ETSF Workshop on

Electronic Excitations 2009

Évora (Portugal), September 14–19, 2009

F. Nogueira (CFC, Univ. de Coimbra),

M. A. L. Marques (LPMCN, Université Lyon I),
L. Wirtz (Univ. Lille)

Program:

Sunday, September 13

20:45	Lunch/Dinner (at the Hotel)

Monday, September 14

12:30	Lunch/Dinner (at the Hotel)
14:00	SC meeting
16:00	Coffee break
16:30	SC meeting
	IT meetings (as arranged by IT convenors and members)
20:30	Lunch/Dinner (at the Hotel - Buffet)

Tuesday, September 15

9:00		Welcome address
9:20	*Steven Louie*	Spectroscopic and Transport Properties of Graphene and Graphene Nanostructures
10:20		Coffee break
10:50	*Patrick Rinke*	Auger recombination rates in nitrides from first principles
11:10	*Hannes Huebener*	Second Harmonic Generation in Bulk Silicon
11:30	*Julien Vidal*	How can ab initio calculations help to improve solar cells?
12:10	*Nicola Spallanzani*	Photo-excitation of light-harvesting supra-molecular triad: a TDDFT study
12:30		Lunch/Dinner (at the Hotel)
14:30	*Gustavo Scuseria*	New models for mixing wavefunctions with density functional theory
15:30		Coffee break
16:00	*Steen Nielsen*	Absorption spectra of chromophore ions obtained from storage ring experiments
17:00	*Adriano Conte*	A theoretical investigation on the first step of the mechanism of vision in living beings
17:20	*Marius Wanko*	Multiscale Approaches for Protein Spectroscopy
17:40		Round Table — Interaction of ETSF with users
20:00		Lunch/Dinner (at "Jardim do Paço" restaurant)

Wednesday, September 16

9:00	*Emily Carter*	Ab Initio Treatment of Excited States and Strongly Correlated Electrons in Crystals
10:00	*Federico Iori*	In strong correlation do we trust? The paradigm of V2O3
10:20		Coffee break
10:50	*Matteo Guzzo*	Exchange and correlation effects in the electronic properties of transition-metal oxides: The example of NiO
11:10	*Martin Stankovski*	Oxidise this: A study of PAW+QPSCGW calculations on Zn and Sn oxides
11:30	*Jim Greer*	Calculation of electron correlations and excitation spectra from a Monte Carlo configuration generation technique
12:10	*Dietrich Foerster**	Extension of the LCAO method to excited states
12:30		Lunch/Dinner (at the Hotel)
14:30	*W. Temmermann*	Electronic and Magnetic Properties of Rare Earths and Actinide Compounds
15:30		Coffee break
16:00	*Xinguo Ren*	Assessing the random phase approximation: CO adsorption and weakly bonded systems
16:40	*Esa Räsänen*	Functionals in low-dimensional systems
17:00	*Ulf von Barth*	Correlation energy functional and potential from time-dependent exact-exchange theory
18:00		Cheese and wine tasting at "Rota dos Vinhos"
20:00		Lunch/Dinner (at "Adeguita do Farrobo" restaurant)

* with Peter Koval

Thursday, September 17

9:00	*Hervé Ness*	Non equilibrium and many-body effects in quantum transport through nanoscale devices
9:40	*Hector Mera*	Are Kohn-Shamm conductances accurate?
10:00	*Valerio Olevano*	Effective 1D theory and generalized Fisher-Lee formula for quantum transport at nanocontacts
10:20		Coffee break
10:50	*Simon Dubois*	Quantum Transport in Graphene Nanoribbons
11:30	*Zeila Zanolli*	Transport properties of carbon atomic wires
11:50	*Aurelien Lherbier*	Charge transport in 2D graphene including dopants/defects: ab initio and tight-binding coupled approach
12:30		Lunch/Dinner (at the Hotel)
14:30	*Juan Garcia-Lastra*	Classical and Many-Body Theory of Image Potentials at Solid-Molecule Interfaces
15:10	*Andreas Gierlich*	All-electron GW Calculations for Perovskite Transition-Metal Oxides
15:30	*J.A. Berger*	GW without empty states
15:50	*Pina Romaniello*	The self-energy beyond GW
16:10		Coffee break
16:40		Poster Session
20:00		Lunch/Dinner (at "Jardim do Paço" restaurant)

Friday, September 18

9:00	*Alberto Castro*	Quantum Optimal Control Theory with TDDFT
9:40	*Ilya Tokatly*	Linear Continuum Mechanics for Quantum Many-Body Systems
10:00		Coffee break
10:30	*Andre Schleife*	From Ideal Bulk to Reality - Interplay of Excitonic Effects with Defects and Doping
11:10	*Claudia Roedl*	Absorption Spectra of Magn. Insulators: Antiferromagn. Trans.-Metal Oxides and Ferrogmagn. CrBr3
11:30	*M. Cazzaniga*	Ab-initio long wavelength dielectric properties of bulk iron
11:50	*Giancarlo Cappellini*	Optical absorption ... polycyclic aromatic hydrocarbons
12:10	*Giovanni Onida*	Spectroscopy of Monoatomic Carbon wires connecting sp2 carbon fragments
12:30		Lunch/Dinner (at the Hotel)
14:30	*Pierluigi Cudazzo*	Ab Initio Description of High-Temperature Superconductivity in Dense Molecular Hydrogen
14:50	*Frank Fuchs*	Ab-initio study of atomic gold-wires on Ge(001)
15:10	*Hansi Weissker*	Temperature effects on the electronic and optical properties of silicon clusters
15:30		Final remarks
15:40		Coffee break
16:00		ETSF Members' meeting
20:00		Lunch/Dinner (Banquet at the Hotel)

Saturday, September 19

9:00		SC meeting
10:30		Coffee break
11:00		SC meeting
12:30		Lunch/Dinner (at the Hotel)

List of Posters:

Irene Aguilera	First-Principles Design of Complex Intermediate-Band Photovoltaic Materials.
Magdalena Birowska	Ab initio study of functionalized carbon nanotubes
Björn Oetzel	Ab-Initio Studies of Electronic and Transport Properties of Graphene Nanoribbons
Michel Bockstedte	The merits of DFT-LDA and going beyond it towards excited states: a perspective from defects in SiC
Duanjun Cai	Accurate color tuning of firefly chromophore by modulation of local polarization electrostatic fields
Fabiana Da Pieve	Magnetic circular dichroism and spin polarization in resonant photoemission
Louise Dash	Non-equilibrium inelastic electronic transport: beyond the self-consistent Born approximation for the electron-phonon interaction
Luiz Cláudio de Carvalho	First-Principles Study of the Structural and Electronic Properties of the (Al,Ga,In)N Compounds
Xavier Declerck	Electronic and transport properties of boron nitride nanoribbons
Christoph Friedrich	EXX within the full-potential augmented-planewave (FLAPW) method
Pablo Garcia Gonzalez	GW calculations in exactly solvable model systems: The problem of the self-interaction errors
Matteo Gatti	Excitonic effects in the absorption spectrum of sodium at high pressure
Paola Gori	Electronic and optical properties of group IV two-dimensional systems
Jim Greer	The ABC's of Many-Electron Correlated Scattering
Ralf Hambach	First-Principles Approach for Spatially-Resolved Electron Energy-Loss Spectroscopy
Yann Pouillon	Structural and optical transitions of biliverdin
Fabrizio Puletti	Large prebiotic molecules in space: photo-physics of acetic acid and its isomers
Yuchen Ma	excited states of the chromophores within many-body perturbation theory
Anna Miglio	Transparent Conducting Oxides (TCO): tin oxides as a case study
Bruce Milne	Time-Dependent DFT for Elucidation of Stereochemistry: Dermacozine E, a Natural Product from the Mariana Trench
Bruce Milne	FMO-TDDFT Studies of Luciferase from the Japanese Firefly Luciola cruciata
Manolo Ramirez López	Many carrier effects in semiconductor nanostructures
Manolo Ramirez López	Photoluminescence spectroscopy of InGaAs/GaAs quantum wells
Tonatiuh RANGEL	Transport properties of molecular junctions from Many-Body Perturbation Theory
Arno Schindlmayr	Do we know the band gap of lithium niobate?
Martin Stankovski	Oxidise this: A study of PAW + QPSCGW calculations on Zn and Sn oxides
Z. Szotek	Structural phase transitions and fundamental band gaps of $Mg_xZn_{1-x}O$ alloys from principles
F. Trani	Ab Initio simulation of photovoltaic materials
José Guilherme Vilhena	Density gradients for the exchange energy of electrons in two dimensions
Ludger Wirtz	The phonon dispersion relations of lead chalcogenides (PbS, PbSe, PbTe)

Oral Communications

Spectroscopic and Transport Properties of Graphene and Graphene Nanostructures

Steven G. Louie

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The low-energy electronic states in graphene (a single atomic layer of carbon in a honeycomb structure) behave like those of two-dimensional (2D) massless Dirac fermions with pseudospin character. Many of the unusual electronic, transport and optical properties of graphene and graphene-based nanostructures originate from this unique electronic structure. Ab initio calculations further showed that, because of reduced dimensionality, electron-electron interaction effects are very important in the electronic and optical excitations of these systems. In this talk, I discuss some of our recent theoretical studies in exploring the fascinating properties of graphene and graphene-based nanostructures. Although pristine graphene and bilayer graphene are semimetallic, many-body interactions alter significantly their spectroscopic properties such as those measured in angle-resolved photoemission and optical experiments. For graphene-based nanostructures, strong excitons exist in and dominate the optical response of both semiconducting and metallic carbon nanotubes. Graphene nanoribbons are semiconductors with unusual electronic, magnetic and optical properties. Owing to the chiral nature of the electronic states, the carrier dynamics in graphene exhibits anomalous anisotropy when subjected to an external periodic potential of nanometer dimensions (called graphene superlattices). Under appropriate conditions, these graphene superlattices are predicted to be electron supercollimators and new generation of massless Dirac fermions may be created. Moreover, a biased bilayer graphene is a semiconductor with tunable excitons.

Auger recombination rates in nitrides from first principles

Patrick Rinke, Kris T. Delaney and Chris G. Van de Walle

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Indium gallium nitride (InGaN) alloys are successfully being used for light emitting and laser diodes in the green to ultraviolet part of the spectrum, but increases in internal quantum efficiency (IQE) are still required to allow broader applications. The IQE of InGaN devices is limited by loss mechanisms that, at high drive currents (i.e., high carrier concentrations) lead to a decrease in IQE, a phenomenon commonly referred to as efficiency droop. We demonstrate by means of rigorous first-principles calculations (density-functional and many-body-perturbation theory [1,2]), in which individual loss processes can explicitly be isolated, that Auger recombination is a key loss mechanism in wurtzite InGaN [2]. Auger recombination had previously been proposed by Shen et al. [3] as a loss mechanism in optically pumped InGaN LED devices, but it is difficult to discriminate between different radiationless processes experimentally. We examine two different mechanisms – inter- and intra-band recombination – that affect different parts of the spectrum (see Fig. 1). In the blue this is the last candidate. next esc will revert to uncompleted text. o green spectral region and at room temperature the Auger coefficient can be as large as 2×10^{-30}cm^{6}s^{-1} and in the infrared even larger [2]. Since Auger recombination scales with the cubic power of the free-carrier concentration, it becomes an important non-radiative loss mechanism at high current densities.

