

O 49: Ab-initio approaches to excitations in condensed matter II

Time: Thursday 10:30–13:30

Location: SCH 251

O 49.1 Thu 10:30 SCH 251

Effects of electron-phonon interaction beyond mean-field approximation in the non-adiabatic dynamics of photo-excited short polyacetylene chains — ●LORENZO STELLA — London Centre for Nanotechnology, London, United Kingdom — University College London, London, United Kingdom

Conjugated polymers, of which polyacetylene is the simplest example, combine good mechanical and electronic properties that may be exploited in future technological applications. To this end, a proper description of photo-generation of charged and neutral excitations is crucial. In particular, if quantum vibrational modes (phonons) can be excited, the adiabatic approximation is no longer applicable and this will affect the transfer of energy from the electronic excitations. I show here that neglecting quantum fluctuations of atoms can lead to a qualitatively wrong account of the relaxation dynamics of photo-excited short polyacetylene chains. Indeed, even at zero temperature, quantum fluctuations of the molecular degrees of freedom can trigger the decay of an excited electronic state, through spontaneous emission of phonons: within a mean-field approach, such a process cannot be described at all. A proper study of this quantum phenomenon is given here by an improved version of Correlated Electron-Ion Dynamics (CEID) which includes quantum fluctuations of atoms about their mean-field trajectories in a converging perturbative way. This method is stable, efficient and provides a smooth evolution for both electronic and molecular degrees of freedom. Implications of the obtained results on the efficiency of conjugated polymer devices are also discussed.

O 49.2 Thu 10:45 SCH 251

Fully relativistic one-step theory of photoemission: chemical disorder and correlation — ●JAN MINAR, JURGEN BRAUN, and HUBERT EBERT — Dep. Chemie und Biochemie, LMU München, Germany

We present a generalized version of the fully relativistic one-step model of photoemission, which takes into account chemical disorder and electronic correlation on an equal footing. The electronic structure input is calculated within the Coherent Potential Approximation (CPA) alloy theory. The spectroscopic analysis itself is based on the configurationally averaged photocurrent first proposed by [1]. Both, electronic structure and photoemission calculations have been performed by use of the upgraded version of the Munich SPR-KKR program package [2]. The formalism is applicable to arbitrary two-dimensional systems and photon energies ranging from the ultraviolet to the hard X-ray regime. Strong electronic correlations are treated by the LSDA-DMFT approach, selfconsistently implemented in the SPR-KKR program. Here, we discuss spectroscopic data from binary intermetallic $\text{Ni}_x\text{Pd}_{1-x}$, $\text{Ag}_x\text{Au}_{1-x}$ and ternary Heusler $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ and $\text{Co}_2\text{Cr}_{1-x}\text{Fe}_x\text{Al}$ alloys as function of the concentration x .

1. P. J. Durham, J. Phys. F: Met. Phys. **11** 2475 (1981).
2. H. Ebert et al., The Munich SPR-KKR package, version 3.6, <http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR> (2008).

O 49.3 Thu 11:00 SCH 251

Transforming Nonlocality into a Frequency Dependence: A Shortcut to Spectroscopy — ●MATTEO GATTI^{1,2,3}, VALERIO OLEVANO^{1,4}, ILYA TOKATLY^{1,3}, and LUCIA REINING^{1,2} — ¹European Theoretical Spectroscopy Facility (ETSF) — ²LSI - Ecole Polytechnique, Palaiseau, France — ³Universidad del País Vasco, San Sebastian, Spain — ⁴Institut Néel, Grenoble, France

Measurable spectra are often derived from contractions of many-body Green's functions. In this way, one calculates hence more information than needed. Here we present and illustrate an in principle exact approach to construct effective potentials and kernels for the direct calculation of electronic spectra. In particular, a dynamical but local and real potential yields the spectral function needed to describe photoemission. We discuss for model solids the frequency dependence of this photoemission potential stemming from the nonlocality of the corresponding self-energy. We also show that our approach leads to a very short derivation of a kernel of time-dependent (current-)density functional theory that is known to well describe absorption and energy-loss spectra of a wide range of materials.

