

# TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS

## 3rd International Workshop and School

Benasque (Spain), August 31 – September 15, 2008

A. Rubio (Univ. País Vasco, ETSF, and DIPC),  
E. K. U. Gross (Freie Universität Berlin),  
M. A. L. Marques (LPMCN, Université Lyon I),  
F. Nogueira (CFC, Univ. de Coimbra)

Supported by:



# School Poster Session

## Electronic structure of topologically modified graphene sheets

Joice Araújo

UFMG - Universidade Federal de Minas Gerais

In this work, we address the electronic structure of graphene sheets modified by the addition of various different concentrations of heptagons and pentagons. An adjacent heptagon-pentagon pair (HPP), also known as a Stone-Waller defect, is a common defect in graphene and graphene-derived carbon forms such as nanotubes and fullerenes. An HPP is formed when a bond in the honeycomb network of graphene is rotated by 90°. Previously, Crespi et al. [1] have considered the electronic properties of planar graphene geometry in which all the hexagons were replaced by HPP's. The structure was shown to behave as a covalent metal, with a non-zero density of states at the Fermi level. In the present work, we consider graphene sheets consisting of dissociated HPP's. The dissociation of HPP's leads to the possibility of both planar and corrugated geometries, the latter being a result of non-null local curvatures at the heptagons and pentagons. We find the corrugated geometries to be more stable than the planar ones, and address the electronic structure of both varieties. We find that graphene sheets consisting of dissociated HPP's could behave as a metal, a semiconductor, or a semimetal, depending on the concentration of HPP's. We also address the electronic structure and energetics of grain-boundaries in graphene, as observed in a recent scanning tunneling microscopy study [2]. The grain boundary (GB) geometry is formed by HPP units along the GB line. We investigate the main electronic and elastic-energy features of GB's in this material as a function of the tilt angle.

[1] Vincent H. Crespi et al, Physical Review B 53, p. 303-305, (1996).

[2] P. Simonis et al; Surface Science 511, p. 319-322 (2002).

## Computations on Metal-Phthalocyanines

Jakub Baran

Tyndall National Institute, University College Cork, Computational Modelling Group

Deposited and/or self-assembled on metal electrodes, metal-phthalocyanine are attractive candidates for novel molecular sensors, memory, and light-harvesting components. The knowledge of their molecular geometry and electronic structure are crucial points in order to understand their interactions with surfaces. To study the adsorption of metal-phthalocyanines (MPc (M=Co, Sn, Pb) bonded parallel on the Ag(111) surface we have performed electronic structure calculations using a cluster representation (55 and 169 silver atoms) of the surface within the framework of density functional theory (DFT) [1]. Our calculations use the generalized gradient approximation (GGA) parameterization by Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation energy [2] and multipole accelerated

resolution of identity method [3]. We have investigated bonding on three surface adsorption sites (hcp-hollow, fcc-hollow and on-top). For each of these systems we have found good agreement in binding geometries with experimental data obtained by normal incidence X-ray standing wave spectroscopy (NIXSW) [4,5]. Binding energies and geometries for all systems are given. We propose flat chemisorption of respective MPcs on Ag(111).

## Absorption geometry and interfacial properties for CH<sub>3</sub>SH self assembled on Cu(110)

Stefania D'Agostino, Letizia Chiodo, Fabio Della Sala, Roberto Cingolani and Rosaria Rinaldi

National Nanotechnology Laboratory, CNR-INFM, I-73100 Lecce, Italy

With the aim to characterize the real nature of the S-Cu bond and to shed light on the interfacial electrostatics for a copper surface, an ab initio study has been carried out for CH<sub>3</sub>SH self-assembled on a Cu(110) substrate [1]. Calculations have been performed in the framework of the Density Functional Theory using the Generalized Gradient Approximation (GGA) [2] and the plane-waves code PWSCF [3] with Ultrasoft Pseudopotentials [4]. Theoretical results suggest that the binding of the methanethiol to the substrate is rather weak and that the molecular structure is correspondingly almost unaffected by the adsorption on metal. Otherwise, when CH<sub>3</sub>SH decomposes by deprotonation producing methanethiolate (CH<sub>3</sub>S), stronger chemical bonds appear between sulfur of CH<sub>3</sub>S-radical and the surface Cu atoms. Experimental results on structural properties for this system give no clear informations on the adsorption site [5,6]. Therefore for a p(2x2) and a c(2x2) CH<sub>3</sub>S coverage, a preliminary structural analysis on the relaxed geometries for various adsorption configurations has been necessary to elucidate the electronic properties at the molecule-substrate interface. By studying the partial density of states (PDOS) and the electrons accumulation/depletion regions in the real space, a strong hybridization among p-orbitals of sulfur and d-states from the metal substrate was deduced. Work function variations of CH<sub>3</sub>S/Cu(110) were also monitored when the coverage changes between 0 ML and 1 ML: theoretical results prove an evident non-linear decrease at increasing coverage and this effect can be explained by the negative dipole of the adsorbate together with the interdipole effects.

[1] S. D'Agostino, L. Chiodo, F. Della Sala, R. Cingolani, R. Rinaldi, *Phys. Rev. B* **75**, 195444 (2007).

[2] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.* **77**, 3865 (1996).