[1] P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, J. Neugebauer, and M. Scheffler, Phys. Rev. B **77**, 075202 (2008).

[2] K. T. Delaney, P. Rinke, and C. G. Van de Walle, Appl. Phys. Lett. **94**, 191109 (2009).

[3] Y. C. Shen, G. O. Mueller, S. Watanabe, N. F. Gardner, A. Munkholm, and M. R. Krames, Appl. Phys. Lett. **91**, 141101 (2007).

Second Harmonic Generation in Bulk Silicon

Hannes Hübener, Ralf Hambach, Eleonora Luppi and Valérie Véniard

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Second Harmonic generation is dipole forbidden in centrosymmetric media, like cubic Si, which makes it a powerfull symmetry selective tool. In experiments, however, multipole contributions to the second harmonic signal are frequently observed and thus provide a major obstacle for accurate non-linear spectroscopies that rely on exactly vanishing components of the second order response tensor, most notably non-linear surface spectroscopy. We investigate the importance of multipole second harmonic generation for materials with and without inversion symmetry by comparing the second order susceptibility calculated in dipole approximation with a calculation accounting for all multipole contributions. This enables us to predict, for example, the bulk contribution to second harmonic measurements of silicon surfaces.

How can ab initio calculations help to improve solar cells?

Julien Vidal

LSI, Ecole Polytechnique, Palaiseau, France

Cu(In,Ga)(S,Se)2 (CIGS) ternary compounds constitute the most promising alternative to the hegemony of silicon-based photovoltaic solar cells. Together with CdTe, they form a new generation of light absorbing materials which can be grown unexpensively using thin-film technologies. Not only record efficiency of CIGS solar cells approaches the record efficiency of silicon solar cell but also CIGS modules show excellent outdoor stability and radiation hardness. Despite the industrial success encountered by this technology, little is known about the material itself except that it shows good absorption properties and sustains high concentration of native defects, resulting in a natural doping and enhanced conductivity. In this presentation, I will review some of the past theoretical works involving Density Functional Theory (DFT) methods and present beyond-DFT results that enlighten new properties of the material and may open new routes towards higher efficiencies for CIGS solar cells.

Photo-excitation of a light-harvesting supra-molecular triad: a Time-Dependent DFT study

N. Spallanzani, C. A. Rozzi, D. Varsano, T. Baruah, M. R. Pederson, F. Manghi, A. Rubio

Department of Physics, University of Modena e Reggio Emilia; INFM-CNR National Research Center "S3",Modena, Italy; European Theoretical Spectroscopy Facility (ETSF); Department of Physics, University of Texas at El Paso; Center for Computational Materials Science, Code 6390, Naval Research Laboratory, Washington; Nano Bio Spectroscopy group, Dpto. de Física de Materiales, Universidad del País Vasco and Centro Mixto CSIC-UPV/EHU and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain.

We study the light harvesting triad carotenoid-diaryl-porphyrin-C_{60}, a novel promising candidate for third generation solar cells. This supramolecular assembly acts both as a photosynthetic antenna site, and a support for long-lived charge-separated states, merging the two main functionalities of the active component of a dye-based solar cell. We perform real-time Time-Dependent DFT, and we show, besides the numerical challenge, that TDDFT is able to provide an accurate description of the excited state properties of the system. In particular we discuss the electronic structure and the optical properties of the assembly, and we propose an interpretation of the photo-excitation and charge-transfer mechanisms in terms of the properties of the isolated component moieties. We find very good agreement between the calculated quantities and the experimental data, and we get useful insight about the photo-induced charge transfer mechanism.

New models for mixing wavefunctions with density functional theory

Gustavo E. Scuseria

Department of Chemistry and Department of Physics & Astronomy, Rice University, Houston, Texas, USA

The recent realization that the ground-state correlation energy of the random phase approximation (RPA) is intimately connected to an approximate coupled cluster doubles (CCD) model [1], opens interesting avenues for mixing RPA with DFT [2]. I will describe some of the recent work done in our research group on RPA, including applications to van der waals and noncovalent interactions [3].

In the second part of this talk, will present a mean-field approach for accurately describing strong correlations via electron number fluctuations and pairings constrained to an active space. Electron number conservation is broken and correct only on average but both spin and spatial symmetries are preserved. Optimized natural orbitals and occupations are determined by diagonalization of a mean-field Hamiltonian. This constrained-pairing mean-field theory (CPMFT) [4] yields a two-particle density matrix ansatz that exclusively describe strong correlations. I will demonstrate CPMFT accuracy with applications to the metal-insulator transition of large hydrogen clusters and molecular dissociation curves. I will also discuss the inclusion of dynamical correlation effects via density functionals.

[1] G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, J. Chem. Phys. 129, 231101 (2008).
[2] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. 130, 081105 (2009).
[3] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. 131, 034110 (2009).
[4] T. Tsuchimochi and G. E. Scuseria, arxiv:0904.2010v2 [cond-mat.mtrl-sci].

Absorption spectra of chromophore ions obtained from storage ring experiments

Steen Broendsted Nielsen

Department of Physics and Astronomy Aarhus University, Denmark

The electronic structure of ions strongly depends on their environment, and gas-phase studies are therefore needed to reveal intrinsic properties. A complication, however, is too few absorbing species for a traditional light transmission experiment. In Aarhus we have developed state-of-the-art apparatus to record gas-phase absorption spectra of macromolecular ions. The technique is based on the combination of an electrospray ion source, an electrostatic ion storage ring, and pulsed tunable lasers, and it relies on the measurement of delayed dissociation of photoexcited ions (action spectroscopy). I will present some of our recent results for chromophores of relevance in materials science and photobiology and discuss how the transition energies depend on the spatial delocalization of the pi electrons, the character of the electronic transition, nearby charges, and, not least, solvation by polar molecules. Our results are used to benchmark quantum chemistry calculations. Finally, if time allows, I will address the electronic coupling between bases in DNA revealed by synchrotron radiation circular dichroism experiments on DNA samples in aqueous solutions.

A theoretical investigation on the first step of the mechanism of vision in living beings

Adriano Mosca Conte[1], Leonardo Guidoni[2], Olivia Pulci[1]

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The mechanism of vision is present in most of the living beings[1]. In superior animals this mechanism is supported by a complex apparatus, but the ability to transform external optical solicitations in chemical signals is also present in the most primitive forms of life such as bacteria. In all the cases the first and most important step of the mechanism is the photoisomerization of the rhodopsin retinal that is a change of the retinal structural geometry (from CIS to $TRANS$) induced by the absorption of a photon. The rhodopsin is a protein located in some rod cells in the retina of the human eye, and is bonded to the retinal (a long organic molecule with more then fifty atoms). A good model reproducing the physical properties of the retinal is the protonated minimal Schiff base model (NC_5H_7). The small size of this photoactive molecule enables to study the photoisomerization process along all its phases by using the most efficient methods of calculation. Despite the simplicity of this system, the accuracy required for the study of its photoisomerization stretches the predictive power of most of the methods for the determination of the optical properties to their limits. In this work we studied the photoisomerization of the Schiff base by the GW method and the Bethe-Salpeter equation. Our results show that this process can be described by a two-state model in agreement with other theoretical works[2]. We then studied this process by TDDFT and analyzed the effect of several possible approximations of the exchange-correlation kernel.

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[2] Olivucci, Am. Chem. Soc. (1997); Filippi, J. Chem. Phys. (2004).

Multiscale Approaches for Protein Spectroscopy

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Our functional understanding of biomolecules at the molecular level is essentially gained by combining steady-state and transient spectroscopic features with structural information, as obtained by xray crystallography. The interpretation of spectroscopic properties and their response to structural changes, mutation, and changes in the environment (temperature, pH, etc.) can be greatly supported by theoretical modeling and spectroscopy. The predictive power of theoretical models depends not only on the level of approximation but more so on the knowledge of the errors and ncertainties incorporated in them. In the popular QM/MM approach, the largest error is usually introduced by the QM method employed to describe the spectroscopically active region of the system. Further, the interaction between this "QM region" and the protein/solvent/membrane environment is most commonly described at the level of a molecular mechanical force field. Hence, the protein electrostatics is described in terms of fixed point charges, neglecting the mutual polarization of QM and MM region and nonclassical dispersion interactions as well as intermolecular and inter-residual charge delocalization.

In this contribution, we present approaches beyond the conventional QM/MM model, discuss the performance of TDDFT and multi-reference QM methods, and present applications to the optical, IR, and NMR spectroscopy in rhodopsins and fluorescence proteins. In particular, the TDDFT description of excited-state properties of biologic chromophores will be discussed.

Ab Initio Treatment of Excited States and Strongly Correlated Electrons in Crystals

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Density functional theory (DFT) has been anointed as the method of choice for a quantum mechanics description of molecules and materials, but it is best used as a qualitative indicator because its quantitative accuracy is still limited by approximate electron exchange and correlation (XC). Moreover, there are cases where DFT fails completely, even in a qualitative sense. Photochemistry, strongly correlated systems, physisorption, and polymers are all at best poorly described within standard DFT implementations. We will discuss two ab initio techniques we have developed to accurately treat excited states and strongly correlated electrons in condensed matter. In particular, we will discuss our embedded correlated wavefunction theory, which offers a locally improved description of XC, and an ab initio version of the DFT+U method for strongly correlated materials. We will present applications of these techniques to problems where DFT fails (for various reasons that shall be outlined in the talk): the Kondo effect (transition metal impurities in nonmagnetic metallic hosts) and properties of first row transition metal oxides. Analysis of our embedded correlation wavefunctions provides the means to understand scanning tunneling spectroscopy measurements probing the Kondo state, while use of our ab initio DFT+U approach provides a non-empirical and hence experiment-independent technique to transition metal oxide properties.