O 49.4 Thu 11:15 SCH 251

Kohn-Sham scheme for frequency dependent linear response — ●RYAN REQUIST and OLEG PANKRATOV — Lehrstuhl für Theoretische Festkörperphysik, Universität Erlangen-Nürnberg

Due to the so-called causality paradox, the Kohn-Sham scheme in time dependent density functional theory cannot be derived from a stationary principle of the form $\delta A/\delta n = 0$, where $A[n]$ is the density functional for the quantum mechanical action. As Vignale has recently shown [1], the density-functional formulation of the action principle contains boundary terms. Therefore, the exact exchange-correlation potential cannot be calculated from the functional derivative of a universal functional. However, we find that the second-order quasienergy, $K_v^{(2)}$, satisfies a stationary principle $\delta K_v^{(2)}/\delta n_\omega^{(1)} = 0$, where $n_\omega^{(1)}$ is the linear response density induced by a harmonic perturbation with frequency ω . This is not inconsistent with Vignale's result because boundary terms vanish in this case. The stationary principle can serve as a basis for the linear response Kohn-Sham scheme. The first-order exchange-correlation potential $v_{xc}^{(1)}$ is the functional derivative of the exchange-correlation part of $K_v^{(2)}$. With the same approach, we also find a stationary principle and linear response Kohn-Sham scheme in the time dependent extension of reduced density matrix functional theory, in which the basic variable is the one-body reduced density matrix.

- [1] G. Vignale, Phys. Rev. A, **77**, 062511 (2008).

O 49.5 Thu 11:30 SCH 251

Time-dependent density functional study of $S_1 \leftarrow S_0$ transition of 2,3-benzofluorene — ●DAVOUD POULADSAZ¹, GAEL ROUILLE², FRIEDRICH HUISKEN², MICHAEL SCHREIBER¹, and REINHARD SCHOLZ³ — ¹Institut für Physik, Technische Universität Chemnitz — ²Labor Astrophysik, Friedrich-Schiller-Universität Jena — ³Walter Schottky Institut, Technische Universität München

We have recently studied the $S_1(^1A') \leftarrow S_0(^1A')$ absorption spectrum of 2,3-benzofluorene (Bzf) [1]; the potential energy surfaces of the $S_n = 0, 1, 2$ states of Bzf have been investigated with calculations based on the time-dependent density functional theory (TD-DFT). At the B3LYP/TZ level of theory, TD-DFT does not deliver a realistic difference between the excited S_1 and S_2 potential energy surfaces, a problem which can be avoided by introducing a reference geometry where this difference coincides with the observation. In this geometry, an expression for the Herzberg-Teller corrected intensities of the vibronic bands is proposed, allowing a straightforward assignment of the observed a' modes below 900 cm^{-1} , including realistic calculated intensities. For vibronic bands at higher energies, the agreement between calculated and observed modes is deteriorated by substantial Dushinsky rotations and nonparabolicities of the potential energy surface S_1 . We consider our calculations to be the best approach to an ab initio study realized for Bzf until now since only parametrized force fields had been used before.

- [1] A. Staicu, G. Rouillé, Th. Henning, F. Huisken, D. Pouladsaz, and R. Scholz, J. Chem. Phys. **129**, 074302 (2008)

O 49.6 Thu 11:45 SCH 251

Ab-initio Study of the Electronic and Optical Properties of MnO, FeO, CoO, and NiO — ●CLAUDIA RÖDL, FRANK FUCHS, JÜRGEN FURTHMÜLLER, and FRIEDHELM BECHSTEDT — Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

Although the electronic properties of MnO, FeO, CoO, and NiO have been studied for decades, the description of the one-particle excitation spectrum of these materials remains a challenge. Quasiparticle calculations using a perturbative treatment of Hedin's *GW* approximation based on (semi)local approaches to exchange and correlation in the subjacent density-functional calculation fail to reproduce the experimental photoemission spectra.

