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# Chapter 1

## List of abstracts

### 1.1 *Nuno Carneiro: Tests in a 1-Dimensional model for Generalised Kohn-Sham schemes*

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 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.

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

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

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

### 1.2 *Martin Stankovski: Vertex corrections in Hedin's equations*

Many-body perturbation theory provides a potentially powerful class of orbital-functional methods, which may be implemented within Kohn-Sham theory, generalized Kohn-Sham theory, or other frameworks. For their successful implementation it is essential to have adequate and tractable models for the self-energy. A non-local operator like the self energy can be consistently calculated through many-body perturbation theory. We have implemented a non-local model vertex correction 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. We will present the theory of vertex corrections in Hedin's equations and the merits of several approaches, both historical and recent, for a starting model of the self-energy will be discussed. Numerical results will be presented for the case of the homogenous electron gas. These are mainly for the static structure factor, the pair-correlation function and possibly for the spectral function of Jellium.

### 1.3 *Jeil Jung*: A simple benchmark system for studying electron correlation

A system of two electrons confined within a sphere constitutes a very simple yet challenging problem due to the complex nature of electron correlation. We will show that the self-interaction can be a serious source of error at low density high correlation regime, preventing widely used semi-local DFT approximations to reach a satisfactory accuracy [1]. Preliminary results based on the more sophisticated  $G_0W_0$  method for total energies and density profiles will be reported.

- [1] J. Jung, P. García-González, J.E. Alvarillos and R. W. Godby, Phys. Rev. A **69** 052501 (2004).

### 1.4 *Gianluca Stefanucci*: Variational Functional Approach to (Current) Density Functional Theory

Successively better exchange-correlation kernels in (current) density functional theory are obtained from the variational approach to many-body perturbation theory. The resulting kernels give rise to response functions which obey several experimentally important conservation laws and consistency requirements like, e.g., the f-sum rule. The so called Exact-Exchange (EXX) approximation follows from our approach when the self-energy is approximated with the Hartree-Fock self-energy.

### 1.5 *Stefano Pittalis*: Optimized effective potentials in Current- Density-Functional theory

The proper description of many-electron systems in the presence of magnetic fields within a density-functional framework requires the current density to be used as basic variable besides the electron density. 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 current-density-functional theory (CDFT) one also allows for the coupling to the orbital currents. Electron-gas-based (LDA-type) approximations of CDFT exhibit derivative discontinuities as a function of the magnetic field whenever a new Landau level is occupied. The corresponding exchange-correlation potentials then become singular which makes these functionals difficult to use in practice. As an alternative, we present an optimized effective potential (OEP) method within a CDFT framework which allows for the use of explicitly orbital-dependent functionals. The derivation of these equations and a numerically tractable scheme for their solution within a KLI-type approximation will be discussed. We present first results at the exchange-only level for open shell atoms and quantum dots in external magnetic fields.

### 1.6 *Nicole Helbig*: The fundamental gap in reduced density matrix functional theory

We present a novel method for calculating the fundamental gap. To this end, reduced density matrix functional theory is generalized to fractional particle number. For each fixed particle number,  $M$ , the total energy is minimized with respect to the natural orbitals and their occupation numbers. This leads to a function,  $E_{tot}^M$ , whose derivative

with respect to the particle number has a discontinuity identical to the gap. In contrast to density functional theory, the energy minimum is generally not a stationary point of the total-energy functional. The formalism is extended to open-shell as well as periodic systems. Numerical results are presented for alkali atoms, for the LiH molecule and for the periodic one-dimensional LiH chain.

## 1.7 *Stefan Kurth*: A Practical Scheme for Quantum Transport using Time-Dependent Density Functional Theory

The Landauer formalism is a popular method to calculate the current of non-interacting electrons through a mesoscopic or nanoscopic system connected to two (or more) macroscopic electrodes in the steady-state. Here we present a *time-dependent* description of transport based on the time evolution of the non-interacting Schrödinger equation. We develop a numerical algorithm for the time propagation of extended states. For simple model systems, the scheme is used to compute the time-dependent current in response to an external dc or ac bias. As expected, for a dc bias the system evolves to a steady state. Using the algorithm in the framework of time-dependent density functional theory allows for the description of transport of *interacting* electrons beyond the Landauer formalism.

