

NANOEXC2004 CONFERENCE

Programme, Abstracts, and Participants List of the conference

# Theory and Modeling of Electronic Excitations in Nanoscience

19 – 23 September 2004

## Conference Organizers

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**PSI-K: Electronic structure calculations for elucidating the complex atomistic behaviour  
of solids and surfaces**

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# Conference Programme

Monday, September 20 2004

## 8:50 **Presentation and general announcements**

- 9:00-9:40 **R. W. Godby**  
*Self-consistency in GW calculations of spectral and ground-state properties*
- 9:40-10:00 **T. Kotani**  
*Quasi-particle self-consistent GW approximation*
- 10:00-10:20 **P. Rinke**  
*Exact-Exchange-Based Quasi-particle Calculations of II-VI Compounds and Group III Nitride*
- 10:20-10:40 **M. Marsili**  
*Electronic band structure of the C(111)2x1 surface within an iterative GW scheme*
- 10:40-11:10 \* Coffee break \*
- 11:10-11:50 **J. Rehr**  
*Local-Field Effects in Calculations of Optical Constants from UV-X-rays*
- 11:50-12:10 **G.P. Brivio**  
*Ab initio treatment of adatom Auger decays*
- 12:10-12:50 **E. Shirley**  
*Bethe Salpeter treatment of core excitations: multiplet effects*
- 13:00-14:30 \* Lunch break \*
- 16:00-16:40 **E.K.U. Gross**  
*Ab-initio theory of superconductivity*
- 16:40-17:00 **E. Chulkov**  
*Electron-phonon interaction and its role in the lifetime broadening mechanism of electron and hole excitations in metallic materials*
- 17:00-17.20 \* Coffee break \*
- 17:20-18:00 **J. Palacios**  
*Electronic transport in nanoscale systems from first principles*
- 18:00-18:20 **P. Bokes**  
*Conductance of metal-vacuum-metal interface from the polarisation function*
- 18:20-18:40 **H. Mera**  
*Exchange in non-equilibrium systems*
- 20:00-21:00 \* Dinner \*
- 21:00 **EVENING POSTER SESSION**

- 9:00-9:40 **F. Bechstedt**  
*Optical spectra of three-, two-, and zero-dimensional systems treated using many-body perturbation theory*
- 9:40-10:00 **R. Del Sole**  
*Calculation of surface optical properties within TDDFT: the bound exciton of Si(111)2x1*
- 10:00-10:20 **P. Eggert**  
*Long-ranged interactions in a supercell approach*
- 10:20-10:40 **L. Chiodo**  
*The energy loss of (110)Ag and (001)Al surfaces*
- 10:40-11:10 \* Coffee break \*
- 11:10-11:50 **G. Rignanese**  
*First-principles study of crystalline and amorphous transition metal oxides and silicates*
- 11:50-12:10 **L. Dash**  
*Ab initio spectra of the low-pressure phases of zirconia*
- 12:10-12:30 **A. Incze**  
*Ab initio study of reflectance anisotropy spectra of a sub-monolayer oxidized Si(100) surface*
- 13:00-14:30 \* Lunch break \*
- 15:00-15:40 **S. Baroni**  
*Time-dependent density-functional perturbation theory*
- 15:40-16:00 **Y. Pouillon**  
*Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism : ground-state and excited-state studies*
- 16:00-16:20 **S. Kurth**  
*Orbital Functionals in Current-Density Functional Theory*
- 16:20-16:40 \* Coffee break \*
- 16:40-17:20 **L. Reining**  
*TDDFT and Many-Body Perturbation Theory: comparisons and combinations*
- 17:20-17:40 **A. Marini**  
*A three-point Many-Body vertex function from Time-Dependent Density-Functional Theory*
- 17:40-18:20 **G. Stefanucci**  
*Excitons from TDDFT as generated by the variational approach to many-body perturbation theory*
- 18:30-20:30 POSTER SESSION (continued)
- 20:30 \* Dinner \*

- 8:30-9:10 **C. Delerue**  
*Quasi-particle gap, dielectric properties and electronic correlations in semiconductor nanostructures*
- 9:10-9:50 **L. Benedict**  
*Optical absorption in hydrogenated Si clusters: BSE vs. TDLDA*
- 9:50-10:10 **L. Ramos**  
*Excitation energies and optical properties of Si nanocrystallites*
- 10:10-10:30 **S. Ossicini**  
*Ab-initio calculation of the structural, electronic and optical properties of Silicon nanoclusters in their ground and excited states*
- 10:30-11:00 \* Coffee break \*
- 11:00-11:40 **A. Franceschetti**  
*Electronic Excitations in Semiconductor Quantum Dots*
- 11:40-12:00 **C. Verdozzi**  
*Tuning the optical and/or magnetic properties of correlated nanoclusters*
- 12:00-12:20 **M. Gatti**  
*Effects of oxygen on the structural, electronic and optical properties of silicon nanocrystals*
- 12:20-12:40 **E. Degoli**  
*Impurities states in hydrogenated silicon nanoclusters*
- 13:00 \* Lunch break \*
- 16:00-16:40 **S. Ismail-Beigi**  
*First-Principle Green's function methods: electronic and optical properties of carbon nanotubes and excited-state forces*
- 16:40-17:00 **E. Chang**  
*Quasiparticle energies and optical properties in carbon nanotubes*
- 17:00-17:40 **L. Wirtz**  
*Excitons in BN-nanotubes: dimensionality effects*
- 17:40-18:00 \* Coffee break \*
- 18:00-18:20 **M. Marques**  
*Absorption spectra of biological systems from TDDFT*
- 18:20-18:40 **A. Seitsonen**  
*Recent applications of TD-DFT in molecular, liquid and solid phases*
- 18:40- 18:50 *Conclusive Remarks*
- 18:50 *Closing of nanoexc2004 and presentation of the 2005 workshop*
- 20:00 **\*\*Pizza Party\*\***

## List of Posters

- 1 Andrey Bogdanov *"Coherent exchange between the forward and backward waves in Bistable optical response of a thin glassy film"*
- 2 Silvana Botti *"Optical properties of complex systems from TDDFT"*
- 3 Fabien Bruneval *"Electronic Excitations of Cu<sub>2</sub>O within GW approximation"*
- 4 Mauro Bruno *"Ab-initio electronic and optical properties of Germanium Quantum wires"*
- 5 Gabriele Butti *"Image potential states and surface electronic structure calculation on the Na/Cu(111) system"*
- 6 Sebastiano Caravati *"Selectivity of auger decays to the local surface environment"*
- 7 Nuno Carneiro *"A novel generalized Kohn-Sham approach for total energy calculations within Density Functional theory"*
- 8 Louise Dash *"Choosing ultrasoft pseudopotentials for spectroscopy calculations"*
- 9 Kris Delaney *"Self-consistent Solutions of Dyson's Equation and Total Energies from the GW Approximation"*
- 10 Christoph Freysoldt *"GW calculations for surfaces"*
- 11 Martin Friak *"Ab-initio calculations of the half-metal to metal transition in magnetite"*
- 12 Christophe Friedrich *"Photocatalytic oxidation of CO at the V<sub>2</sub>O<sub>5</sub>(010) surface: cluster model studies"*
- 13 Maja Garcia-Vergniory *"Self-energy and lifetimes of surface states beyond the GW approximation"*
- 14 Conor Hogan *"Theory of electron energy Loss at surfaces"*
- 15 Aleksey Kuznetsov *"Ab initio study of Fe<sub>3</sub>O<sub>4</sub>(111) surface"*
- 16 Roman Leitsmann *"Nonlinear Optical coefficients from first-principles calculations: Different numerical approaches"*
- 17 Sergey Lisenkov *"Ab-initio study of new polimeric crystals based on fullerenes C<sub>60</sub> and carbynes"*
- 18 Manfred Niesert *"Ab-initio calculations of the optical properties of phase-change materials"*
- 19 Enrico Perfetto *"Microscopic model for a strongly correlated superconductor single-electron transistor"*
- 20 José M. Pitarke *Large crystal local-field effects in the dynamic structure factor of TiO<sub>2</sub>"*
- 21 Stefano Pittalis *"Optimized effective potentials in current-density functional Theory"*
- 22 Victor A. Popa *"Band gaps in GW self-consistent calculations"*
- 23 Sampsa Riikonen *"Ab-initio studies of the Si(557)/Au and Si(553)/Au Reconstructions"*

- 24 Arno Schindlmayr "*Vertex Corrections in a systematic self-energy perturbation theory*"
- 25 Paolo Emilio Trevisanutto "*A bi-exciton mechanism of photo-induced desorption from MgO*"
- 26 Daniele Varsano "*A study of excitonic properties of low dimensional systems with TDDFT*"
- 27 Nathalie Vast "*Phase stability in titanium and its dioxides with ab initio methods*"
- 28 Wojciech Welnic "*Ab-initio calculations of amorphous phase change materials*"

# **Abstracts of talks and posters**

# Time-dependent density-functional perturbation theory

**Marco Saitta (1,2), Brent Walker(2,3), Ralph Gebauer(2,3), and  
Stefano Baroni(1,2,4)**

(1) *Physique des Milieux Condensés, Université Pierre et Marie Curie, Paris, France* (2) *DEMOCRITOS National Simulation Center, Trieste, Italy* (3) *The Abdus Salam International Center for Theoretical Physics, Trieste, Italy*  
(4) *Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy*

In this talk I will discuss some ideas that would allow an extremely efficient calculation of optical spectra within TDDFT. Once some preliminaries have been set up with a numerical effort typical of a *static* DFPT calculation, the *dynamical* polarizability can be obtained at any (not too large) frequency, essentially for free. As it is the case for static DFPT, our method does not make any explicit reference to unoccupied molecular orbitals, so that it is well suited for large-scale plane-wave calculations. At the time when this abstract is being written, we are still working on the algorithm and testing it on a simple toy model. It is hoped that, by the time of the meeting, some meaningful results on a realistic system will be available.

## Optical spectra of three-, two-, and zero-dimensional systems treated using many-body perturbation theory

**F. Bechstedt, P. Hahn, and W.G. Schmidt**

*Friedrich-Schiller-Universität Jena, Institut für Festkörpertheorie und -optik, Max-Wien-Platz 1, 07743 Jena, Germany*

The aim of the present paper is to demonstrate the power of the many-body perturbation theory to describe accurately optical spectra of systems with arbitrary confinement. The method is based on solutions of the Dyson and Bethe-Salpeter equations in the framework of the GW approximation. The dynamical screening is treated by a model dielectric function or by the full frequency-dependent dielectric matrix calculated within the independent-particle approximation. An initial-state formulation of time-dependent polarizability allows spectra computations for systems with many atoms in the unit cell. The treatment of the quasiparticle self-energy effects beyond the first-order perturbation theory is discussed for molecular systems. Applications of the method are demonstrated for bulk compound semiconductors without confinement, hydrogenated Si surfaces with one-dimensional confinement, and molecular systems such as silane, H<sub>2</sub>O molecules as well as molecular crystals (ice) with more or less three-dimensional confinement. Problems of the approximations concerning e.g. the frequency dependence of the self-energy and the mixing of wave functions are discussed.

