

## O 55: Theoretical methods II

Time: Wednesday 16:45–19:15

Location: MA 043

O 55.1 Wed 16:45 MA 043

**Interacting electrons in a quantum dot: A wave packet approach** — ●JOHANNES EIGLSPERGER<sup>1</sup>, SUSMITA ROY<sup>1</sup>, CHRISTIAN BRACHER<sup>2</sup>, and TOBIAS KRAMER<sup>1</sup> — <sup>1</sup>Institut für theoretische Physik, Universität Regensburg, Germany — <sup>2</sup>Physics Program, Bard College, Annandale-on-Hudson, USA

Solving quantum systems with interacting electrons is a complicated task: The antisymmetrization postulate renders calculations more and more cumbersome with increasing particle number  $n$ . The interaction between electrons entangles their dynamics, and the ensuing correlations leads to a full  $n$ -body wave function dependent upon  $n \cdot d$  variables, where  $d$  is the dimensionality of the system, instead of simpler product states of single particle wave functions.

(TD)DFT is a popular and versatile method to describe the properties of these systems in terms of the electron density only, a function of  $d$  variables. However, the quality of the results depends critically on the sophistication of the employed exchange correlation functionals.

Semiclassical techniques based on wave packets offer a complementary approach. In our method, the system is modeled using complex coherent Gaussian states which populate a classical trajectory in phase space. The evolution of the trajectory is governed by Hamilton's equations. We employ this coherent state dynamics model to study  $n$ -electron quantum dots in a magnetic field.

O 55.2 Wed 17:00 MA 043

**DFT based tight-binding with environment-dependent crystal field splittings** — ●ALEXANDER URBAN<sup>1</sup>, MATOUS MROVEC<sup>2,3</sup>, CHRISTIAN ELSÄSSER<sup>2,3</sup>, and BERND MEYER<sup>1</sup> — <sup>1</sup>ICMM/CCC, University of Erlangen-Nürnberg — <sup>2</sup>Fraunhofer IWM, Freiburg — <sup>3</sup>IAM-ZBS, Karlsruhe Institute of Technology

In traditional tight-binding (TB) models the intra-atomic (on-site) matrix elements of the Hamiltonian are approximated by constant atomic values and crystal field splittings are neglected. Using our recently developed scheme for deriving TB bond and overlap integrals from DFT calculations of arbitrary reference configurations it is, however, easy to analyze also the on-site integrals [1]. We find that the values of these matrix elements may depend strongly on the atomic environment, and neglecting the crystal field splittings introduces significant errors in the electronic structure. A new crystal field TB (CF-TB) scheme will be presented which allows to take the environmental dependence of the on-site terms into account [2]. The parameters for this straightforward extension of the Slater-Koster rules are readily accessible using our projection framework [1]. Comparisons of the CF-TB band structures and densities of states for a representative set of benchmark cases with DFT reference results demonstrate an enhanced transferability of the CF-TB parametrization.

[1] A. Urban, M. Reese, M. Mrovec, C. Elsässer, B. Meyer, *Phys. Rev. B* 84 (2011) 155119

[2] A. Urban, M. Mrovec, C. Elsässer, B. Meyer, *in preparation*

O 55.3 Wed 17:15 MA 043

**Ferrocene-Peptide Charge Transfer on Gold Surface: a First Principles Study** — ●FILIPE C. D. A. LIMA<sup>1</sup>, ARRIGO CALZOLARI<sup>2</sup>, and HELENA M. PETRILLI<sup>1</sup> — <sup>1</sup>Universidade de São Paulo, Instituto de Física - Brasil — <sup>2</sup>CNR-NANO Istituto Nanoscienze, Centro S3-Italia

Ferrocene-peptide self-assembled layers are one of the most studied redox-active assemblies on metal surfaces as prototypical models to probe heterogeneous electron transfer at hybrid interfaces. Recent experimental investigations have shown that the electron transfer in peptides can occur across long distances, by separating the donor from the acceptor. From the experimental point of view, it is not clear which charge transfer mechanism occurs in this type of system. We study the interaction of an oligo-peptide chain Fc-Gly-CSA (Ferrocene, Glycine and Cystamine) on the Au(111) from first principles calculations to evaluate its electron transfer mechanism. The method employed is based on the KS-DFT as implemented in the Quantum-ESPRESSO suite of codes, using ultrasoft pseudopotentials and the GGA-PBE exchange correlation functional to evaluate the ground-state atomic and electronic structure of the system. By analyzing the KS orbital at the Fermi Energy we see a high electronic density at the Ferrocene and minor contributions from the solvent and counter ion. On the other

hand, higher energy states mainly contributes to the gold surface. We infer the considered models are able to simulate heterogeneous electron transfer and the results indicates an electron tunneling mechanism from the Ferrocene to the Surface.

