits the characterization of the topography of a intermolecular Potential Energy Surface (PES) in a fully automated fashion. This topographical information will be used to obtain a global description (fit) of the interaction potential, necessary for the dynamical elucidation of spectroscopic properties and reactivity of the adsorbed species. For this, we have developed the Specific Reaction Parameter Multigrid POTFIT (SRP-MGPF) algorithm and software (SRPTucker) [6]. This method computes chemically accurate (intermolecular) PESs through reparametrization of semiempirical methods which are subsequently tensor decomposed using MGPF [7]. This software has been interfaced with the Heidelberg version of the Multiconfiguration Time-Dependent Hartree (MCTDH) software [8].

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Mots-Clés: PES, Semiempirical methods, MCTDH

Relativistic range-separated density functional theory

Julien Paquier * ¹

¹ Laboratoire de chimie théorique (LCT) – Université Pierre et Marie Curie - Paris 6, Centre National de la Recherche Scientifique : UMR7616 – Tour 12-13, 4ème étage, 4 place Jussieu, Case Courrier 137, 75252 PARIS, France

Standard Kohn-Sham density-functional theory (DFT) with the usual approximations is a very efficient tool for calculating electronic properties of systems so long as they do not display near-degeneracy effects. It so happens that systems containing heavy elements usually display both strong correlation and relativistic effects.

An efficient scheme to deal with strong correlation is range-separated density functional theory (rs-DFT) where the electron-electron Coulomb interaction potential is being split into a short-range interaction to be treated in DFT and a complementary long-range interaction to be treated in wave-function theory (WFT). One can then use multiconfigurational WFT to account for the long-range static correlation, and consider the short-range dynamical correlation through a DFT functional. This scheme was later adapted to account for some relativistic effects by O. Kullie and T. Saue through the use of a relativistic four-component long-range MP2 scheme and a complementary non-relativistic short-range functional.

In order to take relativistic effects in account both in the long-range wave function and short-range density functional we started the construction of a four-component range-separated scheme starting from the Dirac equation with a relativistic electron-electron Coulomb-Breit interaction potential. The first step of this work was the construction of a relativistic short-range LDA exchange functional, followed by the implementation of a four-component rs-DFT plugin within the software Quantum Package in order to test it. The second step was the the construction of a relativistic short-range correlation functional, starting from the relativistic short-range RPA.

Mots-Clés: Relativistic chemistry, range, separation, functionals

*Intervenant

Quantum N-body problem in condensed matter physics

Pina Romaniello * ¹

¹ Laboratoire de Physique Théorique - IRSAMC (LPT) – CNRS : UMR5152, Université Paul Sabatier [UPS] - Toulouse III, Université Paul Sabatier (UPS) - Toulouse III – 118 route de Narbonne, 31062 Toulouse Cedex 4, France

In this talk I will give a pedagogical introduction to the quantum mechanical description of extended systems. I will first introduce the concept of band structure and its link to the electronic structure of finite systems. I will then move to the most commonly used ab-initio theories to describe some interesting properties (e.g. photoemission and optical spectra) of these systems. I will focus in particular on density-functional theory [1] (and its extension to time) and on many-body perturbation theory based on Green's functions [2].

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Mots-Clés: Green's functions, extended systems, density functional theory

*Intervenant

Simulating molecular properties on a quantum computer

Bruno Senjean * ¹

¹ Instituut-Lorentz, Universiteit Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands – Pays-Bas

The increase in computational power together with theoretical method developments have played a significant role in our understanding of matter over the last decades. However, technological progress is now threatened by the predicted death of Moore’s law and new strategies have to emerge.

Indeed, the modeling of molecules and materials requires to solve the electronic structure problem, which scales exponentially with the system size. Nowadays, workarounds to this exponential wall problem are the use of truncated wavefunction-based correlation methods, Kohn-Sham density functional theory or Monte Carlo techniques. Unfortunately, large complex systems having strong multiconfigurational character remain challenging either in terms of computational cost or accuracy. Alternatively, quantum embedding theories have been proposed and allow to partition the system such that only the most active part (fragment) is treated by a high-level method, while the rest of the system (environment) is treated by a low-level method. However and despite promising results, the (sometimes drastic) decrease in the size of the Hilbert space in embedding approaches comes with a decrease in accuracy, and they still scale exponentially with the size of the fragment. Therefore, only small fragments can be considered and large complex systems remain intractable on a classical computer. That is when quantum computing enters into the game. Quantum computers promise an exponential speed-up to solve the electronic structure problem, such that modeling chemical reactions and complicated molecular systems has been proposed as the “killer application” of a future quantum computer. In this talk, I will introduce the concept of quantum computing and the two main algorithms developed to extract the ground- (and eventually excited-) state energy, namely the quantum phase estimation and the variational quantum eigensolver. Finally, I will discuss our recent work on determining molecular properties on a quantum computer from the calculation of energy derivatives.

Mots-Clés: Quantum Computing, Quantum Phase Estimation, Variational Quantum Eigensolver, Exponential speedup

*Intervenant

Playing with the reduced density-matrix: representability, functionals and embedding

Matthieu Saubanère * ¹

¹ Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier – Ecole Nationale Supérieure de Chimie de Montpellier, Université de Montpellier, Centre National de la Recherche Scientifique : UMR5253 – France

Going beyond Density-Functional Theory appear today as an important challenge for theoretical chemists and physicists, in particular to improve the accuracy for strongly correlated systems and to access to beyond ground-states properties. In that context, theories based on the reduced density-matrix are appealing but necessitates developments to become practical. In this presentation we present our recent work on the resolution of the density matrix functional theory variational equations and our strategy to construct a density-matrix-based embedding theory. Proofs of concept are presented in the framework of the periodic Hubbard model.