[3] S. Baroni, A. Dal Corso, S. De Gironcoli, P. Giannozzi, <http://www.pwscf.org/> (2001).

[4] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

[5] A. F. Carley, P. R. Davies, R. V. Jones, K. R. Harikumar, M. Wyn Roberts, and C. J. Welsby, *Topics in Catalysis* **22**, 161 (2003).

[6] J. G. Lee and J. T. Yates, *J. Phys. Chem. B* **107**, 10540 (2003).

# Interpretation of valence band and resonant photoemission in the multiple scattering approach

Fabiana Da Pieve

Institut Carnot de Bourgogne, Université de Bourgogne

Valence band photoemission and resonant photoemission are widely used spectroscopic techniques. In particular, energy and angle resolved ultraviolet photoemission is a powerful technique for mapping energy bands of solids, while resonant photoemission has often been exploited to study correlation effects. We have extended the real space multiple scattering approach with the aim of interpreting experimental diffraction patterns and energy spectra obtained from transition metals both in the UV and X-ray regime. The LMTO method has been used for the calculation of potentials in the atomic sphere approximation and the exchange correlation part was calculated in the LDA approximation. For valence band photoemission we show that: 1) the real space multiple scattering approach, based on a finite cluster method, reproduces the band structure of the systems under investigation, as well as heavier band structure calculation 2) a dual behaviour between itinerant and well localized electronic states is observed when analyzing the anisotropy of UV diffraction patterns from Cu(111) when the analysis is performed energy-resolved or energy integrated For resonant photoemission in TiO<sub>2</sub> we show that: 1) we can describe the dependence of the spectra on photon energies and we reproduce the Fano profile originating from the interference between the resonant and the direct emission process. 2) the study of diffraction patterns allows to obtain informations on the delocalization of defect states.

## Semiconducting chains of gold and silver

Frederico Ramos Fioravante

UFMG - Universidade Federal de Minas Gerais

Nanowires (NWs) based on  $4d$  and  $5d$  metals are a topic of intense current interest in the physics of nanomaterials. Understanding the connection between transport and atomic structure [1], in the limit of the ultrathin monoatomic wires that have been produced experimentally [2], is crucial to the future manipulation of metallic wires and electric contacts in nanoscale electronic devices. In order to study this connection we present an investigation of the relation between the atomic structure, energetics, and the electronic structure of ultrathin nanowires. In the limit of low-atomic-density (small diameters) wires, we introduce a geometry for ultrathin Au and Ag wires that *ab initio* calculations indicate to be more stable than previously considered planar geometries for these systems, by about 0.1 eV per atom. This structure is insulating for both metals and for related Ag<sub>0.5</sub>Au<sub>0.5</sub> alloys, with gaps of 1.3 eV for Au, 0.8 eV for Ag, and varying between 0.1 eV and 1.9 eV for the alloys. The insulating nature of the geometry is not a result of Peierls instabilities, and is analyzed in terms of an interplay between geometric and electronic structure effects. We also address more compact nanowires with volumetric structures. We find that gapped structures, with competing formation energies, may occur even for gold and silver, with gaps of 0.02 eV and 0.12 eV for silver and 0.25 eV and 0.13 eV for gold. Generally, we find that hollow tube-like structures are preferred for gold, while filled dimerized structures are more stable in silver nanowires. Our calculations also suggest the possibility of a great variety of structures with formation energies differing by the room-temperature scale, with different

numbers of bands crossing the Fermi level. This would suggest that the interpretation of quantum-conductance measurements must reflect this variety of electronic behaviors for a possibly larger number of degenerate structures.

[1] D. Cheng, W. Y. Kim, S. K. Min, T. Nautiyal, and K. S. Kim, *Phys. Rev. Lett.* **96**, Art. No. 096104, 2006.

[2] J. Bettini, F. Sato, P. Z. Coura, S. O. Dantas, D. S. Galvão, and D. Ugarte, *Nature Nanotechnology* **1**, 182 (2006).

## **CdSe nanocrystals under pressure**

Giorgia Fugallo

King's College London

CdSe is an interesting material because of its efficient room temperature electro-luminescence and nano-electric device applications. In particular CdSe nanocrystals exhibit a range of interesting properties that can be tuned with their size: from the colours they fluoresce with to the way they change structure under pressure. By using and adapting the metadynamics method, which is able to accelerate rare events and to explore the free energy surface of complex systems, we have simulated structural transformations in CdSe nanocrystals close to the transition pressure, without the need to overpressurize the systems typical of conventional constant pressure molecular dynamics. Results for CdSe nanocrystals of different sizes and shapes will be presented.

## **AUTOMATIZATION OF FITTING THE DFTB REPULSIVE ENERGY**

Michael Gaus, Chien-Pin Chou, Henryk Witek, Marcus Elstner

Theoretical Chemistry, TU Braunschweig, Germany

SCC-DFTB is an approximation to density functional theory (DFT), starting from a second order expansion of the DFT total energy [1]. The total energy of a system is described by two contributions: an electronic and a repulsive energy. The fitting procedure for developing accurate and transferable parameters for the repulsive part has been cumbersome in the past. Recently first attempts were made for automating such a fitting procedure [2]. We are developing techniques for automatically producing repulsive parameters, following two approaches: 1) using a genetic algorithm and 2) by solving a linear equation system. We present preliminary results of these parameters for hydrocarbons as well as for small systems containing oxygen and hydrogen.

