

GDR REST General Meeting

The GDR-REST aims to bring together different communities of theoretical spectroscopy which are/were historically separated, but unified under a very precise and important subject: the excited-states spectroscopy of variety of systems (for both weakly and strongly correlated systems, for valence and core electrons, etc.). One of the objectives is also to extend the collaboration to the nuclear physics community which might use very similar approaches based on Green's functions.

Retracing the GDR-REST footsteps, the Roscoff meeting will be of an interdisciplinary nature, in order to establish the state-of-the-art approaches, share knowledge, identify important issues and unresolved problems, and indicate future directions for the different communities.

For this reason four main lectures have been scheduled aiming to introduce the participants to the core electrons spectroscopy, to create a connection with nuclear physics and chemistry communities and to activate discussion on new mathematical developments and algorithms.



The meeting will take place at the Biological Station in Roscoff (SBR <http://www.sb-roscoff.fr/>), Roscoff Marine Station Research and training in marine biology, created in 1872 and affiliated to the CNRS and the University Pierre and Marie Curie. This station, situated on the north coast of Brittany, hosts a CNRS conference centre and is located in Place Georges Teissier, 29680 Roscoff.

All meals (and the poster session) will be served at the Gulf Stream restaurant, located at 800m from the Conference Centre. The accommodation of participants will take place both at the Gulf Stream and at the Hotel de France (located by the Conference Centre).

Organizers:

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Roscoff: a corsair village



Tide tables

High tide in Roscoff: 23/05 (20:06), 24/05 (8:23, 20:37), 25/05 (8:56, 21:11), 26/05 (9:33, 21:49), 27/05 (10:15, 22:34).

Tourisme

Visit the tourisme office (<http://www.roscoff-tourisme.com>) for a selection of possible cultural or gastronomical suggestions (cider/brewery, biscuits confectionery, etc.). For those who stay longer, you can also visit the Isle of Batz (2 miles north of Roscoff). The boat timetable is the following: from Roscoff (13h30, 14h30, 15h30, 16h30, 18h, 19h) and from Batz (14h, 15h, 16h, 17h, 18h30).

Monday

23 May

18:00-19:00 Registration and Welcome Aperitif

18:00-19:00 Poster Up

19:30 Dinner

Tuesday

24 May

09:00 Welcome

9:10-10:40 Keynote Speaker

09:10 Maurits Haverkort (*Max-Planck Institute, Dresden*)

Excitations and dynamics in solids and molecules, from local excitons via resonances to band excitations

10:40-11:10 Coffe Break

11:10-12:10 Core Spectroscopies

11:10 Yves Joly (*Institut Néel, CNRS and UGA, Grenoble*)

Multipole expansion in x-ray spectroscopies

11:40 Nadejda Mas (*IMPMC, Université de Paris VI*)

Ab-initio calculation of XMCD and XNCD at the K-edge

12:10-14:30 Lunch (and poster session)

14:30-15:30 Developments in DFT and beyond

14:30 Germain Vallverdu (*Université de Pau*)

XPS chemical shifts calculations: confrontation of experimental and theoretical investigations

15:00 Odile Franck (*LCT, Université de Paris VI*)

Self-consistent double-hybrid density-functional theory using the optimized-effective-potential method

15:30 Bruno Senjean (*LCQ, Université de Strasbourg*)

Local density approximation in site-occupation embedding theory

16:00-16:30 Coffe Break

16:30-17:30 RPA approaches for total energies

16:30 Dario Rocca (*Université de Lorraine*)

Dielectric matrix formulation of correlation energies in the Random Phase Approximation: Inclusion of exchange effects

17:00 Bastien Mussard (*Université de Lorraine*)

Random Phase Approximation with Fractional Charge and Fractional Spin

19:30 Dinner

09:00-10:30 Keynote Speaker

09:00 Timo Fleig (*LCPQ, Université de Toulouse*)

Atoms and Molecules as Laboratories for Exploring Physics Beyond the Standard Model of Elementary Particles

10:30-11:00 Coffe Break**11:00-12:00 Theoretical Developments (TDDFT and MBPT)**

11:00 Arjan Berger (*LCPQ, Université de Toulouse*)

Advances in Time-dependent Current-density-functional Theory

11:30 Stefano Di Sabatino and Walter Tarantino (*LSI, École Polytechnique, Palaiseau*)

Photoemission spectra from continued fraction representations of the Green's function

12:00-14:30 Lunch (and poster session)**14:30-16:00 Implementations and Methods**

14:30 Ivan Duchemin (*L_Sim, CEA Grenoble*)

Combining the GW Formalism with the Polarizable Continuum Model: a State-Specific Non-Equilibrium Approach

15:00 Maxime Morinière (*L_Sim, CEA Grenoble*)

Linear response TDDFT within cubic and linear BigDFT : case study of N₂ and HBDMI

15:30 Antoine Levitt (*Inria Paris*)

A new construction of Wannier functions

16:00-16:30 Coffe Break**16:30-17:30 Non-linear spectroscopies**

16:00 Valérie Véniard (*LSI, École Polytechnique, Palaiseau*)

Ab initio local field effects for surface second harmonic generation

16:30 Emanuele Coccia (*LCT, Université de Paris VI*)

Time-dependent quantum chemistry for high-harmonic generation spectroscopy

19:00 Banquet

09:00-10:30 Keynote Speaker

09:00 Vittorio Somà (*CEA, Saclay*)

