

356th Wilhelm and Else Heraeus Seminar
**“40 Years of the GW Approximation for the Electronic Self-Energy:
Achievements and Challenges”**

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Abstracts of Lectures

Lars Hedin and the GW approximation—the first 20 years

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The early sixties was a very exciting period in the development of many-body theory as applied to solids. In this talk I will concentrate on the development in the group of Stig Lundqvist, Lars Hedin and Bengt Lundqvist, and the importance of their work for future applications. In particular, the development of the GW theory will be discussed.

Twenty years of GW in Rome

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The microscopic study of complex systems has nowadays reached a high level of accuracy that allows for a deep understanding of the electronic excitations. Ab initio descriptions of experiments such as direct or inverse photoemission, optical absorption, electron energy loss, have become possible thanks to the huge progress in theory and increased computational power. Charged excitations, as well as neutral excitations, can now be studied within the many-body perturbation theory based on the Green’s function formalism. Optical spectra can be calculated with inclusion of the electron-hole interaction by solving the Bethe-Salpeter equation (BSE) within the framework of Green’s function theory. This has been made possible by the seminal work of Lars Hedin in 1965, who derived a set of equations (Hedin’s equations) to describe excited states. Moreover, optical spectra can also nowadays be well described within the time-dependent density-functional theory (TDDFT).

In this seminar I will review some of the work carried out on these topics in Rome since 1985, when a collaboration with Friedhelm Bechstedt started with the purpose of finding a recipe for a fast, simplified, yet accurate, GW method. I will also describe the most recent results, i.e., for the electronic structure and optical properties of diamond and silicon surfaces within the DFT, GW and BSE approaches. A test of the TDDFT approach to the optical properties will be shown for the case of Si(111)-(2×1).

Theoretical spectroscopy: Some developments and applications based on GW

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In this talk, I will give a very brief overview of some work done in our group in Palaiseau, often in collaboration, during the last 10 years. I will focus on subjects for which we were essentially using Lars Hedin's *GW* approximation or starting from it for further developments. The topics in this list range from clusters to bulk materials, from approximate *GW* calculations and technical developments to vertex corrections beyond the random-phase approximation and beyond *GW*.

Excited states in semiconductors and insulators: Ab initio quasiparticle band structures of II-VI compounds, group-III nitrides and high-*k* dielectrics

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Photo-electron spectroscopy has developed into an invaluable experimental tool for the study of electron excitations in bulk solids and surfaces. The success of photoemission spectroscopy (PES) and its inverse counterpart (IPES) owes much to the interpretation of the photo-electron spectra in terms of single-particle excitations or quasiparticles in the language of many-body quantum mechanics. For solids Hedin's *GW* approximation, where *G* refers to the Green's function and *W* to the dynamically screened Coulomb interaction, has become the method of choice for an ab initio calculation of the quasiparticle energy spectrum. The *GW* method is applied to different crystalline phases of HfO₂, which has received considerable interest as an alternative gate material (high-*k*) in complementary metal-oxide semiconductor (CMOS) transistors, to shed light on the structural dependence of the excitation spectrum. For describing systems with semicore electrons like II-VI compounds and group-III nitrides, which are important for the optical industry, a new, alternative approach based on combining *GW* with density-functional theory (DFT) in the exact-exchange formalism (OEPx) will be presented [1].

[1] P. Rinke et al., *New J. Phys.* **7**, 126 (2005).

Quasiparticle excitations of native defects in III-V semiconductors: *GW* approximation

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The III-V systems have received much attention due to their technological applications. Especially, the group-III nitrides form an important class in the major semiconductors that are currently under development for devices requiring wide band gaps. As in all semiconductors, understanding the effects of native defects is required to implementation of devices made from these materials. In this work, we study the structural and electronic properties of various point defects (vacancies and antisites) in III-V semiconductors by ab initio calculations using the pseudopotential plane-wave approach. To model an isolated native defect, a supercell technique was used. Using the spin-polarized *GW* approximation, we examined the electronic structure of defects to provide accurate estimates of defect-induced

levels. The calculated equilibrium atomic configurations of vacancies and antisites obtained within density-functional theory (DFT) show Jahn-Teller-like distortions. Calculated energetic locations of defect levels can be compared with available measurements and explain the nature and the origin of the experimental data.

***GW* calculations for compounds with *d* and *f* electrons**

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Strong correlations are in most cases due to the presence of *d* or *f* electrons. Traditionally, however, the *GW* approach has been applied with the biggest success to *sp* systems. In my talk I will present results of *GW* calculations for systems with *d* and *f* electrons. These test cases are: (i) II-VI compounds, where the shallow but fully occupied *d*-electron shell places this class of materials at the border between weakly and strongly correlated systems, (ii) the *3d* compound MnTe and (iii) the *4f* compound PrO₂.

***GW* calculations on Na and Pt clusters**

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Quantum-chemical ab initio methods such as configuration interaction (CI) and coupled-cluster (CC) approaches accurately predict ground- and excited-state properties of systems without translational invariance and target optical absorption experiments. Green-function methods, on the other hand, yield the state-specific lifetimes of quasiparticles and collective excitations, properties that are very hard to obtain by any correlated quantum-chemical method. Thus, a Green-function approach is a theoretical counterpart of the rapidly developing time-resolved electron spectroscopies, such as 2-photon photoemission (TR-2PPE).

We present an implementation of the *GW* approximation for the calculation of electronic properties of clusters or molecules such as Na_{*n*}⁺ (*n* < 25) and Pt₃ without periodic boundary conditions. We expand all quantities in Gaussian-type basis functions, an approach widely used in quantum chemistry, and compute the Green function, screened interaction and self-energy on the real axis of the frequency domain. The dielectric function $\epsilon(\omega)$ is treated without previously employed simplifications, such as the plasmon-pole approximation. Convolutions are performed using fast Fourier transforms to the real time and back. As a test example we use in particular the widely studied Na₉⁺ cluster where our self-consistent *GW* calculations indicate convergence of relevant quantities (band gap, screened interaction, self-energy and Green function) already after four cycles. Self-consistency reduces the band gap from values of 4.5 eV (Hartree-Fock) and 3.7 eV (non-self-consistent *GW*) to 3.38 eV. Besides, the plasmon peak narrows due to renormalisation of the broadening of the quasiparticle states. Its half-maximum width corresponds to a plasmon lifetime of approximately 4.1 fs in agreement with experiments on similar systems. In order to study substrate effects on lifetimes we also employ quantum chemistry for the system Na₉⁺/Cu(100), where the surface is modelled by an

arrangement of 54 Cu atoms. We find a shift and broadening of the collective excitation as the cluster-surface separation shrinks. This ab initio result is analysed further by a combination of image-charge and Mie theory.

Emission properties of small hydrogenated and oxidised silicon nanoclusters

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Silicon nanocrystals (Si-Nc) are promising as silicon-based light-emitting materials. Recent experimental data have demonstrated that surface chemistry produces substantial impact on the optoelectronic properties of Si-Nc. We have investigated the optical response of Si-Nc with different surface termination using ab initio techniques within the DFT. The absorption and emission energies have been calculated within the Δ SCF approach taking into account the structural rearrangement of the atoms within the cluster geometry both in the ground and excited state. This explains the difference between absorption and emission values, i.e., the Stokes shift. For the calculation of the optical spectra we have used different levels of approximation: RPA with and without the inclusion of the local field, quasiparticle corrections within the *GW* approximation, electron-hole interaction within the BSE and TDDFT approach. These calculations have been performed for both the structural geometry of ground and excited state. In particular we have focused our attention on the *Si*₁₀-Nc considering the fully hydrogen-terminated cluster (Si₁₀H₁₆) and the cluster with oxygen (Si₁₀H₁₄O) with two different types of oxygen bonds at the surface: Si=O double bond and Si-O-Si bridge bond. For all these systems the *GW* shift is quite big and there is a substantial cancellation between self-energy and electron-hole interaction effects. In each structure the optical spectra show at the energy onset a smooth increase of their behaviour, with a single important exception in the emission spectra of the oxidised cluster with O in the bridge. Here a very intense excitonic peak is present. The Stokes shift calculated within the Δ SCF, BSE and TDDFT are quite similar, again the only difference is for the system with the oxygen atom in the bridge configuration.

Quasiparticle energies and optical properties of small fullerenes

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We present theoretical results on the electronic excitations and optical properties of small fullerenes, namely C₂₄, C₂₈, C₃₂ and C₃₆. Quasiparticle-corrected HOMO-LUMO gaps have been computed through the Δ SCF scheme. Photoabsorption spectra have been obtained in the framework of time-dependent density-functional theory. Calibration calculations per-

formed for C_{20} and C_{60} result in good agreement with the available experimental and theoretical data.