[1] M. Elstner et al., *PRB* 58(11) pp. 7260-7268 (1998).

[2] J. Knaup et al., *JPCA* 111(26) pp. 5637-5641 (2007).

# Nickel oxide: spin and exchange effects

Matteo Guzzo

Università Statale di Milano - Bicocca

The issue at the origin of this work is the nature underlying the considerable gap (4.3 eV) of nickel oxide. The question is whether the spin or the exchange interaction could contribute to its formation, or if maybe both could explain it. NiO is historically the prototype of the so-called "strongly correlated materials". The problem of its correct theoretical description was raised by N.F. Mott, since the paramagnetic phase of NiO was badly described by "band theories". He stated that strong correlation (strong d-electrons localization and repulsion) causes gap opening (Hubbard insulator) and prevents a band structure description (independent electrons approximation). The DFT-LDA calculations show us that spin leads to an insulating Kohn-Sham structure, whereas without it the system is in a metallic configuration. This is a well known result in literature. When a HF calculation is performed without accounting for the spin, NiO is still predicted to be a metal, as the DOS is non-zero at the Fermi level. Nevertheless, the density of states is heavily modified and loses most of its weight around the Fermi level. Introducing the spin in LSDA produces an insulating structure with an energy gap of about 0.5 eV, and the subsequent Hartree-Fock calculation predicts an insulator as well, with a high energy gap of about 14 eV (Hartree-Fock is known to highly overestimate the gap).

## Discontinuity of the dielectric function close to Bragg reflections: Graphite.

R. Hambach, C. Giorgetti, N. Hiraoka, Y. Q. Cai, F. Sottile, A. G. Marinopoulos, F. Bechstedt, and Lucia Reining

Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA/DSM, Palaiseau, France;  
European Theoretical Spectroscopy Facility (ETSF); Institut für Festkörpertheorie und  
-optik, Friedrich-Schiller-Universität Jena, Germany; National Synchrotron Radiation  
Research Center, Taiwan; Department of Physics and Astronomy, Vanderbilt University, USA

As an example for layered materials, the loss function of graphite was studied for momentum transfers  $q$  beyond the first Brillouin zone. Surprisingly, near Bragg reflections, the spectra are highly dependent on very small changes in  $q$ , which reminds the non-analyticity of the loss function in the optical limit ( $q \rightarrow 0$ ). The effect is investigated by means of first principle calculations within the random phase approximation and experimentally confirmed by inelastic x-ray spectroscopy measurements. We explain this discontinuity by means of crystal local field effects that become particularly important and cause a strong coupling between excitations at small and large momentum transfers.

# Full-Potential Multiple Scattering Theory with Space-Filling Cells for bound and continuum states

Keisuke Hatada

Multiple scattering (MS) approach has been widely used to solve the Schrödinger equation (SE) (or the associated Lippmann-Schwinger equation) both for scattering and bound states with energy dependent complex exchange correlation potential. Most practical calculations have been done within the so called “Muffin-Tin ( MT ) approximation” using cells of spherical shape, inside which the potential is spherically averaged and constant in the interstitial region. However the MT approximation cannot properly describe a great number of physical systems, ranging from open lattices to molecular systems with substantial anisotropy ( eg. systems of biological interest ), to surfaces and interfaces.

The first practical attempt to go beyond MT approximation with arbitrary shaped potential was done by Williams. [1] However it was soon realized that the method presented convergence problems in the angular momentum (AM) expansion. [2] One of the difficulties was to solve SE for arbitrarily shaped potential cells.

The present approach instead expands in spherical harmonics the wave function rather than the shaped potential, so that the convergence problem is completely avoided and we can treat arbitrarily shaped potential without any approximation. Together with appropriate numerical techniques this approach is seen to overcome the historical problem completely. [3]

We have tested the present FP-MS scheme against the analytical solution of the absorption cross section for hydrogen-like atoms in the case of the  $\text{Li}^{2+}$  atom ( $Z=3$ ) by partitioning the system into 15 cells and an outer sphere. We show applications of the method to the calculation of the absorption spectra of molecules,  $\text{Se}_2$  and  $\text{GeCl}_4$ , and crystalline systems,  $\text{Si}$  and  $\text{SiO}_2$ . We obtained significant improvement over the MT approximation in all cases.

[1] A. R. Williams and J. van W. Morgan, *J. Phys. C: Solid State Phys.* 7 (1974) 37.

[2] Y. Wang et al., *Phys. Rev. B* 49 (1994) 5028.

[3] K. Hatada et al., *Phys. Rev. B* 76 (2007) 060102(R).

## Second order harmonic generation in crystalline semiconductors

Hannes Huebener

LSI, Ecole Polytechnique, Palaiseau, France

A comprehensive understanding of the nonlinear optical properties of solids is crucial for the improvement of nonlinear materials and devices and provides an opportunity to search for new materials. However, the theoretical description of nonlinear effects in solids is a formidable task and important difficulties have delayed any accurate calculations for many years. In principle the optical response of a material depends strongly on local field effects and electron correlations and important advances have been made recently to account for these in the linear response using Time Dependent Density Functional Theory (TDDFT) [1]. We formulate a derivation for the calculation of the second-order susceptibility tensor for crystals of any symmetry within TDDFT. For cubic symmetries, we show how this approach can be simplified and expressed in terms of the second order response function and

of the dielectric function. Numerical results will be presented for several materials with zincblende structure.