## 1.8 *Micael Oliveira*: Optical and magnetic excitations in small transition-metal clusters using TDDFT

We use time dependent density functional theory (TDDFT) to study optical and magnetic excitations of small transition-metal clusters. We mainly focus on two things. First, the role of non-collinear magnetism and spin-orbit coupling in such phenomena. Second, the importance of including the current density as the basic variable (current-density functional theory) that allows to treat, in principle, open-shell systems. The calculations are done within a real-time real-space TDDFT framework using the Octopus code.

We will present some preliminary results concerning the linear response calculations and show how non-collinear effects modify the optical and/or magnetic spectra (including the natural magnetic dichroism spectroscopy).

## 1.9 *Daniele Varsano*: Optical properties of quasi 1d systems

We investigate optical properties and static polarizability of finite and infinite linear chains (Hydrogen chains and polyacetylene) via MBPT and via TDDFT with a recently developed frequency dependent and non-local exchange-correlation kernel. The TDDFT optical spectra calculated with such methods turns out to be indistinguishable and gives very good results when compared with experiments. We also presents results for the static polarizability of such chains as a function of number of monomers. Compared to the Adiabatic Local Density Approximation (ALDA) that systematically overestimates this quantity for such systems we see that the present approximation for the kernel gives good results when compared with quantum chemical calculations. In order to perform these calculations, an exact Coulomb cutoff technique has been developed to treat finite and quasi one dimensional systems, as isolated, in super-cell techniques.

## 1.10 *Wojciech Welnic*: Local atomic order and optical properties in amorphous semiconductors

In this work excited state calculations are presented for GeTe. Due to a significant change of optical reflectivity and electric conductivity upon the phase transition from the amorphous to the crystalline state covalent semiconductors like GeTe or the ternary alloy  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  are promising candidates for future data storage applications.

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 this experimental data a simple structural model of amorphous GeTe was applied to perform *ab initio* ground state and excited state calculations.

The optical spectra are calculated within TDDFT in the Random Phase Approximation. They are in qualitative agreement with experimental data and furthermore explain the profound change of optical absorption upon amorphisation. It is not due to a smearing and broadening of the density of states as commonly assumed for amorphous semiconductors, but rather to a change in the local atomic order. This causes changes in the electronic and then consequently in the optical properties.

## 1.11 *Silvana Botti*: TDDFT from clusters to solids

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.

I will 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.

## 1.12 *Hans-Christian Weissker*: Dielectric properties of silicon: *ab initio* calculations and inelastic X-ray scattering

The present work reports *ab initio* calculations of inelastic x-ray scattering spectra on silicon. We determined spectra for momentum transfers between 0 and 2.4 a.u. along the [100] and [111] directions using the Time-Dependent Local Density Approximation (TDLDA).

In parallel, experiments have been performed at the beam line ID16 of the European Synchrotron Radiation Facility in Grenoble (ESRF). Having a higher resolution than experiments done a decade earlier, they reveal a fine structure that was not reported in the older measurements [1].

Surprisingly, the spectra obtained within TDLDA are in outstanding agreement with the new experiments, in particular at the low-energy side, up to about 30-40 eV. RPA calculations yield consistently worse agreement. The spectra will provide a benchmark to test more refined approximations. We present here preliminary results.

[1] W. Schülke et al., Phys. Rev. B 52, 11721 (1995).

### 1.13 *Andrea Floris*: Density functional theory for superconductors: Applications to MgB<sub>2</sub> and solids under pressure

Understanding and predicting the properties of superconductors is of both fundamental and technological importance. The discovery of superconductivity in MgB<sub>2</sub>, with its rather high critical temperature ( $T_c = 39.5\text{K}$ ) 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  $\mu^*$ . Within this approach, we obtained the  $T_c$  and the two gaps of MgB<sub>2</sub> in good agreement with experiment, taking into account the strong anisotropy of this material.