For this reason, we use the non-local HSE03 exchange-correlation functional to obtain a reasonable starting point for a quasiparticle calculation within first-order perturbation theory and compare to results obtained within the computationally less expensive *GGA+U* scheme. The respective value for the on-site interaction U is determined by a fit to the more sophisticated HSE03+ G_0W_0 band structure.

Furthermore, we examine the optical properties of these materials. Accounting for their antiferromagnetic ordering, we solve the spin-

polarized Bethe-Salpeter equation (BSE) and calculate optical absorption spectra including excitonic and local-field effects.

O 49.7 Thu 12:00 SCH 251

Influence of free carrier absorption on the optical spectrum of ZnO — ●ANDRÉ SCHLEIFE^{1,2}, EMMANOUIL KIOUPAKIS², PATRICK RINKE², CLAUDIA RÖDL¹, FRANK FUCHS¹, CHRIS G. VAN DE WALLE², and FRIEDHELM BECHSTEDT¹ — ¹Institut für Festkörpertheorie und -optik, Jena, Germany — ²Materials Department, University of California, Santa Barbara, USA

For optoelectronic devices such as light emitting or laser diodes as well as solar cells an important aspect is the availability and controllability of transparent conducting materials. Zinc oxide as a transparent conducting oxide is strongly in the focus of scientific interest.

In this *ab-initio* study we investigate the impact of electrons in conduction bands on the optical properties. By employing density functional theory within a generalized-gradient approximation and making use of the projector-augmented wave method, we compute all-electron wave functions. They allow the calculation of optical transition matrix elements. We explicitly elucidate the Burstein-Moss shift due to the occupancy of conduction bands as well as the absorption caused by conduction-conduction band transitions on the level of the random-phase approximation within the independent quasiparticle approximation. Both effects are analyzed regarding their dependence on the free carrier concentration.

Consequences for the transparency of zinc oxide will be discussed including the dependence on the free carrier concentration.

O 49.8 Thu 12:15 SCH 251

Tailoring High-Order Harmonics: A Computational Approach Based on Time-Dependent Density-Functional Theory — ●ALBERTO CASTRO¹, ALI AKBARI², ANGEL RUBIO², and EBERHARD GROSS¹ — ¹Freie Universität Berlin, Berlin, Germany — ²University of the Basque Country, San Sebastián, España

Atoms and molecules react in complex manners when they are irradiated with high-intensity electromagnetic pulses: multi-photon, tunnelling and over-the-barrier ionisation, laser driven photo-induced isomerisations or fragmentations, and high harmonic generation are some of the non-linear effects that are observed. The so-called pulse shaping techniques can be used to design pulses that produce a desired effect. A technologically appealing possibility is to tailor the harmonic emission spectrum: enhancement of some given orders, suppressions of others, etc. We have undertaken the task of exploring this possibility from a theoretical point of view, by making use of time-dependent density-functional theory to describe the electrons, a real-space numerical representation, and various optimization techniques.

O 49.9 Thu 12:30 SCH 251

Optical properties of molecular crystals: Periodicity meets molecular deformation patterns — ●REINHARD SCHOLZ and LINUS GISSLEN — Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, 85748 Garching, Germany