Quasiparticle energies for large molecules: A tight-binding GW approach

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We present a tight-binding-based GW approach for the calculation of quasiparticle energy levels in confined systems such as molecules. Key quantities in the GW formalism like the microscopic dielectric function or the screened Coulomb interaction are expressed in a minimal basis of spherically averaged atomic orbitals. All necessary integrals are either precalculated or approximated without resorting to empirical data. The method is validated against first-principles results for benzene and anthracene, where good agreement is found for levels close to the frontier orbitals. Further, the size dependence of the quasiparticle gap is studied for conformers of the polyacenes ($C_{4n+2}H_{2n+4}$) up to $n = 30$.

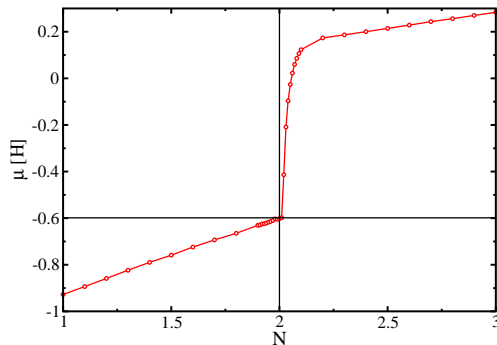
The fundamental gap in reduced-density-matrix-functional theory

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We propose a novel method for calculating the fundamental gap, Δ . This quantity is defined as the difference between the ionisation potential and the electron affinity. Given a system with integer particle number N_0 , the fundamental gap can be expressed rigorously as the discontinuity which the chemical potential $\mu(N)$ exhibits at the integer N_0 , i.e., $\Delta = \mu(N_0 + \eta) - (N_0 - \eta)$, with a positive infinitesimal η . In the context of density-functional theory this formula leads to the famous representation of the gap as $\Delta = \delta\epsilon + \Delta_{xc}$, where $\delta\epsilon$ is the energy difference between the lowest unoccupied and the highest occupied Kohn-Sham orbital, and Δ_{xc} amounts to the discontinuity of the exchange-correlation potential upon adding and subtracting a fractional charge with respect to the N_0 -electron system. Here we investigate the discontinuity of the chemical potential in the context of reduced-density-matrix-functional theory (RDMFT). Employing well-known reduced-density-matrix functionals [1] for the exchange-correlation energy we minimise the total energy with the appropriate constraints ensuring N -representability of the density matrix and conservation of the total particle number. We demonstrate [2] that the resulting discontinuity of the chemical potential represents an excellent measure of the gap, far superior to LDA or GGA calculations. The figure below shows the calculated chemical potential $\mu(N)$ for the H_2 molecule.



Furthermore, we generalise RDMFT to treat open-shell systems by introducing spin-dependent occupation numbers for spin-independent natural orbitals [3]. We demonstrate that the additional constraint of total-spin conservation is indispensable for the proper treatment of open-shell systems: It reduces the difference between calculated and experimental total energies by a factor of 2.

- [1] A. M. K. Müller, Phys. Lett. A **105**, 446 (1984).
- [2] N. Helbig, N. N. Lathiotakis, M. Albrecht and E. K. U. Gross, cond-mat/0504436.
- [3] N. N. Lathiotakis, N. Helbig and E. K. U. Gross, cond-mat/0504435.

A Hilbert-transform-based scheme for efficient computation of response functions and its application to study the optical properties of the oxidised Si(100)-(2×2) surface

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We have formulated an efficient scheme to evaluate the independent-particle dynamic polarisation $\chi^0(\omega)$, used as a starting point in TDDFT to calculate the optical response of a system. The new method has been implemented in the DP ab initio code, improving its time scaling. We demonstrate that this new method is convenient to evaluate the dielectric function of large systems (hundreds of atoms in the unit cell). We applied this method to study the dielectric function of the oxidised Si(100)-(2×2) surface including for the first time the local-field effect in calculating the polarisability and the reflection anisotropy spectra (RAS and SDR).

Electronic and optical properties of Si and Ge nanocrystallites: Influence of oxidation, capping and doping

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Si nanocrystallites (NCs) are interesting structures from the technological point of view, since one can exploit their quantum-confinement properties in electronic devices. For instance, the confinement of carriers in the same region of space can enhance radiative recombination and

make nanostructures of indirect-gap materials like Si emit light. Although in recent years, progress has been achieved to understand the luminescence from Si nanostructures, their application in devices, such as lasers, is not yet a reality. In an attempt to obtain optical gain in Si NCs, many factors that influence the light emission have been identified. Besides the size of the NCs, which determines mainly the quantum-confinement effects, oxidation and the presence of defects are some of the factors that can affect the efficiency of optical transitions in Si NCs. Si nanocrystalline samples usually correspond to an ensemble of Si NCs that makes difficult the interpretation of the physical phenomena involved in light emission. In this sense, theoretical models accounting for isolated NCs are useful to individualise the properties of those particles. By applying an *ab initio* pseudopotential method, we present an investigation of free-standing Si and Ge NCs, concerning their size, passivation, Si oxidation, capping and doping [1]. The main chemical trends for the electronic and optical properties of NCs can be obtained by means of the ground-state treatment provided by density-functional theory, the local-density and generalised gradient approximations. However, to account partially for excitations we also employ the Δ self-consistent-field method, *GW* method, and we solve the Bethe-Salpeter equation to calculate electronic structure and optical absorption spectra. Using those methods, certain aspects of passivation, oxidation, capping, single terminations and substitutional impurities in Si and Ge NCs can be understood [1].

[1] L. E. Ramos, F. Furthmüller and F. Bechstedt, *Phys. Rev. B* **70**, 033311 (2004); **71**, 035328 (2005); **72** (in press).

Quasiparticle effects in inelastic X-ray scattering

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We will present computational results for nonresonant inelastic X-ray scattering (NRIXS) from core electrons in solids. The behavior of the core excited states is dominated by the localisation of the core hole. In practice this means that the problem can be written as an effective single-particle problem for the final-state electron. The effect of the core hole–electron interaction, the final-state electron quasiparticle shifts and the final-state electron lifetime are clearly visible in the spectra.

We apply a band-structure-based approach [1] to the analysis of NRIXS from core-excited states. The role of the electron-hole interaction will be reviewed. We use a simple G_0W_0 approach [2,3] to approximate the quasiparticle effects. Comparison of the calculated spectra with experimental ones clearly shows that accurate quasiparticle corrections are needed for quantitative analysis. The results highlight the capabilities and some limitations of the current *GW*-based scheme. Analysis of the final-state local density of states with respect to the momentum-transfer dependence of NRIXS cross sections will also be discussed.

[1] J. A. Soininen and E. L. Shirley, *Phys. Rev. B* **64**, 165112 (2001).

[2] J. A. Soininen, E. L. Shirley and J. J. Rehr, *J. Phys.: Condens. Matter* **15**, 2573 (2003).

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Ab initio study of the photo-excited state: Nanotubes to self-trapped excitons

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We discuss some recent progress on first-principles study of excited-state properties, in particular the optical response of condensed-matter systems. As examples, we present results on the optical properties of nanotubes and on the phenomenon of self-trapped excitons in SiO₂. The approach involves solving for the quasiparticle and electron-hole excitations of the interacting electron system within the *GW* approximation. In the study of self-trapped excitons, calculation of forces on the atoms in the excited state is further required. Owing to their reduced dimensionality, many-electron effects qualitatively alter the optical spectra of the nanotubes. It is discovered that exciton states in the semiconducting carbon nanotubes have binding energies that are orders of magnitude larger than bulk semiconductors and hence they dominate the optical spectrum at all temperature, and that bound excitons can exist even in metallic carbon nanotubes. Similar studies show that excitonic effects are even stronger in the BN nanotubes. In SiO₂, the excited electron and hole spontaneously distort the crystal, and the exciton self-traps locally to the distortion (to a lower-energy configuration in the excited state) leading to a huge Stokes shift of over 6 eV in the photoluminescence frequency. The calculations provide a microscopic picture of the trapping mechanism and geometry of the self-trapped exciton. The physics behind these phenomena is discussed.

Excitons in germanium nanowires: Quantum confinement, orientation and anisotropy effects

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Within a first-principles DFT framework we show how many-body effects crucially modify the electronic and optical properties of free-standing germanium nanowires. A clear dependence of the excitonic binding energy and localisation length, not only from the wire size, but also from the wire orientation has been found. Moreover, in some of the analysed quantum wires we observe an almost complete compensation of the self-energy and excitonic effects, explaining it in terms of their geometrical atomic structure.

Time dynamics of electron-hole excitations

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We address the time dynamics of excited electronic states, in particular of correlated electron-hole excitations, within ab initio many-body perturbation theory. The excited states are described within the *GW* approach (for electrons and holes) and within the Bethe-Salpeter equation (BSE) for coupled electron-hole pair excitations. In this talk we focus on the resulting time dynamics of the electronic and geometric degrees of freedom. As an example for electronic femtosecond dynamics of excited states we discuss resonant charge-transfer

processes from electronically excited adsorbates to a substrate surface, in particular in the system CO:MgO(001)-(1×1). Picosecond dynamics of the atomic structure, as resulting from electronic excitation, can lead to structural relaxation or to dissociation of a system. As examples, we investigate excited-state relaxation of PPP, as well as atom expulsion from alkali halide surfaces.