As a further application, 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.

### 1.14 *Martin Friak*: Ab initio study of the A<sub>1g</sub> Raman-active phonon mode in magnetite

Half-metals, which are metallic in only one spin channel and can thus sustain ideal 100% polarized currents, are excellent candidates for future spintronic technologies. Factors like strain may destroy this desirable property, but as the spin polarization is difficult to measure directly, there are so far no comprehensive data. We therefore studied thermodynamic properties that are more readily accessible by spectroscopy and can be probed to distinguish the half-metallic and metallic phases. For magnetite we identify the A<sub>1g</sub> Raman-active phonon mode as a possible indicator.

Our density-functional theory (DFT-GGA) calculations, employing the all-electron FLAPW method, predict the mode frequency under equilibrium conditions in good agreement with experiments and also reproduce the observed kink in the frequency as a function of applied pressure around 15 GPa. We explain this behavior as a direct consequence of the strain-induced half-metal to metal transition, which changes the lattice dynamics. Explicit boundaries for the half-metallic phase of magnetite are given for different forms of strain.

### 1.15 *Aleksey Kuznetsov*: Theoretical study of the Fe<sub>3</sub>O<sub>4</sub>(111) surface structure and physical properties

The Fe<sub>3</sub>O<sub>4</sub>(111) surface has been studied intensively since several years due to its potential application in spintronics (Yu. S. Dedkov et al., Phys. Rev. B **65** (2002) 064417). The unreconstructed surface can expose six possible terminations, but only three of them have been clearly resolved experimentally (e.g. N. Berdunov *et al.*, Phys. Rev. B **70** (2004) 085404). Moreover, self-consistent band structure calculations of the Fe<sub>3</sub>O<sub>4</sub>(111) surface are still lacking. We present the results for the different surface terminations, in particular

addressing the stability, electronic structures, and magnetic properties. Employing *ab initio* atomistic thermodynamics we identified the most stable surface termination. All calculations were performed using density-functional theory together with the all-electron full-potential linearized augmented plane-wave method as implemented in the WIEN2k code.

## 1.16 *Christoph Freysoldt*: GW for surfaces

Density functional theory (DFT) is the state-of-the-art method to determine ground state properties from first principles for a wide variety of different materials. In order to treat surfaces one often employs a repeated slab geometry, which allows to use standard software packages that utilise three-dimensional periodic boundary conditions. This is justified because on the level of DFT, the slab is easily decoupled from its periodic image. Only when permanent dipoles are present in the slab an additional correction is required.

Excited-states properties, notably the quasiparticle band structure, are successfully described by correcting the Kohn-Sham band structure with many-body perturbation theory in the GW-approximation.

We show that certain approximations that are commonly made in GW implementations must be carefully validated in order to capture the physical behaviour of the repeated slabs. Our numerical results give evidence that the periodic arrangement manifests itself noticeably in the bandstructure, which is in agreement with an electrostatic model that incorporates the induced dipole effects. Prospects for realistic GW surface calculations are discussed.

## 1.17 *Patrick Rinke*: Combining quasiparticle energy calculations with exact-exchange density-functional theory

We present a systematic *ab initio* study of the electronic structure for selected II-VI compounds and group III nitrides in the zinc-blende structure with special emphasis on analysing the role played by the semicore *d*-electrons. We show that applying density-functional theory (DFT) in the exact-exchange (EXX) approach [1] leads to an improved description of the *d*-electron hybridisation compared to the local-density approximation (LDA). Moreover we find that it is essential to use the newly developed EXX pseudopotentials [2] in order to treat core-valence exchange consistently.

In combination with quasiparticle energy calculations in the *GW* approximation we achieve very good agreement with available photoemission data. Since the DFT energies and wavefunctions serve as input for the *GW* calculation we conclude that for these materials EXX constitutes the better starting point.