Recent progress in ab initio approaches to the nuclear many-body problem

10:30-11:00 Coffe Break**11:00-12:00 Developments in Many-Body approaches**

11:00 Lucia Reining (*LSI, École Polytechnique, Palaiseau*)

Theoretical spectroscopy: some thoughts on old and new ideas

11:30 Pina Romaniello (*LPT, Université de Toulouse*)

Unphysical and Physical Solutions in Many-Body Theories: from Weak to Strong Correlation

12:00-14:30 Lunch (and Poster Session)**14:30-16:00 Excitonic properties**

14:30 Mads Trolle (*LSI, École Polytechnique, Palaiseau*)

Optical response in lateral graphene/hBN super-lattices

15:00 Giorgia Fugallo (*LSI, École Polytechnique, Palaiseau*)

Exciton Dispersion in Layered Materials

15:30 Pierluigi Cudazzo (*LSI, École Polytechnique, Palaiseau*)

Plasmon and exciton dispersion in in two dimensions

16:00-16:30 Coffe Break**16:30-17:30 Chemistry developments and Applications**

16:30 Carlo Adamo (*Chimie Paristech*)

Hybrid and double-hybrid parameter-free functionals

17:00 Hugo Gattuso (*SRSMC, Université de Lorraine*)

Computation of optical properties of DNA and DNA-sensitizer aggregates. Coupling molecular dynamics and quantum chemistry

19:30 Dinner

09:00-10:30 Keynote Speaker

09:00 Christian Brouder (*IMPMC, Université de Paris VI*)
Relativistic effects and gauge invariance in spectroscopy and scattering

10:30-11:00 Coffe Break

11:00-11:30 European action for core spectroscopies

11:00 Didier Sébilleau (*Institut de Physique, Université de Rennes*)
EUSpec, Modern Tools for Spectroscopy on Advanced Materials: a European Modelling Platform

11:30 Closing remarks

12:00-14:30 Lunch

Departures

Oral Contributions

Excitations and dynamics in solids and molecules, from local excitons via resonances to band excitations

Maurits Haverkort

Max Planck Institute for Chemical Physics of Solids, Dresden

Abstract

The theoretical description of excitations and with that the dynamics can be divided into three categories. For some materials and or energy of the excitation one can think of the excited state as an excited electron and hole moving in the potential of the original ground-state configuration. Excitations are explained as transitions between occupied orbitals and unoccupied orbitals. Band transitions in a solid. For some materials and excitation energies one needs to consider that once the electrons move the potentials change. This can be approximated as an effective interaction between the created hole and the added electron. These interactions will shift spectral weight to lower energy with sharp peaks at the edge called a resonance. If the interaction between the created hole and extra electron is large in an insulating material a bound state might be formed, a so called exciton.

The theoretical description of excitons and resonances can be quite challenging. In many cases it is not sufficient to assume a time dependent potential. Where the ground-state to some degree can be approximated by a single Slater determinant this is much less the case for excited states. Using several examples I will in the first part of my talk exemplify the different excitation types and the minimal level of treatment needed to describe these.

In the second half of this talk I will show how a newly developed post density functional theory method merging ideas from quantum chemistry and renormalization group theory can capture band-excitations, resonances and excitons including their involved multiplet structure. The method merges the local many body cluster calculations used for the interpretation of excitonic x-ray absorption spectra of correlated compounds with band structure methods used to calculate the less correlated spectra.

Multipole expansion in x-ray spectroscopies

Yves Joly

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Abstract

X-ray spectroscopies, as the optic ones, can often give fruitful pieces of information on material not only from the energy dependence of the response signals, but also analyzing their angular dependences. X-ray absorption spectroscopy is sensitive not only to the electric dipole (E1) interaction term, but also to the following terms in the expansion (E2, and probably E3). More challenging, contrary to optics is the search of the dipole magnetic interaction term (M1). Furthermore, X-Raman is able to probe electric monopole transition, and Resonant Elastic X-ray Scattering, a photon-in photon-out process, give more possibilities to probe independently all these terms. The purpose is to make some connections between optics and x-ray terminology and in examples such as low quartz to verify the corresponding sensitivity on birefringence, linear or circular dichroism. We shall see the benefits of the tensorial approach to analyze these transition terms and the crossed channels (E1E1, E1E2, E2E2, E1M1...) and make the connection with the physical properties related to the symmetry of the material.

Ab-initio calculation of XMCD and XNCD at the K-edge

Nadejda Mas^{1,2}, N. J. Vollmers³, Ph. Sainctavit^{1,2}, Ch. Brouder¹, F. Baudelet², M. Calandra¹, U. Gerstmann³, Amélie Juhin¹