Work done in collaboration with N.-P. Wang, P. Krüger, J. Pollmann, E. Artacho, M. Côté, P. D. Haynes, R. J. Needs and C. Molteni.

GW approximation for electronic excitations beyond standard treatment

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We demonstrate the power of many-body perturbation theory in the *GW* approximation to describe single-particle and pair excitations in complex systems. The method is based on solutions of the Dyson and Bethe-Salpeter equations and the dynamically screened Coulomb interaction. Together with the supercell approach it can be applied to complex systems, e.g. molecules on surfaces, which involve both extended and localised states. On the single-particle level we discuss effects beyond G_0W_0 , pure electronic screening and first-order perturbation theory. A possible approach is presented to treat systems with a wrong energetical ordering of the Kohn-Sham states. It is shown that an initial-state formulation of the time-dependent optical polarizability allows computations of optical spectra for systems with many atoms in the unit cell. The effect of dynamical screening and $\delta W/\delta G$ contributions to the interaction kernel is studied on the two-particle level. Applications of the *GW* approximation to single-particle and pair excitations are presented for three classes of materials: molecules (silan, water), surfaces (hydrogenated Si surfaces) and polar crystals (InN, ice, NaCl).

Converged all-electron GW approximation in the augmented-plane-wave basis-set limit

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The *GW* approximation for the electronic self-energy is known to yield quasiparticle band structures in much better agreement with experimental measurements than the local-density approximation (LDA) for a large class of materials. However, almost all actual implementations so far are based on the plane-wave pseudopotential approach, which effectively restricts applications to simple metals and *sp*-bonded semiconductors. In order to overcome this limitation, we have developed an alternative implementation within the all-electron full-potential linearised augmented plane-wave (FLAPW) method, which is also applicable to systems with localised electrons like transition metals or rare-earth elements. Additional simplifications, such as plasmon-pole models, are avoided. While the FLAPW method treats the core electrons explicitly and does not suffer from the uncontrolled pseudisation of the wave functions, another source of errors resulting from the linearisation is frequently overlooked. This arises because the radial wave functions in the muffin-tin spheres are expanded around fixed reference energies. Irrelevant for the valence bands in density-functional theory, it cannot be

ignored in the GW approximation, where unoccupied states more than 100 eV above the Fermi level must typically be included in the self-energy to guarantee converged results. To eliminate this error, we have improved the FLAPW basis set by including second and higher energy derivatives of solutions to the radial scalar-relativistic Dirac equation in the form of local orbitals. With this modification, we show that the eigenstates converge systematically towards the exact APW spectrum, which contains no linearisation errors. This careful approach finally allows us to comment on the controversial apparent discrepancy between pseudopotential and all-electron GW results addressed in several recent studies [1,2]. For the example of silicon, we demonstrate that the inclusion of a much larger number of unoccupied states and the elimination of linearisation errors both contribute to an increase of the band gap. While a certain deviation from pseudopotential calculations remains, it is smaller than previously claimed, and both results lie in comparable proximity to the experimental value.

We benefitted from intensive discussions with T. Kotani and G. Bihlmayer on this subject. This work was funded by the Deutsche Forschungsgemeinschaft (SPP 1145) under the Priority Programme 1145.

[1] W. Ku and A. G. Eguiluz, Phys. Rev. Lett. **89**, 126401 (2002).

[2] M. L. Tiago, S. Ismail-Beigi and S. G. Louie, Phys. Rev. B **69**, 125212 (2004).

Local atomic order and optical properties in amorphous and laser-crystallised GeTe with ab initio methods

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In this work we present optical spectra calculations for crystalline and amorphous GeTe, a prototype phase-change material. Recent experimental data reveals that GeTe exhibits a profound change in local atomic order upon the phase transition from the crystalline to the amorphous state. Based on these findings a simple structural model of amorphous GeTe was constructed to perform ab initio ground-state and excited-state calculations to reveal the change in optical properties. The optical spectra are calculated in the random-phase approximation. The eigenvalues are corrected with the GW approximation and two-particle excitations are taken into account within the framework of the Bethe-Salpeter equation. The results are in good qualitative agreement with experimental data and furthermore explain the profound change in absorption upon amorphisation. It is found that the change in optical absorption is correlated to a change in the local atomic order.

Silicate chain formation in the nanostructure of cement-based materials

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The present works reports our findings arising from ab initio calculations on the stability of silicate chains which aim to shed light on the silicate chain formation in the nanostructure of cement-based materials. Our ab initio study focuses on the growth and merging of silicate chains, which could improve our understanding of the cement-hydration process. It also addresses the pivotal role of certain ionic species on the chain-forming mechanisms. In particular, our results predict the empirically observed rule of number of silicon atoms in the silicate chains ($m = 3n - 1$, m being the number of silicon atoms with $n = 1, 2, \dots$) and confirm the experimental evidence that dimers arise from a growth mechanism and pentamers from a merging process. Besides, we demonstrate that charged chains are predominant over neutral species at equilibrium. These results will lead to a better understanding of the cementitious matrix nanostructure formation and are a strong basis to improve the mechanical and durability properties of cement-based materials. Furthermore, the implications and the scope of our findings can be easily transferred to other similar systems and materials, such as clays, porous silicate materials, sol-gel materials and more generally any silicate-based materials.

A TDDFT-based formalism for the response of solids, nanostructures and biomolecules

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We will review the recent implementations of TDDFT to study the optical absorption of biological chromophores, one-dimensional polymers and layered materials. In particular we will show the effect of electron-hole attraction in those systems. We will follow two routes: one based on solving the Bethe-Salpeter equation and the other on an orbital-dependent OEP method on top of the GW approximation for the self-energy. Virtues and deficiencies of both methods will be illustrated. In particular we will illustrate a new implementation of the adiabatic-connection fluctuation-dissipation theorem (ACFDT) to treat correlation effects within a (time-dependent) density-functional-based approach (TDDFT). In this approach, the correlation energy is calculated from the knowledge of the interacting density response. We will make links to the linearised Sham-Schlüter equation that determines the exchange-correlation potential with the electron self-energy of many-body perturbation theory. Both approaches are equivalent, however the numerical implementation is different. We will show some results for the structural properties of simple solids (Si, NaCl) and layered systems. For the latter there are evident discrepancies between the KS and the TDDFT binding energies. This is due to the presence of long-ranged correlations that cannot be described at all by mean-field approximations. All these effects are illustrated taking as example hexagonal boron nitride, where all the structural properties including phonon frequencies are very well described by this approach. We will also show how exchange-correlation kernels with the proper q -dependence can be obtained from this approach and how they can be used to unify many-body and TDDFT-based schemes. Applications to Si and LiF would be used as examples of the theory.

Work done in collaboration with A. Castro, M. Marques, L. Wirtz, A. Marini, M. Grüning, L. Wirtz and D. Varsano and supported by the NANOQUANTA Network of Excellence.

A TDDFT study of excited states of DNA bases and base assemblies

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We present the results of an investigation of optical absorption spectra of DNA bases and base pairs, carried out by means of time-dependent density-functional theory calculations. The spectra for the isolated bases are compared to available theoretical and experimental data and used for assessment of the method. A particular attention is placed to the relative role of hydrogen-bonding and π -stacking in the modification of optical fingerprints.

An ab initio theory of transport using TDDFT and nonequilibrium Green functions

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We present an ab initio theory for describing the motion of interacting electrons through nanoscopic constrictions. Our theory is based on time-dependent density-functional theory (TDDFT) and nonequilibrium Green functions. We consider the electrode-device-electrode system initially contacted and in equilibrium, therefore the scheme is thermodynamically consistent. Besides the steady-state responses one can also calculate physical dynamical responses. We show that the steady-state current results from a dephasing mechanism provided the electrodes are macroscopic and the device is finite. In the dc case, we obtain a Landauer-like formula when the effective potential of TDDFT is uniform deep inside the electrodes. A computationally tractable scheme is also presented. We first extract the set of initial states by diagonalising the spectral function in the device region. These states will then be propagated in time with proper transparent boundary-condition at the device/electrode interface. This is possible due to a new modified Crank-Nicholson algorithm that allows an efficient time-propagation of open quantum systems. We illustrate the method in one-dimensional model systems as a first step towards a full first-principles implementation.