## Optical absorption in hydrogenated Si clusters: BSE vs. TDLDA

**L. X. Benedict**

*Lawrence Livermore Lab, L-045, 7000 East Ave, USA*

We have performed calculations of the optical absorption spectra of nm-sized hydrogenated Si clusters using two related approaches, an approximate Bethe-Salpeter equation treatment, and TDLDA. We find that the gross features of the results are similar for the larger clusters, but are

highly discrepant for  $SiH_4$ . The similarities and differences will be discussed, as they illustrate the relation between the two theoretical approaches. In the end, I offer some suggestions as to why the TDLDA spectra for  $SiH_4$  and other small systems seems to be in such good agreement with experiments.

## **Coherent exchange between the forward and backward waves in Bistable optical response of a thin glassy film**

**A. A. Bogdanov and A. I. Zaitsev**

*A.I.Herzen Russian State Pedagogical University, naberezhnaya reki Moiki 48, St. Petersburg, 191186 Russia  
aabogdanov@mail.ru*

The generation of reflected and transmitted waves in the dense two-level absorber for an intense plane wave under normal-incidence conditions is investigated. A region of parameters is intentionally selected for which one needs to take into account strong atom-field coupling, which results in the appearance of polaritons. The near-zone dipole-dipole interaction is taken into account within the local-field approach. We also discover the possibility of optical hysteresis of transparence and the dependence of the instabilities of several states on length of a sample. If the length of the sample increases, time of transition to the mode of transparency increases too. Thus the impulse regime of the reflected field is formed. Possibility of change of conditions of bistables behaviour under influence of the inhomogeneous broadening is researched too.

The nonlinear resonant optical properties of dense dielectric two-level media have been a subject of interest during the past two decades. We mainly focus our study on the analysis of the nonlinear reflection and transmission from a vacuum to two-level medium, varying the driving parameters over a region in which the system shows bistable behavior. This problem was partly studied by us in a recent publication [2]. The coherent cooperative phenomenon has been mainly studied in the unidirectional approximation, where the reflection from the boundaries of an inverted medium is ignored [1]. The amplitudes are usually assumed to be slowly varying in both time and space. The inclusion of reflection implies that we should abandon the approximation of slowly varying amplitudes in space [3]. In the presence of reflection, an atomic system may generate waves propagating in both directions, although the external field initiates generation of only one wave.

The medium is described by the modified Bloch equations in which the field acting on each atom of the system consists of two parts: the first is the average (Maxwell) field, and the second is the local-field correction  $(4\pi/3)P$  (where  $P$  is the electric polarization of the medium), when one takes into consideration the resonant dipole-dipole interaction.

$$\dot{R} = i\Delta R + E(2\rho - 1) - R\gamma_2 \quad (1)$$

$$\dot{\rho} = -ER^* - E^*R - \rho\gamma_1 \quad (2)$$

$$\begin{aligned}
E(t, x) = & -i\frac{2}{3}(\tau_\lambda)^{-1} \int_{\omega} R(t, x, \omega)g(\omega)d\omega + A(t)e^{ikx} \\
& + (\tau_\lambda)^{-1} \int_0^L \int_{\omega} R(t, x', \omega)e^{ik|x-x'|}g(\omega)d\omega dx'
\end{aligned} \tag{3}$$

where the dots denote time derivatives;  $\rho$  are the elements of the atomic density matrix at a point with coordinate  $x$  at the moment of time  $t$ ;  $\Delta$  is the detuning of an atom and light. We include effects related to homogeneous and inhomogeneous broadening in our analysis.  $\tau_\lambda$  is the characteristic time. The amplitude of the quasi-resonant external field increases and then decreases, as we want to research the phenomenon of a hysteresis.

Since the fields of transmitted and reflected waves are determined by the values of the field on the boundaries of the sample, the kinetics of these fields can be understood only through the analysis of field and atomic characteristics in the medium. From our point of view, the investigation of spatial and kinetic characteristics of our system should be supplemented by the analysis of the kinetics of the mode structure of the field, i.e., the spatial spectrum of the field inside the sample: Many features of the studied phenomena can be better understood in terms of the normalized spatial spectrum of the field inside the sample. For the analysis of integral dependences of the field kinetics, we will also employ the fraction of the forward wave.

In our opinion, it is also useful for the analysis of the process under study to separate the field inside the sample into the forward and backward waves, which can be reconstructed by the inverse Fourier transform over the spatial spectrum in the positive and negative regions of wave numbers. From our point of view, the use of these quantities allows the process under study to be understood in a more detailed way.

The shift of the resonance frequency, which is due to the dipole-dipole interaction, as well as the dependence of the resonance frequency on the population, which reflects the nonbosonic character of the collective excitations (excitons), are described in an adequate manner. We use the concept of polaritons to analyze qualitatively the spectral regions into which one can separate the effects generated by the local-field non-linearity from those caused by self-reflection, as well as when such separation is impossible. The possibility of a stable reflectivity hysteresis loop is also demonstrated. The mutual action of the local-field and the saturation nonlinearities is analyzed. We pursued only one aim, namely, to check how the results obtained in our previous study will change when the local-field correction is considered.

[1] M. G. Benedict, A. M. Ermolaev, V. A. Malyshev, I. V. Sokolov, and E. D. Trifonov, *Super-radiance: Multiatomic coherent emission*, Institut of Physics Publishing, Bristol - Philadelphia, 1996.

[2] A.A.Bogdanov, I.V. Ryzhov, A.I.Zaitsev, V. A. Malyshev, J. Knoester, "Optical response and bistability of an thin film consisting of molecular aggregates", *Proc. SPIE*, **4605**, pp. 325-332, 2001.

[3] A.A.Bogdanov, A.I.Zaitsev, *Generation of Transmitted and Reflected Waves in Induced Superradiance*, Laser Physics, Vol. **11**, No. 3, pp. 1 V15, 2001.

# Conductance of metal-vacuum-metal interface from the polarisation function

**Peter Bokes<sup>(1)</sup> and Rex Godby<sup>(2)</sup>**

*(1) Department of Physics, Slovak University of Technology (FEI STU), Ilkovičova 3, 812 18 Bratislava, Slovakia.*

*(2) Department of Physics, University of York, Heslington, York YO10 5DD, U.K.*

Recently we have suggested a novel approach for calculation of the conductance of quantum junctions from the polarisation function [1]. The method, unlike all other available approaches, does not rely on a single-particle approximation and can effectively take advantage of well developed many-body techniques, particularly the GW method. Here we present results of calculation for a metal-vacuum-metal interface at the SCF-DFT level and discuss problems met in actual numerical implementation of the approach.

[1] P. Bokes and R. W. Godby, arXiv:cond-matt/0403204, to appear in Phys. Rev. B (2004).

## Optical properties of complex systems from TDDFT

**Silvana Botti, Fabien Bruneval and Lucia Reining**

*Laboratoire des Solides Irradiés, UMR 7642 CNRS/CEA, École Polytechnique, F-91128 Palaiseau, France*

Time-dependent density functional theory (TDDFT) allows to study the electronic excitations involved in spectroscopic experiments, possibly conserving a computational effort comparable to that of ground-state density functional theory (DFT). In practice, its use is still restricted to some classes of systems, due to the difficulty in finding general approximations for the exchange and correlation (xc) terms.

Here we discuss applications of TDDFT to the calculation of the optical properties of a variety of systems: from clusters and nanostructured materials to bulk crystalline and amorphous systems. We will consider different approximation schemes, showing that results in agreement with experiments do not necessarily come from a single scheme. Finally, we present a simple model to account for the energy dependence of the long range xc kernel of TDDFT.

## Ab initio treatment of adatom Auger decays

**G.P. Brivio<sup>1</sup>**

*1-Dipartimento di Scienza dei Materiali - Università di Milano Bicocca, Italy*

We calculate the core-core-valence (CCV) Auger profiles of an adatom on a periodic surface within the DFT framework by using an approximate method based on the local density of states (LDOS), with a core hole on the atom, in the neighbourhood of the impurity. To verify the validity of this simpler approach we compare the Auger rates worked out with the Fermi golden rule with those obtained via the LDOS for a substrate jellium model. In this way we show that the radius of the sphere in which we compute the LDOS is the relevant parameter of the latter simpler approach. We investigate the CCV lineshapes of Na on Al(111), a system in which two

ordered phases are observed at room temperature. From a detailed comparison of the calculated spectra with the experimental ones measured at the Elettra synchrotron for the KL23V lineshape of Na, we prove that a joint experimental and theoretical effort (based on DFT) can allow for determining different surface geometries for a given adsorption system, and also for unravelling different adsorbate components coexisting in the signal.

## **Electronic Excitations of $\text{Cu}_2\text{O}$ within GW approximation**

**F. Bruneval, N. Vast, L. Reining**

*1-Laboratoire des Solides Irradiés, CNRS, CEA, Ecole Polytechnique, Palaiseau, France*

Cuprous oxide has been extensively studied during the last decades, mainly because of its exciton series in the optical range.  $\text{Cu}_2\text{O}$  is a good starting point to address the fundamental issue of  $3d$  electrons of metals in oxides. This semiconductor material has indeed a cubic structure, a closed  $d$  shell, and is non-magnetic. This is now a very important topic: it is known that density functional theory fails to predict a gap in various insulating oxides like CoO, CuO. We performed band structure calculations on  $\text{Cu}_2\text{O}$  within Density Functional Theory and GW approximation. We carefully studied the role of semicore states ( $3s^23p^6$ ). Though deep in energy, these states have a large overlap with valence bands. Their influence is slight on the Kohn-Sham band structure. However, we state that the semicore states have to be included in the GW calculation to get meaningful results.

Even a GW calculation including semicore states largely underestimates the quasiparticle gap. Further approximations are usually used to perform a “standard” GW calculation: the use of a plasmon pole model to describe the dynamical screening, a first-order perturbation scheme, an assumption that LDA and GW wavefunctions are equal... We extensively discuss many of them and conclude that they are reliable.

Then the failure of GW may lie in the neglect of the vertex part of the self-energy. We therefore propose a scheme to include some local vertex corrections, thanks to Time-Dependent DFT.

## **Ab-initio Electronic and Optical Properties of Germanium Quantum Wires**

**Mauro Bruno<sup>1</sup>, Maurizia Palumbo<sup>1</sup>, Rodolfo Del Sole<sup>1</sup>, Stefano Ossicini<sup>2</sup>**

*1-Dipartimento di Fisica Università Tor Vergata Roma*

*2-INFN-S3 nanoStructures and bioSystems at Surfaces, Dipartimento di Scienze e Metodi dell'Ingegneria,  
Università di Modena e Reggio Emilia*

We have performed first principles calculations, in order to understand the influence of spatial orientation on the electronic band structure and optical properties of hydrogenated germanium quantum wires. Such calculations have been performed by means of a plane wave basis set code [1]. In particular we have analyzed how the geometrical relaxation affects the electronic and optical properties. Further we have compared our results with existing similar calculations (see

Ref. [2]) where ideal bulk truncated atomic positions have been used. What we have found is that atomic relaxation determines a small changing (modification) in the wires band structure. Moreover some optical spectra beyond the one-particle approach will be shown. Important GW correction and strong excitonic effects have been found. Nevertheless an almost complete compensation of these two contributions seems to happen.