[1] F. Sottile, V. Olevano et L. Reining, Phys. Rev. Lett. 91, 056402 (2003).

## A relativistic optimized potential method for spin-polarized systems

Diemo Koedderitzsch

LMU Muenchen, Dept. Chemie/Biochemie

We present the first implementation of a **spin-polarized relativistic** optimized potential method (ROPM) for solids in the framework of spin-density functional theory. We have reformulated the ROPM in terms of Green's functions and sketch our subsequent implementation within the framework of the KKR multiple-scattering theory for solids. This method is an all electron approach. All quantities are expanded in a fully relativistic spin-angular representation; spin-orbit coupling is treated **non**-perturbatively. Core-core interactions are determined along the lines of the method presented in Ref. [1], core-valence (band states) and valence-valence interactions are expressed in terms of the relativistic multiple-scattering representation. We used exact exchange (EXX) as a first step towards a complete exchange correlation functional. Results for simple metals are discussed.

[1] D. Ködderitzsch, H. Ebert, E. Engel, Phys. Rev. **B77**, 045101 (2008)

## DFT analysis of the structural, electronic, and spectral properties of zFP538 chromophore

Karina Kornobis

UNIVERSITY OF LOUISVILLE, KY, USA

The yellow fluorescent protein zFP538 isolated from button polyp *Zoanthus* belongs to a family of GFP-like proteins. The unique ability to form chromophore in an auto-catalytic reaction makes the group an attractive tool in biotechnology considering for instance applications like monitoring gene expressions or localizing proteins in living cells. Although numerous studies of the photophysical properties of GFP homologues, up to date, little is known about the nature of zFP538. The structure of its chromophore is of special interests, as the excitation and emission maxima have been found right between those of GFP and DsRed. The recently proposed structure of zFP538 chromophore contains an additional heterocyclic ring with the C=N bond comparing to GFP. As a result of increased conjugation in the chromophore the red shifts in spectra are being observed.

The main purpose of this study was the investigation of the structural, electronic and spectral properties of the chromophore zFP538 using theoretical methods. Based on Density Functional Theory (DFT) different protonation states of cis and trans isomers of zFP538 chromophore have been studied. The employed calculations let to analyse the dependence of zFP538 properties on environmental changes. To predict electronic excitation bands Time Dependent DFT (TDDFT) method has been chosen. All results presented in this work are significant in understanding details of zFP535 chromophore nature, as well as, bring new insights into the spectral properties of GFP-like proteins.

# Optical Properties of Silicon Nanoclusters

Olli Lehtonen and Dage Sundholm

Department of Chemistry, University of Helsinki, Finland

Light emitting silicon nanoclusters have been studied extensively during last years. However, the actual mechanism responsible for the strong optical activity of the nanoclusters has remained unsolved. The molecular structures and electronic excitation spectra of silicon nanoclusters up to  $\text{Si}_{329}\text{H}_{196}$  have been studied using time-dependent density functional theory. The computed excitation energies are often in good agreement with the experimental observations, but the oscillator strengths of the transitions are usually significantly smaller than reported in experiments. We have also proposed new class of silicon nanoclusters with silane modified surfaces, which have both energies and oscillator strengths in accordance with experiments, as possible candidates for strongly luminescent silicon nanoclusters.

## Time-dependent density functional theory in projector augmented wave method

Lauri Lehtovaara

Helsinki University of Technology

In recent years, the time-dependent density functional theory has become a popular tool for calculating excited state properties such as linear and non-linear optical response. We have implemented the time-dependent density functional theory (TDDFT) using the projector augmented wave (PAW) method into the electronic structure program GPAW. Two different approaches, linear response and time propagation, are available. The real-space PAW has several advantages for both ground state and time-dependent calculations: single convergence parameter (grid spacing), different boundary conditions, reduced number of grid points (compared to pseudopotentials), and efficient parallelization using domain decomposition. As an example, we show a direct comparison of the linear absorption spectrum of the benzene molecule obtained via the time-propagation after a delta pulse and via the linear response calculation. We also demonstrate the excellent parallel performance of the time-propagation approach.

## Quantum transport with correlations in Kadanoff-Baym approach

Petri MYÖHÄNEN

University of Jyväskylä, Finland

We consider an interacting two-level system coupled to macroscopic non-interacting electron reservoirs (leads). We apply the theory of non-equilibrium Green's functions to study the transient properties of the system driven by time-dependent bias voltage in different many-body approximations. Concepts such as history dependence, correlations and memory effects are also studied and analyzed.

# The Lieb-Oxford lower bound on the exchange-correlation energy of atoms, molecules, solids and model Hamiltonians

Mariana Odashima

Universidade de São Paulo, Brazil

Density-functional theory (DFT) is one of the most popular and reliable approaches to the electronic-structure of matter. In DFT, ever better exchange-correlation functionals are required for the ever more precise description of many-body effects on electronic structure. Important ingredients in the construction of improved functionals are universal constraints, obeyed by all possible systems. Here we investigate one such universal property on approximate density functionals, the Lieb-Oxford lower bound on the exchange-correlation energy [1]. In a recent study [2,3] we showed, via case studies of atoms, ions, molecules, solids, and some model Hamiltonians, that the presently accepted value of this lower bound can be substantially reduced, leading to a tighter bound. We also point that different classes of systems can be classified with respect to class-specific (but not fully universal) similar bounds. A substantial change in this bound will have consequences for the performance of modern exchange-correlation functionals. Connections with the construction of such functionals will be explored.