Ab initio study of the excited-state properties of liquid water

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In the last decades, we have witnessed an increasing interest on water and many studies on the geometry and ground-state properties have appeared in the literature. Nevertheless, its excited-state properties have not been investigated yet. We present here ab initio calculations, in the framework of many-body Green's function formalism, of liquid water. We use snapshots taken from classical molecular dynamics as input geometries for the study of the electronic and optical spectra. The excitation spectra are first obtained within the density-functional theory (DFT) and then corrected within the GW approximation. We obtain an average HOMO-LUMO gap of 4.85 eV at the DFT-LDA level, in good agreement with previous calculations. The electronic gap is then modified by the GW corrections up to 9.0 eV. The optical absorption spectra are calculated by solving the Bethe-Salpeter equation; they result modified, with respect to the DFT spectra, suggesting the presence of important excitonic effects at low energies.

GW and beyond

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The GW approximation is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W . It may be thought of as exact exchange (Hartree-Fock), together with a partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ , the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as GW . In applying GW to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises from Σ is particularly important: G_0W_0 , GW_0 and fully self-consistent GW , where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. Our recent formulation [1] of the conductance of a nanosystem which permits the inclusion of electronic correlation effects in time-dependent DFT and GW -like frameworks. I shall also present early results [2] from an approach to vertex corrections in order to include correlation beyond the GW level.

[1] P. Bokes and R. W. Godby, Phys. Rev. B **69**, 245420 (2004); P. Bokes, H. Mera and R. W. Godby (to be published).

[2] M. Stankovski and R. W. Godby (to be published).

Fully self-consistent GW calculations for atoms and molecules

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We want to emphasise the importance of electron correlation in single-molecule charge and energy transport. To satisfy the conservation laws, we have to use a Φ -derivable scheme. For this, we use a self-consistent Green's function, obtained from the Dyson equation, to calculate the self-energy and to construct the screened interaction W , within the Φ -derivable GW approximation. The self-consistent equations were solved in time-space, in a basis of Slater functions, using finite temperature formalism. We have applied this scheme to calculate total energies of atoms and diatomic molecules. These are, to the best of our knowledge, the first self-consistent GW calculations for total energies of atoms and molecules. We also show that these total energies are very close to the energies obtained from Luttinger-Ward functional, with simple input Green's functions.

Beyond the GW approximation

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Band structures are routinely calculated from static density-functional theory, but there is no theoretical foundation for interpreting the calculated one-electron energies as real excitation energies—and the agreement is often quite poor. Not even within time-dependent density-functional theory does one yet have a direct way of obtaining one-electron excitation energies. Instead, such energies are traditionally calculated from many-body perturbation theory (MBPT). Within MBPT, the so-called GW approximation (GWA) proposed by Hedin and others in the mid sixties has been remarkably successful for obtaining band structures and band gaps in a variety of different systems. The GWA is a simple extension of the Hartree-Fock method in which the bare Coulomb interaction is screened by the dielectric function of the system and where the latter is usually calculated at the level of the RPA. Despite its well known advantages, the GWA has a number of deficiencies. Most notable is perhaps its inaccurate description of satellite structure. Less well known is the fact that band widths obtained from the GWA are consistently too large compared to experiment in most materials. And there are reasons to believe the GWA to be totally inadequate in cases where the electrons are strongly correlated. What is left out of the GWA is, per definition, referred to as vertex corrections and correspond physically to, e.g., the attraction of the outgoing electron by the hole left behind in a photoemission process. There is thus a strong need to go beyond the GWA and include such effects.

We have previously shown how to construct conserving approximations to response functions within TDDFT. Such approximations necessarily include vertex effects. As it turns out, such conserving response functions allow for the extraction of approximate vertex functions which are local in space and time and which can be used to construct improved electronic self-energies beyond the GWA. We here test some self-energies obtained along these lines and we conclude that this is not an adequate procedure due to the very nonlocal character of a true vertex. We here suggest a cure for this problem based on the observation that, in localised systems, an expansion order by order in the Coulomb interaction seems preferable to infinite summations of particular sets of Feynman graphs. Combining this with the necessity to screen the long-range part of the Coulomb interaction in extended systems leads to the proposal to

split the Coulomb interaction in two parts, one weak long-ranged part and a second, strong and short-ranged part. We then screen the long-ranged part as within the GWA and go to second order in the short-ranged part. We hope to be able to present some preliminary results of this new method at the meeting.

Quasiparticle self-consistent *GW* method

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We present some progress in our “quasiparticle self-consistent *GW* (QPsc*GW*) method” based on the all-electron, full-potential LMTO method [1]. The object of the QPsc*GW* method is to obtain the (nonlocal but static) one-body Hamiltonian H_0 (or G_0) which best describes the quasiparticles (QP). The *GW* approximation generates the Green function G as a functional of any given H_0 . In QPsc*GW*, this H_0 is chosen self-consistently so that the QP part in G is well reproduced by H_0 . The QP from H_0 can be used directly within the one-particle picture to evaluate quantities, e.g., in the construction of the Boltzmann equation.

We applied our QPsc*GW* to a wide range of materials. Our results show systematic improvement over LDA and one-shot *GW* from LDA. As recent results, we will mainly show these points.

1. Theoretical justification:

The self-consistency of QPsc*GW* does not require a total-energy minimization but the stability of the ground state by H_0 as for the QP excitations. We define a kind of norm $\|G^{-1} - G_0^{-1}\|$ and discuss that its minimization can approximately give the fundamental equation of the QPsc*GW*.

2. ϵ_∞ vs. band gap:

QPsc*GW* tends to give somewhat larger band gaps than experiments. The tendency is systematic, and the difference may be because we do not include electron-hole correlation in the dielectric function.

3. *f*-systems:

We applied QPsc*GW* to *f*-systems like Gd, GdN, ErAs and CeO₂. We will discuss trends of these result.

4. Spin susceptibility (in progress):

We will show results of the spin susceptibility of Ni and Fe based on QPsc*GW*.

[1] S. V. Faleev, M. van Schilfgaarde and T. Kotani, Phys. Rev. Lett. **93**, 126406 (2004).

Electronic structure of Cu₂O within self-consistent *GW*

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It is known that Kohn-Sham density-functional theory (DFT) experiences dramatic problems with *d* electrons in solids. In particular, it fails to predict a gap in various insulating oxides like

CuO. Cu₂O seems to be a good starting point to address the fundamental issue of $3d$ electrons in metal oxides. This semiconductor material has indeed a cubic structure, a closed d shell, and is nonmagnetic. We carried out a study of the electronic structure of Cu₂O within DFT, and then within the GW approximation [1], based on pseudopotentials plus plane-waves basis set. We showed that the GW approximation using the standard technical approximations unexpectedly fails concerning the band gap of Cu₂O, even when the semicore states are properly included in the GW calculation [2]. We therefore performed a self-consistent GW calculation on Cu₂O, using the constrained self-consistent scheme of Faleev *et al.* [3]. We show that small changes in the wave functions can produce large changes in the Hartree potential that are mainly compensated by the changes in the exchange operator. The band gap comes out in good agreement with experiment. Furthermore, when the self-consistent GW band structure and screened Coulomb interaction are used in the solution of the Bethe-Salpeter equation, one obtains a very good optical absorption spectrum compared to experiments, although the optical absorption spectrum of Cu₂O is complex, with several exciton series.

[1] L. Hedin, Phys. Rev. **139**, A796 (1965).

[2] A. Marini, G. Onida and R. Del Sole, Phys. Rev. Lett. **88**, 016403 (2002).

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Merging first-principles and model approaches: $GW+DMFT$

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First-principles calculations reveal a lot more details about the system than model calculations can hope to do. On the other hand, model approaches are often theoretically more sophisticated than first-principles approaches. By combining the GW method and dynamical mean-field theory (DMFT), which is traditionally applied to study strongly correlated systems in the model context, we obtain a first-principles scheme that incorporates the strength of DMFT in treating systems with strong onsite correlations. In this scheme, the Hubbard U is calculated self-consistently and the so-called double counting is taken into account properly. The new scheme was tested in ferromagnetic nickel with encouraging results.