Selected References:

S. Sharifzadeh, P. Huang, and E. A. Carter, "All-Electron Embedded Correlated Wavefunction Theory for Condensed Matter Electronic Structure," Chem. Phys. Lett., 470, 347 (2009). P. Huang and E. A. Carter, "Ab initio explanation of tunneling lineshapes for the Kondo impurity state," Nano Letters, 8, 1265 (2008). P. Huang and E. A. Carter, "Self-consistent embedding theory for locally correlated configuration interaction wave functions in condensed matter," J. Chem. Phys., 125, 084102 (2006). P. Huang and E. A. Carter, "Local electronic structure around a single Kondo impurity," Nano Letters, 6, 1146 (2006). N. J. Mosey and E. A. Carter, "Shear Strength of Chromia across Multiple Length Scales from First Principles," Acta Materialia, 57, 2933 (2009). N. J. Mosey and E. A. Carter, "Ab initio LDA+U Prediction of the Tensile Properties of Chromia across Multiple Length Scales," J. Mech. Phys. Solids, 57, 287 (2009). N. J. Mosey, P. Liao, and E. A. Carter, "Rotationally-Invariant ab initio Evaluation of Coulomb and Exchange Parameters for DFT + U Calculations," J. Chem. Phys., 129, 014103 (2008). N. J. Mosey and E. A. Carter, "Ab initio Evaluation of Coulomb and Exchange Parameters for DFT+U Calculations," Phys. Rev. B, 76, 155123 (2007).

In strong correlation do we trust? The paradigm of V2O3

Federico Iori[1], Matteo Gatti[2] and Lucia Reining[1]

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Aim of our work is to study through an ab initio theoretical approach the paramagnetic insulating phase of V_2O_3 compound, in order to understand better the metal-insulator phase transition subdues by V_2O_3 [1,4]. It has been shown that at DFT level it's not possible to describe properly the insulating paramagnetic phase because of a poor treatment of the strong electronic correlation for such systems with d- or f- incomplete shell. Moreover the comparison of DFT density of state with the experimental one is not possible until including many body effect such the ones arising from a direct photoemission spectroscopy. Within a traditional ab initio density functional scheme, the Kohn-Sham eigenvalues can' t be used for an appropriate description of the electronic bands structures, leading in particular for such a system (VO_2, V_2O_3) [2] to an underestimation or even to a closure of the photoemission band gaps [5]. Moreover, from the experimental point of view, it has been shown that adding small amount of Cr into the V_2O_3 a sharp metal-insulator transition arises as a function of both Cr concentration and pression at room temperature. Since to the best of our knowledge all the theoretical calculation present in the literature concern only V_2O_3 without really taking into account the Cr dopant atom [1], we decide to perform ab initio calculation by considering Cr-doped V_2O_3 supercell system in order to point out which role the presence of the dopant plays on the electronic structure during the metal-insulator paramagnetic transition of the V_2O_3 .

[1] G. Keller et al., Phys. Rev. B **70**, 205116 (2004)
[2] M. Gatti et al., Phys. Rev. Lett **99**, 266402 (2007)
[3] S.-K. Mo et al., Phys. Rev. Lett. **90**, 186403 (2003)
[4] A. I. Frenkel et al., Phys Rev. Lett. **97**, 195502 (2006)
[5] W. G. Aulbur et al., Solid State Phys. **54**, 1 (1999)

Exchange and correlation effects in the electronic properties of transition-metal oxides: The example of NiO

Matteo Guzzo[1], Matteo Gatti[2], Lucia Reining[1]

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The purpose of this work is to investigate the role of exchange and correlation effects on the electronic structure of nickel oxide (NiO), in particular on the nature of the insulating energy-gap, by means of ab-initio methods. As a prototype of strongly-correlated materials, the electronic structure of NiO has been extensively studied, experimentally and theoretically [1,2,3,4]. However, the origin of its gap is still under debate. Direct and inverse photoemission experiments are the most direct experimental way to measure the band structure of solids. From a theoretical point of view, we have to describe changes in the number of particles of the system. Many-Body Perturbation Theory (MBPT) — where the key quantity is the one-particle Green's function, i.e. the propagator of an electron/hole — is the appropriate tool to describe and understand photoemission. The GW approximation from MBPT [5] includes dynamical screening and correlation effects beyond H-F. The standard GW approach calculates first-order corrections of the LDA eigenvalues, but is not reliable on NiO since the Kohn-Sham band structure is too poor to be used as a starting point. It is thus necessary to go beyond standard GW. I used the COHSEX approximation [5,6], a static approximation of GW, to achieve self-consistency in energies and wavefunctions, to obtain a better starting point for the GW step. The GW+COHSEX photoemission spectrum gives an energy-gap of about 5 eV, in good agreement with experiment. In particular, I obtain similar results as another more time-consuming approach beyond perturbative GW [4]. In GW the screening is due to classical noninteracting charges. An improvement to GW would consider the screening between quantum interacting particle instead. An attempt to follow this way in the $GW\Gamma$ approximation [7] has shown no improvement in the spectrum.

[1] Mott, N.F., *Metal–Insulator transitions*, Taylor & Francis, London (1990).
[2] Sawatzky, G. A. and Allen, J. W., Phys. Rev. Lett. 53 (1984) 2339.
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Oxidise this: A study of PAW + QPSCGW calculations on Zn and Sn oxides

Martin Stankovski, Anna Miglio, Matteo Giantomassi, Gian-Marco Rignanese and Xavier Gonze

UCL, Louvain-la-Nevue, Belgium

The Zinc and Tin oxides represent a particularly troublesome example of transparent conducting oxides (TCOs) in ab-initio calculations. TCOs are a technologically very important class of wide-gap semiconductors with high electrical conductivity, and have been the focus of many recent ab-initio efforts. The failure of the one-shot G_0W_0 method is well documented in the case of ZnO and is hitherto largely uninvestigated for the tin oxides. Taking quasiparticle self-consistent GW [1] as a theoretically well-defined target, we investigate - for ZnO - the suitability of several starting points: LDA, GGA, $LDA+U$, $GGA+U$ and $COHSEX$ taken with various GW implementations. Illustration will be made on the crucial importance of! including semi-core states, some details of state-of-the-art Projector Augmented Wave (PAW) calculations, and also the need for employing well-constructed PAW atomic datasets in PAW+GW calculations. Finally, we present a comparison of features and results of ZnO with experiment and report on some trials and tribulations of calculations on the tin oxides.

[1] T. Kotani, M. van Schilfgaarde, S. V. Faleev, Phys. Rev. B. **76**, 165106 (2007).

Calculation of electron correlations and excitation spectra from a Monte Carlo configuration generation technique

Jim Greer

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Arbitrarily accurate solutions to the many-body Schrödinger equation are possible through a brute force expansion of the wave function, the so called configuration interaction (CI) or superposition of configurations method, although the length of the expansions required renders the approach intractable except for few-electron problems. A Monte Carlo technique for sampling configurations and evaluating their contribution to the energy or many-electron wavefunction has been developed and applied to a variety of molecular problems. Recently using this Monte Carlo CI (MCCI) method, singlet and triplet electronic excitation energies have been calculated for Ne, CH_2, C_2, N_2, and H_2O. We find that excitation energies can be predicted to within a few tens of meV (¡ 1%) of full CI (FCI) results using expansions consisting of only a few thousand configuration state functions as compared to the $O(10^8)$ configurations occurring in the corresponding FCI expansions. The method provides a consistently accurate and balanced description of electronic excitations with accuracy for small molecular systems comparable to the equation-of-motion coupled cluster method with full triples [1].

By considering the form of the energy resulting from truncation of the many-particle expansion space, electron correlations may be extracted from estimates of average or effective energy contributions while maintaining a reduced dimension for the expansion space. An energy formula expressed as a rational function of the expansion vector length is determined, allowing for estimates of asymptotic limits of many-body correlations [2], and hence an estimated of neglected correlations in a truncated many-body basis.

Interactions between molecular bound states and continuum states can be modeled exactly by using the (energy-dependent) self-energy or approximately by using a complex potential. We discuss the relation between the two approaches and give a prescription for using the self-energy to construct an energy-independent, nonlocal, complex potential [3]. This allows for a rigorous treatment of molecular correlations on a subsystem while 'opening' the system to allow interaction with larger systems such as electrodes in molecular physics, localized defect states, or for molecules-surface interactions.

We will also report on recent results for porting the method to the IBM Blue Gene and discuss scaling of the algorithm in massively parallel environments.

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Extension of the LCAO method to excited states

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We present an extension of the LCAO method to excited states. As a first application, we construct the Kohn Sham response function and molecular spectra within TDDFT linear response both in $O(N^2)$ operations where N represents the number of atoms of the molecule/cluster under study.

The first half of this report by D.F. describes the underlying mathematical idea while the second half by P.K. presents the results obtained.

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Electronic and Magnetic Properties of Rare Earths and Actinide Compounds

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An introduction is given to the Self-Interaction-Corrected Local-Spin-Density (SIC-LSD) method and its application to the rare earths in order to determine, without adjustable parameters, the valence of the rare earth in the elemental rare earths and their compounds.[1,2] The results of calculations of the rare earth's valence in 130 rare earth pnictides and chalcogenides are presented. Calculations for actinide carbides and nitrides are also presented [3] as well as actinide oxides [4]. This leads to a discussion of the degree of localisation in the 5f's and in the 4f's carbides and nitrides. Furthermore a comparison is made in the oxidation behaviour of the 4f's and 5f's. In addition, it is shown that the finite temperature SIC-LSD generalization allows the study of phase diagrams. The charge and magnetic fluctuations are treated with the Coherent Potential Approximation (CPA) and the Disordered Local Moment (DLM) formalisms respectively. This has allowed the determination of the critical point in Cerium [5] and the Curie temperatures, as well as the incommensurate Q-vectors, of all the late rare earths, from Gd onwards. This has resulted in a phase diagram of finite temperature magnetism of the heavy rare earths [6].

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Assessing the random phase approximation: CO adsorption and weakly bonded systems

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Local- and semilocal density approximations (LDA/GGA) to density functional theory (DFT), although tremendously successful in electronic structure calculations, suffer from, amongst others, severe self-interaction errors and the absence of long-range van der Waals (vdW) interactions. These deficiencies can lead to qualitative failures, as exemplified by the "CO adsorption puzzle" where LDA and GGA predict the wrong adsorption site for a CO molecule on (111) surfaces of Cu, Rh, and Pt or the considerable underbinding of two graphene layers. The recent resurgence of the "CO adsorption puzzle" and the renewed interest in vdW interactions are tied to the more fundamental quest of finding an "optimal" electronic structure method, that combines accuracy and tractability with transferability across different chemical environments. In this context the random-phase approximation (RPA) offers a promising avenue, because it overcomes the deficiencies of LDA/GGA by combining "exact exchange" and a correlation energy based on the renormalized (screened) Coulomb potential that is finite for metallic systems and takes vdW interactions into account automatically. The RPA is currently experiencing its own revived interest – facilitated in parts by the steady increase in available computer power – and a critical assessment of the RPA is beginning to emerge.