[1] [www.abinit.org](http://www.abinit.org)

[2] A. N. Kholod, V. L. Shaposhnikov, V. E. Borisenko, F. Arnaud D Avitaya, S. Ossicini, accepted on Phys. Rev. B

## **Image potential states and surface electronic structure calculation on the Na/Cu(111) system**

**G. Butti<sup>2</sup>, S. Caravati<sup>1</sup>, M.I. Trioni<sup>1</sup>**

*1-Dipartimento di Fisica - Università di Milano Bicocca*

Image potential states are a common feature of all metal surfaces; these states are originated by the long range character of the image potential. This long range behavior is usually not accounted for within standard DFT calculations because of the local character in the common approximation of the exchange and correlation potential. In our Green's function embedding approach we overcome this limitation imposing the correct long range behavior by gradually matching the DFT effective potential with a model one. Within this framework we manage to reproduce the Rydberg series of image states and obtain an excellent agreement with experimental results, in a fully ab-initio way. Unfortunately given the static character of our calculation, we are not able to estimate any intrinsic linewidth, a feature which seem to have drag very recently a lot of theoretical and experimental attention. The system we chose for testing our approach is Na/Cu(111) for which a consistent volume of data is available; as an aside we also give a detailed picture of its surface electronic structure.

## **Selectivity of Auger decays to the local surface environment.**

**S. Caravati<sup>1</sup>, G.P. Brivio, M.I. Trioni<sup>1</sup>**

*1-Dipartimento di Fisica - Università di Milano Bicocca*

In recent years, alkali metals adsorption on metal surfaces has been a matter of both theoretical and experimental investigation. In particular Na on Al(111) is a nice prototype to study the interaction between simple metals and alkali atoms. This system show unusual adsorption geometries inducing different kinds of surface reconstructions depending on temperature and coverage conditions.

We focus on two ordered structures, both observed at room temperature: a  $(\sqrt{3} \times \sqrt{3}) R30^\circ$  with a Na atom in a substitutional site and a  $2 \times 2$  structure presenting an intermixing between Al and Na atoms, resulting in a "surface alloy". We investigated the electronic properties of the Al(111) surface and of the two systems described above, applying the embedding method, proposed by Inglesfield and extended by Ishida. In such a way we are able to consider a real, semi-infinite

substrate within the DFT framework, using a Green's function formalism and adopting a full-potential LAPW basis set.

We then calculated the Auger lineshape for the Na  $KL_{23}V$  transition for each of two reconstructions considered. Although in principle, in this work one has to deal with excited state due to the presence of a core hole, and with the consequently screening effects, nevertheless, because of the simple electronic structure of the particular system studied, we show that a good approximation of the Auger lineshape can be obtained within standard Kohn-Sham approach from the local DOS around the excited sodium atom.

Calculated Auger spectra present marked differences suggesting the possibility to use such experimental technique to investigate structural properties. We also show here the results of the experimental investigation performed on the same kind of systems at the TASC Lab, using ALOISA beamline. The measured Auger lineshapes perfectly agree with theoretical predictions, confirming the suitability of combining Auger lineshape analysis and theoretical calculations to determine local surface morphology.

## **A novel generalized Kohn-Sham approach for total energy calculations within Density Functional theory**

**N. Carneiro and R. Godby**

*Department of Physics, University of York, Heslington, York YO10 5DD, UK*

Generalised Kohn-Sham (GKS) theory [1],[2], provides a variety of possible generalisations of the well-known Kohn Sham implementation of density functional theory for the calculation of total energies of systems of interacting electrons such as molecules and solids. We present an assessment of various GKS schemes for a one-dimensional model semiconductor. Comparison is made with previous quantum Monte Carlo calculations [3] and with previous GW calculations within many-body perturbation theory for this system. Further GW calculations suggests a new GKS approach based on a GW formulation of the total energy, which will lead to a new version of density functional theory for efficient practical calculations which circumvents the problem of approximating the usual Kohn Sham exchange correlation energy functional.

[1] A. Seidl, A. Görling, P. Vogl, and J. A. Majewski and M. Levy; Physical Rev. B 53, 3764 (1996)

[2] P. Sánchez-Friera and R. W. Godby, Phys. Rev. Letters 85, 5611 (2000)

[3] W. Knorr and R.W. Godby. Phys. Rev. Lett. 68, 639-641 (1992)

## **Quasiparticle energies and optical properties in carbon nanotubes: a first-principle study**

**Eric K. Chang\*, Giovanni Bussi, Alice Ruini, and Elisa Molinari**

*INFN National Center on nanoStructures and bioSystems at Surfaces (S3)*

*and Physics Department, University of Modena and Reggio Emilia*

*41110 Modena, Italy*

We present the results of our calculations of excitonic effects and optical properties of carbon

nanotubes. We adopt a first-principles approach and use many-body methods such as the Bethe-Salpeter Equation (BSE), which has been used with considerable success to calculate excitonic effects in bulk semiconductors<sup>1,2,3</sup> and most recently, in one-dimensional systems, such as polymers.<sup>4</sup> The success of the latter reinforces the applicability of the BSE to one-dimensional systems such as nanotubes. The novelty of our approach consists in the symmetry analysis of the nanotube in which we take advantage of the invariance of the tube with respect to screw-symmetry operations. Such an analysis not only reduces the computation effort required, but also offers a better understanding of the physics involved, including the nature of the excitons and of the optical transitions. We show results for the GW quasiparticle corrections, optical absorption and Raman spectra.

[1] M. Rohlfing and S.G. Louie, Phys. Rev. Lett. **80** (11): 2312 (1998).

[2] L.X. Benedict, E.L. Shirley, and R.B. Bohn, Phys. Rev. Lett. **80** (20): 4514 (1998).

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[4] A. Ruini, M. J. Caldas, G. Bussi and E. Molinari, Phys. Rev. Lett. **88**, 206403 (2002).

## **The energy loss of (110)Ag and (001)Al surfaces by *ab initio*, all electron calculations.**

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Since the milestone paper by A. Liebsch [1], aimed to overcome the limitation of the jellium model to evaluate the loss properties of transition and noble metals, further improvements to the model [2] yield only qualitative agreement with experimental results. For the purposes of material science, however, model representation of metals are highly unsatisfactory and unsuitable for comparison with to-date experiments. We present energy loss functions and surface plasmon dispersions of (110)Ag and (001)Al surfaces, based for the first time on *ab initio*, all electron calculations, performed within DFT-LDA. We use a Full-Potential Linear Muffin Tin Orbital code, particularly efficient for metals. In this way, the simple metal aluminum, considered a prototype of the jellium model, and silver, with *d*-electrons, are treated on the same footing. The linear upward dispersion of the surface plasmon of Ag(110) is recovered, in quantitative agreement with measurements [3]. It originates from the specific dielectric response of the surface layer.

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# **Electron-phonon interaction and its role in the lifetime broadening mechanism of electron and hole excitations in metallic materials**

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Departamento de Física de Materiales and CentroMixto CSIC-UPV/EHU, Facultad de Ciencias Químicas, UPV/EHU, Apdo.1072, 20080 San Sebastián/Donostia, Basque Country, Spain; Donostia International Physics Center (DIPC), Paseo de Manuel Lardizabal 4, 20018 San Sebastián/Donostia, Basque Country, Spain Ab-initio study of electron-phonon interaction and its contribution to the lifetime broadening of excited electrons and holes in metallic materials is reported. The energy and momentum resolved Eliashberg function and electron-phonon coupling parameter are calculated for simple and transition metals. The electron-phonon contribution calculated at different temperatures is analyzed for sp and d-bands as a function of momentum and energy. It is shown that the electron-phonon coupling matrix elements strongly modify phonon density of states suppressing some phonon modes contribution. The relative role of electron-electron and electron-phonon interaction in the lifetime broadening of excited quasiparticles is analyzed.

## **Ab initio spectra of the low-pressure phases of zirconia**

**Louise Dash, Tiphaine Tesson, Virginie Quéquet and Nathalie Vast**

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We have developed ultrasoft pseudopotentials intended to be used in calculations for *ab initio* spectra beyond DFT. Ultrasoft pseudopotentials can be of several forms, but the most widely used are those using methods developed by David Vanderbilt [1] and by Rappe, Rabe, Kaxiras and Joannopoulos (RRKJ) [2], both of which have produced excellent results for many problems. For spectroscopy calculations using plane-wave techniques, however, we demand a high level of convergence in the calculations in order to obtain reliable results. We have found that many Vanderbilt-type ultrasoft pseudopotentials suffer from poor absolute convergence, even at extremely high plane-wave cutoffs, and are therefore unsuitable for many applications in spectroscopy.

Using examples of both types of ultrasoft pseudopotentials, as well as norm-conserving Bachelet, Hamann and Schlüter (BHS) pseudopotentials, we demonstrate this convergence problem and the implications for calculations of electronic spectra.

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# Choosing ultrasoft pseudopotentials for spectroscopy calculations

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and Nathalie Vast**

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We have developed ultrasoft pseudopotentials intended to be used in calculations for *ab initio* spectra beyond DFT. Ultrasoft pseudopotentials can be of several forms, but the most widely used are those using methods developed by David Vanderbilt [1] and by Rappe, Rabe, Kaxiras and Joannopoulos (RRKJ) [2], both of which have produced excellent results for many problems. For spectroscopy calculations using plane-wave techniques, however, we demand a high level of convergence in the calculations in order to obtain reliable results. We have found that many Vanderbilt-type ultrasoft pseudopotentials suffer from poor absolute convergence, even at extremely high plane-wave cutoffs, and are therefore unsuitable for many applications in spectroscopy.

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## Impurities states in hydrogenated silicon nanoclusters

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In this work we show an *ab-initio* study of impurity states in silicon nanocrystals. It is known that doping semiconductor nanocrystals results in a much less efficient increasing of the carriers density than for the bulk crystal. In fact, impurities states can be far apart from band edges, due to confinement effects, so leading to ionisation thresholds much higher than for the bulk system [1]. Studies on doped semiconductor nanocrystals are still lacking [2]. Here, we study the main structural and electronic properties of doped silicon nanoclusters from *ab initio* calculations. The PWscf package [3] has been used, based on density functional theory, pseudopotentials (the GGA approximation for the exchange-correlation functional is considered) and plane waves basis set. Spherical silicon nanocrystals are built adding bulk silicon shells around a central Si atom, up to a given radius. The surface is then passivated with hydrogen atoms, in order to prevent the cluster from surface reconstruction phenomena.