Hedin's equations and enumeration of Feynman diagrams

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To evaluate dressed correlators for interacting fermions, one must sum over classes of diagrams of all orders of perturbation theory in v . It might be useful, or at least interesting, to know in advance how many diagrams are required at each order of the approximation, and how many are left out. The counting problem is much simpler and is obtained by translating the recursive equations at hand to zero dimensions. I show how Feynman diagrams can be enumerated for the exact theory and GWA starting from Hedin's equations [L. G. Molinari, Phys. Rev. B **71**, 113102 (2005)]. The vertex equation is first written in terms of the Hartree propagator g , in place of the full one. In $d = 0$ four Hedin's eqs. become algebraic, with variables g and v , and the functional derivative is an ordinary one. After removing i factors

and replacing (-2) with a parameter ℓ that counts the same loops, they are: $G = g + g\Sigma G$, $W = v + v\Pi W$, $\Sigma = GW\Gamma$, $\Pi = \ell G^2\Gamma$ and $\Gamma = 1 + g^2\partial\Sigma/\partial g$. By searching solutions as a series in the variables v and ℓ , one obtains coefficients that count all Feynman graphs, with weight one, that contribute to a perturbative order (the power of v), with a given number of fermionic loops (the power of ℓ). Omission of vertex corrections makes the number of diagrams grow with a power law, instead of factorially. For example, the numbers for the self-energy are ($x = g^2v$):

$$\begin{aligned}\Sigma/vg &= 1 + (2 + \ell)x + (10 + 9\ell + \ell^2)x^2 + (74 + 91\ell + 23\ell^2 + \ell^3)x^3 \\ &\quad + (706 + 1063\ell + 416\ell^2 + 46\ell^3 + \ell^4)x^4 + \dots \\ &= 1 + 3x + 20x^2 + 189x^3 + 2232x^4 + 31130x^5 + \dots\end{aligned}$$

(at order v^3 (x^2 -term) there are 20 diagrams: 10 with no fermion loop, 9 with a single loop and 1 with two loops),

$$\begin{aligned}\Sigma_{GW}/vg &= 1 + (1 + \ell)x + (2 + 4\ell + \ell^2)x^2 + (5 + 15\ell + 9\ell^2 + \ell^3)x^3 \\ &\quad + (14 + 56\ell + 56\ell^2 + 16\ell^3 + \ell^4)x^4 + \dots \\ &= 1 + 2x + 7x^2 + 30x^3 + 143x^4 + 728x^5 + \dots\end{aligned}$$

The high-density electron gas and the peculiarities of its reduced densities, its self-energy and the Hugenholtz–van Hove identity

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The long-range Coulomb repulsion makes the correlation energy e_c and its kinetic and potential components, t_c and v_c , as well as μ_c , the correlation contribution to the chemical potential, logarithmically divergent for $r_s \rightarrow 0$, namely $e_c \rightarrow a \ln r_s$, $t_c \rightarrow -a \ln r_s$, $v_c \rightarrow 2a \ln r_s$, $\mu_c \rightarrow a \ln r_s$ with $a = (1 - \ln 2)/\pi^2$ [energies in a.u.]. This is known from the seminal work of W. Macke [1], from the virial theorem and from the definition of μ . It is shown which peculiarities of the momentum distribution $n(k)$ and of the static structure factor $S(q)$ cause the divergent behavior of t_c and v_c , respectively [2]. μ_c is related to the correlation part of the self-energy $\Sigma_c(k, \omega)$ through the identity $\mu_c = \Sigma_c(k_F, \mu)$. Therefore the small- r_s behavior of $\Sigma_c(k_F, \mu)$ is studied with the help of the Gell-Mann/Brueckner trick [3]. It is shown that the GW approximation yields the correct result $a \ln r_s$ for $G \rightarrow G_0$ and W within RPA screened Coulomb repulsion. Contrary to this, using $G =$ Green's function of the interacting system and $W \rightarrow$ bare Coulomb repulsion gives higher-order terms $\propto r_s(\ln r_s)^2$ and $\propto r_s \ln r_s$ [4] beyond the correct asymptotics $a \ln r_s$.

[1] W. Macke, Z. Naturf. **5a**, 192 (1950).

[2] P. Ziesche and J. Cioslowski, Physica A (in press).

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[4] J. Cioslowski and P. Ziesche (submitted).

Many-body properties of a jellium slab

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The study of many-body properties of jellium in geometries different from the bulk one is a fruitful current subject of research: for example, surface image states and resonances have recently been investigated for a small jellium cluster and for a semi-infinite one, respectively. In this work we study metallic jellium slabs of different thickness. As a starting method we use DFT in the LDA. In this framework we compute the bulk and surface contributions to the total energy, which display a good accord with earlier estimates. Individual kinetic, Coulombic and exchange-correlation contributions to the total surface energy (surface tension) oscillate as a function of the slab thickness, with nontrivial phase relations. A detailed analysis reveals the origin of these oscillations and their link with the surface dipole layer originated by the charge spill-out. Next we treat the eigenvalues of the system, resolved in the wave vector (\vec{k}_{\parallel}) parallel to the surface. The many-body solution, worked out in the GW approach and in the plasmon-pole approximation for the dielectric function, modifies the behaviour obtained in the LDA. As also found for bulk jellium, the dispersion is nonparabolic. At variance with the bulk case, we observe small gaps (~ 0.3 eV) opening at the Fermi energy in the \vec{k}_{\parallel} dispersion. The origin of these gaps is presently unknown but may be due to an imperfect cancellation of corrections in the numerical GW implementation.

Lifetimes of Shockley electrons and holes at the Cu(111) surface

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A theoretical many-body analysis is presented of the electron-electron inelastic lifetimes of Shockley electrons and holes at the (111) surface of Cu. For a description of the decay of Shockley states both below and above the Fermi level, single-particle wave functions have been obtained by solving the Schrödinger equation with the use of an approximate one-dimensional pseudopotential fitted to calculations and experiment indicates that inelastic lifetimes are very sensitive to the actual shape of the surface-state single-particle orbitals beyond the $\bar{\Gamma}$ ($\mathbf{k}_{\parallel} = 0$) point.

First-principles description of transport including electron correlation

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The field of nanotechnology has undergone a remarkable growth in the last few years. This development has been fueled by the expectation that unusual properties of matter, which become evident as the size of the structural components of a device shrinks below 10–100 nm, may be exploited. In this work, we first present an original approach to the calculation of ballistic transport properties of nanostructures from first principles. Then we move beyond the mean-field approach, by addressing the effect of electron-electron interactions on coherent electronic transport through nanoscale conductors. The study of the coherent transport is based on a matrix Green’s function methodology, as implemented in the WanT code (freely available at <http://www.wannier-transport.org>). The approach adopts the maximally localised Wannier functions as basis set. In the case of electron-electron correlated systems, the standard Landauer approach breaks down, and a more general theory is needed to evaluate the electronic transport properties. For this purpose, we derive a generalised Landauer-like expression for the current, valid also in the e-e interacting case. We focus on the strong e-e correlation regime. We apply the above described method to a range of nanosized conductors such as molecular bridges, free-standing and substrate-supported atomic chains. We discuss electronic and linear-response transport properties in the mean-field and interacting case.

GW approximation for correlated systems within the multiple-scattering theory

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The ab initio study of semiconductors and insulators as well as systems with strongly localised electrons entails great difficulties involved by the treatment of excitation energies and many-body effects. The most successful first-principles method, the density-functional theory (DFT) within the local-spin-density approximation (LSDA), is designed for ground-state properties and can not provide a proper description of band structures of semiconductors and insulators. If some localised electrons are present in the system, like $3d$ -electrons in the transition-metal oxides, the local-density approximation can be essentially improved by the so-called self-interaction correction (SIC). In this approximation the self-interaction of single-particle charges, which are present in the LSDA, can be canceled out for the localised electrons. However, the self-interaction correction within the LSDA is still not sufficient for a proper description of the excitation energies and band gaps. It is possible to do accurately from first principles by solving Hedin’s set of equations for the full Green’s function. The implementation of this formalism is very difficult, one neglects commonly the vertex correction (the random-phase approximation), and the self-energy is calculated in this case within the so-called *GW* approximation. The non-self-consistent *GW* approximation was successfully implemented within several first-principles methods, but most of the existing implementations are generally designed for systems with delocalised (fast) electrons.

Here we present a general ab initio approach designed for the study of electronic properties of solids, in which on base of the Korringa-Kohn-Rostoker (KKR) method we implemented the self-interaction correction for strongly localised electrons and the non-self-consistent *GW* approximation for the inclusion of many-body effects. We illustrate our approach by the electronic structure study of some semiconductors and transition-metal oxides.

Wave-function-based determination of the quasiparticle band structure of solids

and polymers

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By exploiting the predominantly local character of electron correlation it is possible to set up schemes which allow to determine the ab initio many-body wave function of excited electron-hole and attached electron states of solids and other periodic systems by means of quantum-chemical post-Hartree-Fock correlation methods such as multi-reference configuration interaction (MR-CI). Two different approaches will be presented. The first is a divide-and-conquer algorithm which is based on a strictly local representation of the many-body Hamiltonian of the system by means of suitable localisation schemes. The individual matrix elements of this local Hamiltonian can be obtained from fragment calculations. Diagonalising that local Hamiltonian directly yields the band structure of the systems under consideration with the electron correlation effects being fully included on the quantum chemical level chosen for the fragment calculations. The second approach is an efficient Green's function formalism which effectively sums up infinitely many proper self-energy diagrams. It is implemented with Gaussian-type basis functions. Locality is exploited by representing all quantities in terms of localised Wannier functions and consequently applying spatial configuration selection schemes. The two methods turned out to yield very similar correlated band structures, and the calculated band gaps are found to be much better than those extracted from Hartree-Fock or Kohn-Sham orbital energies.