[1] E. H. Lieb and S. Oxford, *Int. J. Quantum Chem.* 19, 427 (1981).

[2] M. M. Odashima and K. Capelle, *J. Chem. Phys.* 127, 054106 (2007). [3] M. M. Odashima and K. Capelle, *Int. J. Quantum Chem.* (accepted).

## Accelerating RI-MP2 quantum chemistry calculations with graphical processing units

Roberto Olivares-Amaya

Harvard University

We present an algorithm to accelerate quantum chemistry calculations taking advantage of the graphical processing units (GPUs) as co-processors using CUDA and CUBLAS. We implement a method to virtually expand the GPU's memory in the face of data intensive calculations. Finally we also present 1.X precision, a method that circumvents the GPU's current ability to only give single precision calculations.

## Non-adiabatic dynamics from ab-initio excited state potential energy surfaces

T. Olsen, J. Gavnholt, and J. Schiøtz

Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark.

We have generalized the method of  $\Delta$ SCF-DFT to include situations where the relevant excited state is a superposition of Kohn-Sham orbitals as is the case for adsorbates on metal surfaces. From these

surfaces we can extract non-adiabatic coupling parameters and calculate probabilities for hot substrate electrons to transfer energy to the adsorbate. We find that at the level of single electrons we always need to treat the adsorbate quantum mechanically while given a thermal distribution of hot electrons we can treat the adsorbate semiclassically at the picosecond timescale when  $T > 1000$  K.

## Hunting double excitations processes

D. Sangalli, P. Romaniello, and G. Onida

Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia (CNISM); Physics Department, Università degli Studi di Milano, I-20133 Milan, Italy; European Theoretical Spectroscopy Facility (ETSF)

The spectra of isolated systems is known to be described quite well by Casida's approach to Time-Dependent Density-Functional-Theory (TDDFT) for many closed shell systems, within the adiabatic approximation. On the other hand the same framework is known to perform quite poorly for open shell systems. The reason of this deficiency can be found in the failure of the adiabatic approximation in describing double excitations, that leads, therefore, to the break of the spin symmetries of the system [1]. One would encounter analogous deficiencies using the Bethe Salpeter (BSE) approach with a static kernel  $W_{\text{RPA}}(\omega = 0)$ . A solution to the problem is the use of dynamical kernels. This work aims to scrutinize the dynamical structure that the BSE kernel and/or the exchange correlation kernel of TDDFT should have in order to describe double excitations. Following the same line of previous works on the study of removal/addition of electrons [2] and of excited states of nuclei [3, 4], we obtain the Feynman diagrams which should be included in the kernel. We show some preliminary tests on model systems and we give some guidelines for future developments.

- [1] Mark E. Casida, J. Chem. Phys. **122**, 054111 (2005).
- [2] L. S. Cederbaum and J. Schirmer, Z. Physik **271**, 221-227 (1974).
- [3] D.J. Rowe, Nuclear Collective Motion, Methuen, London (1970).
- [4] C. Yannoules, M. Dworzecka, J.J. Griffin, Nucl.Phys. **A379**, 239 (1983).

## Efficient $O(N^2)$ approach to solve the Bethe-Salpeter equation for excitonic bound states

A. Schleife, F. Fuchs, C. Rödl, and F. Bechstedt

Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität and European Theoretical Spectroscopy Facility (ETSF), Max-Wien-Platz 1, 07743, Jena, Germany

The accurate calculation and parameter-free prediction of optical spectra including excitonic effects is highly desirable for both fundamental and applied research. Excitonic effects can be treated in the framework of many-body perturbation theory by solving the Bethe-Salpeter equation (BSE), which can be recast in an eigenvalue problem for the electron-hole Hamiltonian  $\hat{H}$ .

Although for the computation of excitonic optical spectra in an extended frequency range efficient methods are available, the determination and analysis of individual exciton states (e.g. excitonic

bound states or dark excitons) still requires the diagonalization of the electron-hole Hamiltonian  $\hat{H}$ . We present a numerically efficient approach for the calculation of exciton states with quadratically scaling complexity, which significantly diminishes the computational costs compared to the commonly used cubically scaling direct-diagonalization schemes. The accuracy and performance of this approach is demonstrated by solving the BSE numerically for the Wannier-Mott two-band model in k space and the semiconductors MgO and InN. For the convergence with respect to the k-point sampling a general trend is identified, which can be used to extrapolate converged results for the binding energies of the lowest bound states.

## **Ab initio study of the mechanism of production of photosensitized singlet oxygen by means of phenalenone**

Mireia Segado and Mar Reguero

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo, s/n-Campus Sescelades, 43007 Tarragona, Spain

The first excited state of molecular oxygen, singlet oxygen, is a reactive species that can mediate the oxidative degradation of many molecules. For most practical purposes, singlet oxygen is conveniently generated in a photosensitizing process wherein a molecule absorbs light and transfers a fraction of the excitation energy to the triplet ground state of oxygen to form singlet molecular oxygen.