Next, doped nanocrystals are obtained replacing one atom by a trivalent or pentavalent impurity (substitutional B and N respectively). Non equivalent positions of the impurity within each cluster are considered, with the aim of investigating the dependence of the calculated properties on the distance of the impurity itself from the surface. Moreover, the impurity states are investigated as a function of the nanocluster size. The starting hydrogenated nanoclusters which have been considered are  $\text{Si}_{29}\text{H}_{36}$  and  $\text{Si}_{87}\text{H}_{76}$ , whose radii are 0.45 and 0.71 nm respectively. For each cluster, full relaxation with respect to the atomic positions is carried out. The structural properties (reconstruction around the impurity, bond lengths and angles, etc.) have been determined. It is obviously expected that the starting Td symmetry is broken, giving rise to atoms arrangement. Neutral impurities show lower symmetry due to a missing or an extra electron. Charged impurities (negatively charged B and positively charged N), instead, retrieve the original symmetry (tetravalent electronic configuration). Formation energies for both neutral and charged impurities have been determined. Care has been taken in determining total energy of charged systems within a supercell calculation, applying the Makov-Payne correction [4]. Finally, an attempt has been done to calculate ionisation thresholds of each impurity species as a function of size.

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## **Self-consistent Solutions of Dyson's Equation and Total Energies from the $GW$ Approximation**

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We present details of the use of many-body perturbation theory, within the  $GW$  approximation, in computing ground-state total energies for finite-sized systems. We study the total energy using the Galitskii-Migdal formula with a Green function derived from the non-, partially- and fully-self-consistent  $GW$  approximation.  $GW$  total energy calculations have been successfully applied for systems with high symmetry [1,2,3], motivating further investigation.

We present the results of these calculations for a family prototype finite-sized systems known as jellium spheres, and an analysis of the role of the approximate exchange-correlation functional of the preceding DFT calculation in the accuracy of the  $GW$  total energies.

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# **Quasi-particle gap, dielectric properties and electronic correlations in semiconductor nanostructures.**

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Electronic excitation spectra of semiconductor nanostructures are particularly interesting quantities to calculate because they can be related to many experimental results in optical or electrical spectroscopy. On a fundamental point of view, it is also instructive to understand how the spatial and quantum confinement affect the spectra, in particular the gap. In this talk, we present recent theoretical works [1-4] concerning the quasi-particle gap of nanostructures, which required to consider the dielectric properties of the nanostructures.

Thus, in a first part, we consider the following question: how the dielectric properties of semiconductor nanostructures differ from those of the bulk material? We present calculations explaining why the average dielectric constant changes with size of the systems. We demonstrate that this evolution is not due to quantum effects (opening of the gap) and that it may be explained starting from the bulk dielectric function [1].

In a second part of the presentation, we discuss the influence of these dielectric properties on the exchange-correlation potential  $V_{xc}$  which is a central quantity in density functional theory since there is no explicit definition of this quantity. It is well-known that  $V_{xc}$  has a discontinuity within the gap of semiconductors and insulators. In this context, we have studied the dependence of this discontinuity in confined systems. Using a tight binding version of the GW theory [2,3], we show that the discontinuity of  $V_{xc}$  has a non monotonic behavior with respect to the dimensionality of the systems, from 0D (= zero dimension = dots), 1D (wires), 2D (wells) to 3D (bulk). We demonstrate that this behavior is due to the presence of polarization charges at the surface of the nanostructures arising from the exchange-correlation hole. We explain why the local density approximation gives comparatively better results for 0D systems than 2D or 1D ones. Finally, we hope to present preliminary results concerning metallic dots.

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## **Calculation of surface optical properties within TDDFT: the bound exciton of Si(111)2x1**

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In recent years it has been possible to develop methods [1] for calculating optical spectra with inclusion of the electron hole interaction by solving the Bethe Salpeter equation (BSE) within the framework of Green's function theory. The calculated spectra are in good agreement with experiments, although the computational effort is very heavy, since one has to solve a two-particle equation, for the electron and the hole. A promising alternative method is that based on

Time Dependent Density Functional Theory (TDDFT)[2], which treats an effective one-body problem, where all many-body effects are included in the so called exchange-correlation kernel,  $f_{xc}(r, r'; \omega)$ . The kernel is the crucial -yet unknown- quantity needed to calculate accurate spectra.

In the last three years a breakthrough in the knowledge of  $f_{xc}$  has been obtained by comparing TDDFT with the well tested -yet more complex-BSE method. Two different approaches [3,4] have yielded the same (approximate) formula for  $f_{xc}$ ; this has been shown to work very well for bulk systems, for both semiconductors and insulators, for bound excitons and unbound electron-hole pairs[3,4,5]. It also works, within the simplest TDLDA approximation, for small systems as clusters. However, the TDDFT approach has never been applied so far to surfaces.

In this work we consider the test case of the Si(111)2x1 surface, where an exciton with binding energy of about 0.27 eV results from BSE calculations and we show that the same result is obtained within TDDFT. To our knowledge, this is the first time that TDDFT is applied to calculate surface optical properties.

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## Long-ranged interactions in a supercell approach

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In today's *ab initio* electronic structure calculations plane wave basis sets are widely used due to certain numerical advantages. For systems without translational invariance such as surfaces, clusters and quantum wires, however, the plane waves introduce an artificial periodicity. A surface for example is thereby represented by a repeated slab geometry, with vacuum separating the individual slabs. Vacuum and slab form the repeated unit, the so called supercell for the calculation. On the level of DFT the issue of spurious long-ranged interactions between these repeated units has been studied in detail. Through the non-local screened Coulomb potential, however, for non-charged systems *GW* becomes more long-ranged than the local DFT-LDA formalism. In a cluster *GW* calculation for the sodium tetramer long-ranged interactions up to 40 bohr of vacuum have been observed [1]. Our *GW* calculations using the space-time approach [2] indicate that long-ranged interactions also play a dominant role for surfaces. We explain this

behaviour by an electrostatic effect and show that only a cutoff of the long-ranged interactions leads to converged quasiparticle energies. The need to cutoff the long-ranged interactions has been also discussed very recently for semiconducting nanotubes [4].

As an application, we compare our quasiparticle band structure for the Si(001) c(4×2) surface with recent two-photon photoemission data [3].

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## **Electronic Excitations in Semiconductor Quantum Dots**

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Semiconductor quantum dots can now be synthesized with a high degree of control over their size, shape, and composition. Recent advances in measurement and characterization techniques have lead to a wealth of experimental information on the physics of electronic excitations in these nanostructures. The challenge for theory is to accurately predict the behavior of complex electronic excited states (such as multi-excitons, charged excitons, etc.) in semiconductor quantum dots containing typically  $10^3$  to  $10^6$  atoms. These nanostructures are too large for first-principles calculations to be practical, and too small for continuum models, such as effective mass or k.p, to be accurate. I will discuss here a semi-empirical method, based on pseudopotential wave functions, to calculate electronic excitations in million-atom semiconductor quantum dots with accuracy comparable with computationally more expensive first-principles methods. This approach requires the solution of an atomistic pseudopotential Schroedinger equation to determine the single-particle energies and wave functions of the quantum dot, followed by a configuration-interaction-like expansion of the excited-state wave functions to obtain the many-particle excitations. I will present results on: (i) Multi-exciton radiative and non-radiative recombination in colloidal and self-assembled quantum dots, (ii) Auger electron-hole scattering and electron cooling in CdSe free-standing nanocrystals, (iii) Dark and bright exciton lifetimes as a function of temperature and size, and (iv) Mechanisms for direct carrier multiplication in quantum dots.

# GW calculations for surfaces

**Christoph Freysoldt<sup>1</sup>, Philipp Eggert<sup>1</sup>,  
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The combination of density functional theory (DFT) and many-body perturbation theory in the *GW* approximation has become an important tool for *ab-initio* band structure calculations and is typically in very good agreement with experiment [1]. In order to treat surfaces one often employs a repeated slab geometry (for computational convenience). However, electric multipole moments in the slabs lead to a slowly decaying electrostatic interaction between the slabs. This can be corrected for in DFT total energy calculations in order to obtain a fast convergence to the limit of an isolated slab [2]. Within *GW*, multipoles may occur dynamically even if the time-averaged ground state exhibits no dipole.

Although we avoid direct interactions between periodic images in our approach [3] by integrating the self-energy in real space, our calculations showed no convergence with respect to the vacuum spacing in the numerically accessible range. A step-by-step analysis reveals that the divergent behaviour is introduced by the head and wing elements of the dielectric matrix which are calculated using  $k \cdot p$  perturbation theory. In anisotropic systems such as surfaces, head and wings become directionally dependent, which reflects the non-analytic behaviour of the dielectric function for  $q \rightarrow 0$ . We show how the full angular dependence of head and wings can be incorporated into the inverse dielectric matrix in an efficient manner. However, the convergence problem persists in the angle resolved implementation.

An alternative approach to suppress the unwanted interaction that leads to a sufficiently fast convergence with respect to the slab separation is presented for silicon surfaces.

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## Ab initio study of the electronic structure of magnetite

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We analyzed the influence of internal and external conditions on the electronic structure of magnetite, specifically the half-metal to metal transition. The latter leads to a loss of the material's desirable half-metallic properties. Total energies, electronic structure, and magnetic

moments are calculated by density functional theory (DFT) using the FP-LAPW method. Results obtained within the generalized gradient approximation are in excellent agreement with experimental findings. In response to uniaxial, biaxial or triaxial pressure, a half-metal to metal transition occurs, which shifts the Fermi energy from the gap of the majority-spin electrons under the top of the valence band so that both spin channels become metallic. We also performed an analysis of different structural and spin configurations simulating the substitution  $\text{Fe}_{2.5}\text{X}_{0.5}\text{O}_4$  ( $\text{X} = \text{Mn}, \text{Co}, \text{Ni}$ ). The Mn-doped crystal is metallic whereas Co- and Ni-doped ones are half-metallic.

## **Photocatalytic Oxidation of CO at the $\text{V}_2\text{O}_5(010)$ Surface: Cluster Model Studies**

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While the catalytic behavior of vanadium oxide has been known and utilized for a long time many microscopic details of oxidation reactions at vanadium oxide surfaces are still not fully understood. Experiments indicate that  $\text{CO}$  binds weakly at the clean  $\text{V}_2\text{O}_5$  surface but can adsorb strongly at oxygen vacancies of the reduced surface. In addition, there is experimental evidence that local electronic excitations at the clean  $\text{V}_2\text{O}_5$  surface can facilitate  $\text{CO}$  oxidation involving surface oxygen. In this work we use embedded cluster models as large as  $\text{V}_{10}\text{O}_{31}\text{H}_{12}$  together with DFT methods to examine the effect of local electronic excitations and the influence of  $\text{O}$  vacancies on the interaction of  $\text{CO}$  with the  $\text{V}_2\text{O}_5(010)$  surface. The electronic structure of the surface in its ground state is modelled by the singlet cluster while local excitations are introduced by singlet to triplet excitations. Our calculations show, in qualitative agreement with experiment, that local excitations of the  $\text{V}_2\text{O}_5$  surface can promote oxidation of  $\text{CO}$  while oxygen vacancies do not facilitate this reaction. Molecular  $\text{CO}$  adsorption can, however, take place at oxygen vacancy sites.

## **Self-energy and lifetimes of surface states beyond the GW approximation**

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We report many-body calculations of the self-energy and the lifetime of Shockley and image states on the (100) and (111) surfaces of Cu. The self-energy is computed either in the absence of short-range correlation effects (GW approximation) or by including short-range correlation effects both in the screened interaction  $W$  (beyond the random-phase approximation) and in the expansion of the self-energy in terms of the  $W$  (beyond the GW approximation). Different approximations have been chosen to describe the exchange-correlation kernel, and the impact of these approximations will be discussed.