Investigations using the pseudopotential SIC-LSDA method into the role of n-type defects in DMS ZnO:Co

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We discuss results from ab initio density-functional theory (DFT) calculations using the pseudopotential SIC-LSDA (pseudo-SIC) method of Filippetti et al. [1] to investigate the possible role of n-type native defects in the DMS behaviour of dilute (3%) Co-doped ZnO. We find that the pseudo-SIC method overcomes the major shortcomings of the local-spin-density approximation (LSDA) in describing ZnO:Co viz., the band-gap error and incorrect positioning of Co 3d-levels. Results obtained within this improved description for ZnO:Co in the presence of zinc interstitials (I_{Zn})/oxygen vacancies (V_O) suggest that the centres responsible for long-range ferromagnetism in ZnO:Co might be defect-dopant pairs such as I_{Zn} -Co and/or V_O -Co.

[1] Alessio Filippetti and Nicola A. Hill, cond-mat/0303042.

Self-interaction-corrected (SIC) pseudopotential for Ti and TiO₂

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We have studied the phase diagram of titanium metal and dioxide by means of ab initio

total-energy calculations in DFT-LDA with pseudopotentials. The phases of interest for titanium metal are the α phase (hcp), the high-temperature phase β (bcc) and the high-pressure phase ω (hex); for TiO_2 the rutile phase (stable) and the anatase phase (metastable). With the pseudopotential method we have to separate core electrons (treated within the frozen-core approximation) from valence electrons (explicitly treated). However titanium, a transition element, has semi-core electrons. These semi-core states are atomic-like, but their exchange interaction with valence electrons is important. Stabilisation between the different phases changes a lot depending on whether or not we include the semi-core states, whereas structural properties (equilibrium volume and bulk modulus) are only slightly perturbed. Thus in standard calculation with semi-core states in the valence, the ω phase is more stable than the α phase and the anatase phase more stable than the rutile phase, contrary to the experimental results. Furthermore other problems appear without semi-core states, e.g., for electron energy-loss spectra [1]. In order to correct the LDA error on localised states as the semi-core states, we have introduced an atomic SIC (self-interaction correction) at the level of our pseudopotential in the spirit of [2]. We have extended the formalism to allow one to take into account several orbitals per angular momentum. We present the method developed and discuss the results obtained for the first time on a transition metal and its oxides.

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Orbital- and energy-dependent exchange-correlation functionals

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Orbital- and energy-dependent functional have raised considerable interest recently, because they are potentially able to overcome limitations of commonly used approximations like the local-density approximation, the generalised-gradient approximation or hybrid methods, especially in the description of Van der Waals forces. We show that density-functional theory within the random-phase approximation (RPA) for the exchange-correlation energy provides a correct description of bond dissociation in H_2 in a spin-restricted Kohn-Sham formalism, i.e., without artificial symmetry breaking. However, the RPA dissociation curve displays unphysical repulsion at larger but finite bond lengths. We also calculate the band-gap energy of a solid using the RPA and find that it is similar to the one obtained from nonrenormalised GW calculations, non-self-consistently, i.e., the G_0W_0 approximation. This provides a well-defined and meaningful interpretation to G_0W_0 quasiparticle band-gap calculations but questions the physics behind the renormalisation factors in the expression of the band-gap energy.

A novel generalised Kohn-Sham scheme

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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 and a three-dimensional spherical system. Comparison is made with previous quantum Monte Carlo calculations [3] and with previous *GW* calculations within many-body perturbation theory for these systems. Further *GW* calculations suggest 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.

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Density-functional theory for superconductors: Applications to MgB₂, Pb and solids under pressure

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Understanding and predicting the properties of superconductors is of both fundamental and technological importance. The discovery of superconductivity in MgB₂, with its rather high critical temperature ($T_c = 39.5$ K) and the presence of multiple gaps, has renewed the interest for conventional, phonon-driven superconductors. In this talk, we present several applications of a novel approach to superconductivity that allows one to calculate material-specific properties, such as the gap and the T_c , in a truly ab initio fashion without using any adjustable parameter, such as the Coulomb pseudopotential μ^* . Within this approach, alternative to the Eliashberg theory, we obtained the T_c and the two gaps of MgB₂ in good agreement with experiment, taking into account the anisotropy of this material. As a further application, solving a fully k -resolved gap equation, we found the presence of two gaps also for Pb, due to a different electron-phonon coupling in the two bands crossing the Fermi level. Finally, we have studied the behaviour of T_c in Li and Al as a function of pressure. Despite their simple metal structure, these two materials show a different behaviour upon pressure. While Li undergoes several transitions favouring superconductivity, in Al the electron-phonon coupling decreases with pressure, leading to a complete suppression of superconductivity around 8 GPa.

Abstracts of Posters

Ultra-nonlocality in the TDDFT and MBPT description of quantum transport

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Our recently developed linear-response formulation for conductance [1] is particularly suitable for TDDFT and MBPT analysis. Our first system to study is the interacting homogeneous electron gas (HEG). We can express the change of the conductance of the interacting HEG with respect to that of the noninteracting HEG directly in terms of the exchange-correlation kernel within the TDDFT, or alternatively, via the irreducible polarisation within the MBPT. Assuming that the conductance of the interacting HEG does not change, we derive a restrictive conditions on the form of the exchange-correlation kernel at small wave vector and small imaginary frequency. In particular, we find that a frequency-dependent ultra-nonlocal term needs to be present within the f_{xc} . We generalise the ultra-nonlocal HEG kernel for an inhomogeneous gas and compare the predictions of our approach to the estimates recently obtained within time-dependent current-density-functional theory [2].

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The physics of CdSe nanocrystals

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In the past years, nanometer-sized CdSe clusters have attracted a large interest from the community. These nanocrystals can be prepared with a very narrow size distribution and have found important applications as chemical markers. In most experiments, the nanocrystals are formed by kinetically controlled precipitation and are terminated with capping ligands (e.g., the TOPO molecule) which provide stabilisation of the otherwise reactive dangling orbitals at the surface. Of course, when unsaturated bonds exist, they drive strong reconstructions which modify the electronic properties. However, the extent to which the cluster atomic structure resembles the corresponding bulk, as well as how the reconstruction of the surface affects the electronic properties are not well understood.

We performed extensive density-functional calculations of structural properties and absorption spectra of small CdSe nanocrystals, with a diameter ranging from 0.5 to 1.5 nm. We considered unsaturated clusters, obtained by structural relaxation of wurtzite bulk-like fragments, clusters whose surface was passivated with TOPO molecules and fullerene-like cages. We found that the unsaturated systems exhibited very strong surface reconstructions. However, by passivating the Cd atoms at the surface with TOPO molecules, the clusters remained bulk-like, even for very small diameters. The optical spectra were obtained within

time-dependent density-functional theory. The optical absorption is strongly dependent on the size and the geometrical properties of the clusters. Furthermore, our results allowed us to interpret recent experiments of absorption in CdSe nanocrystals.

Spin-polarisation in metastable deexcitation spectroscopy

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The polarisation of emitted electrons in the deexcitation of metastable helium impinging on metal surfaces is investigated from the theoretical point of view. We calculate the Auger emission rate, considering the He* atom at various distances from jellium surfaces with different work functions. We make use of the embedding Green's function method combined with density-functional theory, which allows us to consider the helium atom over a semi-infinite substrate fully accounting for their mutual interaction [N. Bonini et al., Phys. Rev. B **68**, 35408 (2003)]. We will show that the different degree of spin polarisation in the deexcitation probability on different surfaces is strictly related to the energy position of the 2s resonance with respect to the Fermi level of the substrate: The 2s level being higher than the Fermi one causes a fairly small magnetisation around He*, giving consequently a weakly polarised signal. On the contrary, a small-work-function substrate leaves the 2s level fully occupied, causing a strong polarisation in the emitted electrons. These results are in very good agreement with previous experimental findings.

Electronic properties of thin oxide films

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Ultrathin films have gained large interest over the last years due their current or potential application in catalysis, electronic devices and protective coatings. It is often argued that the structural, elastic and electronic (response) properties of these films may differ noticeably from their counterparts with mesoscopic thickness.

We present density-functional theory calculations for the large-gap oxides α -quartz SiO₂ (amorphous SiO₂ is the gate material in standard silicon-based transistors), α -alumina Al₂O₃ (a common support material in catalysis) and hafnia HfO₂ (a promising candidate for replacing SiO₂ in future nanoscale microelectronic devices). We find that the electronic structure becomes bulk-like for very few atomic layers if the local bonding of the bulk material is preserved. This observation stands in contrast to semiconductors that show quantum-size effects up to the nanometer range. This has important consequences for applications and device design. The results are analysed in view of the localised bonding in these oxides. For SiO₂, quasiparticle corrections in the *GW* approximation have been calculated. We find size-dependent quasiparticle shifts in qualitative agreement with simple models.