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Abstract

X-rays Circular Dichroism is the difference between absorption spectra obtained from right and left circularly polarized X-rays. It occurs when the symmetry is broken. X-ray Natural Circular Dichroism (XNCD) occurs in non-centrosymmetric materials in which the inversion symmetry is broken. In a magnetic sample the breaking of time-reversal symmetry permits X-ray Magnetic Circular Dichroism (XMCD). XNCD presents a fundamental interest as it gives access to stereochemical information; it can, for example, be used to identify enantiomeric crystals. Ab initio calculation of the phenomena could be very useful for the investigation of the natural circular dichroism in new optically active materials. XMCD is a powerful tool for the study of the magnetic structure of complex systems as it gives element-specific information on the magnetic properties of the sample. Performing the experiments with hard X-rays is mandatory to probe samples at high pressure as diamond anvil cells are highly absorbing media. Studying the properties of matter under pressure is a good way to test our understanding of the electronic structure as pressure changes the local environment of the atoms, giving rise to new bulk properties. For 3d transition elements, measurements of XMCD at the K-edge are the main way to probe magnetism under pressure. Now, unlike the $L_{2,3}$ absorption edges for which well-established sum rules allow to extract spin and orbital contributions, the quantitative analysis of K-edge XMCD spectra is far from straightforward. The crucial support of theoretical interpretations is, yet, required to understand the experimental results. We will present the different operators contributing to the XAS, XMCD and XNCD cross section in a relativistic framework and we will discuss in detail their physical meaning. In order to calculate the spectra ab initio, these different contributions have been implemented in a monoelectronic plane-waves code based on Density Functional Theory: the XSpectra package of Quantum Espresso. The idea is to compute the charge density in the presence of a core-hole and then compute the absorption cross section using Lanczos algorithm. The calculated XAS and XMCD spectra obtained for metals (Fe, Co, Ni) and XAS and XNCD spectra of the gyrotropic crystal LiIO_3 will be carefully compared with experimental ones and the weight of each term (most important multipole and relativistic contributions) of the cross section will be discussed. We plan to use this method to calculate XAS and XMCD spectra of 3d transition metals in various spinels and intermetallic systems. We also plan to apply this formalism to compute the dependence of the absorption of non-polarized light on the direction of the magnetization in magnetized chiral systems: X-ray magneto-chiral dichroism.

XPS chemical shifts calculations: confrontation of experimental and theoretical investigations

Germain Vallverdu, Émilie Guille, Yann Tison, Isabelle Baraille

Université de Pau et des Pays de l'Adour, IPREM CNRS UMR 5254, Technopole Hélioparc, 2 av. du Président Pierre Angot, 64053 Pau cedex 9, France

Abstract

X-ray photoemission spectroscopy (XPS) is a surface characterisation technique among the most widely used in order to investigate chemical properties of material surfaces. XPS spectra are interpreted from the chemical shifts of the elements composing the material with respect of a given reference. One can then obtain information on the electronic structure of this element and the chemical bonds in its first coordination sphere. The binding energy of an electron in a given core level is computed from the energy difference of the N electrons system, called the initial state, and the $N-1$ electrons system, called the final state. Chemical shifts of one element can then be decomposed in an initial state effect, mainly due to the chemical environment of the element and a final state effect due to the electronic relaxation of the cation. Quantum chemistry methods can help at the interpretation of chemical shifts and to quantify the contribution of the final state and the initial state effects.

In this scope, we investigated a solid electrolyte, $Li_xPO_yN_z$, widely studied from an experimental point of view and otherwise already employed in commercial devices. Experimentally, the synthesis of thin films of $Li_xPO_yN_z$ is made by use of radiofrequency magnetron sputtering and starts from an amorphous form of γ - Li_3PO_4 , this material being then submitted to an N_2/Ar flux. Because of the amorphous structure of this compounds, the first step aims at finding a structural model of this electrolyte, adapted to periodic density functional theory calculations and able to reproduce the experimental data, composed of XPS and Raman spectra. The calculations of XPS shifts permit us to obtain a structural pattern for the electrolyte and to suggest a new coordination for nitrogen atoms which have not ever been considered in the experimental interpretation of XPS spectra. The possible existence of monovalent nitrogen atoms seems to be confirmed by vibrational and thermodynamic calculations and leads to a new point of view on the structure of the amorphous electrolyte and on the migration mechanism of Li^+ ions in the electrolyte.

Further Reading

- [1] Guille, É.; Vallverdu, G.; Tison, Y.; Bégué, D.; Baraille, I. J. Phys. Chem. C **2015**, 119 (41), 23379–23387.
- [2] Guille, É.; Vallverdu, G.; Baraille, I. The Journal of Chemical Physics **2014**, 141 (24), 244703.

Self-consistent double-hybrid density-functional theory using the optimized-effective-potential method

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Abstract

Double-hybrid density-functional methods [1, 2] combining DFT with second-order Møller-Plesset perturbation theory (MP2) are commonly used but usually the MP2 term is not calculated self-consistently. Some methods were proposed to improve that point such as an orbital-optimized double-hybrid scheme proposed by Peverati *et al.* [3]. In this study we compare the results with calculations performed using an alternate self-consistent double-hybrid scheme by using an OEP double-hybrid approximation (1DH-OEP). We consider fractional occupation numbers to evaluate the ionization potentials (IP) and electronic affinities (EA) using a one parameter double-hybrid MP2 method (1DH).

Further Reading

- [1] S. Grimme, *J. Chem. Phys.* **124**, 034108 (2006)
- [2] K. Sharkas, J. Toulouse, A. Savin, *J. Chem. Phys.* **134**, 064113 (2011)
- [3] R. Peverati, M. Head-Gordon, *J. Chem. Phys.* **139**, 024110 (2013)

Local density approximation in site-occupation embedding theory

Bruno Senjean¹, Masahisa Tsuchiizu², Vincent Robert¹, Emmanuel Fromager¹

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Abstract

Modelling strongly correlated electronic systems, such as materials and molecules containing transition metals, remains a challenge for quantum chemists and condensed matter physicists. In order to deal with these systems, the Hubbard Hamiltonian is usually employed, and solved either by the frequency-dependent dynamical mean-field theory (DMFT) [1] or the more recent frequency-independent density-matrix embedding theory (DMET) [2] which decompose the whole system into a small subsystem called impurity, embedded in the rest of the system referred to as the bath. In this talk, an alternative frequency-independent embedding scheme called site-occupation embedding theory (SOET) [3] will be presented. SOET is a density-functional theory (DFT)-based method which relies on the extension of DFT to model Hamiltonians. In this context, the density is the collection of sites occupation. The embedding of the impurity system within SOET is in principle exact and obtained from a site-occupation correlation functional for the bath. The difficult task is to provide an approximate functional, and the so called impurity local density approximation (ILDA) [4] as well as its implementation will be presented.