# Effects of oxygen on the structural, electronic and optical properties of silicon nanocrystals

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Silicon clusters are ideal models to study the effects related to the reduction in size of semiconductors. In these systems, both quantum confinement effects (opening of quasiparticle gap, enhancement of excitonic effects), and surface effects (passivation, oxidation, reconstruction, defects) play a fundamental role.

Starting from the equilibrium geometry of the ground state of  $\text{Si}_{10}\text{H}_{16}$  computed with the Car-Parrinello method in DFT-LDA, we have studied how the structure of this cluster changes when an O atom replaces a couple of H atoms, in the case of formation of either a double Si=O bond or a bridge Si-O-Si bond.

Then we have calculated the absorption spectra of these clusters, at different degrees of approximation. In particular, we have studied within RPA the effects of the non locality of the pseudopotentials, those due to local fields and, finally, the effects of geometrical relaxation in the excited state.

## Self-consistency in GW calculations of spectral and ground-state properties

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The  $GW$  approximation is, of course, the first-order term in an expansion of the self-energy operator  $\Sigma$  in powers of the dynamically screened electron-electron interaction,  $W$ . From  $\Sigma$ , the one-electron Green's function  $G$  may be calculated, from which various spectral and ground-state properties are available. Different ways of deriving the approximation from exact theory yield different choices of whether  $G$  and/or  $W$  are made to be consistent with the Green's function that arises from  $\Sigma$ :  $G_0W_0$ ,  $GW_0$  and fully self-consistent  $GW$ , where  $G_0$  generally indicates the LDA Green's function. We present results for finite and infinite systems at all three levels of self-consistency, including both spectral and total-energy calculations [1-3]. These include converged total energies resulting from the incorporation of self-consistency and  $GW$  total-energy techniques into our general-purpose GWST "space-time" supercell code suite [4],

which interfaces with pseudopotential plane-wave DFT calculations as its input. This opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

We also discuss the role of pseudopotentials in  $GW$  calculations and the interplay with self-consistency[5].

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Further details at <http://www-users.york.ac.uk/~rwg3/>.

## Ab-initio theory of superconductivity

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One of the great challenges of modern condensed-matter theory is the prediction of material-specific properties of superconductors. The traditional model of Bardeen, Cooper and Schrieffer (BCS) properly describes the universal features of (conventional) superconductors but is not able to make accurate predictions of material-specific properties such as the critical temperature. To tackle this problem, a density functional formalism has been developed which describes superconductors in thermal equilibrium in terms of three quantities: the ordinary electron density, the superconducting order parameter, and the nuclear N-body density matrix. These three ”densities” are determined by a set of Bogoliubov-type Kohn-Sham equations representing the electronic degrees of freedom, and a Schrödinger equation with an N-body interaction describing the nuclear motion. These equations are coupled to each other via exchange-correlation (xc) potentials which are universal functionals of the three densities. Approximations of these xc functionals will be derived on the basis of many-body perturbation theory. In this way, a true ab-initio description is achieved which does not contain any empirical parameters. Numerical results will be presented for the critical temperatures and the gaps of simple metals, of  $MgB_2$ , and of Li and Al under pressure. Superconductors with strong and with weak electron-phonon coupling are equally well described. For other than phonon-driven superconductors, we will discuss how an effective particle-particle interaction and hence the superconducting mechanism can be identified, once an approximation for the universal exchange-correlation functional is given.

# Theory of electron energy loss at surfaces

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Electron energy loss spectroscopy is a frequently exploited technique for characterizing materials. When carried out at low energies, a substantial proportion (about 1%) of electrons are backscattered inelastically as they excite a variety of transitions within the surface region. Depending on the incident and loss energy regimes, these excitations may be related to very different processes, such as atomic vibrations, bulk or surface plasmons, interband and intraband transitions (both core and valence), and so on.

Correspondingly, different theoretical approaches have been developed to interpret the observed spectra. In the 1-20 eV range, where spectral features are predominantly related to interband transitions and surface plasmons, bandstructure effects should be most important. Hence, a proper description of the loss function should incorporate the full microscopic inverse dielectric function of the vacuum-surface interface, calculated ab-initio, and including the effects of local fields and q-dependence.

We present a new method that accounts for these features within the limit of dipole scattering theory, improving on previous approaches based on three-layer models. The flexibility of the model is illustrated via studies of the loss anisotropy of some typical semiconductor surfaces and the surface plasmon dispersion in a simple metal.

## **Ab initio study of reflectance anisotropy spectra of a sub-monolayer oxidized Si(100) surface**

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The effects of oxygen adsorption on the reflectance anisotropy spectrum (RAS) of reconstructed Si(100):O surfaces at sub-monolayer coverage (first stages of oxidation) have been studied by an ab initio DFT-LDA scheme within a plane-wave, norm-conserving pseudopotential approach. Dangling bonds and the main features of the characteristic RAS of the clean Si(100) surface are mostly preserved after oxidation of 50% of the surface dimers, with some visible changes: a small red shift of the first peak, and the appearance of a distinct spectral structure at about 1.5 eV. The electronic transitions involved in these changes have been analyzed through state-by-state and layer-by-layer decompositions of the RAS. We suggest that new interplay between present theoretical results and reflectance anisotropy spectroscopy experiments could lead to further clarification of structural and kinetic details of the Si(100) oxidation process in the sub-monolayer range.

# First-Principle Green's function methods : electronic and optical properties of carbon nanotubes and excited-state forces

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Ab initio predictions of electronic and optical properties of materials within the GW-Bethe Salpeter Equation (GW-BSE) formalism have proved accurate and reliable. The formalism allows for the study of electronically excited states and outputs experimentally measurable quantities such as band gaps and optical spectra. We present two recent research results in this area: the optical spectra of carbon nanotubes and the calculation of excited-state forces.

The work on small-diameter single-walled carbon nanotubes underlines the physics of Coulomb interactions of electron-hole pairs in one-dimensional systems and its crucial effect on optical properties. In addition, inclusion of all the relevant excited-state many-body effects produces results in quantitative agreement with experiment. This accuracy allows for theoretical assignment of various observed absorption lines to particular nanotube chiralities.

The ability to compute excited-state forces allows us to move beyond fixed atomic configurations. This advance opens the door to the calculation of the atomic rearrangements of electronically excited-systems as well as concomitant modifications of optical properties such as Stokes shifts and changes in luminescent intensity. We outline the theoretical background and tests on molecular systems. We illustrate the method with an application to an interesting solid-state problem: exciton self-trapping in quartz.

## Quasi-particle self-consistent GW approximation

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We present some progress in the development of a semi self-consistent GW method based on the all-electron, full-potential LMTO method. By iterating the GW Hamiltonian, whose energy dependence is ignored in a few reasonable ways (we tested some possibilities), self-consistency in both the eigenfunctions and eigenvalues is achieved. Our intent is to obtain a reasonable approximation for the best quasi-particle (QP) eigenfunctions and eigenvalues. QPscGW gives directly the QP density of states (QP-DOS) in the sense of independent-particle picture, which can be justified by the Landau's Fermi liquid theory. Thus we call our semi self-consistent GW method as the QP self-consistent GW (QPscGW) method. The QP bands can be used directly within a one-particle picture to evaluate quantities, e.g. response functions, optical properties, magnetic moments, transport, and in the construction of the Boltzmann equation.

In addition, we think that the independent-particle picture should be a rigid starting point even when we try to go beyond the one-particle picture. The method may be viewed as a way construct the most suitable quadratic part of the full Hamiltonian for many-body perturbation theory. As for the spectrum DOS (SP-DOS), the imaginary part of the full Green function

$G$ , it can be calculated by a one-shot GW calculation (or GW+extensions) from the QPscGW result. This situation is in contrast with the full self-consistent GW method (full scGW), which makes SP-DOS self-consistent. Compared the full scGW, QPscGW is advantageous in two ways: (1) It is numerically easier and more stable. We have successfully applied it to wide range of materials. (The ability to do so is also due to a mixed-basis expansion of the Coulomb interaction, as will be described.) (2) There is self-consistency in both the QP bands and the dynamically screened Coulomb interaction  $W$  (they are obtained at the same time). By contrast, the full scGW may give problematic  $W$ , or more precisely it should be identified not as the dynamical screened interaction but as an intermediate construction during calculation. There are theoretical predictions that the full scGW would give poor  $G$ .

We applied our QPscGW to metals, semiconductors, oxides, magnetic materials, f-electron materials (in progress) and so on. Our results show very systematic improvement over LDA compared with experiments. We present two key findings: (1) large improvements are found for materials where one-shot GW fails. (2) The discrepancies with experiment are very systematic, and can be explained in terms of what GW theory omits from the exact hamiltonian. As for semiconductors, not only band gaps but many other properties are improved, such as effective mass. For NiO and MnO, d-d splitting and relative positions of oxygen 2p bands move closer to experimental results. Transition metals show a small, systematic d-band width narrowing relative to LDA. We also present recent results for MnGaAs and half-metallic compounds.

Finally, we report some progress on attempts to solve the Luttinger-Ward functional to compute the total energy.

## **Orbital Functionals in Current-Density Functional Theory**

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A proper description of many-electron systems in an (external or internal) magnetic field within a density functional framework requires the use of the current-density functional theory (CDFT) of Vignale and Rasolt [1]. Unlike in ordinary spin-density functional theory, where only the coupling of the magnetic field to the spin degrees of freedom is taken into account, in CDFT one also allows for coupling to the orbital degrees of freedom. Such a CDFT formalism most likely is required for a proper description of open-shell systems where the ground state may carry a finite current. The usefulness of CDFT in practice depends on the availability of accurate approximations to the exchange-correlation (xc) energy. A local-density approximation based on the xc energy per electron of the uniform electron gas exposed to a uniform magnetic field has been suggested. However, since this xc energy has derivative discontinuities as function of the field whenever a new Landau level is occupied, the corresponding xc potential becomes singular and difficult to handle in practice.

Here we investigate the use of explicitly orbital-dependent functionals as alternative route. In fact, one might expect orbital functionals to be well suited for this situation since the appearance of Landau levels intrinsically is an orbital effect. We show the equivalence of two different formulations of CDFT if certain conditions on the xc energy functional are satisfied. We also

elucidate the connection to ordinary spin-DFT for ground states with vanishing currents. We then use the optimized effective potential (OEP) formalism for CDFT recently developed in our group [2] to derive integral equations for the xc scalar and vector potentials. Simplifying approximations to these integral equations lead to a numerically tractable scheme to calculate the xc potentials. First results on atomic systems will be presented.