[1] M. Städele *et al*, Phys. Rev. Lett. **79** 2089 (1997)

[2] M. Moukara *et al*, J. Phys.: Condens. Matter **12** 6783 (2000)



## 1.18 *Myrta Gruening*: Density functional theory from many-body perturbation theory: optical absorption spectra of semiconductors and insulators

Optical absorption spectra of semiconductors and insulators calculated with the (adiabatic) local density approximation ((A)LDA) -or any other local or gradient approximation- for the exchange-correlation (xc) potential and kernel present two main shortcomings: the spectra are shifted towards lower energies and excitonic effects are not taken into account. In this study first, we try to understand in which measure the LDA for the xc potential is responsible for the downward-shift in the optical absorption spectra; second, we look for approximations for the kernel that can reproduce excitonic effects.

To achieve the first objective we calculated self-consistently the KS band structures with the xc potentials that corresponds via the optimized effective potential equation to the Hartree-Fock and the GW (G: Green's function; W: screened Coulomb interaction) approximations to the many-body self-energy operator.

To achieve the second objective we compare the optical absorption spectra calculated with approximations to the exact-exchange kernel: the Petersilka-Gossman-Gross (PGG) kernel and the kernel obtained from the common energy denominator approximation (CEDA) for the KS Green function. Both these approximations avoid the summation on the conduction bands that makes the calculations of the exact-exchange kernel expensive, but only the CEDA has the proper  $q \rightarrow 0$  behavior.

We present results for the band structures and optical absorption spectra of bulk Si and bulk LiF.

## 1.19 *Andrei Incze*: Ab initio study of reflectance anisotropy spectra of oxidized Si(100) surfaces

The effects of oxygen adsorption on the reflectance anisotropy spectrum (RAS) of reconstructed Si(100)(2x2):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, oxidizing 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. We suggest that new interplay between present theoretical results and reflectance anisotropy spectroscopy experiments at low coverage could lead to further clarification of structural and kinetic details of the Si(100) oxidation process in the sub-monolayer range.

## 1.20 *Frank Fuchs*: Origin of the optical anisotropy oscillations during the oxidation of Si(001)

The oxidation of silicon is both of great fundamental and technological interest. Despite decades of effort, the microscopic mechanisms of oxide growth are still under consideration. Recent experiments indicate the high potential of Reflectance Anisotropy Spectroscopy (RAS) for the study of oxide growth on Si(001), where RAS could represent a powerful supplement to conventional surface characterisation techniques. Here we present the results of our ab initio study on the origin of the RAS oscillations measured during oxide

growth. Our results demonstrate the relation of the RAS oscillations to the layer-by-layer oxidation of Si(001). The major contribution to RAS is found to result from the interface, while the RAS signal from the oxide-overlayer is found to vanish due to surface disorder. The progression of the local strain field accompanying the oxygen-insertion into Si-Si bonds at the interface is proposed as the actual origin of the RAS oscillation.

## 1.21 *Katalin Gaal-Nagy*: Optical Properties of the Si(113) surface

In this contribution recent results for the optical properties of the Si(113) surface are presented. From the reconstructions considered by the group of F. Bechstedt [1], the Si(113)  $3\times 2$  ADI surface is the most stable one. For our calculations it was necessary to reduce the thickness of the slab used by [1]. Tests on the atomic geometry and the electronic structure confirmed the reliability of the new unit cell. We have been calculating the  $x$  and  $y$  contribution to the imaginary part of the polarizability. Our results show a shift of the  $x$  contribution to higher energies, which is not visible in tight-binding results. In order to study the origin of this shift we have been analysing the slab layer by layer. It turns out that this shift can be obtained even in the bulk-region of the slab. Presently we are searching for the reasons of this anisotropy.