Further Reading

- [1] Georges, A., Kotliar, G., Krauth, W., and Rozenberg, M. J., *Rev. Mod. Phys.* **68**, 13 (1996).
- [2] Knizia, G., and Chan, G. K. L., *Phys. Rev. Lett.* **109**, 186404 (2012).
- [3] Fromager, E., *Mol. Phys.* **113**, 419 (2015).
- [4] Senjean, B., Tsuchiizu, M., Robert, V., and Fromager, E., arXiv preprint arXiv:1602.02547 (2016).

Dielectric matrix formulation of correlation energies in the Random Phase Approximation: Inclusion of exchange effects

Dario Rocca

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Abstract

Starting from the general expression for the ground state correlation energy in the adiabatic connection fluctuation dissipation theorem (ACFDT) framework, it is shown that the dielectric matrix formulation, which is usually applied to calculate the direct random phase approximation (dRPA) correlation energy, can be used for alternative RPA expressions including exchange effects [1]. Within this framework, the ACFDT analog of the second order screened exchange (SOSEX) approximation leads to a logarithmic formula for the correlation energy similar to the direct RPA expression. Alternatively, the contribution of the exchange can be included in the kernel used to evaluate the response functions. In this case the use of an approximate kernel is crucial to simplify the formalism and to obtain a correlation energy in logarithmic form. Through the use of a compact auxiliary basis set, this dielectric matrix-based formalism can be efficiently implemented both in localized and plane-wave basis sets [1, 2, 3]. A series of test calculations on atomic and molecular systems shows that exchange effects are instrumental to improve over direct RPA results. Work in collaboration with A. Dixit, B. Mussard, S. Lebègue, G. Jansen, and J. G. Ángyán. This work was supported by Agence Nationale de la Recherche under grant number ANR-15-CE29-0003-01.

Further Reading

- [1] B. Mussard, D. Rocca, G. Jansen, and J. Angyan, *J. Chem. Theory Comput.* (2016), to appear
- [2] Y. Ping, D. Rocca, and G. Galli, *Chem. Soc. Rev.*, 42, 2437 (2013)
- [3] D. Rocca, *J. Chem. Phys.* 140, 18A501 (2014)

Random Phase Approximation with Fractional Charge and Fractional Spin

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Abstract

An systematic analysis of the self-interaction error and the error in strong correlation of different versions of RPA is proposed. The analysis is done by calculations on systems with fractional charges and fractional spins. The clear connection between the errors and these fractionally occupied systems is explained.

Atoms and Molecules as Laboratories for Probing Physics Beyond the Standard Model

Timo Fleig

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Abstract

The search for physics beyond the standard model of elementary particles today is a highly interdisciplinary field, involving researchers from high-energy, nuclear, and atomic physics [1]. Electric dipole moments (EDMs) which give rise to spatial parity (P) and time-reversal (T) non-conserving interactions are an important probe of such New Physics in the low-energy regime [2], and their investigation allows for detecting/constraining (CP)-violation [3] required for solving several problems in fundamental physics, among them the Baryon Asymmetry of the Universe. I will present numerous aspects of relativistic electronic-structure investigations on atoms and molecules in the framework of the search for EDMs. These very often include elaborate studies of excited-state spectra of the systems in question and relativistic electronic-structure methods capable of addressing complex electronic structure [4]. Recent developments as well as theoretical results [5, 6, 7, 8] required in conjunction with experimental measurements [9, 10] on state-of-the-art atomic and molecular systems will be presented.

Further Reading

- [1] J. Engel, M. J. Ramsey-Musolf, and U. van Kolck, *Prog. Part. Nucl. Phys.*, **71** 21 (2013)
- [2] M. Pospelov, A. Ritz, *Ann. Phys.*, **318** 119 (2005)
- [3] M. Raidal et al., “Flavor physics of leptons and dipole moments”, *Eur. Phys. J. C*, **57** 13 (2008)
- [4] T. Fleig, “Invited Review: Relativistic Wavefunction-Based Electron Correlation Methods”, *Chem. Phys.*, **395** 2 (2012)
- [5] M. Denis, M. N. Pedersen, H. J. Aa. Jensen, A. S. P. Gomes, M. K. Nayak, S. Knecht, M. K. Nayak, T. Fleig, *New J. Phys.*, **7** 043005 (2015)
- [6] T. Fleig, M. K. Nayak, *J. Mol. Spectrosc.*, **300** 16 (2014)
- [7] T. Fleig, M. K. Nayak, *Phys. Rev. A* **88** 032514 (2013)
- [8] T. Fleig, M. K. Nayak, M. G. Kozlov, *Phys. Rev. A* **93** (2016) 012505
- [9] J. Baron and W. C. Campbell and D. DeMille and J. M. Doyle and G. Gabrielse and Y. V. Gurevich and P. W. Hess and N. R. Hutzler and E. Kirilov and I. Kozyryev and B. R. O’Leary and C. D. Panda and M. F. Parsons and E. S. Petrik and B. Spaun and A. C. Vutha and A. D. West, *Science* **343** 269 (2014)
- [10] H. Loh and K. Cossel and M. C. Grau and K.-K. Ni and E. R. Meyer and J. L. Bohn and J. Ye and E. A. Cornell, *Science* **342** 1220 (2013)

Advances in Time-dependent Current-density-functional Theory

Arjan Berger

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Abstract

In this work we solve the problem of the gauge dependence of molecular magnetic properties (magnetizabilities, circular dichroism) using time-dependent current-density functional theory [1]. We also present a parameter-free exchange-correlation functional that accurately describes the optical absorption spectra of insulators, semiconductors and metals [2].