## **Ab initio study of the $\text{Fe}_3\text{O}_4$ (111) surface**

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Metal oxides represent an important class of materials found in environmental science, electrochemistry, biology, chemical sensor technology, catalysis, magnetism and other fields. However, our understanding of basic metal oxide surface chemistry and mechanisms of catalytic reactions on metal oxides greatly lags behind that of semiconductors and metals. Magnetite ( $\text{Fe}_3\text{O}_4$ ), the oldest known magnet, is one of the most abundant transition metal oxides. The  $\text{Fe}_3\text{O}_4$  (111) surface can be considered as a stack of layers containing either metal cations or oxygen anions. The stacking of layers with opposite charges gives rise to a large dipole moment perpendicular to the surface, which the system may reduce by large interlayer relaxations. Moreover, for such oxide surfaces different surface compositions are possible and should be taken into account. Despite a large amount of research, the  $\text{Fe}_3\text{O}_4$  surface structures and properties have not been understood fully yet. Our calculations are performed employing the full-potential linearized augmented plane-wave method (WIEN2k). We will describe our project and show first results for the relative stability of different  $\text{Fe}_3\text{O}_4$  (111) terminations and their electronic and magnetic properties.

## **Nonlinear optical coefficients from first-principles calculations: Different numerical approaches**

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Different numerical and methodological approaches for the ab initio calculations of the nonlinear optical response are used in the literature[1,2]. On the one hand, the formulas used are not easily seen to be equivalent. On the otherhand, the numerical results even for well characterized bulk systems like GaAs do neither agree well with each other nor with experiment[3]. We revisit the derivation of the relevant expressions for the second harmonic generation and show analytically the equivalence of the approaches[1,2] within the independent-particle approximation. In addition, numerical results for bulk GaAs are presented which show the large influence of technical parameters on the final results.

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# **An *ab initio* study of new polymeric crystals based on fullerene $C_{60}$ and carbynes**

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The most basic fullerene structure is the  $C_{60}$  molecule. Since its discovery in 1985,  $C_{60}$  has been used as the fundamental component of a variety of new carbon nanostructures. Examples include endohedral fullerenes, peapod nanotubes,  $C_{60}$  dimers, and single-molecule transistors.

Using density-functional calculations, we study a new polymeric form based on fullerene  $C_{60}$  and linear chain of carbon atoms (cumelens). The structures considered in the work contain from two to six carbon atoms in cumelens chain between fullerenes  $C_{60}$ . Two different stable states of these structures have been found. For odd numbers of carbon atoms, adjacent fullerenes in the chain are rotated in  $90^\circ$  with respect to each other. For even numbers of carbon atoms between fullerenes the effect did not occur.

We found, that all structures are semiconductors with band gap of the range 1.19 - 1.36 eV. It also shown that structure containing two carbon atoms between fullerenes is energetically most favorable. We have compared the energy per atom of all polymeric structures with different dimensional with two carbon atoms between fullerenes. The most energetically favorable structure is 3D structure.

## **A three-point Many-Body vertex function from Time-Dependent Density-Functional Theory**

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Thanks to the recently developed Many-Body expressions for the exchange-correlation kernel  $f_{xc}$  Time-Dependent Density-Functional Theory (TDDFT) has become an extremely powerful technique to calculate correlation effects in the microscopical polarization function. In this talk we will investigate the relation between the Many-Body  $f_{xc}$  and the self-energy vertex function. We will show that it is possible to obtain a practical and general expression for the three-point vertex function based on the two-point exchange-correlation kernel. Taking LiF as a test case we will prove that, in contrast to previous results for the electron gas, simple metals and semiconductors, vertex corrections in the self-energy and in the screening function do not compensate each other.

# Absorption spectra of biological systems from TDDFT

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Not surprisingly, the theoretical understanding of biophysical processes is a very active field of research. In particular, there have been spectacular advances in the characterisation of structural and dynamical properties of complex biomolecules by a combination of quantum-mechanical and classical-molecular mechanics methods (QM-MM). However, and in spite of the large amount of experimental work in photo-active molecules, the theoretical description of the interaction of these molecules with external time-dependent fields is very much in its infancy. Photo-active molecules relevant for biology include the green fluorescent protein (GFP), retinal, chlorophyll, etc. On the other hand, time dependent density functional (TDDFT) theory has proved to be an invaluable tool for the calculation of excitation spectra of molecules. We will present a way to combined QM-MM methods (for the ground state) with TDDFT (for the description of the excited states) to calculate optical absorption spectra. Our first test case, the GFP, yielded remarkably good results. Very recent work on the blue fluorescent protein and on the DNA basis will also be reviewed.

## **Electronic band structure of the C(111)2x1 surface within an iterative GW scheme**

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Theoretical calculations show that the most stable reconstruction for the (111) surface of diamond is consistent with a Pandey Chain model, being the atoms on the chain neither buckled nor dimerized. Experimental data, while confirming the absence of dimerization, cannot exclude the presence of buckling. The electronic band structure related to the fully relaxed (111) surface of diamond appears semimetallic within DFT, in contrast with experiments which show a gap of at least 0.5 eV. The underestimation of the electronic gap could be due to a wrong theoretical equilibrium geometry (absence of buckling) and/or to the usual DFT band gap problem. Introducing quasiparticle corrections within a self-consistent GW scheme, using an iterative procedure for updating the quasiparticle energies, we found for this surface an electronic gap of 0.5 eV. Preliminary results on the optical properties are also presented and discussed.

## **Exchange in non-equilibrium systems**

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State-of-the-art simulation tools for non-equilibrium quantum transport systems typically take the current-carrier occupations to be described in terms of the equilibrium distribution functions of two particle reservoirs characterised by two different electrochemical potentials, while for the description of electronic exchange and correlation, the Local Density Approximation (LDA) to Density Functional Theory is generally used[1],[2]. However, this involves an inconsistency because the LDA is based on the homogeneous electron gas in equilibrium, while the system is not in equilibrium (and may be far from it).

In this work we remove this inconsistency by deriving local density approximations for the non-equilibrium *exchange* potential, based on non-equilibrium homogeneous electron systems modelled in the spirit of Landauer-Büttiker theory. I-V characteristics calculated with both, equilibrium and non-equilibrium, local exchange potentials are then compared for a simple model non-equilibrium metal-vacuum-metal junction.

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[2] N. D. Lang, Phys. Rev. B. 52, 5335 (1995)

## **Ab-initio calculations of the optical properties of phase-change materials**

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The results of ab-initio calculations of the dielectric function and the reflectivity of bulk GeTe and AgTe systems will be presented. These materials are promising candidates for memory devices exploiting the change of the optical properties depending on the structural phase-change and are thus subject of intensive investigations. Different atomic configurations have been computed and the influence on the dielectric function has been investigated. We focus on the degree of symmetry, comparing cubic with lower symmetry. The dielectric function considering the long-wavelength limit and neglecting local-field effects, is implemented within the FLEUR code, an implementation of the full-potential linearized augmented plane-wave (FLAPW) method.

## **Ab-initio calculation of the structural, electronic and optical properties of Silicon nanoclusters in their ground and excited states**

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Silicon-based light emitting materials, such as porous silicon and Si nanocrystals, have attracted a lot of interest in the last years because of the promising applications in advanced electronic

devices based on nanoscale technology. Understanding and improving the properties of these novel semiconductor materials requires to learn more about the atomistic aspects of their structure and fabrication. Passivated-surface silicon clusters are the ideal theoretical model to achieve this aim. The most part of first principle calculations and empirical simulations have used hydrogen as passivating agent for the Si surface, focusing the efforts mainly on the role of quantum confinement effects. Yet, it has been recently pointed out that also the surface chemistry produces substantial impact on the Si clusters properties. Here we investigate the structural, electronic and optical properties of small Si clusters using different approaches (pseudopotential methods, TDDFT, GW-BSE) within the Density Functional Theory. To explain the observed Stokes shifts between the absorption and emission energies we have performed calculations for each cluster both in ground and excited state configuration considering as the excited state the electronic configuration in which the highest occupied single-particle state (HOMO) contains a hole (h), while the lowest unoccupied single-particle state (LUMO) contains the corresponding electron (e). Structural relaxations have been fully taken into account in all cases through total energy minimization calculations. We have first considered clusters covered by hydrogen and then we have substituted some H with O both double bonded or in a bridge configuration with respect to Si. The substitution of H with O as passivating agent results in a different cluster geometry and in a reduction of the energy band gap depending on the type of O-Si bond. Moreover also the optical properties strongly depend on the different O-Si bond type. The results provide a consistent interpretation of the photoluminescence redshift observed in oxidized samples and of recent outcomes on Si single quantum dot photoluminescence bandwidth. We have also performed calculations for the optoelectronic properties of small Si clusters embedded in a SiO<sub>2</sub> matrix; the equilibrium structure shows a deformation of the SiO<sub>2</sub> cage only in the neighborhood of the cluster. This strained interface region, about 1 nm thick, participates to the light emission processes as supported by experimental results, too.

Work done in collaboration with R. Magri (1), E. Degoli(2), E. Luppi(1), M. Luppi(1), O. Bisi(2), G. Cantele(3), D. Ninno(3), G. Onida(4), M. Gatti(4), A. Incze(4), O. Pulci(5), R. Del Sole(5)

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## **Electronic transport in nanoscale systems from first principles.**

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I will review some of the key issues concerning ab initio electronic transport in nanosystems, focusing on the achievements and limitations of Landauer formalism. This widely accepted formalism, when properly combined with first principles calculations, can give very satisfactory

results both at zero and finite bias voltages in a range of situations. Its application in the latter case, however, cannot be fully justified and remains an open issue. As illustration, various results for metallic nanocontacts will be presented.

## **Microscopic model for a strongly correlated superconductor single-electron transistor**

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We show how we can model a Superconducting Single-Electron Transistor (S-SET) operating by purely repulsive electron-electron interactions. The model consists of properly linked Hubbard clusters placed between electrodes and capacitively coupled to a gate potential. In the linear regime the conductance exhibits well separated peaks due to Andreev reflection, reproducing the typical response of a S-SET. This illustrates the  $W=0$  pairing mechanism and its potential to describe the superconducting behavior of properly symmetric Hubbard systems.

## **Large crystal local-field effects in the dynamic structure factor of $\text{TiO}_2$**

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We present ab initio time-dependent-density-functional calculations and non-resonant inelastic x-ray scattering measurements of the dynamical structure factor of rutile  $\text{TiO}_2$ . Our calculations are in very good agreement with experiment and prove the presence of large crystal local-field effects below the Ti M-edge, which yield a sharp loss peak at 14 eV featuring a remarkable non-monotonic dependence on the wave vector. These effects, which impact the excitation spectra in the oxide more dramatically than in transition metals, provide a signature of the underlying electronic structure.

## **Optimized Effective Potentials in Current-Density Functional Theory**

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In a density functional framework, the description of many-electron systems moving in (external or internal) magnetic field is achieved by current-density functional theory (CDFT) [1]. Using the Optimized Effective Potential (OEP) formalism for CDFT [2] with the exact exchange functional, we investigate an old problem in DFT: in an open-shell atom with, e.g., one occupied p-orbital, the density will be different depending on whether the p-orbital with magnetic quantum number  $m = 0$  or  $m \neq 0$  is occupied. Therefore, ordinary DFT will incorrectly give different total energies. The problem can be alleviated [3], by using current density functionals.

Here we present a practical scheme which allows for the calculation of the exchange-correlation scalar and vector potentials of the OEP-CDFT approach as well as first numerical results for atoms.