O 55.4 Wed 17:30 MA 043

**Redshift of excitons in carbon nanotubes caused by the environment polarizability: A BSE study** — ●MICHAEL ROHLFING — Fachbereich Physik, Universität Osnabrück

Optical excitations of molecular systems can be modified by their physical environment. We analyze the underlying mechanisms within many-body perturbation theory (GW approximation and Bethe-Salpeter equation, BSE), which is particularly suited to study non-local polarizability effects on the electronic structure. Here we focus on the example of a semiconducting carbon nanotube, which observes redshifts of its excitons when the tube is touched by another nanotube or other physisorbates. We show that the redshifts mostly result from the polarizability of the attached ad-system. Electronic coupling may enhance the redshifts, but depends very sensitively on the structural details of the contact.

O 55.5 Wed 17:45 MA 043

**xcitons in solids captured with bootstrap approximation for the exchange-correlation kernel of time-dependent density functional theory** — ●SANGEETA SHARMA, J. K. DEWHURST, A. SANNA, and E. K. U. GROSS — Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

The ab-initio calculation of optical absorption spectra of nanostructures and solids is a formidable task. The current state-of-the-art is based on many-body perturbation theory: one solves the Bethe-Salpeter equation (BSE). Unfortunately, solving the BSE involves diagonalizing a large matrix making this method computationally very expensive.

Time-dependent density functional theory (TDDFT) is another method able to determine neutral excitations of a system. Although formally exact, the predictions of TDDFT are only as good as the approximation of the exchange-correlation (xc) kernel. There are only a few xc-kernels which correctly reproduce the excitonic effect, but these kernels suffer from either being computationally as expensive as solving BSE or depend upon external parameters.

In our latest work we propose a new approximation[1] for xc-kernel, and demonstrate that this kernel is nearly as accurate as BSE and has the correct  $1/q^2$  behavior. The computation cost for the bootstrap kernel is minimal and no system-dependent external parameter is required.

1. S. Sharma, J. K. Dewhurst, A. Sanna, E. K. U. Gross, *Phys. Rev. Lett.*, 107, 186401 (2011).

O 55.6 Wed 18:00 MA 043

**One-particle excitation energies and optical spectra of alkali-metal fluorides, oxides and nitrides** — ●CHRISTOPH SOMMER, PETER KRÜGER, and JOHANNES POLLMANN — Institut für Festkörpertheorie, Universität Münster, D-48149 Münster, Germany

We present a comparative study of one-particle excitation energies and excitonic properties of the alkali-metal fluorides LiF, NaF and KF, oxides Li<sub>2</sub>O, Na<sub>2</sub>O and K<sub>2</sub>O as well as nitrides Li<sub>3</sub>N and Na<sub>3</sub>N. To this end, we have calculated band structures based on self-interaction corrected (SIC) pseudopotentials as well as quasiparticle energies within the GW approximation. It turns out that DFT-SIC improves the band gaps of the alkali compounds considerably in comparison to the results of standard density-functional calculations. For the alkali fluorides and oxides, the SIC band gaps are very close to those of the quasiparticle bands while somewhat larger deviations occur for the nitrides. In particular, we find for Na<sub>3</sub>N band gaps of 0.8 and 1.6 eV in SIC and GW, respectively. In LDA, on the other hand, Na<sub>3</sub>N turns out to be metallic in contradiction to experiment. We have evaluated the optical spectra of the alkali compounds by solving the Bethe-Salpeter equation for a thorough comparison with experimental results that have been derived mainly from optical data for these materials. The influence of going towards self-consistency in the screened interaction  $W$  or using SIC as a starting point for GW is also discussed. On this basis, the experimental electronic band gaps available in the literature are examined

closely.