Optical properties of the Si(113) surface

Katalin Gaál-Nagy, Emiliano Ponzio and Giovanni Onida

We have investigated the optical properties of the 3×2 ADI reconstruction (which is the most stable one [1]) of the (113) surface of silicon. The slab used in [1] was reduced in thickness for computational reasons, and tests on the atomic geometry and the electronic structure confirmed the reliability of the new unit cell. For the optical properties we have been calculating the x and y contribution to the imaginary part of the polarisability, from which the RAS (reflectance anisotropy spectra) can be obtained. In order to discriminate the surface contributions a layer-by-layer analysis has been performed. The calculations have been done within the plane-wave pseudopotential approach to the density-functional theory as implemented in ABINIT and TOSCA. The optical properties have been derived using the matrix elements of the momentum operator. Electronic bands and optical properties have been obtained also within a semi-empirical tight-binding approach, allowing a much denser \mathbf{k} -point sampling.

[1] A. A. Stekolnikov, J. Furthmüller and F. Bechstedt, Phys. Rev. B **67**, 195332 (2003).

Ab initio calculations of layered systems based on C and BN

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We calculate with ab initio methods electronic properties of graphite and hexagonal boron-nitride systems, as well as derived systems (like simple or bilayers). We study the validity of simple models simulating the distance between layers, from the bulk distance to isolated layers. These calculations will allow us to study the influence of the geometry and of the interaction between layers on absorption and electron energy-loss spectra. The band-structure calculations are done using Abinit with *GW* corrections [1]. The spectra are calculated in TDDFT using DP [2].

[1] <http://www.abinit.org>

[2] <http://theory.lsi.polytechnique.fr/codes/dp/dp.html>

Ab initio study of optical spectra for oxidised Si(100) surfaces

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The effects of oxygen adsorption on the reflectance anisotropy spectrum (RAS) of reconstructed Si(100)-(2 \times 2):O surfaces at low coverages (0.5–1.5 ML) have been studied by an ab initio DFT-LDA scheme within a plane-wave, norm-conserving pseudopotential approach. At 0.5 ML coverage, oxidising only one of the two dimers does not induce noticeable changes in the surface optical anisotropy. On the other hand, backbond oxidation of each surface dimers is enough to strongly reduce the surface optical anisotropy. Coverages close to saturation (1

and 1.5 ML) have the effect of cancelling the surface anisotropy up to 3 eV, as seen in the experiments.

Performance of GW total energies in a simple inhomogeneous benchmark system

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A system of two electrons confined within a sphere constitutes a very simple yet challenging problem where the degree of correlation can be controlled by setting the value of the radius R . Bearing in mind that the performance of GW is subject to errors coming from an incomplete cancellation of self-interaction, we will make a comparative study, with respect to the exact solutions, of the total energies and density profiles. We will present the calculations and the analysis of the results starting from the G_0W_0 , then the partially self-consistent GW_0 and finally the completely self-consistent GW level.

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All-electron GW code based on FP-(L)APW+lo

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We report on the development of an all-electron GW code based on the Wien2k implementation of the FP-(L)APW+lo method. The optimised basis [1] for the matrix representation of nonlocal operators allows the inclusion of core and semicore states on the same footing with a reasonable computational cost. To be able to address metallic systems, we extended the linearised tetrahedron method to calculate Brillouin-zone convolutions. The dielectric matrix at the Γ -point in our program is solved analytically instead of being approximated from the surrounding points. The self-energy is calculated from first principles, without relying on the plasmon-pole approximation for the frequency-dependence of the dielectric function. We show the preliminary results obtained with our code on Si and GaAs. The \mathbf{q} -dependent integration for metals is tested by comparing the dielectric function for the free electron gas with the standard Lindhard function. Macroscopic dielectric functions including local-field effects are calculated and compared with the results of other methods and experiments [2].

[1] F. Aryasetiawan in *Strong Coulomb Correlations in Electronic Structure Calculations*, edited by V. I. Anisimov (Gordon and Breach, New York, 2000).

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Quasi-particle effects in 1D polymer chains: The case of red and blue forms in PDA

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Quasi-1D polymer chains are very interesting systems as quantum-wire models [1]. Moreover, they can be used in optoelectronic applications due to their luminescence properties. Polydiacetylene (PDA) has been synthesised in form of isolated chains [2]. Bulk PDAs are known to exist in either of two electronic structures, so-called red and blue phases, showing intense excitonic absorptions near 2.4 and 2.0 eV, respectively. Blue chain fluorescence is extremely weak. On the contrary, red chains have a high fluorescence [2], indicating that the exciton-relaxation scheme has to be very different from the blue one. This scheme is still an open question since experimentally no conformal difference between the two types of chains could be detected yet. It has been postulated that the difference between both forms could come from a tilting of the building units giving an identical mean structure. As a first step to the comprehension of PDA isolated chains and crystal structures, we will present a *GW*-BSE study on the evolution of the quasiparticle energies as well as optical excitations as a function of the tilting angle between building units.

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Ab initio calculation of the spin susceptibility for real materials

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The magnetic response of a material to an applied field is the key quantity to understanding its magnetic behaviour. A thorough characterisation is a prerequisite for the selection of optimal materials for modern technological applications in the field of magneto-electronics and spintronics with ever smaller sizes and switching times. The change in magnetisation $\vec{m}(\vec{r}, t)$ with respect to an external magnetic field $\vec{B}(\vec{r}', t')$ is given by the dynamic spin susceptibility. Of particular interest is the transverse component $\chi^{-+}(\vec{r}, \vec{r}'; \omega)$, because its spectral function reveals the energy and lifetime of spin excitations, which correspond to poles in the complex frequency plane. It can be understood as describing the propagation of an additional spin under the influence of its interaction with the rest of the system. Despite the importance for real-world applications, theoretical studies are still mostly based on simple lattice systems with empirical parameters, such as the Heisenberg model, due to the complicated exchange and correlation effects in solids. Constrained density-functional theory can give some information about the adiabatic regime, but dynamic properties like excited-state lifetimes are only accessible within a more general framework like many-body perturbation theory or time-dependent density-functional theory. The feasibility of both approaches has been successfully demonstrated for spin excitations in simple systems [S. Y. Savrasov, *Phys. Rev. Lett.* **81**, 2570 (1998); K. Karlsson and F. Aryasetiawan, *Phys. Rev. B* **62**, 3006 (2000)], but so far there exists no universal implementation capable of describing on an ab initio basis the spin susceptibility of more complex materials like multi-component devices or surfaces.

As a first step towards a full ab initio treatment, we investigate the magnetic response function at the level of the Kohn-Sham susceptibility. This approach is inherently dynamic and already gives a good account of single-particle spin-flip processes on an eV energy scale, the so-called Stoner excitations. Our implementation is based on the full-potential linearised augmented plane-wave (FLAPW) method. We illustrate the performance by applications to different magnetic materials. In the future, we intend to enhance our calculations by including dynamic exchange-correlation effects, which give rise to collective excitations like spin waves in the low-energy part of the spectral function.

During the work we benefitted from intensive discussion with T. Kotani on this subject.

EXCITON: A many-body code interfaced to CRYSTAL

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CRYSTAL is a well-known Hartree-Fock (HF), density-functional theory (DFT) and hybrid HF/DFT code which exploits space-group symmetry to a high degree, which makes calculations on large unit cells feasible. EXCITON is a Gaussian-orbital many-body code interfaced to CRYSTAL. The present version of EXCITON may be used to perform *GW* and Bethe-Salpeter calculations using a plasmon-pole approximation for the dielectric function. Band-structure and optical excitation spectra for solid Ne and Ar computed using EXCITON are presented. Real-space algorithms used in CRYSTAL for computing operators are now being implemented in EXCITON and this will allow many-body calculations to be performed on larger unit-cell systems using either a DFT, hybrid HF/DFT or HF mean-field Hamiltonians.

Band gaps in pseudopotential self-consistent *GW* calculations

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For materials which are incorrectly predicted by density-functional theory to be metallic, an iterative procedure must be adopted in order to perform *GW* calculations. In this paper we test two iterative schemes based on the quasiparticle and pseudopotential approximations for a number of inorganic semiconductors whose electronic structures are well known from experiment. Iterating just the quasiparticle energies yields a systematic, but modest overestimate of the band gaps. Iterating the quasiparticle wave functions as well gives rise to an imbalance between the Hartree and Fock potentials and results in band gaps in far poorer agreement with experiment.