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## **Band gaps in GW self-consistent calculations**

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The GW approximation of the self-energy has been very successful in describing single particle excitations. For example it leads to correct band gaps in inorganic semiconductors and insulators. However, for systems wrongly predicted by LDA to be metallic (LDA wave functions and eigenvalues are used as starting point for GW calculations), the standard perturbative approach of GW is no longer effective. We go beyond this approach, by iterating the GW procedure in two alternative schemes: (i) only on quasiparticle eigenvalues and (ii) on eigenvalues and eigenfunctions (full charge self-consistency). In this contribution the two iteration schemes are compared. In addition, the effect of semicore states is investigated. The calculations are performed on a range of systems and the band gaps are compared to the experimental values.

## **Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism : ground-state and excited-state studies**

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There is a growing need for exchange-correlation (XC) functionals going beyond the Local-Density and Generalized-Gradient Approximations (LDA and GGA), as these do not account for long-range correlations occurring for instance in weakly-bonded compounds and biomolecules. In such systems van der Waals (vdW) interactions play a crucial role and can only be taken into account by means of fully non-local XC functionals. Contrary to the LDA and GGA cases, most of the latter depend on the Kohn-Sham orbitals and their energies. One way to build such a functional is to resort to the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem [1] [2] in conjunction with the Random-Phase Approximation (RPA). The RPA captures the physics of the vdW interactions and has been tested non self-consistently on some atoms, diatomic molecules, and solids.

However, a spurious maximum in the dissociation curve was evidenced for the N<sub>2</sub> [3] and H<sub>2</sub> [4] molecules. It may result from either (a) the RPA being insufficient to describe the dissociation

regime, or (b) the lack of self-consistency, as well as (c)  $H_2$  and  $N_2$  being pathological cases, without forgetting (d) a possible bug in the implementation. In parallel with studies concerning points (a), (b) and (d), we are tackling point (c) by examining the dissociation of several diatomic molecules within the ACFD-RPA framework as well as their excitation energies through Time-Dependent DFT (TDDFT) and  $\Delta$ SCF calculations. We compare some of their ground-state properties with the results obtained from LDA/GGA approximations too. In addition of being heteroatomic, and composed of low  $Z$  atoms, the LiH molecule presents very peculiar properties and is often used as a test case for new computational methods. That is why we have decided to put a particular emphasis on it. To further enhance our understanding of weakly-bonded systems we are also considering the van der Waals molecules  $Be_2$  and  $Mg_2$ . In particular, it is known that the vdW interaction is quite larger in the latter than in all those previously tried.

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## **Excitation energies and optical properties of Si nanocrystallites**

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Nanostructures and porous materials based on Si are an appealing research topic due to their promising applications in optoelectronics, data storage devices, and solar cells. By exploiting the three-dimensional quantum confinement of nanocrystallites, their luminescence properties can be enhanced and optical gain can in principle be achieved. Recent theoretical investigations on nanocrystallites have been focused in the electronic excitations and screening effects. Several attempts have been made in order to model a dielectric function of Si nanocrystallites, but so far the applicability of these methods is not clear. We present an investigation of Si nanocrystallites by means of an ab initio pseudopotential planewave method. By applying the  $\Delta$ -selfconsistent field method in the framework of the density-functional theory and the local-density approximation, we calculate the electron-hole pair-excitation energies. We also discuss different approaches to compute the quasiparticle gaps by combining a GW approximation and an effective medium theory applied to the crystallites. An estimate of the excitonic effects is made by evaluating the Coulomb integral with the highest occupied molecular orbital and lowest unoccupied molecular orbital. The quasiparticle gap calculated by means of the difference between ionization potentials and electron affinities, and the influence of Coulomb effects are taken in consideration with respect to the supercell size. Our results intend to find reliable procedures to calculate excitation energies in Si nanocrystallites and to model screening effects in these structures.

# Local-Field Effects in Calculations of Optical Constants from UV - X-rays\*

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There has been dramatic progress in recent years both in calculations and in the interpretation of x-ray absorption spectra (XAS). For deep core x-ray absorption an independent-electron approximation with final state potentials including a core-hole is often adequate [1]. However, corrections to the independent particle approximation due to local fields are often important, even far above an absorption edge. These local fields arise from the screening of the external x-ray field and the coupling to the core-hole. Their treatment requires a theory that goes beyond the independent-electron approximation. We have developed an efficient approach for treating these effects in solids and molecules based on a combination of the Bethe-Salpeter equation (BSE) and time-dependent density functional theory (TDDFT). First the TDDFT response function is calculated with a local exchange-correlation functional [2]. This first step alone is adequate over a wide spectral range above the edge. In the near-edge region where non-local effects can be important, the full BSE response is then calculated using a local projection operator approach, with a screened core-hole potential  $W$  calculated within the RPA [3]. This combined approach can be appended straightforwardly to our self-consistent real-space Green's function code FEFF8, and makes possible efficient calculations of optical constants from the UV to x-ray energies. The approach is illustrated with a number of examples.

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## **”TDDFT and Many-Body Perturbation Theory: comparisons and combinations”**

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Today, one of the big challenges of theoretical condensed matter physics is to find ways for describing accurately and efficiently the response of electrons to an external perturbation. In fact, the knowledge of response functions allows one to directly derive spectra (such as absorption or electron energy loss); moreover, response functions enter the description of correlation effects, for example through the screened Coulomb interaction  $W$  in Hedin's GW approximation to the electron self-energy. Two main developments for the *ab initio* calculation of response functions of both finite and infinite systems are, on one side, the solution of the Bethe-Salpeter equation (BSE), and, on the other hand, Time-Dependent Density Functional Theory (TDDFT). Both approaches are promising, but suffer from different shortcomings: the

solution of the Bethe-Salpeter equation is numerically very demanding, whereas for TDDFT, despite recent progress a generally reliable but at the same time very efficient description of exchange-correlation effects has still to be developed.

We will review the two approaches focussing on their comparison. The meaning and importance of different contributions to the induced potentials will be analyzed for various systems, ranging from atoms to bulk semiconductors and insulators, from graphite to nanotubes. We will then show various ways to combine TDDFT and the BSE approach, that are all leading to a similar class of exchange-correlation kernels. These kernels yield excellent results for absorption and energy loss spectra; moreover, they can be used to determine vertex corrections beyond the GW approximation. We will discuss the links between these methods as well as the relation with other work (e.g., Goerling's EXX), show results and give perspectives.

## **First-principles study of crystalline and amorphous transition metal oxides and silicate**

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Until recently, silicon dioxide has been the dielectric of choice in integrated MOS devices. By 2004, the thickness of this insulating layer is expected to decrease to 1.0 nm to 1.5 nm (about five silicon atoms deep) precluding its effective use due to severe leakage problems. An alternative high-permittivity (high- $\kappa$ ) gate dielectric is required. In this framework, transition metal oxides and silicates have attracted considerable attention as possible substitutes. Their dielectric properties constitute an issue of great practical relevance. In particular, it is highly desirable to develop a better understanding of how the permittivity is related to the underlying microstructure. This is the aim of the present work.

Using first-principles calculations, we investigate the electronic and dielectric properties of group IVB transition metal (Ti, Zr, and Hf) oxides and silicates. We consider various crystalline phases for the oxides (cubic, tetragonal, and rutile) and for the silicates (zircon), as well as amorphous silicates. The electronic properties are first calculated in the framework of the density functional theory, and then corrected using the *GW* approximation. For the dielectric properties, we introduce a scheme which relates the dielectric constants to the local bonding of silicon and metal atoms. This scheme is based on the definition of parameters characteristic of the basic structural units formed by silicon and metal atoms and their nearest neighbors, and allows us to avoid heavy large-scale calculations, which are beyond current computational capabilities. Applied to amorphous Zr silicates, our scheme provides a good description of the measured dielectric constants, and highlights the role of sixfold coordinated metal atoms.

# Ab-initio studies of the Si(557)/Au and Si(553)/Au Reconstructions

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Gold deposited on silicon surfaces at the monolayer regime results in a variety of reconstructions. The most interesting ones are the (quasi-) one dimensional phases, featuring monatomic wires of gold. They promise exotic physical phenomena, such as the Luttinger liquid [1]. These wires can be grown on the flat Si(111) surface which yields three possible directions for the wires to grow [2]. Stepped silicon surfaces avoid this problem; the wires grow parallel to the step edges. These systems have now been manufactured for years [3].

We present ab-initio studies of the Si(557)/Au and Si(553)/Au reconstructions using the Siesta ab-initio code [4].

The Si(557)/Au surface, resulting from the deposition of 0.2 ML of gold, has been intensively studied, due to the rich physical phenomena observed in it. Our ab initio calculations show that spin-orbit coupling is crucial to understand the electronic structure of the Si(557)-Au surface [5]. The spin-orbit splitting originates the two one-dimensional bands observed in photoemission, which were previously attributed to spin-charge separation in a Luttinger liquid [6]. This spin splitting might have relevance for future device applications. We also show that the apparent Peierls-like transition observed in this surface by scanning tunneling microscopy is a result of the dynamical fluctuations of the step-edge structure, which are quenched as the temperature is decreased [7].

In the case of the Si(553)/Au reconstruction, we study a recently proposed model [3] and give some alternative models that yield bandstructures that are in good agreement with the photoemission data [8]. The role of the spin-orbit coupling is also studied.

## Exact-Exchange-Based Quasiparticle Calculations of II-VI Compounds and Group III Nitride

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We present a systematic *ab initio* study of the electronic structure for a wide range of II-VI compounds and group III nitrides in the zinc-blende structure. The challenge from a computational point of view is to capture the exchange-correlation (XC) effects arising from the shallow semicore *d*-electrons of the cation, which we explicitly treat as valence states in our pseudopotential approach.

In order to correctly describe the dominant exchange interaction we apply density-functional theory (DFT) in the exact-exchange (EXX) approximation. Although the EXX Kohn-Sham

bandstructure compares well with experiment for standard semiconductors [1] the bandstructure as measured by photoemission is an excited state property. We therefore apply many-body perturbation theory in the  $GW$  approximation to the EXX groundstate.

The hierarchy of our approach allows us to systematically investigate the role of XC in these materials from first principles. Our results show that it is crucial to treat XC on the same footing at every stage. To achieve this in our EXX calculations we employ the newly developed EXX-pseudopotentials [2]. Furthermore we obtain  $GW$  bandstructures in very good agreement with existing all-electron  $GW$  calculations.

Our results indicate that, in contrast to common believe, a pseudopotential approach including only the  $d$ -electrons of the semicore shell in question, is sufficient to accurately describe the electronic structure if treated in the EXX+ $GW$  formalism.

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## Vertex Corrections in a systematic self-energy perturbation theory

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The perturbative implementation of the  $GW$  approximation, in which the self-energy is evaluated non-self-consistently with Kohn-Sham orbitals, has proved to be very successful in practical applications and yields accurate quasiparticle band structures for a wide range of materials. While this approach originally suggested itself naturally due to its numerical simplicity, expanding computational resources have now made it possible to perform self-consistent calculations and to explore vertex corrections beyond the simple functional form of the  $GW$  approximation. However, it has proved hard to achieve systematic improvements, which depend on a careful balance between counteracting self-energy contributions. Starting from density-functional theory, I here develop a perturbation expansion of the self-energy that converges systematically. The first-order correction to the Kohn-Sham eigenvalues resembles the  $GW$  approximation but includes some modifications that make the approach internally consistent. The implications are illustrated by numerical results for the homogeneous electron gas.