Further Reading

- [1] N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger Phys. Rev. Lett. **114**, 066404 (2015)
- [2] J.A. Berger, Phys. Rev. Lett. **115**, 137402 (2015)

Photoemission spectra from continued fraction representations of the Green's function

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Abstract

In the past two decades, the one-body Green's function calculated in the GW approximation has become a major tool in estimating quasiparticle band structures and direct/inverse photoemission spectra of materials. Despite its success, the approach bears some intrinsic limitations, motivating the search for extensions/alternatives. We here present an on-going work on the development of an alternative approach, based on a different yet equivalent definition of the Green's function, expressed as a continued fraction [1]. Within this framework, approximate schemes arise from truncation of such a fraction and the way certain static quantities are estimated. Some preliminary results on model systems and bulk NiO [2], in which static quantities are calculated via RDMFT [3, 4], are shown. Model systems spectra are accurately described both in the weak and the strong coupling regime, while the approximate NiO spectrum is qualitatively correct both in the antiferromagnetic and paramagnetic phases, improving on standard mean-field approximations, for which the paramagnet is a metal.

Further Reading

- [1] R. Haydock, *Comput. Phys. Commun.* **20**, 11 (1980).
- [2] S. Di Sabatino, et al. Submitted (2015).
- [3] T. L. Gilbert, *Phys. Rev. B* **12**, 2111 (1975).
- [4] S. Sharma, et al., *Phys. Rev. B* **78**, 201103 (2008).

Combining the GW Formalism with the Polarizable Continuum Model : a State-Specific Non-Equilibrium Approach

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Abstract

We have implemented the Polarizable Continuum Model within the framework of the many-body Green's function GW formalism for the calculation of electron addition and removal energies in solution. The present formalism includes both ground-state and non-equilibrium polarization effects. In addition, the polarization energies are state-specific, allowing to obtain the bath-induced renormalization energy of all occupied and virtual energy levels. After a brief introduction of the present formalism, I will show some validating examples by comparisons with Δ SCF calculations performed at both the Density Functional Theory and Coupled-Cluster Single and Double levels for solvated nucleobases. The present study opens the way to GW and Bethe-Salpeter calculations in disordered condensed phases of interest in organic optoelectronics, wet chemistry and biology.

Linear response TDDFT within cubic and linear BigDFT : case study of N₂ and HBDMI

Maxime Morinière, Luigi Genovese, Thierry Deutsch, Ivan Duchemin

CEA Grenoble, DRF/INAC/MEM/L_Sim

Abstract

The Linear Response - Time Dependent Density Functional Theory (LR-TDDFT) was implemented and tested within the BigDFT code in 2012. It was only done through the solving of Casida's equations under the Tamm-Dancoff approximation (TDA) within the cubic BigDFT version. The solution of the full Casida's equations has now been tested, and we report results, obtained at the LDA level, concerning the N₂ and HBDMI molecules. We compare them to those given by NWChem. We will see with these examples the advantages and the drawbacks of an approach based on real-space basis sets. While systematically improving the description of the orbitals with diffuse properties, it also exhibits the so-called collapse of the continuum states, which is greatly impacting the LR-TDDFT spectra obtained. This problem is analysed in detail in the second part of our work, where recent developments in BigDFT allowed to use the wavefunctions computed using the linear BigDFT version to build the coupling matrix, which is the main ingredient of Casida's equations. In this case, the continuum collapse is not experienced, and the density of virtual states allows the description of transitions at higher energies. We will therefore present how these results compare to both the cubic BigDFT and the NWChem results we already introduced.

A new construction of Wannier functions

Eric Cances¹, Antoine Levitt¹, Gianluca Panati², Gabriel Stoltz¹

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Abstract

In this talk, I will present a new construction of real localized Wannier functions for systems with time-reversal invariance. Inspired by a recent proof of D. Fiorenza, D. Monaco and G. Panati, we introduce a new numerical method which does not require any initial guess, and is more robust than the Marzari-Vanderbilt approach of minimizing the localization of the Wannier functions.

Ab initio local field effects for surface second harmonic generation

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Abstract

A comprehensive understanding of the nonlinear optical properties of solids is crucial to improve the design and the analysis of new optical devices and provides an opportunity to search for new materials. Among these processes, Second-Harmonic Generation (SHG) is probably one of the most studied and has become, through the years a very powerful-non-invasive technique to characterize materials, because of its particular sensitivity to the symmetry of a system. In materials where inversion symmetry is present, optical Second Harmonic Generation is forbidden within the dipole approximation. But at a surface or an interface between two such materials, the inversion symmetry is broken and SHG is allowed. Crystal local fields are generated by the induced microscopic response of the system to an external perturbation. As a consequence their effects will be particularly important close to discontinuities as interfaces or surfaces. Local fields are important for a good description of optical properties of materials, but their effects on surface SHG have never been studied. We present here a new *ab initio* formalism that allows us to calculate the frequency-dependent surface second-order susceptibility $\chi^{(2)S}$ within TDDFT, where the local field effects are fully included and we have applied this formalism to Silicon surfaces.