*Intervenant

Relativistic equation of motion coupled cluster theory

André Severo Pereira Gomes ^{* 1}, Valérie Vallet ¹, Florent Réal ¹, Loïc Halbert ¹

¹ Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique : UMR8523 – France

Heavy elements ($Z > 31$) are widely used in technological applications (catalysts, strong magnets, nuclear fuels etc) and, as such are intimately linked to major societal issues (nuclear waste, pollution). This makes it a pressing concern to understand their behavior in complex environments, and nowadays simulations play a key role in such efforts.

These elements, however, are often not easy to simulate since, in order to understand their properties it is essential to incorporate relativistic effects (scalar relativistic effects and spin-orbit coupling) into the electronic structure calculations. This has to be done at the same footing as the treatment of electron correlation, as both effects are now understood to be non-additive [1].

In this contribution we discuss our current work in the development of the equation of motion coupled cluster approach based on 4-component Hamiltonians [2], including its combination with quantum embedding approaches based on the frozen density embedding framework [3], so that both ground and excited states of complex systems can be accurately treated and predicted whenever experiments are too difficult to perform.

These approaches are showcased with examples of the determination of electron binding energies and electronically excited states of actinides in the gas phase [4], and of electron binding energies halogenated species in water droplets [5]. We will also outline our current efforts to treat larger molecular systems and other molecular properties in the DIRAC (<http://diracprogram.org>) program.

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*Intervenant

Mots-Clés: Coupled cluster, quantum embedding, relativistic effects, ionization energies, excitation energies

Insights into chemiluminescence from ab initio molecular dynamics simulations and machine learning analysis

Morgane Vacher * ¹

¹ Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation – Centre National de la Recherche Scientifique : UMR6230 – France

Chemiluminescence is the emission of light as a result of a non-adiabatic chemical reaction. One of the simplest molecules with chemiluminescent properties is 1,2-dioxetane. While the yield of the chemiluminescent process is observed to be low in 1,2-dioxetane (0.3%), it increases to 35% by substituting the hydrogen atoms by methyl groups. The reason for this impressive increase has remained an outstanding question. Firstly, we address it using ground-state and non-adiabatic dynamics of the decomposition reaction, and a simple kinetic model. While simulations are key to the understanding of chemical reactions, a current challenge is the in-depth analysis of the large amount of data produced, in order to provide valuable insight. Here, we present machine learning models trained to predict directly a specific outcome quantity of ab initio molecular dynamics simulations of chemiluminescent reactions. Our results show that in order to make accurate predictions, the models evidence empirical rules that are, today, parts of the common chemical knowledge. This paves the way for conceptual breakthroughs where machine analysis would provide a source of inspiration to humans.

Mots-Clés: chemiluminescence, non, adiabatic dynamics, machine learning

*Intervenant

Striking many-body effects in a simple oxide: the B₂O₃ case

Guillaume Ferlat * ¹, Maria Hellgren , Michele Casula

¹ Université Pierre et Marie Curie - Paris 6 (UPMC) – Institut de minéralogie, de physique des matériaux et de cosmochimie – 4 place Jussieu - 75005 Paris, France

Boron oxide is a prototypical network-forming system made of trigonal units [1-4]. Of particular relevance is the existence of some specific units, called boroxol rings, which are the analogue of benzene rings in these oxides [1]. Here, we will show the striking effects of many-body, mostly van der Waals, contributions to the energy and structure of these materials using ab initio methods, including DFT at different levels up to RPA and QMC calculations [2]. This was achieved on a set of polymorphic crystalline structures which were predicted a few years ago [3]. The results, not only enrich the B₂O₃ phase diagram and explain anomalies of the glassy phase, but could also be used for the benchmarking of ab initio methods and for the calibration of new force-fields [4].

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Mots-Clés: polymorphism, oxide, DFT, RPA, QMC

*Intervenant

Liste des participants

- Abadie Claire
- Agostini Federica
- Amadon Bernard
- Ammar Abdallah
- Ancarani Ugo
- Assfeld Xavier
- Bardenet Rémi
- Berger Arjan
- Biermann Silke
- Bonnet Eric
- Brémond Éric
- Briquez Stephane
- Caffarel Michel
- Carniato Stéphane
- Cassam-Chenaï Patrick
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- Etienne Thibaud
- Ferlat Guillaume

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- Maday Yvon
- Marut Clotilde
- Miradji Faoulat

- Mitrushchenkov Alexander
- Mladenovic Mirjana
- Moncomble Aurélien
- Nava Paola
- Oher Hanna
- Opoku Richard Asamoah
- Outerovitch Robinson
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- Pelaez Ruiz Daniel
- Porro Andrea
- Réal Florent
- Reinhardt Peter
- Robert Vincent
- Romaniello Pina
- Rouabhia Tarek Imed
- Saubanère Matthieu
- Scemama Anthony
- Schira Romain
- Sekaran Sajanthan
- Senjean Bruno
- Severo Pereira Gomes André
- Sisourat Nicolas
- Toubin Céline
- Toulouse Julien
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- Vallet Valérie
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