## Recent applications of TD-DFT in molecular, liquid and solid phases

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Time-dependent density functional theory (TD-DFT) can be used to efficiently calculate excitation energies, with excitonic effects included. In molecular systems the energies of valence excitations are usually quite accurate, however Rydberg and especially charge-transfer excitations are badly described with the adiabatic LDA or GGA functionals. Here we compare the GGA-PBE functional [John P Perdew *et al*, Phys. Rev. Lett. **77** (1996) 3865], the TPSS

meta-functional [Jianmin Tao *et al*, Phys. Rev. Lett. 91 (2003) 146401], the asymptotically corrected SAOP potential [P R T Schipper *et al*, J. Chem. Phys. 112 (2000) 1344] and the PBE0 hybrid functional [C. Adamo and V. Barone, J. Chem. Phys. 110 (1999) 6158]. Except for the charge-transfer excitations the excitation energies are generally improved by the SAOP potential and PBE0 functional.

## **Bethe Salpeter treatment of core excitations: multiplet effects**

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We present a Bethe-Salpeter treatment of core excitations in solids that can be used to include multiplet effects. This accounts for electron spin degrees of freedom, as well as core-hole quantum numbers, L, M and S. The advantage of this approach over other approaches (atomic, Anderson impurity model) is that it allows for the natural inclusion of many chemical and solid state effects. The approach should be usable in molecular and cluster calculations as well, so that it can help study multiplet effects in core-hole spectra for nanosystems. Issues regarding charge-transfer excitations and multiple electron excitations will also be discussed.

## **Excitons from TDDFT as generated by the variational approach to many-body perturbation theory**

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It is rather well known that the optical or density response function of electronic systems can be obtained from time-dependent density-functional theory (TDDFT) in terms of an exchange-correlation kernel ( $f_{xc}$ ). This approach is computationally far simpler as compared to solving the Bethe-Salpeter equation of many-body perturbation theory (MBPT). In actual fact, within TDDFT, no systematic route toward successively better approximations has, so far, been available. In the present work we construct such a scheme based on our variational action functionals. In terms of the one-electron Green function of MBPT these functionals give stationary expressions for the total action of the system at hand - or the total energy in the case of time independent problems. From a stationary action it is rather straight-forward to construct the time dependent density response function. Building the functionals from the PHI derivable theory of Baym and Kadanoff, always results in response functions which obey a large number of physical constraints like particle or energy conservation. The simple idea of the present work is to restrict the variational freedom of the functionals to the domain of Green functions which are non-interacting and given by a local one-electron potential. According to the Runge-Gross theory this restriction immediately results in a density-functional theory the quality of which is determined by the sophistication which is build in to the choice of PHI derivable approximation for the action functional.

# A bi-exciton mechanisms of photo-induced desorption from MgO

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Recent experimental data clearly demonstrate that using both femto- and nano-second laser pulses with photon energies tuned to excite particular surface features at the MgO surface, one can achieve a very effective desorption of atomic O and Mg species. In this presentation we demonstrate a new bi-exciton mechanism responsible for desorption of oxygen atoms and draw analogies with the exciton mechanism of desorption of alkali halides.

Recently we demonstrated that photo-induced desorption can be used for probing surface spectroscopic features [1-3]. The technique is sensitive enough to detect energy shifts between the bulk and surface excitons as small as 0.2 eV. In addition, a significant degree of control over the desorbed species can be achieved if the knowledge of the surface electronic structure is fully exploited [1-3]. We extended this approach to more complex oxide surfaces. The experimental and theoretical studies demonstrate that excitation energies of corner and step sites at the MgO (001) surface are strongly shifted with respect to the bulk and terrace exciton energies [4]. Recent experiments demonstrated that selective excitation of the kink and corner surface features using 4.7 eV laser pulses leads to desorption of O atoms with average kinetic energies of about 0.3 eV. Since the valence of anions in MgO is twice that of anions in alkali-halides, the desorption mechanism is expected to be more complex and involve several steps.

To model the photon-induced processes in MgO we employ an embedded cluster approach, which combines a quantum-mechanical treatment of a site of interest with a self-consistent classical description of the remaining part of the system. The method is implemented in a computer code GUESS; it allows one to account consistently for the ionic and electronic contributions to the defect-induced lattice polarisation and for their effect on the defect itself, and to treat excited states using different ab initio techniques. We modelled desorption from a 3-coordinated oxygen corner site at an MgO surface and developed a two-step mechanism for this process. The results of our calculations suggest that the first photon of ca. 4.5 eV can induce an optical transition at the oxygen corner site. This first excited state relaxes with a significant displacement of the corner oxygen away from its original site. The relaxed state corresponds to a charge transfer exciton configuration  $O V E Mg^+$ . This system can be further excited with another photon at about 4.8 eV creating a bi-exciton, where the oxygen species becomes effectively neutral. The adiabatic potential energy surface for the second excited state is such that oxygen atom prefers to leave the surface with the maximum kinetic energy of several tenths on an eV. The surface site relaxes with the formation of a neutral F centre at the corner site previously occupied by the desorbed oxygen atom. Our results are in good agreement with the experimental photon energies and kinetic energies of desorbed species.

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# A study of excitonic properties of low dimensional systems with TDDFT

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We investigate the optical, electron energy-loss spectra and static polarizability, of polyacetylene, a conjugated polymer, via Time Dependent Density Functional Theory (TDDFT). The results obtained using our recently developed frequency dependent and non-local exchange-correlation kernel  $f_{xc}(r, r'; \omega)$ , are compared with the state-of-the-art Many Body Perturbation Theory (MBPT) calculations. The TDDFT optical and energy-loss spectra of the isolated infinite chain turns out to be practically indistinguishable from the MBPT results and from the experiment. As the proposed xc-kernel has been tested only on bulk solids, the present results confirm its applicability and stability for the case of quasi one dimensional systems. We present also results for the static polarizability  $\alpha$  of the finite chain as a function of the numbers of the monomers. Compared to the Adiabatic Local Density Approximation (ALDA) that systematically overestimate  $\alpha$  for such systems, the present approximation for  $f_{xc}$  yields very good results when compared with quantum chemical calculations.

## Phase stability in titanium and its dioxides with *ab initio* methods

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We have studied the crystal structures of titanium metal and dioxides by means of *ab initio* total-energy calculations. The phases of interest for titanium metal are the  $\alpha$  phase (hcp), the high-temperature phase  $\beta$  (bcc), and the high-pressure phase  $\omega$  (hex), and for  $TiO_2$  the rutile phase (stable) and the anatase phase (metastable). For rutile the electron energy loss spectra have already been studied in our laboratory [1].

We have used density functional theory (DFT) with a plane-wave basis set and the pseudopotential method [2]. We have calculated the relaxed lattice parameter for each structure and the energy differences between the phases. Different pseudopotentials were used, where 3*sp* semicore states were explicitly treated, or implicitly via a non linear core correction. The relative stability of the different phases is found to change a lot depending on the treatment of the semicore states.

In order to provide a better treatment of the semicore states, we have taken into account an approximate self-interaction correction (SIC) for the semicore states in our pseudopotentials. The results for titanium metal will be presented.

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# Tuning the optical and/or magnetic properties of correlated nanoclusters

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Due to its technological relevance, the microscopic tailoring of nanoclusters electronic properties is currently one of the most active areas of condensed matter research.

We report here of recent and in progress activity in the characterization of the optical and magnetic response of nanoclusters. The theoretical approach is based on exact diagonalization (ED), supplemented by many-body perturbation theory, depending on the systems and phenomena considered.

In one part of the presentation we will show results for magnetic clusters\* with dense Kondo-type impurities. For such systems, controlling  $T_K$  upon varying the energy spacing is acquiring increasing importance since it may allow to tune the cluster magnetic behavior and to encode quantum information. Our calculations reveal that tunes the interplay between the local Kondo and non-local RKKY interactions, giving rise to a Doniach phase diagram for a nanocluster. We will also show that for specific couplings and parameters, electron-phonon coupling may enhance the local moment and affect the RKKY vs. Kondo interplay, thus changing the phase boundaries domains of the Doniach phase diagram.

In the other part of the presentation, we will illustrate our progress about a characterization of the optical and Auger response of supported semiconductor quantum dots. We are addressing single-dot and clustered dots geometry, without specific assumptions about dot shapes, in the effective mass-approximation. This is conveniently done using a Gaussian basis approach and with the inclusion of e-e, h-h, e-h correlation (Coulomb) effects. We will characterize the methodology with some numerical examples and overview the experimental phenomena and subsequent technical developments we plan to address.

\* Work done by CV with Y.Luo and N.Kioussis

## Ab initio Calculations of amorphous phase change materials

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Chalcogenide alloys, which show a significant change of optical reflectivity and electric conductivity under phase transformation from the amorphous to the crystalline structure are widely used for optical data storage today (e.g. DVD-RW). As they can also be used as non volatile memories (Phase-Change-RAM), they are furthermore promising candidates for future electronic data storage techniques. In this work ground state and excited state calculations are presented for GeTe, the basic phase-change-material. It is reported to crystallize in a cubic rocksalt phase and in a trigonal phase, which can be described as a distorted cubic structure. From literature relatively little is known about the amorphous structure, but the available data hints towards a tetragonal, diamond-like local coordination. The focus of the project is on the

relation between optical properties and geometrical structure in the amorphous phase compared to the crystalline phases. The origin for the difference of the optical and electronic properties in the crystalline and the amorphous state -which is crucial for the application- is examined. The problem of obtaining a realistic amorphous structure is approached in two different ways: on one side we employ ab initio molecular dynamics within a 64-atom supercell and on the other side we use a simple model structure which reproduces the local configuration reported in earlier experimental work. The electronic structure is presented in the GW-correction and the theoretical spectra are calculated within TDDFT and GW-RPA. They are compared with experimental data of thin film GeTe-samples. Differences between theory and experiment are discussed as well as the changes in the optical and electronic properties upon phase transition from the crystalline to the amorphous state.

## **Excitons in BN-nanotubes: dimensionality effects**

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Optical absorption spectroscopy is an important tool for the characterization of nanotubes. The first order explanation in terms of single-particle excitations from occupied to unoccupied states is straight-forward. For quantitative predictions, however, a simple calculation based on the assumption of non-interacting particles and on the electronic band-structure on the DFT level is not accurate enough. In particular, electron-hole interaction has a large impact on the absorption spectra of BN structures and leads to excitonic peaks with a binding energy of up to 2 eV. We have calculated these excitonic effects through the solution of the Bethe-Salpeter equation. We discuss the resulting spectra of bound excitonic peaks in the quasi-one dimensional tubes and compare with the spectra of the quasi-two dimensional single sheet of hexagonal BN and of bulk hexagonal BN. The sheet and tube exhibit strong excitonic effects that overcome the quasiparticle correction to the DFT-bandstructure. This give rises to bound states in the quasiparticle gap that are not present in the case of the layered structure.

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