RPA has recently been implemented in the electronic structure code FHI-aims [1]. We perform our RPA calculations as a post-correction to either a self-consistent DFT or Hartree-Fock (HF) ground-state calculation. For CO@Cu(111), we demonstrate that RPA does overcome the pathologies of LDA/GGA and the correct (on-top) adsorption site is recovered [2]. The adsorption energies themselves are also in good agreement with available experimental data [2]. The underlying mechanism behind this improvement is then analyzed in terms of the excitation spectrum of CO@Cu(111) computed with the GW method. For two graphene layers we show that the RPA binding energy is in excellent agreement with the experimental value. This is due to the fact that dispersion forces, which are accurately described by RPA, dominate for this system. We further demonstrate for a large set of weakly bonded molecules that the vdW description intrinsic to RPA indeed leads to bonding, however, with a tendency to underbind. Insight into the origin of this underbinding is offered by analyzing the influence of different input orbitals (KS or HF) on "exact exchange" and correlation separately.

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Functionals in low-dimensional systems

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Practical success of density-functional theory depends on finding good approximations for exchange and correlation. So far, most density functionals have been developed in three dimensions (3D) with a view to studying the properties of atoms, molecules, and solids. Such efforts for two-dimensional (2D) systems have been relatively scarce despite the rapidly increasing theoretical, experimental, and technological interest in 2D structures such as semiconductor layers and surfaces, quantum Hall systems, graphene, and various types of quantum dots.

Here we first briefly review the rapid progress of low-dimensional physics, and then we present our very recent advances in the development of non-empirical 2D density functionals for both exchange and correlation. For finite, inhomogeneous 2D systems, all these functionals lead to considerably more accurate results than the commonly used 2D local spin-density approximation (LSDA).

For the exchange, adapting the strategy of Becke and Roussel to 2D, and thus modeling the cylindrical average of the exchange hole, we derive both implicit and explicit 2D density functionals for the exchange energy. Both functionals lead to accurate results when compared with exact reference data for the uniform 2D electron gas (2DEG) and few-electron quantum dots, respectively. Further generalization of the functional to ring topology leads to accurate description of the electronic exchange in quantum rings, even in the quasi-one-dimensional limit, where the (2D) LSDA is explicitly shown to fail. Parallel to this approach, we have also derived a more standard generalized gradient approximation for the 2D exchange, which reduces the error of the LSDA by a factor of four.

For the correlation, which is of extraordinary importance in low-dimensional systems, we have developed two functionals. The first one is based on modeling of the correlation-hole functions satisfying a set of exact properties. Excellent performance is obtained in comparison with numerically accurate quantum Monte Carlo data for quantum dots in magnetic fields, as well as for the 2DEG. Our second correlation functional originates from an extension of the Colle-Salvetti approach to 2D, supplemented by a Gaussian approximation for the pair density. The resulting local approximation for the correlation energy broadly outperforms the LSDA, and it is very straightforward to implement.

Correlation energy functional and potential from time-dependent exact-exchange theory

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A new functional for the correlation energy can be obtained via the Hellman-Feyman theorem as applied to the strength of the Coulomb interaction starting from the exact-exchange (EXX) approximation within time-dependent density functional theory (TDDFT). The resulting correlation energies are accurate to within 5%. The correlation potential obtained by taking the functional derivative with respect to the density turns out to be remarkably accurate for a number of atoms studied here. This potential has been used within the EXX formalism to calculate ionization potentials, static polarizabilities and van der Waals coefficients with results in close agreement with experiment.

Non equilibrium and many-body effects in quantum transport through nanoscale devices

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Using a non-equilibrium Green's functions technique, we study the effects of the interaction between electrons and atomic vibrations (vib) in the context of electronic transport through molecular devices within the steady-state regime.

We discuss the effects of the e-vib interaction and of the potential drops on the current and on the inelastic electron tunneling spectra. We suggest the possibility of using a single-molecule junction to built a nanoscale switch.

Finally we discuss the so-called non equilibrium distribution function (i.e. a non equilibrium extension of the well known Fermi-Dirac distribution for electrons at equilibrium), its universal behaviour and its use for transport calculations in complex systems.

Are Kohn-Sham conductances accurate?

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Using a correlated two-level two-electron model and the Friedel sum rule we discuss the accuracy of exacty and approximated Kohn-Sham density functional theory for the calculation of the electrical conductance.

Effective 1D theory and generalized Fisher-Lee formula for quantum transport at nanocontacts

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We introduce a new quantum transport formalism based on a map of a real 3-dimensional lead-conductor-lead system onto an *effective 1-dimensional system*. The resulting effective 1D theory is an in principle exact formalism to calculate the conductance. Beyond to be more efficient than the principal layers approach, it naturally leads to a *5-partitioned* workbench (instead of 3) and a *generalized Fisher-Lee formula* which allow a better physical insight into the contact resistance mechanisms. A similar generalization of the Meir-Wingreen formula is derived for correlated systems. We present an application to graphene nanoribbons.

Quantum Transport in Graphene Nanoribbons

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Remarkable transport properties related to the very high electron/hole mobilities have been reported in graphene monolayers, suggesting its potential use in future nanoelectronic. However, since truly two-dimensional graphene is a zero gap semiconductor, its direct integration in active electronic devices such as field effect transistor is prevented. The lithographic patterning of graphene into nanographites provides an easy way to overcome this drawback. Among the patterned nanographites, graphene nanoribbons (GNRs) have attracted considerable attention due to the strong relation between their electronic structure and their topology (more specifically the nature of their edges). Hydrogenated GNRs with armchair edges exhibit a band gap which arises from both quantum confinement and termination effects. In GNRs with zigzag shaped edges, an energy gap due to edge magnetization is found depending on the hydrogen coverage of the terminations. Regarding their synthesis, bottom-up fabrication techniques are very promising for the achievement of accurately defined ribbons geometries. However, GNRs produced are unlikely to be pristine graphene fragment with atomically perfect edges, but rather contains both topological and edges defects, playing the role of scattering centers. In the present work, the spin-polarized density functional theory is used to investigate the electronic and transport properties of GNRs with various edges geometries in the presence of topological and edge defects. The nature of the defect is found to play a key role in the band gap engineering of these graphene ribbons. In addition, our results gives some clues about the use of zigzag GNRs as possible components for spin-based electronic devices.

Transport properties of carbon atomic wires

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The quest for the miniaturization of electronic devices has incentivated the study of the electron transport properties of single molecules and few-atoms systems as the ultimate basic components of nanoscale circuits. In particular, carbon-based nanostructures are among the promising candidates to complement silicon-based electronics and/or give rise to all-carbon electronics [1]. For this kind of devices, the smallest possible interconnect is a monoatomic carbon wire, whose formation has been suggested to explain the behaviour of graphene-based switches [2] and of carbon nanotubes with a 'core' thinned down to atomic dimensions [3].

Motivated by the recent production and characterization of atomic carbon wires connecting graphene-like nanostructures [4, 5], first-principles and non-equilibrium Green's functions techniques have been used to investigate the spin-polarized electron transport properties of monoatomic carbon chains covalently connected by graphene-like fragments and graphene nanoribbons. It has been found that chains consisting of an even or odd number of carbon atoms are, respectively, not magnetic or magnetic, suggesting possible applications in spintronics.

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Charge transport in 2D graphene including dopants/defects investigated using an ab initio and tight-binding coupled approach.

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The Kubo-Greenwood formalism developed in real space [1] allows to investigate mesoscopic transport regimes, including localization phenomena [2] in nanostructures. In the present work, such approach is used to predict the quantum transport in 2D graphene including various dopants/defects using a tight-binding technique correlated to ab intio calculations. Indeed, first-principles calculations are performed in order to extract accurate on-site energies, hopping parameters and defect potentials which are then included in the tight-binding Hamiltonian to simulate transport. Large nanostructures of 2D graphene ($> 10^6$ atoms) are constructed and generic transport properties such as conduction mechanisms, mean-free paths, mobilities and conductivities scalings are derived for various concentrations of randomly distributed chemical dopants [3] and topological defects such as Stone-Wales, divacancies, ...

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Classical and Many-Body Theory of Image Potentials at Solid-Molecule Interfaces

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We discuss how dynamical image potentials affect the orbital energies of a benzene molecule when physisorbed on different surfaces ranging from metallic over semiconducting to insulating. At physisorption distances z=4.5 A, the energy gaps between occupied and unoccupied molecular orbitals vary between 10.4 and 7.0 eV depending on the type of substrate and the surface atomic structure. In particular, for semiconducting substrates the presence of metallic surface states can have a dramatic influence on the gap. For each surface the effective image plane position and surface dielectric constants are extracted by fitting the distance dependence of the gap to a classical image charge model. For the metallic surfaces, the LDA energies for the occupied molecular orbitals are in fair agreement with the GW results due to significant cancellation of errors. Finally, we discuss the results in terms of many-body perturbation theory by evaluating the GW self-energy explicitly to second order in the electron-electron interaction.

All-electron *GW* Calculations for Perovskite Transition-Metal Oxides

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The *GW* approximation for the electronic self-energy, which combines bare exchange with the dynamical screening of the many-electron system within the random-phase approximation, yields quasiparticle band structures in very good agreement with experiment. While most implementations today employ the pseudopotential approximation, our recently developed realization (http://www.flapw.de/spex) is based on the all-electron full-potential linearized augmented-plane-wave (FLAPW) method, where core and valence electrons are treated on the same footing. Within this method a large variety of materials can be treated, including d- and f-electron systems, oxides and magnetic systems. In this work we present results for selected perovskite transition-metal oxides, such as $SrTiO_3$, $BaTiO_3$, $PbTiO_3$ and others, which are widely used in technical applications. Their band gaps are difficult to measure experimentally and have been under debate for a long time. Most *ab initio* studies so far were based on density-functional theory and showed a strong underestimation of the band gap. Our all-electron *GW* calculations overcome this problem and yield band gaps very close to the best experimental estimates.

GW without empty states

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The GW approximation (GWA) to the self-energy[1] has proved to be very successful in the calculation of quasi-particle energies for a wide range of solids. However, the GWA is computationally expensive which is mainly due to the slow convergence with the number of unoccupied states that have to be taken into account in its standard sum-over-states expression.

In order to overcome this problem one can either use a simplified approximation to the self-energy such as the COHSEX approximation[1] in which no unoccupied states are required, or look for a numerically more efficient approach to the calculation of the GW self-energy such that only a small number of unoccupied states are needed[2]. However, in the former approach one obtains quasi-particle energies that are, in general, not close to the GW energies and in the latter approach one still has to deal with unoccupied states.

In this work we will show that the expression for the GW self-energy can be rewritten in such a way that no unoccupied states enter. This approach leads to a hierarchy of expressions for the self-energy which converges rapidly. We use a similar scheme to rewrite the sum-over-states expression for the polarizability such that only very few unoccupied states are required.