Phenalenone (also called perinaphthenone, PN, fig.1) is a universal reference for sensitization of singlet oxygen. It's soluble in a large variety of solvents and its quantum yield for singlet oxygen production,  $\Phi_{\Delta}$ , is close to unity in most of the solvents. PN is present as a pollutant in the environment, and it is the skeleton of a lot of secondary metabolites that plants create for defence against pathogens. Its photodynamic therapy is demonstrated.

PN possesses an  $\pi,\pi$ -conjugated carbonyl group that is the main responsible for its photophysical and photochemical properties. After initial absorption to the second singlet excited state, the main deactivation process leads the system to the triplet state through an intersystem crossing with a quantum yield close to unity. Whereas triplet  $n\pi^*$  states undergo photochemical reactions such abstraction of hydrogen, triplets  $\pi\pi^*$  states show very efficient energy transfer reactions such as energy transfer to molecular oxygen. Therefore,  $\pi\pi^*$  depends on the quantum yield of intersystem crossing and the character and the relative energies of the lowest triplet states.

The purpose of this work is to know the energetics and character of the lowest excited states of PN and elucidate the reaction path that populates the triplet state responsible of the sensitization of molecular oxygen. With this aim we have performed high level ab initio calculations with the protocol CASSCF/MS-CASPT2 to characterize the potential energy surfaces of the lowest singlet and triplet excited states of PN. We have calculated the vertical spectrum of the ground state minimum, located the critical points and crossing points (singlet-triplet crossing points and conical intersections) of the lowest PES, compute minimum energy paths (MEP's) and calculate spin-orbit couplings when necessary.

# Characterization of (BN)<sub>n</sub> Cage Emission Band Gaps exploiting Massively Parallel Analytical TDDFT Gradients

Huub J. J. van Dam and Stephen A. Shevlin

STFC Daresbury Laboratory; University College London

Time dependent density functional theory is a main stream method for studying excitations in molecules and clusters. Gradients of the excitation energy [1] are needed to study the potential energy surface of excited states effectively. To extend the capabilities of existing implementations we have implemented time dependent density functional theory gradients in a modified version of NWChem [2] targeting massively parallel computing platforms. The resulting implementation has been demonstrated to scale up to at least 1000 processors. As a demonstration of the potential of this implementation we studied the optical properties of Boron-Nitride clusters. Boron-Nitrides are members of a family of III-IV semi conductors which can exhibit lasing as well as light emission. Of particular interest are cage structures that can be formed. The structure-property relationships were characterised focussing on absorption band gap modification by size selection and defects [3]. Exploiting the new capabilities the work was extended to characterise the emission band gaps as well.

[1] Furche, F.; Ahlrichs, R. *J. Chem. Phys.* 2002, 117, 7433.

[2] Kendall, R. A.; Aprà, E.; Bernholdt, D. E.; Bylaska, E. J.; Dupuis, M.; Fann, G. I.; Harrison, R. J.; Ju, J.; Nichols, J. A.; Nieplocha, J.; Straatsma, T. P.; Windus, T. L.; Wong, A. T. *Comp. Phys. Comm.* 2000, 128, 260.

[3] Shevlin, S. A.; Guo, Z. X.; van Dam, H. J. J.; Sherwood, P.; Catlow, C. R. A.; Sokol, A. A.; Woodley, S. M. *Phys. Chem. Chem. Phys.* 2008, 10, 1944, doi:10.1039/b719838h.

## Optical excitations of surface defects in realistic nanoscale silica cluster

Martijn Zwijnenburg

Universitat de Barcelona

We will discuss our work on predicting the absorption and luminescence spectra of realistic nanoscale silica cluster using TD-DFT and CASPT2. Special attention will be paid to a class of charge transfer defects that seem to require hybrid density functionals with an elevated fraction of Hartree-Fock like exchange for a proper description.

# Workshop Poster Session

## Theoretical spectroscopy for finite systems

Arjan Berger

LSI, Ecole Polytechnique, Route de Saclay, 91128, Palaiseau, France

This work deals with the calculation of linear-response properties of finite systems using time-dependent density-functional theory as well as many-body perturbation theory, namely GW and the Bethe-Salpeter equation. In particular we are interested in the performance of these methods when applied to large finite systems, e.g. biological systems. The existing theory we use for extended systems needs to be reformulated in order to make these calculations for large finite systems feasible. In this work we will discuss how we can obtain an efficient formulation for these systems.

## GPAW: Projector-augmented wave method on real-space grids

Jussi Enkovaara

CSC - Scientific Computing, Helsinki, Finland

We have developed a program package GPAW for density functional calculations using real-space grids together with the projector augmented wave method. Real-space description allows flexible boundary conditions, efficient multigrid algorithms, and efficient parallelization with domain decomposition, while projector-augmented wave method enables accurate calculations for the whole periodic table. We present some applications of the method and demonstrate its efficiency especially in large scale parallel calculations.