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

## 1.22 *Luis Ramos*: Electronic and optical properties of Si and Ge capped nanocrystallites

Although Si is by far the semiconductor most used in devices, the benefits of combining Si and Ge in devices has been only recently acknowledged. The compatibility of Ge with the Si technology is higher than the compatibility of III-V and II-VI compounds what suggests for instance the development of Si-Ge-based devices to work in the infrared region of the spectra. Capped nanocrystallites (NCs) with a core-shell structure are common in II-VI compounds and oxidized Si NCs also have such a structure. The quantum confinement (QC) properties of II-VI NCs with a core-shell have important consequences for their electronic excitations and optical transitions. Changes due to the capping in the NCs can enforce localization of holes and electrons either at capping shells or at the core of the particle.

The charge-storage mechanisms in NCs due to QC are useful for memory devices, whereas the modifications in the QC resulting from the capping of NCs can make them suitable for other applications such as photodetectors and solar cells. The lattice mismatch of Si and Ge as well as the high miscibility of the SiGe alloy in principle prevents very sharp Si-Ge interfaces. However, investigations on ideal Si-Ge nanostructures can be helpful to interpret measurements and perhaps suggest new applications. By means of the ab initio pseudopotential approach implemented in the VASP code, we investigate the structural, electronic, and optical properties of ideal Si-capped Ge NCs and Ge-capped Si NCs. We show that the localization of the highest-occupied and lowest-occupied molecular orbitals, Stokes shifts, and radiative lifetimes are very sensitive to the type of capping and core of the NCs. A compensation effect involving the NC composition and QC is observed in the peaks of optical absorption for Si-capped Ge NCs. We take advantage of the meeting to report other research activities connected to the NANOQUANTA network and other collaborations.

## 1.23 *Jelena Sjakste*: Electron-phonon interaction and intervalley scattering in zinc-blende semiconductors

Highly excited (hot) electrons, subject for example to strong electric fields, can be scattered from a lowest conduction band minimum to the higher minima (usually called 'valleys'), changing their mass and the performance of the devices [1]. These processes are accompanied by emission or absorption of short wavelength (intervalley) phonons. This same mechanism governs other phenomena such as the absorption of light in indirect semiconductors and the relaxation of photoexcited carriers.

This is why the corresponding electron-phonon interaction parameters, – the intervalley deformation potentials, are of particular interest in the characterization of hot electron transport, Gunn effect, hot electron photoluminescence [2] and other more fundamental properties of semiconductors such as temperature-dependent shift and broadening of electronic levels.

In this work we carry out self-consistent *ab initio* DFT (LDA) calculations for the intervalley deformation potentials in some zinc-blende-type semiconductors (GaAs, GaP). 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 [3,4].

[1] J.B. Gunn, Solid State Commun. **1** (1963) 88.

[2] D.Y. Oberli, J. Shah, T.C. Damen, Phys. Rev. B **40** (1989) 1323.

[3] J.Q. Wang, Z.Q. Gu, M.F. Li, W.Y. Lai, Phys. Rev. B **46** (1992) 12358.

[4] V. Aninkevičius, V. Bareikis, R. Kailius, J. Liberis, I. Matulioniene, A. Matulionis, P. Sakalas, and R. Šaltis, Phys. Rev. B **53** (1996) 6893.

## 1.24 *Mauro Bruno*: Electronic and Optical properties of Ge-nanowires beyond the one particle approach

Within a first-principle DFT framework we have calculated the structural, electronic and optical properties of hydrogenated Germanium nanowires of different sizes and different spatial orientations. We have analyzed how the geometrical relaxation affects the optoelectronic properties. Moreover for the smallest structures, we have calculated the electronic and optical properties overcoming the one-particle approach. Large self-energy corrections, compared to the bulk ones, have been found together with strong excitonic effects. An important anisotropic behavior of local-field effects is observed for light polarized parallel and perpendicular to the wire axis as in other one dimensional systems. The influence of the wire-wire interaction on the electronic and optical properties has been also studied.