Time-dependent quantum chemistry for high-harmonic generation spectroscopy

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Abstract

We explore the computation of high-harmonic generation spectra by means of Gaussian basis sets by propagating the time-dependent Schrödinger equation in the TD-CIS framework. We investigate the efficiency of Gaussian functions specifically designed for the description of the continuum proposed by Kaufmann *et al.* [1]. We assess the range of applicability of this approach by studying the hydrogen atom, i.e. the simplest atom for which “exact” calculations on a grid can be performed, and we apply our method to the helium atom and to H_2^+ . Moreover, we propose an alternative way to compute finite lifetimes for modeling the electron loss due to ionization, based on the fit of the radial profile of continuum wave functions.

Further Reading

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Recent progress in ab initio approaches to the nuclear many-body problem

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Abstract

In low-energy nuclear physics, ab initio methods aim at describing nuclear systems in terms of structureless nucleons and interactions between them. The two main difficulties in such an approach are the modelling of inter-nucleon forces and obtaining a controlled solution of the many-body Schrödinger equation. Recently, considerable progress has been made in both directions, with ab initio approaches reaching out to a good fraction of existing nuclei. I will give an outline of these advances, with emphasis on selected results from the Green's function approach in finite nuclei and in infinite nuclear matter.

Theoretical spectroscopy: some thoughts on old and new ideas

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Abstract

Many-body perturbation theory is a powerful tool to describe properties of materials. For example, Hedin's GW approximation [2] has become a standard approach for the calculation of bandstructures. However, often this self-energy to first order in the screened Coulomb interaction W is not sufficient. This is for example the case when one is interested in satellite structure beyond the quasi-particle peaks in the spectral function, or in the case of strong coupling, where the quasi-particle picture is no longer adequate. The natural next step would be to include second-order terms, but this is neither easy nor necessarily a good idea. In this talk I suggest to discuss pros and cons of some commonly adopted or suggested approaches, like the use of a self-energy, Dyson equations, cumulants, functionals, or non-perturbative approaches. The aim is to evaluate possible strategies for making a qualitative step forward in the description of electronic excitations.

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Unphysical and Physical Solutions in Many-Body Theories: from Weak to Strong Correlation

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Abstract

Many-body theory is largely based on self-consistent equations that are constructed in terms of the physical quantity of interest itself, for example the density. Therefore, the calculation of important properties such as total energies or photoemission spectra requires the solution of non-linear equations that have unphysical and physical solutions [1, 2]. In this work we show in which circumstances one runs into an unphysical solution, we illustrate the dramatic consequence that many-body theories become unpredictable, and we indicate how one can overcome this problem [?]. Our findings indicate that currently used strategies to develop approximations are only valid in a regime of weak to moderate interaction strength, and that they have to be completely changed in the strong-correlation regime. We propose a new strategy for strong correlation.

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Optical response in lateral graphene/hBN super-lattices

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Abstract

Two dimensional semiconductors have recently attracted a tremendous amount of attention, with monolayers of hexagonal boron nitride (hBN) representing a prime example. Reduced screening and confinement effects in this materials leads to an optical response completely dominated by strongly bound excitons. Graphene, on the other hand, is a semi-metal in which excitonic effects are much less pronounced. This fundamentally different optical behavior spurs the question as to the importance and underlying physics of excitons in hybrid graphene/hBN monolayer materials. This is especially true given the recent experimental realization of such hetero-structures by various experimental groups. In the present work, we study the optical response of graphene/hBN in-plane (lateral) super-lattices, which are essentially adjacent nano-ribbons composed of alternating graphene and hBN. We model the electronic structure of smaller unit-cells using DFT, and scale to larger super-lattices using a tight-binding model fitted to the DFT results. We model the dielectric screening, finding this to be highly anisotropic, scaling with the hBN/graphene filling factors. Finally, we model excitonic optical spectra and exciton binding energies, again finding a drastic modulation of the optical spectra with respect to hBN/graphene contents.

Exciton Dispersion in Layered Materials

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Abstract

Bethe-Salpeter Equation (BSE) in its recent extension [1, 2] is able to describe the dispersion of localized and delocalized excitons on equal footing and represents a key step for the ab initio study of the exciton mobility and the off-diagonal elements of the dielectric function in reciprocal space. This allows the ab initio simulation of spectra measured by electron energy-loss spectroscopy and inelastic X-ray scattering well beyond the optical limit. I here present the analysis of two prototypical layered materials, hBN and MoS₂ [3, 4] and discuss the change in the exciton dispersion observed passing from their 3D structure to the 2D case.

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Plasmon and exciton dispersion in in two dimensions

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Abstract

The investigation of neutral excitations (namely excitons and plasmons) is one of the most powerful ways to understand, predict, and tune the properties of materials. In particular the study of their dispersion as a function of the momentum transfer determines the way they propagate inside the crystal and transport their excitation energy. This property is of crucial relevance for all applications involving light harvesting, and also provides fundamental knowledge about exciton (or plasmon) mobility and migration. Using state-of-the-art Green's function many body approach we present a first principle study of the neutral excitations in two dimensional (2D) materials. In particular we investigated the exciton dispersion in graphene and hBN [1] and the plasmon dispersion in metallic Transition metal dichalcogenides [2]. From our results we provide a general picture of the mechanisms governing the dispersion of neutral excitation in 2D systems and of the role played by the confinement of the electronic charge in setting the exciton binding energy [3, 4].