## Time-dependent natural orbitals with a phase

Klaas Giesbertz

VU University, Amsterdam

Density matrix functional theory (DMFT) has proven to be quite successful in producing ground state energies of bond breaking systems. Recently a also excited state curves became accessible by writing down the time-dependent DMFT equations [1,2]. However, the adiabatic approximation does not coincide with the static response equations in an earlier publication by Pernal [3]. This incompatibility can be lifted by an explicit treatment of a phase factor of the natural orbitals (NOs), although they are traditionally not defined, since the NOs are defined to be the eigenfunctions of the one-body reduced

density matrix. An additional advantage is that the two-electron system can truly be treated exactly, i.e. all single, double, triplet excitations are reproduced by the response equations that include the phase of the NOs.

[1] K. Pernal, O. Gritsenko and E.J. Baerends, Phys. Rev. A 75, 012506 (2007)

[2] K. Pernal, K. Giesbertz, O. Gritsenko and E.J. Baerends, J. Chem. Phys. 127, 214101(2007)

[3] K. Pernal and E.J. Baerends, J. Chem. Phys. 124, 014102 (2006)

## **Linear density response function within the time-dependent exact-exchange approximation**

Maria Hellgren

Lund University

We have calculated the frequency-dependent exact exchange (EXX) kernel of time-dependent (TD) density functional theory employing our recently proposed computational method based on cubic splines. With this kernel we have calculated the linear density response function and obtained static polarizabilities, van der Waals coefficients and correlation energies for all spherical spin compensated atoms up to Argon. Some discrete excitation energies have also been calculated for Be and Ne. As might be expected, the results of the TDEXX approximation are close to those of TD Hartree-Fock theory. In addition, correlation energies obtained by integrating over the strength of the Coulomb interaction turn out to be highly accurate.

## **Excitation Energy Transfer from a TDDFT real-time propagation approach**

Dirk Hofmann, Stephan Kümmel

Department of Theoretical Physics, University of Bayreuth, 95440 Bayreuth, Germany

Excitation energy transfer is a key process in the light-harvesting mechanism initializing the energy-converting machinery of plants and photosynthetic bacteria. Understanding how energy is transferred from one molecule to another one is a prerequisite for the tailored design of organic materials that serve in applications such as light-emitting diodes and organic solar cells. The standard method to interpret experimental data of excitation energy transfer between two molecules separated by a distance  $R$  is the so-called Förster theory. This theory considers separated donor and acceptor molecules interacting via a Coulomb interaction that is approximated as a dipole-dipole coupling. One of this theory's characteristics is a  $R^{-6}$ -dependence of the energy transfer rate. The aim of our work is to describe excitation energy transfer in the framework of TDDFT with real-time propagation. This approach in principle allows to go beyond the approximations of the standard (Förster) theory. Therefore, the method can be a valuable tool to distinguish between Förster like and non-Förster like excitation energy transfer.

# Self-interaction correction and the Optimized Effective Potential

T. Körzdörfer and S. Kümmel

University of Bayreuth, Germany

Self-interaction is one of the most substantial problems in present-day density functional theory. A widely used approach to overcome this problem is the self-interaction correction (SIC) proposed by Perdew and Zunger. However, the thus given functional does not only depend on the orbitals explicitly, but it is also variant under unitary transformation of the orbitals. Here, we present a recently developed generalized version of the Optimized Effective Potential (OEP) equation which is able to deal with both problems in one go [1]. To exemplify our approach we present calculations on organic molecular semiconductors. For these pi-conjugated systems semilocal functionals have recently been shown to suffer from large self-interaction errors [2]. In addition, we investigate the influence of the self-interaction error on the polarizabilities of molecular chains [3].

[1] T. Körzdörfer, M. Mundt, and S. Kümmel, J. Chem. Phys., accepted.

[2] N. Dori et. al, Phys. Rev. B 73, 195208 (2006).

[3] T. Körzdörfer, M. Mundt, and S. Kümmel, Phys. Rev. Lett. 100, 133004 (2008).

## A density functional theory for symmetric radical cations from bonding to dissociation

Ester Livshits and Roi Baer

Institute of Chemistry and the Fritz Haber Center for Molecular Dynamics, the Hebrew University of Jerusalem, Jerusalem 91904 Israel

It is known for quite some time that approximate density functional (ADF) theories fail disastrously when describing the dissociative symmetric radical cations  $R_2^+$ . Considering this dissociation limit, previous work has shown that Hartree-Fock (HF) theory favors the  $[R^{+1}-R^0]$  charge distribution while DF approximations favor the  $[R^{+0.5}-R^{+0.5}]$ . Yet, general quantum mechanical principles indicate that both these (as well as all intermediate) average charge distributions are asymptotically energy degenerate. Thus HF and ADF theories mistakenly break the symmetry but in a contradicting way. In this letter we show how to construct system-dependent long-range corrected (LC) density functionals that can successfully treat this class of molecules, avoiding the spurious symmetry breaking. Examples and comparisons to experimental data is given for  $R=H$ , He and Ne and it is shown that the new LC theory improves considerably the theoretical description of the  $R_2^+$  bond properties, the long range form of the asymptotic potential curve as well as the atomic polarizability. The broader impact of this finding is discussed as well and it is argued that the widespread semi-empirical approach which advocates treating the LC parameter as a system-independent parameter is in fact inappropriate under general circumstances.