## 1.25 *Xinzheng Li*: Extension of the linearized tetrahedron method for q-dependent integrations

Brillouin Zone (BZ) integrations are a crucial part of any code for calculating electronic properties. In the case of metals, convergence is lowered by the fact that the integration volume is not the whole BZ but only the region surrounded by the Fermi surface. The

most efficient method in this case is the linearized tetrahedron method, which, through the linearization of the bands allows a more accurate determination of the integration region.

In the GW method, the calculation of the polarization and the selfenergy requires BZ-integrations of operators depending on two k-points (or one k point and the vector  $q$  joining them). With the purpose of treating metals with the all-electron GW-code we are developing, we have extended the linearized tetrahedron method into the case of  $q$ -dependent integration. Our results show an excellent agreement with the analytical solutions for the free electron gas with a reasonable number of k-points.

## 1.26 *Roman Leitsmann*: Nonlinear optical coefficients including electron-hole interaction

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 other hand, 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 (SHG) and show analytically the equivalence of the approaches[1,2] within the independent-particle approximation. In addition, we develop an approach to include excitonic effects in the SHG spectra over a wide energy range. Numerical results for bulk GaAs are presented which show the large influence of technical parameters on the final results.

[1] J.L.P. Hughes and J.E. Sipe, Phys. Rev. B 53, 10751 (1996).

[2] B. Adolph and F. Bechstedt, Phys. Rev. B 57, 6519 (1998).

[3] S. Bergfeld and W. Daum, Phys. Rev. Lett. 90, 036801 (2003).

## 1.27 *Viviana Garbuio*: Ab-initio study of the excited state properties of liquid water

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 so called GW approximation to take fully into account exchange and correlations effects. We obtain an average HOMO-LUMO gap of 4.44 eV at DFT-LDA level, in good agreement with previous calculations. The electronic gap is then modified by the GW corrections up to 7.80 eV. The optical absorption spectra are calculated by solving the Bethe-Salpeter equation, which includes excitonic effects by explicitly introducing the electron-hole coulomb interaction. The many-body absorption spectra result modified, with respect to the DFT spectra, suggesting the presence of important excitonic effects at low energies.

## 1.28 *Yann Pouillon*: Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism

There is a growing need for exchange-correlation (XC) functionals going beyond the Local-Density and Generalized-Gradient Approximations (LDA and GGA), in particular in systems where van der Waals (vdW) interactions play a crucial role. These can only be taken into account by means of fully non-local XC functionals, which often 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).

However, a spurious maximum in the dissociation curve was evidenced for the  $N_2$  [3] and  $H_2$  [4] molecules. It may result from either (a)  $H_2$  and  $N_2$  being pathological cases, or (b) the lack of self-consistency, as well as (c) the RPA being insufficient to describe the dissociation regime. In order to tackle point (a), we are examining the dissociation of several diatomic molecules, such as  $LiH$ ,  $Be_2$ ,  $Mg_2$  and  $Ca_2$  both within the LDA/GGA and the ACFD frameworks. Nevertheless, the calculations we have already carried out on  $Be_2$  using ABINIT default pseudopotentials show a huge bump at intermediate range too. We are now exploring thoroughly the influence of several parameters, such as cell size, number of bands, and pseudopotential on both the quality of the final results and the characteristics of the bump.

[1] W. Kohn, Y. Meir, and D.E. Makarov, *Phys. Rev. Lett.* **80**, 4153 (1998).

[2] M. Fuchs and X. Gonze, *Phys. Rev. B* **65**, 235109 (2002).

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## 1.29 *Francesco Sottile*: Optical absorption spectra of porphyrins

The electronic excitation spectra of porphyrin-based systems are of central importance for biological processes like, just to cite one of the most important, the capture of light of chlorophyll (photosynthesis). We perform ab initio calculations of optical spectra of porphyrin-based systems in the framework of time dependent density functional theory: particular accent is posed on the role of the central transition-metal atom as well as role of the environment. We discuss the results obtained and illustrate what are the next steps in our studies of the photoexcited dynamics of porphyrin-based complexes.