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The self-energy beyond GW

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It is commonly accepted that the GW approximation for the electron self-energy is successful for the description of the bandstructure of weakly to moderately correlated systems, whereas it will fail for strongly correlated materials. Here we discuss two important aspects of this approximation: first, the 'self-screening error', which is due to an incorrect treatment of induced exchange; second, the atomic limit, in which, instead, correlation is directly responsible for the observed problem. Using GW for the exactly solvable two-site Hubbard model, we discuss the effects of the self-screening error as well as the atomic limit, and we suggest how one could cure these two deficiencies of the GWA.

Quantum Optimal Control Theory with Time-Dependent Density-Functional Theory

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Atoms and molecules react in complex manners when they are irradiated with high-intensity electromagnetic pulses: multi-photon, tunneling and over-the-barrier ionization, laser driven photo-induced isomerizations or fragmentations, and high harmonic generation are some of the non-linear effects that are observed. The so-called pulse shaping techniques can be used to design pulses that produce a desired effect. We have undertaken the task of exploring this possibility from a theoretical point of view, by making use of time-dependent density-functional theory to describe the electrons, a real-space numerical representation, and various optimization techniques. For this purpose, the set of techniques known as "Quantum Optimal Control Theory" have to be married with Time-Dependent Density-Functional Theory. We exemplify the result with the design of a laser pulse capable of transferring the charge between the two wells of a double two-dimensional quantum dot, and with the design of a laser that achieves the isomerization of the formaldimine molecule.

Linear Continuum Mechanics for Quantum Many-Body Systems

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I develop the continuum mechanics of quantum many-body systems in the linear response regime, which can be viewed as an exact TDDFT in the nonadiabatic extreme. The basic variable of the theory is the displacement field, for which I derive a closed equation of motion under the assumption that the time-dependent wave function in a locally co-moving reference frame can be described as a geometric deformation of the ground state. This equation of motion is exact for systems consisting of a single particle, and for all many-body systems at sufficiently high frequency, and it leads to an excitation spectrum that has the correct integrated strength. The theory is illustrated by simple model applications to one- and two-electron systems.

From Ideal Bulk to Reality – Interplay of Excitonic Effects with Defects and Doping

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Intrinsic point defects often critically influence the properties of realistic systems. Dopants, on the other hand, are defects that are introduced into a crystal to generate free carriers. Both may dramatically change the optical or more generally the spectroscopic properties of the material. Reaching a microscopic understanding of the physical and chemical properties of defects in solids has long been a goal of first-principles electronic structure methods. Here we focus on the first principles calculation of optical properties from many-body perturbation theory through the solution of the Bethe-Salpeter equation (BSE). With the advent of high-performance computing even advanced electronic-structure methods such as the BSE can now be applied to realistic systems and a first principles understanding of defects, free-carriers and many-body effects and their interplay is emerging.

We will first discuss recent advances in the numerical solution of the BSE together with their advantages and disadvantages. For example, hybrid k-point meshes in combination with a conjugate-gradient approach for calculating the lowest excitonic bound states provide meV resolution of the absorption edge [1]. At the same time, a large photon-energy range can be covered by applying a time-propagation scheme to compute the dielectric function for large Hamiltonians. The underlying quasiparticle band structures are computed efficiently using a GGA+U+Δ approach, which is parameterized from HSE03+GW calculations. These concepts lead to a thorough description of the bulk optical properties of MgO, ZnO, and CdO [2].

We then apply the BSE approach to defects and dopants in the wide-gap group-II oxides MgO and ZnO that are important in the context of micro- and optoelectronics and catalysis. For the oxygen vacancy in MgO we show that the binding energy of defect-bound excitons in different charge states is significant. For a description of the influence of doping and free carriers on the optical properties of group-II oxides we incorporate Thomas-Fermi screening of the free electron gas into the screening function as well as the Pauli-blocking factor. This allows us to study temperature effects and the influence of the electron concentration from first principles. We interpret the resulting excitonic features that occur in the absorption spectrum as Fermi-edge singularities or Mahan excitons. The comparison with experimental spectra is gratifying, but the Mott transition of the excitons is difficult to observe.

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Absorption Spectra of Magnetic Insulators: Antiferromagnetic Transition-Metal Oxides and Ferromagnetic CrBr$_3$

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Magnetic materials attract more and more interest for technological applications, e.g. in the field of spintronics. Nevertheless, describing their excitation properties using first-principles methods remains a considerable challenge. We calculate optical absorption spectra solving the Bethe-Salpeter equation (BSE) within the framework of collinear spin polarization for some prototypical magnetic insulators: the antiferromagnetic transition-metal oxides MnO, FeO, CoO, and NiO, which are often considered as benchmark materials, as well as the insulating ferromagnet CrBr$_3$.

We discuss the absorption spectra of these compounds with respect to the influence of excitonic and local-field effects and in terms of optically allowed and forbidden transitions. The underlying electronic band structures are determined using the hybrid functional HSE03 and adding GW corrections in first-order perturbation theory. For the computation of the BSE spectra these band structures are considered as a benchmark and fitted by computationally less expensive GGA+U band structures with an additional scissors shift.

Ab initio long wavelenght dielectric properties of bulk iron

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We compute the optical properties of ferromagnetic iron with ab initio methods. This interesting system presents many theoretical challenges at the same time: this material is metallic, it has 3d electrons, and it is magnetic. In particular we account for the intraband contribution to the dielectric response function with a new method based on a Taylor expansion of the band dispersion across the Fermi energy. The computed RPA response function compares favorably with experiment, even though electron-electron correlations in the 3d bands are described at an independent quasiparticle level. The theoretical loss function is in even better agreement with the experiment. The inclusion of the semicore in the pseudopotential allows to account also for the edge at 55 eV. Our calculation allows to analyze the origin of the different structures in the EEL spectra.

Optical absorption, excitonic effects, and reorganization energies of homologous classes of polycyclic aromatic hydrocarbons. A systematic (time-dependent) density functional theory study

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Homologous classes of Polycyclic Aromatic Hydrocarbons (PAHs) in their crystalline state are presently among the most promising materials for organic opto-electronics. As a part of a more extensive research on PAHs, and following our previous works on oligoacenes, we present a systematic comparative study of the electronic, optical, and transport properties of oligoacenes, n-phenacenes, and oligorylenes. Using density functional theory (DFT) and time-dependent DFT we computed: (i) electron affinities and first ionisation energies; (ii) quasiparticle correction to the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap; (iii) molecular reorganization energies; (iv) electronic absorption spectra. We estimated the excitonic effects occurring in these molecules through the comparison between the optical gap and the quasiparticle corrected HOMO-LUMO energy gap. We discuss general trends as a function of molecular size.

Spectroscopy of Monoatomic Carbon wires connecting sp^2 carbon fragments

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Ab-initio calculations within Density Functional Theory combined with experimental Raman spectra on cluster-beam deposited pure carbon films provide a consistent picture of sp-carbon chains stabilized by sp3 or sp2 terminations, the latter being sensitive to torsional strain. This unexplored effect promises many exciting applications since it allows one to modify the conductive states near the Fermi level and to switch on and off the on-chain pi-electron magnetism [1]. We present and discuss theoretical results for typical sp+sp2 structures, and compared them with measured Raman spectra of cluster-deposited pure carbon films and with recent TEM experiments [2].

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[2] Phys. Rev. Lett. 102, 205501 (2009).

Excitonic effects on the optical properties of Graphane

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We present first-principles calculations of many-body effects on the optical response of graphane using the GW-Bethe Salpeter equation approach. Due to the electron-hole interactions two nearly degenerate bound excitons are formed in this two dimensional insulator. These result in the formation of an absorption peak at 1.6 eV below the GW gap. We found that the excitations are localized Frenkel excitons with the electron transfer from the C-C bonding state (localized on the C-C bond) to the C-H antibonding state (mostly localized on H-atom). Finally we speculate on the possibility of the Bose Einstein condensation of the excitons gas.

Ab-initio study of atomic gold-wires on Ge(001)

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Deposition of a sub-monolayer amount of gold on the Ge(001) surface results in a self-organized formation of atomic wires [1]. In STM images, these wires appear as almost perfect 1D structures that are strictly separated by a 16Å spacing (cf. Fig. 1). Due to its long-range order, experimental techniques operating in reciprocal space can be applied to the surface: LEED experiments give strong evidence for a c(8x2) translational symmetry of the surface, while ARPES indicates a metallic band structure. There are some indications that this system is a candidate for the observation of Luttinger liquid behavior. Yet the atomic geometry of the wires remains unknown. Therefore, the scope of the presented work is to construct, investigate, and evaluate structural models for the surface by ab-initio calculations. They are carried out in the framework of density functional theory using the VASP code. For each model, surface formation energy, STM images, and band structure are calculated. The computed properties are compared to experimental data in order to evaluate the different models.

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Temperature effects on the electronic and optical properties of silicon clusters

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The simulation of nanostructures has been a topic of great interest over the last years. In particular the *ab initio* calculation of the optical and electronic properties, i.e., of those properties which are important for the construction of solar cells and opto-electronic devices, has developed rapidly.

However, these *ab initio* calculations are numerically very demanding. They have been limited to relatively small systems and mostly to zero temperature. Full molecular dynamics in order to study temperature effects due to lattice vibrations are restricted to small systems. The combination of semi-empirical methods for the determination of geometries and of lattice vibrations in nanocrystals is a promising way to overcome these limitations.

In the present work we treat temperature effects on the optical spectra and on the electronic structure of silicon-hydrogen clusters. The geometry including temperature-dependent lattice vibrations is treated using model-potential molecular-dynamics simulations [1], while *ab initio* calculations are used to obtain the electronic and optical properties. Comparison with TDLDA results shows that already independent-particle spectra provide a reliable description as far as *changes* in the optical properties due to temperature are concerned. We find a strong broadening of the optical spectra with increasing temperature, as well as a linear decrease of the HOMO-LUMO gaps.

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Posters

First-Principles Design of Complex Intermediate-Band Photovoltaic Materials.

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Intermediate-band materials represent one of the most promising proposals in the quest of high efficiency solar cells. The compounds we present here are derived from chalcopyrites and spinels host semiconductors. In these compounds, some of the group-III atoms are substituted by transition metals to give rise to the intermediate-band. Their particular electronic structure allows these materials to absorb low energy photons, creating electron-hole pairs not only by the promotion of an electron directly from the valence band to the conduction band, but also due to the absorption of two low-energy photons using the intermediate band as a middle step. This more efficient use of the solar spectrum could in principle increase the efficiency of the cell up to 63.2

In order to propose the best candidates for intermediate-band materials and to predict their suitability for high efficiency photovoltaic purposes, it is necessary to study their properties theoretically. Our aim is to describe and predict by *ab-initio* methods their properties and especially the contribution of the new intermediate band to their absorption. For that purpose we need a precise description of the electronic structure of the systems and since this precision is not reached with standard DFT methods, the use of other advanced ab-initio methods is necessary. This work is thus focused on the analysis and understanding of the optical behavior of intermediate-band materials within different advanced theoretical approaches, in particular, DFT+U, GW and Time-Dependent Density Functional Theory.