# Modeling the non-adiabatic vibrational excitation of HCl on Au(111)

Ilja Makkonen

University of Liverpool

Understanding the mechanisms playing a role in energy transfer when gas atoms impinge on metal surfaces is essential to understanding processes such as sticking, diffusion and reactivity. In addition to the mechanical energy transfer between molecule and surface, molecular vibrations may interact directly with electron-hole pair excitations of the solid. Recent measurements of the vibrational excitation probability of HCl molecules incident on a Au(111) surface suggest that there is a change in excitation mechanism as a function of the surface temperature from an electronically adiabatic mechanism to one involving excitation of electron-hole pairs [1]. This observation raises the question of whether the non-adiabatic coupling really is strong enough to explain the transition. We study the coupling of the HCl vibrations to electron-hole pair excitations by calculating first the non-adiabatic vibrational damping rate of the internal stretch mode for the adsorbed HCl molecule on Au(111) using time-dependent density-functional theory in the quasi-static limit [2]. Only the electronically non-adiabatic vibrational excitation is considered. We focus on constrained HCl collision trajectories along the surface normal with fixed molecule orientation and surface site. The vibrational damping rate and potential energy of the HCl molecule are calculated as a function of distance from the surface. The probability of the  $n = 0 \rightarrow 1$  vibrational excitation is obtained by solving the master equation for the vibrational population using the calculated rates. Preliminary results for a few selected trajectories show that the calculated vibrational excitation probabilities are one order of magnitude larger than the experimental ones, a finding providing strong support for the hypothesis that non-adiabatic mechanisms play an important role in vibrational excitation of an HCl molecule when it scatters from a metal surface.

[1] Q. Ran, D. Matsiev, D. J. Auerbach and A. M. Wodtke, *Phys. Rev. Lett.* 98, 237601 (2007).

[2] N Lorente and M Persson, *Faraday Discuss.* 117, 277 (2000).

## Double excitations in finite systems

Pina Romaniello

Ecole Polytechnique, Palaiseau, France

Time-dependent density-functional-theory (TDDFT) is widely used in the study of linear response properties of finite systems. However, there are difficulties in properly describing excited states which have double- and higher-excitation character, particularly important in molecules with open-shell ground-state. These states would be described if the exact TDDFT kernel were used; however, within the adiabatic approximation to the exchange-correlation (xc) kernel the calculated excitation energies have strict single-excitation character, and are fewer than the real ones. A frequency-dependent xc kernel could create extra poles in the response function, which would describe states with multiple-excitation character.

We introduce a frequency-dependent xc kernel which can reproduce, within TDDFT, double excitations in finite systems. In order to achieve this, we use the Bethe-Salpeter equation with a dynamical

screened Coulomb interaction  $W(\omega)$  which can describe these excitations. We test this kernel on a two-electron model systems, and we find that poles corresponding to double excitations are produced. However, together with the expected energies, other poles corresponding to unphysical states appear. We attribute this deficiency to the self-screening problem the description of  $W(\omega)$  suffers from.

## **Ultrafast manipulation of electron spins in a double quantum dot device: A real-time view**

G. Stefanucci, E. Perfetto, and M. Cini

Universita di Roma Tor Vergata

We consider a double quantum dot system with two embedded and non-aligned spin impurities to manipulate the magnitude and polarization of the electron spin density. The device is attached to semi-infinite one-dimensional leads which are treated exactly. We provide a real-time description of the electron spin dynamics when a sequence of ultrafast voltage pulses acts on the device. The numerical simulations are carried out using a spin generalized and modified version of a recently proposed algorithm for the time propagation of open systems [Phys. Rev. B **72**, 035308 (2005)]. Time-dependent spin accumulations and spin currents are calculated during the entire operating regime which includes spin injection and read-out processes. The full knowledge of the electron dynamics allows us to engineer the transient responses and improve the device performance. An approximate rate equation for the electron spin is also derived and used to discuss the numerical results.

## **Contribution of electron-ion correlations to the non-adiabatic dynamics of conjugated oligomers**

Lorenzo Stella

London Centre for Nanotechnology and University College London

Non-adiabatic processes play a central role in energy transfer between electronic and ionic degrees of freedom in photoexcited conjugate polymers due to their strong electron-phonon coupling. In particular, we are interested in modelling the photogeneration of topological excitations — polarons and excitons — following an earlier vertical transition from the fully relaxed ground state to a low-lying dipole-allowed electronic level. A crucial quantity to study is the ratio between the number of charged and neutral excitations generated because the efficiency of many organic electronic devices strongly depends on it. Here we present the application of a numerical scheme based on Correlated Electron-Ion Dynamics (CEID) to a simple model of conjugated oligomers and we show that electron-ion correlations can effectively suppress the photogeneration of charged topological excitations (polarons) even when electron-electron correlations are not included. Our findings are in agreement with recent experiments and they can shed more light on the physics of organic electronic devices.

# Time-dependent density-functional theory for electron-atom scattering

Meta Van Faassen

VU University, The Netherlands

We present a method to obtain single-channel elastic electron-atom scattering phase shifts from time-dependent density functional theory (TDDFT). The system is placed in a spherical box, and TDDFT is used to calculate its discrete spectrum, from which phase shifts are deduced. Results for scattering from different atoms are shown. We also show scattering results using a finite Slater type basis set (STOs), which simplifies implementation in existing bound-state DFT computer codes.