Further Reading

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Hybrid and double-hybrid parameter-free functionals

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Abstract

The longstanding quest for representing the unknown part of the Kohn-Sham (KS) total energy in Density Functional Theory (DFT), that is the exchange- correlation term, has produced a relevant number of models, which can be grouped following the Perdew's ladder [1], a pictorial yet effective ranking of DF approximations (DFAs). This ranking is associated, in a rather heuristic way, with an improvement of the numerical performances so that higher rungs should correspond to more accurate functionals. However, the best "climbing line" on this ladder is not defined and two routes have been explored: a semi-empirical approach, where functionals are parameterized over a defined number of properties and systems, and first-principle models, which do not contain any fitted variables. Here we show that the latter approach, which can be defined as "the cleanest line on the steepest part of the face" [2], leads to the definition of robust exchange- correlation functionals belonging to the highest rungs of the ladder [3]. In particular, starting from the work of Perdew, Burke and Ernzerhof (PBE) [4], global (PBE0) [5] and double (PBE0-DH, QI-DH) [6, 7] hybrids will be derived and tested for a large number of systems and properties.

Further Reading

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Computation of optical properties of DNA and DNA-sensitizer aggregates. Coupling molecular dynamics and quantum chemistry.

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Abstract

In our current modern society, we are more and more in contact with synthesized unnatural chemicals. Most of them are metabolized and processed by our body and are of no harm for our health, but some of them, after passing through membranes, may accumulate in cells and nuclei and eventually reach DNA to form long living aggregates. In many cases, upon non-covalent interactions the global structure of DNA is not affected. Unfortunately the DNA-bound compounds may absorb in the visible or near UV region of the spectrum and eventually trigger photodegradation of DNA components such as nucleobases or the sugar backbone ultimately causing harmful damages. Depending on the structure of these sensitizers and due to the double-helical arrangement of the DNA double-strand, specific binding interactions will happen. A standard technique used experimentally to monitor such association is electronic circular dichroism (ECD). The inconvenience of such method is that it provides no clear information of the actual binding mode, thus it gives no direct exploitable clue to unravel the possible sensitization pathways. This problem can be tackled using molecular modeling. Indeed molecular dynamics allows us to assess the stability of multiple binding modes, and by comparing the modeled ECD for each case with the experimental one we will be able to conclude on the actual binding mode. For systems of biological interests such as DNA, modeling spectroscopic signals such as ECD is however far from being straightforward since it requires the computation of excited states for a relatively high number of atoms and coupled chromophores. To this aim using a combination of QM/MM calculations and Frenkel exciton theory we developed a protocol able to model efficiently and rapidly ECD of nucleic acid structures, also taking into account dynamic effects thanks to the coupling with molecular dynamics. In the present talk we will present the application of this technique to B-DNA and G-quadruplexes.

Relativistic effects and gauge invariance in spectroscopy and scattering

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Abstract

Magnetic x-ray scattering and relativistic effects in x-ray spectroscopy are calculated by using a Hamiltonian proposed by Blume in 1985, which is not correct for time-dependent fields such as a plane wave. Using the correct Hamiltonian is also not satisfactory because its matrix elements do not approximate the relativistic ones.

Besides, the gauge invariance of absorption and scattering cross sections is still a controversial question. We propose to solve both problems in one stroke by pushing a fully relativistic approach as far as possible, and making the Foldy-Wouthuysen transformation at the end of the calculation.

EUSpec, Modern Tools for Spectroscopy on Advanced Materials: a European Modelling Platform

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Abstract

I will describe our COST Action EUSpec which started 2 years ago and will run for another two years. The main objective of this COST Action is to gather theory activities in the field of spectroscopy to supply outstanding high level and up-to date support for demanding and sophisticated spectroscopy experiments which are being performed using advanced large-scale facilities or laboratory radiation sources within academic as well as industrial fundamental and applied research laboratories. At present, this Action involves about 190 members (physicists and chemists) from 29 countries.

Posters

Exploring density-functional theory at fractional electron numbers

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Abstract

Within exact density-functional theory, we investigate Kohn-Sham (KS) potentials, orbital energies, and noninteracting kinetic energies of the fractional ions of Li, C, and F. We use quantum Monte Carlo densities as input, which are then fitted, interpolated at noninteger electron numbers N , and inverted to produce accurate KS potentials $v_s^N(r)$. We study the dependence of the KS potential on N , and in particular we numerically reproduce the theoretically predicted spatially constant discontinuity of $v_s^N(r)$ as N passes through an integer. We further show that, for all the cases considered, the inner orbital energies and the noninteracting kinetic energy are nearly piecewise linear functions of N .

UV-Visible Absorption Spectra of Silver Clusters from TDDFT Calculations

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Abstract

The UV-visible absorption spectra of silver clusters containing between one and a hundred atoms are investigated in the framework of the time-dependent density-functional theory (TDDFT) using a range-separated hybrid (RSH) functional. The experimental spectra of Ag_n clusters, usually interpreted in the framework of classical optics in term of plasmon excitations due to the s electrons (Mie Theory), are shown to be well reproduced by TDDFT calculations. This approach gives us a description of the plasmon phenomenon from a quantum point of view. We can access the contribution of the orbitals and characterize the different type of excitation that are involved in the plasmon phenomenon. TDDFT calculations are performed both in the gas phase and in a rare-gas matrix.

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Thermal expansion of bismuth from first principles

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Abstract

Some anisotropy in both mechanical and thermodynamical properties of bismuth is expected. A combination of density functional theory total energy calculations and density functional perturbation theory in the local density approximation is used to compute the elastic constants at 0 K using a finite strain approach and the thermal expansion tensor in the quasiharmonic approximation. The overall agreement with experiment is good. Furthermore, the anisotropy in the thermal expansion is found to arise from the anisotropy in both the directional compressibilities and the directional Grüneisen functions.