A special attention is paid to the optical properties of Ti-substituted $CuGaS_2$ and M-substituted $MgIn_2S_4$ (with M=Ti,V). Optical spectra within the RPA approximation and within the Time Dependent DFT approach have been obtained. Absorption coefficients, reflectances and transmittances, are predicted for the IB materials and compared with those of the host semiconductors and experimental data when available.

Ab initio study of functionalized carbon nanotubes

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We study the effects of functionalization of CNTs with simple organic molecules CHn and NHn. We determine binding energies of the functionalized CNTs, the dependence of the binding energies on the density of the adsorbed molecules, and the changes in the geometry and electronic structure of the functionalized CNTs. All these factors influence the electrical properties of the CNTs and are important for sensor characteristics. Our studies are also relevant for the problem of composite materials, where weak materials (like polymers) are enforced with functionalized CNTs. Our studies are based on the ab initio calculations in the framework of the density functional theory. We use the generalized gradient approximation (GGA) for the exchange-correlation density functional and supercell geometry within the numerical package SIESTA. The positions of all atoms in the supercell have been optimized to get vanishing forces on atoms.

Ab-Initio Studies of Electronic and Transport Properties of Graphene Nanoribbons

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In recent years, graphene and its derivatives have gained enormous interest due to their remarkable electronic properties such as very high electron mobilities and signatures of the quantum Hall effect at room temperature. Graphene nanoribbons (GNRs) are particularly interesting for nanoelectronics as they are envisioned as the central element of graphene-based nanotransistors. We present ab-initio DFT calculations for various hydrogen-terminated armchair and zigzag GNRs. The calculations are performed using the Vienna Ab-Initio Simulation Package (VASP) by means of the supercell approach and GGA functionals. We focus our attention on the band structures and energy gaps as a function of the nanoribbon width. Furthermore we study the influence of spin polarization and spin ordering on the band structure and the magnetic behavior of zigzag GNRs. The electronic bandstructures are then converted into transmission functions using a number-of-states approach derived from the Landauer-Büttiker formalism. For several groups of armchair and zigzag GNRs, the similarities and differences of the quantum transport are discussed.

The merits of DFT-LDA and going beyond it towards excited states: a perspective from defects in SiC

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Density functional theory (DFT) has become a popular frame work within which a detailed and realistic defect theory down to the electronic structure is possible. Its well-known short coming, the band gap failure, hamper the quantitative prediction of ionization levels and correspondingly of the stability of defect charge states. Nevertheless, it has proven rather successful and often quantitative in the prediction of several important defect properties. In Silicon Carbide, for instance, the carbon clustering was predicted by theory and proven by the identification of small carbon-clusters via calculated and measured localized vibrational modes. Vacancy-related defects were identified via calculated hyperfine tensors that describe the interaction of the spin of a localized defect electron with the nuclear spin of the surrounding atoms. The quantitative description of these defect fingerprints by DFT in conjunction with the local density approximation (LSDA) enabled the identification of these fundamental defects in SiC and layed ground for a consistent theoretical interpretation of the defect kinetics observed in experiments. Nevertheless, DFT is a ground state theory and as such there is no access to the excited state often characterized in experiments. Many particle perturbation theory within the GW-approximation yields quasiparticle energies and corrects for the DFT band gap failure. The interaction of the excited electron with the hole is treated in the Bethe-Salpeter-equation. Within this frame work, excitation spectra in excellent agreement with experiment were obtained for a variety of systems. Applications in the defect theory however are scarce. Here this approach is applied to the case of the positive carbon vacancy. For this defect photo-EPR experiments exist. The interpretation of the spectral features of the steady state spectra in terms of thresholds for the quenching of the paramagnetic state and its re-ionization are in conflict with the Frank-Condon shifts predicted within the DFT. The inclusion of quasiparticle and excitonic effects beyond the DFT-LSDA picture does not resolve the discrepancies, but rather suggest a different interpretation of the spectra, which takes band structure effects into account and predicts a different sequence of charge states in the excitation process. A sizeable electron-hole attraction is found that results in a divation between the ionization levels and the excitation threshold of 0.23eV. The theory is discussed in the light of recent time resolved experiments that confirm our interpretation. This demonstrates the relevance of this demanding theoretical approach for the interpretation of defect spectra.

Accurate color tuning of firefly chromophore by modulation of local polarization electrostatic fields

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In molecular biology, fluorescent proteins have become a unique marking tool for gene expression, environmental pollutants, and monitoring the dynamics of AIDS virus and single-molecule motors.[1-3] Particularly, mutagenesis method is employed to produce mutants of fluorescent chromophore for color shifts.[4, 5] However, due to the uncertainty and complexity of the mutation effect on emission light wavelength, real color modulation for special need of target marking remains unavailable. In this work, we report a method for the accurate and continuous color tuning of firefly chromophore (oxyluciferin) by controlling the surrounding polarization electrostatic fields. Systematic calculations of time-dependent density functional theory (TDDFT) absorption spectra of gas-phase oxyluciferin molecules are carried out using Octopus. Results show that the polarization electrostatic field applied on the long molecular axis shifts the light wavelength most significantly, whereas that on the short axis in the molecular plane affects gradually. On the contrary, the electric field along the out-of-plane direction imposes zero effect on the optical properties. The color shifts of both the first and second absorption peaks show a simply linear relation with the in-plane electrostatic fields, except that of the first peak under strong negative field along the long molecular axis. Such linear relationship of wavelength shift indicates a realizable modulation technique for very accurate intentional color tuning of fluorescent proteins, which can meet the need of any special marking application by careful design of the local polarization electrostatic fields.

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Magnetic circular dichroism and spin polarization in resonant photoemission

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Valence band photoemission is a powerful tool to study electronic states of materials: in the angle resolved mode it allows to map the electronic states and to study the Fermi surface topology. Magnetic circular dichroism in valence band photoemission (with or without the spin resolution) adds further important informations allowing the study of spin electronic states. However, recently, we have observed a strong interest in using resonant techniques, like resonant photoemission or resonant inelastic X-ray scattering. These processes generally enhance the corss section of the corresponding direct process and allow to study the dynamics of the many body system in a more detailed way and to access to a big amount of information. Resonant photoemission is the opening of an indirect core-hole assisted process, i.e. core level absorption followed by an autoionization process, in which the final state is degenerate with the one in valence band photoemission. This channel resonates with the direct valence band photoemission and generally leads to a strong increase of the cross section. Magnetic circular dichroism and spin polarization in resonant photoemission give access to higher multipole moments with respect to those accessible through the well known sum rules in absorption. We present here the first ab-initio approach based on the multiple scattering approach for this kind of spectroscopy. Preliminary results on 3d ferromagnets are particularly encouraging, and we present here calculations of spin resolved magnetic circular dichroism from Fe. We also solve a debate between some experimentalists at ESRF and people at Daresbury Laboratory, about the possibility or not to measure, using resonant photoemission, local magnetic moments in disordered magnetic structures.

Non-equilibrium inelastic electronic transport: beyond the self-consistent Born approximation for the electron-phonon interaction

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We consider the problem of the interaction between particles (electrons e and phonons ph) in the context of electronic transport in nanoscale devices. We use the Keldysh Green's functions technique and consider the non-equilibrium steady state regime. The many-body effects are included in the form of self-energies treated within a self-consistent conserving approach. Different levels of approximation are used for the corresponding e-ph self-energy. We consider the lowest order diagram in the e-ph coupling (i.e. the self-consistent Born approximation SCBA) and second order diagrams (i.e. double exchange diagram or lowest order GW-like diagram).

Results for the equilibrium and non-equilibrium spectral functions as well as for the current are presented for a wide range of parameters. We show that it is necessary to go beyond the commonly-used SCBA to obtain correct results for all the range of e-ph coupling.

First-Principles Study of the Structural and Electronic Properties of the (Al,Ga,In)N Compounds

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Over the last decade group III-nitride compounds received a lot of attention due to their optoelectronic applications, e. g. their great potential for the fabrication of light-emiting diodes, photovoltaic cells and lasers working in a wide spectral range. Thus, their structural, electronic and optical properties have been extensively studied theoretically and experimentally. Being based on density functional theory (DFT) most of these studies, however, suffer from the so called band-gap problem. At least in the case of InN this cannot even be corrected by a perturbative quasiparticle correction, due to a wrong band-ordering of the band-edges at the Γ-point of the Brillouin zone. A manner that was found to partially correct this problem is to use DFT hybrid functionals in the spirit of an iterative solution of the quasiparticle equation with an exchange-correlation (XC) potential resembling the self-energy in Hedin's GW approximation. The final quasiparticle band-structures are obtained by means of a G_0W_0 correction, using a fully frequency-dependent screening for the calculation of W. The accuracy of this approach has been demonstrated recently for a large variety of materials, even for systems where pure DFT methods fail to predict an energy band-gap. In the present work, we perform a systematic study of the structural and electronic properties of the III-nitrides semiconducting compounds AlN, GaN and InN, in the zinc-blende and wurtzite phases. We use the DFT as implemented in the Vienna Ab-Initio Simulation Package (VASP) with the PBE-GGA and HSE03 approximations for the XC-potentials. The calculated structural parameters, bulk moduli, density of states, and band structures are presented and compared with previously reported ab-initio studies and experimental data. Quasiparticle band structures and their consequences for spectroscopic properties are presented and discussed.

Electronic and transport properties of boron nitride nanoribbons
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Carbon-based nanostructures have been extensively studied during the past few years. However, boron nitride (BN) which presents a strong structural analogy to carbon at the macroscopic level (cubic or hexagonal BN) has been less investigated at the nanoscale although synthesized experimentally (BN fullerenes and BN nanotubes). These observed BN nanostructures always exhibit semiconducting behaviours. Recently, the field emission properties of porous BN nanourchins have been measured [1], suggesting for the first time the possibility of metallic BN nanoribbons. BN nanoribbons are investigated using the density functional theory within the local spin density approximation as implemented in the ABINIT and SIESTA codes. The electronic properties of BN ribbons presenting similar widths are predicted for various shaped edges (zigzag and armchair). When the edge of the BN ribbon is passivated with hydrogen, it exhibits a semiconducting behaviour. However, when the edges are not passivated, zigzag BN nanoribbons are found to be metallic [2]. Furthermore, when spin effects are taken into account, three stable spin-polarized configurations are stabilized at the edges of the ribbon. Finally, based on calculations with SMEAGOL, a first characterization of the transmission properties are shown, suggesting a possible use of zigzag BN nanoribbons as spin-valve devices.