In the calculation of the dielectric properties of molecular pigments, one has to reconcile the deformation of an excited molecule with the periodicity of the crystal. For a set of six perylene-based chromophores, we demonstrate that the excited geometry can be obtained most reliably when applying DFT to a modified occupation of the frontier orbitals, whereas the deformations obtained in TD-DFT remain systematically too small. In the crystalline state, electron and hole transfer mix neutral molecular excitations with charge transfer (CT) states, and as the largest transfer parameters occur along the stacking direction, they can easily be determined by *ab initio* calculations of a stacked dimer. The transition dipoles of molecular excitations and CT states can be derived from TD-DFT applied to a stacked dimer. These DFT-based calculations leave two essential parameters of the system undetermined: The transfer of a neutral excitation to its neighbours, and the energetic difference between neutral excitations and CT states. Albeit estimates for these quantities can be obtained from *ab initio* schemes, they are most precisely obtained from an exciton model accounting for the mixing of neutral molecular excitations and CT states,

together with the deformation patterns of excited and charged molecular states. From the calculated lineshapes, one can derive quite precise energies of the CT states, a key parameter for device applications.

O 49.10 Thu 12:45 SCH 251

The multiconfigurational time-dependent Hartree-Fock method for excited states: Theory and application to conjugated polymers — ●RAFAEL P. MIRANDA¹, ANDREW P. HORSFIELD², and ANDREW J. FISHER¹ — ¹Department of Physics and Astronomy, University College London, London, United Kingdom — ²Department of Materials, Imperial College London, London, United Kingdom

The solution of the time-dependent Schrödinger equation for systems of interacting electrons is generally a prohibitive task, for which approximate methods are highly desirable. One of the simplest schemes, known as the time-dependent Hartree-Fock (TDHF) approximation, consists in restricting the electronic wavefunction to a single Slater determinant. However, several physical processes of interest involve excited states which can not be properly described by a single determinant. For instance, in a photoexcitation process, absorption of a photon creates an open-shell singlet state, and thus devising a scheme which retains the proper spin symmetry requires two Slater determinants. In this work, we extend the TDHF method to such multiconfigurational states. Based on a time-dependent variational principle, we derive the optimal equations of motion for the single-particle molecular orbitals. This method, together with a classical description of the ionic degrees of freedom (mean-field approximation), is then applied to study the dynamics of photoexcitations in conjugated polymers. We show the relaxation of electron-hole pairs to form excitons and charged polarons, and discuss the modifications to the relaxation process predicted by the inclusion of the Coulomb interaction between the carriers.

O 49.11 Thu 13:00 SCH 251

Reduction of the number of orbital products and computation of molecular spectra from the Gross-Petersilka-Grabo equation — ●DIETRICH FOERSTER and PETER KOVAL — CPMOH, Université de Bordeaux 1, 351 cours de la Libération, 33405 Talence, France

Electronic excitations in molecular systems live in a space of orbital products the dimension of which is too large for effective computation.

To circumvent this well known difficulty, we identify a smaller subspace of linearly independent "dominant directions" that span the original space of products with exponential accuracy.

As a first application, we compute molecular spectra by solving, in this subspace of reduced dimensions, the Gross-Petersilka-Grabo equations rather than the equations of Casida.

Possible applications of our method include the study of excitons in molecular systems.

Reference: D. Foerster, "Elimination, in electronic structure calculations, of redundant orbital products", J. Chem. Phys. 128 (2008) 43108.

O 49.12 Thu 13:15 SCH 251

Product basis set in TDDFT: molecular absorption spectra within linear response. — ●PETER KOVAL and DIETRICH FOERSTER — CPMOH, Université de Bordeaux 1, 351 Cours de la Libération, 33405, Talence, France

We propose a new basis set [1] and corresponding method [2] to calculate of the Kohn-Sham density response function $\chi_0(\omega, \mathbf{r}, \mathbf{r}')$. Computational cost of our method scales comparatively cheaply with the number of atoms N .

Here we discuss the application of our technique to the computation of molecular absorption spectra. Spectra are calculated directly in $O(N^2)$ operations from the Gross-Petersilka-Grabo equations [3].

References:

[1] Foerster D, J. Chem. Phys. 128 034108 (2008)

[2] Foerster D, Phys. Rev. B 72 073106 (2005)

[3] Petersilka M, Gossmann U J and Gross E K U, Phys. Rev. Lett. 76 1212 (1996)