Optical Properties of Nanoalloys of Cu and Au

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Abstract

The Surface-Plasmon Resonance (SPR) in noble metal nanoclusters has led to a large range of applications in biological sensing/detecting technology and other fields. The effect of composition and configuration on the optical properties of nano-alloys have widely been studied experimentally and theoretically. In particular, full quantum calculations of bi-metallic clusters of up to about 150 noble metal atoms have been performed using time-dependent density-functional theory (TDDFT) for Ag-Au [1, 2]. Experimental investigations on Au-Cu nanomolecules or clusters had recently revealed that incorporation of Cu gives rise to a SPR-like peak which is absent in both pure Cu and pure Au nanomolecules [3]. Furthermore, a recent theoretical study reported that Cu induces a plasmonic resonance in bimetallic Au-Cu nanoclusters [?]. We systematically study the effect of alloying on the optical properties of Au-Cu nano-clusters, showing that no such effect is found due to alloying Au with Cu. TDDFT calculations of the optical absorption are performed in the visible and near-UV ranges.

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Application of the GW method to strongly correlated electron systems

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Abstract

Strongly correlated electron systems present both strongly and weakly correlated electrons. The strong, short-range correlations cannot be described properly by DFT within the usual exchange-correlation functional approximations such as LDA and GGA. Methods designed for treating strong correlations, such as DFT+DMFT [1], improved the description of these systems. Furthermore, the GW approximation [2] enables to treat at least weak, long-range correlations. Combination of GW and DFT+DMFT have been proposed [3] for strongly correlated electron systems. In the purpose of developing such combinations in the ABINIT code [4], we have performed, and present here, preliminary GW calculations on several strongly correlated systems (bulk cerium and uranium dioxide). We discuss more particularly about the role of self-consistency in the GW loop.

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Study of the frequency-dependence of the short-range exchange-correlation kernel in time-dependent range-separated density-functional theory

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Abstract

The key quantity in linear-response time-dependent density-functional theory (TDDFT) is the exchange-correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ which has to be approximated in space and time. To correctly describe the space dependence of f_{xc} the “range-separated” version of TDDFT is often used [1, 2]. In range-separated TDDFT the electron-electron interaction is separated, by a parameter μ , in a short-range part which is described by standard TDDFT and in a long-range part described by wave-function or Green’s function methods. This approach corrects most of TDDFT deficiencies. For example, it is capable to recover the correct asymptotic behaviour of charge-transfer excitation energies. Instead, the frequency dependence of f_{xc} still remains very difficult to treat and in most of the applications it is just neglected which is referred to as the adiabatic approximation. Despite this crude approximation, the adiabatic f_{xc} provides reasonably accurate low-lying valence electronic excitation energies of molecular systems. However, the adiabatic approximation has also some serious failures. Most notably, it does not account for double (or multiple) excitations.

In this study, we considered range-separated linear-response TDDFT and we focused on the frequency-dependence of the short-range exchange-correlation kernel. We started by generalising the frequency dependent exact-exchange kernel [3, 4] to the case of range-separated TDDFT. We studied the performance of the frequency-dependent exact-exchange kernel as a function of the parameter μ and compared with the adiabatic LDA for He and H₂. We observed that the adiabatic approximation is exact at short range. Then we also considered the frequency-dependent correlation part of the kernel and we analysed its exact behaviour in the frequency space for the simple model H₂ in minimal basis set.

Further Reading

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Above-Threshold Ionization of Quasiperiodic Structures by Low-Frequency fields

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Abstract

We investigate the theoretical problem of the photoelectron cutoff and yield change in periodical structures induced by an infrared laser field. We use a one-dimensional Kronig-Penney potential including a finite number of wells, and the analysis is fulfilled by resolving the time-dependent Schrödinger equation. The electron spectra, calculated for an increasing number of wells, clearly show that a plateau quickly appears as the periodic nature of the potential builds up, even at a moderate intensity (10 TW/cm²). Varying the intensity from 10 to 30 TW/cm² we observe a net increase of both the yield and accessible energy range of the ionization spectrum. In order to gain insight into the dynamics of the system at these intensities, we use an analytical approach, based on exact solutions of the full Hamiltonian in a periodic potential. We show that the population transfers efficiently from lower to upper bands when the Bloch and laser frequencies become comparable. The model leads to a quantitative prediction of the intensity range where ionization enters the nonperturbative regime. Moreover, it reveals the physics underlying the increase of the photoelectron energy cutoff at moderate intensities, as observed experimentally.

Further Reading

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Which model for the alpha-gamma phase transition in cerium: A DFT+DMFT study using Wannier orbitals

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Abstract

We clarify the orbital mechanism of the $\alpha - \gamma$ transition in cerium. First we built an sdf Wannier orbital basis to describe the electronic structure of cerium. Second, we use this basis to study the relative role of several orbital hoppings upon compression of cerium. Third, we use DFT + DMFT calculations to quantify the impact of these hoppings on spectral functions. Our conclusion is that upon compression of γ cerium, the change of hybridization is due to both interatomic ff and fd hopping integrals. In particular, neglecting ff hoppings leads to an important renormalization of both the hybridization and the quasiparticle peak. Thus, neither the Kondo volume collapse nor the Mott transition model are sufficient to describe the isostructural transition in cerium.

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Notes