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EXX within the full-potential augmented-planewave (FLAPW) method
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The success of density-functional theory (DFT) relies on the availability of accurate approximations for the exchange-correlation (xc) functional. Standard xc functionals, such as the local-density and the generalized-gradient approximation, suffer from several shortcomings: an unphysical electronic self- interaction, no discontinuity of the xc potential at integral particle numbers, wrong asymptotic behavior etc.. Orbital-dependent functionals are a promising new generation of xc functionals. The simplest variant, consistent with the Kohn-Sham theory requiring a local xc potential, is the exact-exchange (EXX) functional. It does not exhibit the above mentioned deficiencies. We implemented the EXX functional within the full-potential augmented-planewave (FLAPW) method using a specifically designed auxiliary basis set for the optimized effective potential (OEP) equation. We demonstrate that the auxiliary and FLAPW basis must be properly balanced to avoid spurious oscillations in the exact exchange potential and show first results for prototype semiconductors and insulators.

GW calculations in exactly solvable model systems: The problem of the self-interaction errors

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Many-body perturbation theory under Hedin's GW approximation is presently the method of choice to evaluate quasiparticle properties in condensed matter theory. However, issues related to the intrinsic self-interaction errors in the GW approximation need to be clarified. With this objective in mind we have carried out GW calculations in simple exactly solvable model systems with very different electron correlation regimes. Whereas for standard weakly correlated systems the GW excitation energies are close to the exact values, self-interaction errors are evident in medium and strong correlation regimes. We have also analyzed the importance of the input electron density to check how much affected are the final G0W0 results. As expected, we have found that the final results inherit the errors from the input data and that only accurate quasiparticle energies can be achieved if the input electron density is very close to the exact one.

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Excitonic effects in the absorption spectrum of sodium at high pressure

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At ambient conditions sodium is the prototype of a nearly free-electron metal. Under pressure one would expect an increase of the bandwidth and hence a more free-electron-like behavior. Instead, at high pressure, sodium undergoes a phase transition becoming an insulator with a large gap [1,2]. Here we study excitonic effects in the absorption spectrum of the insulating phase of sodium. We show that the spectrum is characterized by a relevant polarization anisotropy and suggest its measurement as a stringent test for the determination of the crystal structure of the recently discovered phase [2].

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Electronic and optical properties of group IV two-dimensional systems

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The recent experimental realization of graphene, a truly two-dimensional carbon system with peculiar electronic, magnetic, mechanical and thermal properties [1], has brought an explosion of theoretical and experimental activity. Also attracting appears the possible existence of other group IV honeycomb structures made of Si or Ge. In particular silicene, the silicon counterpart of graphene, if endowed with similar properties, would provide a more direct way for their exploitation by virtue of its compatibility with the existing silicon-based microtechnology.

The next logical step in the study can be the chemical functionalization of graphene and graphene-like structures with the aim of tuning its properties. In particular, a conceptually simple way to open a gap is to adsorb atomic hydrogen on the two faces of the atomic sheet to turn the hybrization of carbon from sp^2 into sp^3, saturating the dangling bonds that give rise to the conducting π bands in graphene. Graphane, that is how this new system has been called, has been first theoretically predicted [2] and then experimentally produced [3].

We present here a study of the structural, electronic and optical properties of graphene-like structures composed by silicon or germanium and we compare them with the corresponding properties of graphene. The respective hydrogenated versions are also investigated and contrasted. Band structures are calculated within GGA-DFT and band gaps, when present, are corrected by GW calculations. The optical properties are obtained within the random phase approximation and by taking into account local-field effects.

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The ABC's of Many-Electron Correlated Scattering

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A many-electron correlated scattering (MECS approach to calculation of transport in molecular electronics has been applied to various problems in molecular electronics, including benzene dithiol [1], alkane dithiol/diamine [2], siliane dithiols/diamine [3], and point contacts.

Recently, a study of the MECS approach in the linear response regime questions the manner in which the method imposes the boundary conditions and suggested the method is not able to reproduce well-known phenomena such as conductance quantization.

We present a simple analytical model to demonstrate how the MECS approach in the limit of non-interacting elctrons reproduces conductance quantization for a single channel with unity electron transmission. We further demonstrate that the boundary conditions in this limit are consistent with a Landauer description of quantum electronic transport. We discuss the difference in implementation of the approach within a perturbation or linear response approach and for variational calculations.

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First-Principles Approach for Spatially-Resolved Electron Energy-Loss Spectroscopy

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The recent progress in electron microscopy to achieve atomic resolution in electron energy-loss experiments (EELS) opens a new way to investigate nanostructures. Within the framework of time-dependent density functional theory (TDDFT), first principles calculations [DP] have been successfully applied to study momentum resolved electron energy-loss spectra (EELS) of solids and molecules. We try to extend the current approach to spatially resolved EELS in the low loss region ($E < 40eV$).

First, we performed preliminary tests for a single layer Graphene sheet. In contrast to previous calculations, non-local effects are included in the microscopic dielectric function. Second, we visualized the collective electronic response to an external perturbation in Graphite, explicitly taking into account the inhomogeneity of the system on the atomic level. That analysis in space and time shows directly which electrons contribute to the excitation. The relation to plasmons is discussed.

[DP] DP-code: `http://www.dp-code.org`; V.Olevano et.al., unpublished.

Structural and optical transitions of biliverdin

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Phytochromes constitute a widespread family of photoreceptors found in plants and bacteria, where they act as photomorphogenesis regulators. It is now well-established that they exists in two forms: the P_r, physiologically inactive and absorbing red light, and the P_{fr}, absorbing in the far-red domain. It has also been shown that the P_r-P_{fr} transition mechanism involves an isomerisation process. Yet the actual transition path is still an open question, since it has only been possible to directly observe the P_r form so far, and several models are still being debated.

Biliverdin is the phytochrome found in bacteria, and has been recently observed as a crystal in its P_r form within the surrounding protein. Its P_r-P_{fr} transition has been studied both experimentally and theoretically. The most involved region of the molecule around the chromophore has been identified, though no definitive answer has been given for the final geometry. The protonation state of the P_{fr} form is not clear either, and the mechanisms of the possible proton transfers occuring are still unknown. Adding to the confusion, recent studies suggest that the transition might involve a rotation around a single bond in addition to isomerisation. Due to steric clashes, the rotation would in turn cause further conformational changes in the protein environment. Until now this process has been eluded because of its complexity.

All these considerations clearly call for a finer-grained theoretical insight, that we aim at providing the experimentalists with. The chromophore itself being composed of a few dozens of atoms, we are able to study it by means of *ab initio* DFT calculations. When adding the protein environment, the number of atoms immediately goes above 1500, requiring a different level of approximation, and we are exploring several available frameworks. In all cases we are evaluating and comparing the possible protonation states, in addition to systematically study the aforementioned single-bond rotation. In order to compare our results with experiments, we calculate the infrared, Raman, and optical spectra of all the structures we investigate.

Not only will the knowledge of the P_{fr} form give the correct mechanism of the photochemical transition, as it will open the way to the description of the reverse transition (called *dark reversion*), which is orders of magnitude slower and follows obviously a different path. It will then become possible to understand how the metabolic state of the cell, in particular oxygen levels, influence both transitions.

Large prebiotic molecules in space: photo-physics of acetic acid and its isomers

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An increasing number of large molecules have been positively identified in space. Many of these molecules are of biological interest and thus provide insight into prebiotic organic chemistry in the protoplanetary nebula. Among these molecules, acetic acid is of particular importance due to its structural proximity to glycine, the simplest amino acid. We compute electronic and vibrational properties of acetic acid and its isomers, methyl formate and glycolaldehyde, using density functional theory. In particular we use the program package TURBOMOLE, with the functional-basis combination B3LYP-TZVP, to obtain the electronic ground state geometry and the vibrational spectrum for the three species. Finally we compute the complete photo-absorption cross-section for each molecule using the TD-DFT implementation of OCTOPUS in the local-density approximation, with the exchange-correlation energy density of the homogeneous electron gas. From computed photo-absorption cross-sections, we obtain the corresponding photo-absorption rates for solar radiation at 1 AU and find them in good agreement with previous estimates. We also discuss glycolaldehyde diffuse emission in Sgr B2(N), as opposite to emissions from methyl formate and acetic acid that appear to be concentrate in the compact region Sgr B2(N-LMH).

excited states of the chromophores within many-body perturbation theory

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The excited states of chromophores (photoactive yellow protein chromophores and schiff-base retinal chromophores) are studied using ab-initio many-body perturbation theory (GW approximation and Bethe-Salpeter equation). Calculation beyond the Tamm-Dancoff approximation is needed for an accurate description of the lowest $\pi \rightarrow \pi^*$ excitations, which affects the excitation energy by 0.4 eV. The huge exchange interaction between the electron and hole leads to the unnegligible coupling between the resonant transition and the antiresonant counterpart. Accurate description of the lowest $n \rightarrow \pi^*$ excitation requires inclusion of the dynamics effect in the electron-hole screening.

Transparent Conducting Oxides (TCO): tin oxides as a case study

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TCOs are a class of oxides with increasing importance in many technological applications like solar cells and flat panel displays. They are optically transparent, wide gap semiconductors or insulators which also display good electrical conductivity, due to doping or intrinsic defects. Among the TCOs most widely used, we have focused on tin oxides ($SnO2$ and the less stable SnO) as a case study. In order to explore their electronic bulk properties, we first performed DFT ground state ab-initio calculations within a PAW implementation as well as standard norm conserving pseudopotential approach, employing both LDA and GGA exchange-correlation functionals. The Sn semi-core s, p and d states, relevant especially in $SnO2$, are explicitly taken into account as valence states in the PAW atomic data sets. To improve the description of the band gap, we have subsequently applied one-shot GW corrections.

Time-Dependent DFT for Elucidation of Stereochemistry: Dermacozine E, a Natural Product from the Mariana Trench

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Dermacozine E is a novel chiral phenazine natural product obtained from the Mariana Trench actinobacterium Dermacoccus abyssi. TDDFT has been applied to the calculation of circular dichroism spectra for Dermacozine E in order to aid in the elucidation of the stereochemistry of the enantiomer found in the D. abyssi extract.

In tests performed within the ORCA software package [1], TDDFT seems to perform well for this type of calculation and the simple LDA method was capable of providing good results. The basis set dependence was found to be very modest and quite small basis sets seem to be suitable for this type of calculation.