One- and two-photon absorption spectra of carbon nanotubes

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Coulomb interactions are significantly enhanced in low-dimensional systems and are known to

give rise to peculiar phenomena of central importance for applications. Quasi-one-dimensional single-walled carbon nanotubes are therefore thought to be dominated by electron-electron interactions, even if their optical spectra have often been interpreted in terms of van Hove singularities so far. In the present work the optical properties of large-diameter SWNTs have been investigated from first principles with the inclusion of excitonic effects. We employed an original symmetry-based approach [1] to implement a state-of-the-art formulation based on many-body perturbation theory. Both self-energy corrections to the single-particle energies and excitonic effects are incorporated, allowing for direct comparison with experiment. Taking advantage of the screw-symmetry of the system, we may afford calculations on tubes with more than a hundred of atoms per unit cell, otherwise unfeasible in standard approaches. In addition, this picture gives a more complete understanding of the excited-state properties, of the degeneracies and group character of the single-particle bands and of the selection rules involved in determining optical spectra. We computed one- and two-photon absorption spectra, achieving excellent agreement with recent experiments [2]. We discover that for all the tubes studied, excitonic effects are very strong, with binding energies ranging between 0.3 and 0.9 eV, and crucial in both the peak shapes and positions.

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Spin-dependent *GW* approximation

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Effects due to collinear and noncollinear spin polarisation as well as spin-orbit coupling play an important role in many solid-state systems containing transition metals or heavy elements, respectively. We examine the consequences of including these effects in the system of Hedin's equations. For this purpose we extend the existing theory using Schwinger's functional-derivative formalism to a Hamiltonian with an external magnetic field and the spin-orbit coupling term. The expression for the self-energy is approximated in *GW*. A discussion will be given, which physical effects can be described within such an approximation and which lie beyond the *GW* approach. Additionally, the spin structure of the Bethe-Salpeter equation for the polarisation function in the spin-polarised case is studied. In order to illustrate the analytical results we apply the formulas in the case of collinear spin polarisation to the antiferromagnetic insulator MnO. We perform a spin-polarised density-functional calculation using the generalised gradient approximation and the projector-augmented-wave method to obtain band structures. They are improved by adding quasiparticle shifts. The screening is described by means of a model dielectric function, including a simplified treatment of the dynamical effects.

Self-energy of nickel oxide in spin-polarised *GW* approximation

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NiO is a prototypical strongly correlated magnetic insulator. As is well known, DFT treatments of such systems suffer from the notorious band-gap problem. *GW* corrections improve the situation but do not in general give full agreement with experiment. Beginning with a hybrid DFT-HF Hamiltonian, we calculate the self-energy of NiO in the spin-polarised *GW* approximation, using an all-electron basis of localised Gaussian orbitals and a plasmon-pole approximation to the dielectric function. Varying the amount of Hartree-Fock exchange in the initial calculation allows us to tune the quasiparticle band gap to its exact experimental value, whilst the inclusion of RPA screening in *GW* yields corrections to the relative positions of energy bands which are not present at the mean-field level. This approach may also prove useful in tackling other strongly correlated transition-metal oxides.

Quasiparticle calculations of high-*k*-material band offsets with silicon

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The size reduction of MOS transistors requires the usage of alternative materials as gate oxide layers. In this work we have studied the energy-band alignments of a high-dielectric material, namely, ZrSiO₄ in contact with Si. We have used first-principles DFT calculations within the local-density approximation. The many-body corrections were included as calculated by the *GW* approximation. The calculated band offsets were found to be 2.03 and 2.28 eV for VBO and CBO, respectively. This result suggests that ZrSiO₄ can be a promising candidate to replace SiO₂ in future MOSFET technology.

Electronic deexcitation by intervalley scattering: Ab initio study in GaAs and GaP

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In a number of semiconductors under strong electric field, the carriers can be scattered from the conduction-band minimum to energetically higher satellite minima (“valleys”). These processes are accompanied by the emission and absorption of short-wave phonons (“intervalley phonons”). Intervalley scattering plays an important role in many phenomena such as absorption of light in indirect semiconductors, relaxation of electrons after pulsed optical excitations, negative differential resistance and Gunn effect [1,2]. This is why the corresponding electron-phonon interaction parameters, the intervalley deformation potentials, are of particular interest in the characterisation of optical and transport properties of semiconductors and heterostructures designed to have many-valley band structure.

In this work we calculate, in the framework of density-functional perturbation theory [3], the intervalley deformation potentials in GaAs and GaP. We consider scattering between high-symmetry points as well as in arbitrary directions in the Brillouin zone. Our results show very strong dispersion and anisotropy of the deformation potentials, which depend on the

wave vectors of the initial and final electronic states. So, we find a qualitative agreement with previous theoretical results of Ref. [4], in which the empirical pseudopotential method and rigid-ions model were used. Quantitatively, however, our results are very different from the results of Ref. [4]. Finally, we show how to calculate the contribution of intervalley-scattering times to the lifetime of the electronic excitation and compare our preliminary results to available experimental and theoretical data [4,5].

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Nonlocal vertex corrections in Hedin's equations

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Many-body perturbation theory provides a potentially powerful class of orbital-functional methods, which may be implemented within Kohn-Sham theory, generalised Kohn-Sham theory or other frameworks. For their successful implementation it is essential to have adequate and tractable models for the self-energy. A nonlocal operator like the self-energy can be consistently calculated through many-body perturbation theory. We are implementing local and nonlocal vertex corrections in Hedin's equations and are investigating various quantities which have to be adequately described if such a model is going to be successful in fully self-consistent calculations. So far these quantities have been the static structure factor, the pair-correlation function and the spectral function of the homogeneous electron gas. We also hope to present total-energy calculations. The effect of a local vertex correction on jellium is investigated and results are used to determine a tractable model self-energy.

Electronic excitations: Ab initio calculations of electron energy-loss spectra

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In this work, we address the question of the theoretical prediction and interpretation of experimental spectra obtained by the excitation of valence electrons, such as valence photoemission spectra, electron energy-loss spectra (EELS) or absorption spectra, or by deexcitation of an incoming electron into the conduction band, like in bremsstrahlung isochromat spectroscopy (BIS). We particularly expose the case of the transition metal oxides ZrO₂ [1,3], TiO₂ [2,3] and Cu₂O [3], and compare our theoretical results with experimental data. In ZrO₂ [3], we show which levels of theory are appropriate, starting either from the density of occupied or empty states or from the joint density of states obtained from ground-state density-functional calculations, to the effect of the inclusion of matrix elements of the dipolar operator (random-phase approximation RPA) and the inclusion of off-diagonal elements in the response function

(RPA with crystal local-field effects). Additional exchange and correlation local fields within the adiabatic time-dependent local-density approximation and many-body effects in the quasiparticle and in the TDDFT frameworks [4,5] are presented in order to explain the reasons why the RPA turns out to be a level of approximation appropriate for electron energy-loss spectroscopy, in those materials as well as in a test case like bulk silicon.

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Strong field ionisation using time-dependent density-functional theory

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Time-dependent density-functional theory appears to be a valuable tool to study multiphoton ionisation of atoms or molecules. However, some difficulties appear for high laser intensities, when multiple ionisation becomes possible. Photoionisation of atoms, submitted to an intense laser pulse, is studied within this framework. In order to gain some insight in the dynamics of the process, the kinetic-energy spectra of the emitted electrons are analysed. Particular attention is paid to the problem of determining the photoelectron spectra, as no direct physical meaning can be attributed to the electronic orbitals in DFT calculations. A method to calculate the spectra, based on the electronic density only, is proposed.

Time-dependent quantum transport in 1D model systems with electron-phonon interactions

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We investigate the role of phonons in the time-dependent current response of one-dimensional systems. A finite (central) chain described by the Holstein model is contacted to the left and

to the right with two semi-infinite free-electron leads. We consider different phonon-couplings in the chain, namely strong vs. weak regimes. We drive the whole system out of equilibrium by exposing the electrons to an external time-dependent electric field. The influence of the leads is taken into account via an exact embedding scheme, and the central system is evolved by treating the phonons in the semi-classical limit. By studying the time-dependent current in different points of the chain, we provide some generic remarks about the influence of the phonon-electron interaction on both the transient and steady-state regime.

Dynamic structure factor of silicon: RPA, *GW*-RPA and TDLDA calculations and inelastic X-ray-scattering experiments

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Our recent work shows excellent agreement between the dynamic structure factor of Si as measured by inelastic X-ray scattering and the result of standard TDLDA. TDLDA reproduces the shape, position and intensity of the experimental results. Small discrepancies arise on the high-energy side of the spectrum [1]. In the present contribution we compare the spectra calculated within RPA, *GW*-RPA and TDLDA in order to illustrate the question up to which degree many-body effects are contained in the TDLDA exchange-correlation kernel. The results are compared to the literature [2] as well as to the experiments which have been carried out in parallel. We analyse not only the overall shape and position of the plasmon peak but also secondary structures on the plasmon. Possible implications for the application of the *GW* approximation are discussed.

[1] H.-Ch. Weissker, J. Serrano, V. Olevano, F. Bruneval, F. Sottile, S. Huotari, G. Monaco, M. Krisch and L. Reining (to be published).

[2] W. Schülke, J. R. Schmitz, H. Schulte-Schrepping and A. Kaprolat, Phys. Rev. B **52**, 11721 (1995).