Whilst LDA performed well, the PBE0 hybrid functional did poorly. This is contrary to expectations based on the available literature relating to this subject. Possible reasons why the LDA calculations were successful in this case are discussed. Future work will attempt to address the apparent failure of the hybrid approach.

[1] Available from the University of Bonn: http://www.thch.uni-bonn.de/tc/orca/index.php

FMO-TDDFT Studies of Luciferase from the Japanese Firefly Luciola cruciata

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Firefly bioluminescence involves the reaction of luciferin (LH2) with oxygen in the presence of ATP and Mg2+ to produce excited state oxyluciferin (OLH2) which then decays to the ground state emitting a photon of light [1]. This reaction is mediated by the enzyme luciferase (Luc). Depending on the species involved, at pH 7-8 yellow-green light of 560 nm is emitted whilst at pH 5-6 the light is red with a wavelength of 620 nm.

In the present work electronic structure calculations have been performed on the crystallographically determined structure of the luciferase active site of the Japanese firefly Luciola cruciata (PDB ID = 2D1R). Calculation of the binding energies and electronic absorption energies for oxyluciferin were performed at the MP2/6-311G(d,p) and TD-B3LYP/6-311G(d,p) levels, respectively. The Fragment Molecular Orbital (FMO) method [2] was used to speed up the calculations and permit interaction energy analysis.

The results obtained with this model favour the enol-phenolate form of oxyluciferin as the emitting species in this system. This is in agreement with the most recent experimental studies on oxyluciferin [3].

[1] H. Fraga, Photochem. Photobiol. Sci., 2008, 7, 146-158
[2] D.G. Fedorov and K. Kitaura, J. Phys. Chem. A, 2007, 111, 6904-6914
[3] Naumov, P. et al., J. Am. Chem. Soc., 2009, 131, 11590-11605

Many carrier effects in semiconductor nanostructures

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We have investigated many carrier effects in semiconductor nanostructures. Single quantum wells (SQWs) were grown by molecular beam epitaxy and characterized by photoluminescence (PL) spectroscopy using different excitation power. The sample consists of four InGaAs/GaAs SQWs with thickness of 20, 10, and 5 nm. The laser spot excitation was changed from 100 to 600 mW in PL spectroscopy. The two-dimensional carrier density in the QW's was controlled by mean excitation power. A PL peak down shift was observed when excitation power was increased because many body interactions between carriers produce a renormalization on the active band-gap. To understand this behavior we calculate the effective energy of confined electrons and holes considering the interaction of a single electron-hole pair with the plasmons in the QW. We found that the two-dimensional optically created carrier density increase non-linearly with the excitation power but the effective recombination energy decrease linearly with the excitation power. The theoretical model as a function of the carrier density, QW width and nanostructure temperature are in good agreement with the experimental PL peak behavior.

Photoluminescence spectroscopy of InGaAs/GaAs quantum wells

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InGaAs/GaAs quantum wells (QWs) were grown by molecular beam epitaxy and characterized by photoluminescence (PL) spectroscopy using different excitation power. The sample consists of three InGaAs/GaAs QWs with nominal thickness of 20, 10, and 5 nm. The laser excitation power in PL measurements was changed from 100 to 600 mW at 80 K, thus varying the two-dimensional carrier density in the QWs. We investigated many carrier effects in the QWs. A red-shift in the PL peak was observed when excitation power was increased because many body interactions between carriers produce a renormalization on the active band-gap. In order to understand this behavior we calculate the effective energy of confined electrons and holes considering the interaction of a single electron-hole pair with the plasmons in the QWs. We found that the two-dimensional optically created carrier density increase non-linearly with the excitation power, but the effective recombination energy decrease linearly with the excitation power. The results of a theoretical model as a function of the carrier density, QW width, and nanostructure temperature are in good agreement with the experimental PL peak behavior.

Transport properties of molecular junctions from Many-Body Perturbation Theory

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In recent years, several conductance measurements of single organic molecules have been reported. Concomitantly, considerable efforts have been dedicated to describing transport through such molecular junctions using ab initio methods like density functional theory (DFT). However, the theoretical results often differ by orders of magnitude from the experimental values. Many explanations are possible for such a mismatch. Among others, the transmission functions computed from DFT have resonances at the non-interacting Kohn-Sham excitation energies, which in general do not coincide with the true excitation energies.

In this work, many-body perturbation theory (MBPT) within the GW approximation is used to correct the DFT excitation energies and compute the transport properties for a benzene-dithiol molecule linked to gold leads. The MBPT calculations rely on the extrapolar approximation to reduce the required memory and computer time. The quantum transport calculations are performed using Wannier functions as a minimal and localized basis set. Particular attention is devoted to the study of interactions between different supercells and of surface polarization.

Do we know the band gap of lithium niobate?

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Given the vast range of technical applications of lithium niobate (LiNbO3), the knowledge of its electronic and optical properties is surprisingly limited. No photoemission measurements of the band structure have been reported so far, and the value of 3.78 eV for the direct band gap of the ferroelectric room-temperature phase, frequently cited in the literature, is concluded from optical experiments. A recent theoretical investigation [W. G. Schmidt et al., Phys. Rev. B 77, 035106 (2006)] obtained a much larger band gap but also found that the electronic band structure and optical properties are very sensitive to quasiparticle and electron-hole attraction effects, which were included using the GW approximation for the electronic self-energy and the Bethe-Salpeter equation for the optical absorption spectrum, respectively, both based on a model screening function. To resolve this discrepancy, we performed first-principles GW calculations for lithium niobate within the full-potential augmented-plane-wave (FLAPW) method. Instead of a model screening function we use the parameter-free random-phase approximation, which gives a more realistic description of the nonlocality and the frequency dependence of the screened Coulomb potential. The calculated band gap is thus reduced, although still larger than the experimental value, which we attribute to excitonic effects in the optical absorption.

Oxidise this: A study of PAW + QPSC*GW* calculations on Zn and Sn oxides

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The Zinc and Tin oxides represent a particularly troublesome example of transparent conducting oxides (TCOs) in ab-initio calculations. TCOs are a technologically very important class of wide-gap semiconductors with high electrical conductivity, and have been the focus of many recent ab-initio efforts. The failure of the one-shot G_0W_0 method is well documented in the case of ZnO and is hitherto largely uninvestigated for the tin oxides. Taking quasiparticle self-consistent GW [1] as a theoretically well-defined target, we investigate - for ZnO - the suitability of several starting points: LDA, GGA, $LDA + U$, $GGA + U$ and $COHSEX$ taken with various GW implementations. Illustration will be made on the crucial importance of including semi-core states, some details of state-of-the-art Projector Augmented Wave (PAW) calculations, and also the need for employing well-constructed PAW atomic datasets in PAW+GW calculations. Finally, we present a comparison of features and results of ZnO with experiment and report on some trials and tribulations of calculations on the tin oxides.

[1] T. Kotani, M. van Schilfgaarde, S. V. Faleev, Phys. Rev. B. **76**, 165106 (2007).

Structural phase transitions and fundamental band gaps of $Mg_xZn_{1-x}O$ alloys from first principles

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The structural phase transitions and the fundamental band gaps of $Mg_xZn_{1-x}O$ alloys are investigated by detailed first-principles calculations in the entire range of Mg concentrations x, applying a multiple-scattering theoretical approach (Korringa-Kohn-Rostoker method). Disordered alloys are treated within the coherent potential approximation (CPA). The calculations for various crystal phases have given rise to a phase diagram in good agreement with experiments and other theoretical approaches. The phase transition from the wurtzite to the rock-salt structure is predicted at the Mg concentration of $x = 0.33$, which is close to the experimental value of $0.33 - 0.40$. The fundamental band gap, typically underestimated by the local density approximation, is considerably improved by the self-interaction correction. The increase of the gap upon alloying ZnO with Mg corroborates experimental trends. Our findings are relevant for applications in optical, electrical, and in particular in magnetoelectric devices.

Ab Initio simulation of photovoltaic materials

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During the past years, $Cu(In,Ga)(Se,S)_2$ (CIGS) thin-film solar cells emerged as a technology that could challenge the current hegemony of silicon solar panels. CIGS compounds conserve to a very high degree their electronic properties in a large non-stoichiometric range and are remarkably insensitive to radiation damage or impurities. Moreover, thin film solar cells require transparent contacts. In practice, these contacts are built from insulating oxides that for a certain range of doping become conductive while retaining transparency in the visible spectrum. Thin films of compounds of the delafossite family, namely $Cu(Al,Ga,In)O_2$, are particularly interesting as they show bipolar conductivity.

The origin of the exceptional electronic properties of these two classes of materials is still not understood, despite the large amount of experimental and theoretical works dedicated to this purpose. This is a serious restraint when it comes to designing new materials for more efficient photovoltaic energy conversion.

We show that only the use of state-of-art ab-initio tools, namely self-consistent GW techniques, allowed us a reliable description of the optical properties of these materials.

Density gradients for the exchange energy of electrons in two dimensions

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We derive a generalized gradient approximation to the exchange energy to be used in density functional theory calculations of two-dimensional systems. This class of approximations has a long and successful history, but it has not yet been fully investigated for electrons in two dimensions. We follow the approach originally proposed by Becke for three-dimensional systems [Int. J. Quantum Chem. 23, 1915 (1983); J. Chem. Phys. 85, 7184 (1986)]. The resulting functional depends on two parameters that are adjusted to a test set of parabolically confined quantum dots. Our exchange functional is then tested on a variety of systems with promising results, reducing the error in the exchange energy by a factor of 4 with respect to the simple local density approximatio

The phonon dispersion relations of lead chalcogenides (PbS, PbSe, PbTe)

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The lead chalcogenides are remarkable materials due to their rock-salt crystal structure and their narrow direct band-gap. Furthermore, they are near-ferroelectric materials. Also their phonon dispersions relations have some surprising features. We present ab-initio calculations of the phonons of PbS, PbSe, and PbTe. The acoustic branches are in very good agreement with inelastic neutron-scattering data. The pronounced minimum of the transverse optical branch at Γ due to the near-ferroelectricity of the lead chalcogenides is qualitatively reproduced. In addition, we find a pronounced kink in the longitudinal optical branch at Γ. This kink was previously explained as the effect of "free carriers". Our calculations, however, demonstrate that this anomaly is also present in the pure lead chalcogenides. We explain this kink as a "near" Kohn-anomaly due to the peculiar electronic band-structure: The lead chalcogenides have a narrow direct gap (200-300 meV) at the high symmetry point L. The gap strongly depends on the lattice constant. By (artificially) squeezing the lattice one can reduce the gap to zero and obtain a linear crossing of the conduction and valence band at L. In this case, LO and TO modes are degenerate and the LO mode displays a Kohn-Anomaly in analogy to the case of graphene with its point-like Fermi-surface.