O 55.7 Wed 18:15 MA 043

**The Role of van der Waals Interactions for Non-Metallic Solids** — •GUO-XU ZHANG, ALEXANDRE TKATCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Cohesion in non-metallic solids arises mainly from covalent bonding and/or electrostatic interactions, and it is typically assumed that van der Waals (vdW) forces play a minor role. Nevertheless, the qualitative and quantitative role of vdW interactions has been a matter of discussion for quite some time. In particular, most state-of-the-art functionals, based on the generalized gradient approximation (GGA), meta-GGA, or (screened) hybrid functionals yield systematic deviations for the lattice constants, cohesive energies, and bulk moduli for a wide range of solid-state systems. We recently demonstrated that vdW interactions play an important role for the quantitative description of cohesive properties of benchmark semiconductors and ionic solids [1]. Here we extend our study to a wide range of materials including ionic crystals, semiconductors, and insulators. The vdW energy is computed using our recently developed DFT+MBD method [2], which includes short- and long-range Coulomb screening effects, and computes the many-body vdW energy to infinite order in the dipole approximation. We show that many-body vdW interactions play a significant role for cohesive properties of non-metallic solids.

[1] G.-X. Zhang *et al.*, Phys. Rev. Lett., in print (2011); [2] A. Tkatchenko, R. A. DiStasio Jr., R. Car, and M. Scheffler, submitted.

O 55.8 Wed 18:30 MA 043

**Dispersion corrected DFT studies of molecule-surface interactions** — •KATRIN TONIGOLD and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

The interfaces between soft and condensed matter are of vital importance for technological applications as well as in biological systems. Thus, a thorough description of both the substrate-adsorbate and the adsorbate-adsorbate interactions occurring at the interface is needed. In many cases these interactions are dominated by dispersion. Unfortunately, commonly used GGA density functionals are not able to describe these long-range correlation effects and more sophisticated methods are often computationally too demanding to be applied to extended surfaces.

Therefore, we employ and try to validate DFT-GGA calculations with semiempirical corrections for dispersion effects (DFT-D) regarding the adsorption of different kinds of molecules on (metallic) surfaces. Not only for the physisorption of aromatic molecules [1] or the interactions of the rest groups of chemisorbed thiolate molecules, but also for the adsorption of rather small inorganic molecules, such as water bilayers on metallic surfaces, dispersive interactions were found to be important [2].

[1] K. Tonigold and A. Groß, J. Chem. Phys. **132**, 224701 (2010).

[2] K. Tonigold and A. Groß, J. Comput. Chem., *accepted*.

O 55.9 Wed 18:45 MA 043

**A High-Dimensional Neural Network Potential for Water: First Applications to Water Clusters** — •TOBIAS MORAWIETZ, VIKAS SHARMA, and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Large-scale atomistic simulations using molecular dynamics or Monte Carlo methods require a reliable but efficient representation of the interatomic potential. In recent years, artificial neural networks (NNs) have been shown to provide accurate potential-energy surfaces (PESs) for complex systems. NNs are flexible functions, which allow to interpolate a set of energies and forces obtained from electronic structure data but can be evaluated several orders of magnitude faster. Here we present an application of our generalized NN scheme for high-dimensional systems [1], which incorporates long-range electrostatic interactions based on environment-dependent atomic charges [2], to water clusters [3]. We show that binding energies and vibrational frequencies for several stationary points on the NN-PES are in excellent agreement with reference DFT data.

[1] J. Behler, and M. Parrinello, PRL **98**, 146401 (2007).

[2] N. Artrith, T. Morawietz, and J. Behler, PRB **83**, 153101 (2011).

[3] T. Morawietz, V. Sharma, and J. Behler, submitted (2011).

O 55.10 Wed 19:00 MA 043

**Static and Frequency Dependent Dipole Polarizabilities from the Ground-State Electron Density** — •VIVEKANAND GOBRE<sup>1</sup>, ROBERT DiSTASIO JR.<sup>2</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, and ALEXANDRE TKATCHENKO<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>Princeton University, Princeton, NJ, USA

Molecular polarizability is an essential observable, and its accurate determination is important, e.g., for calculation of van der Waals interactions. Accurate polarizability calculations in principle require computationally expensive electronic structure methods with an explicit treatment of many-electron excitations. These methods can only be applied to systems with less than about 100 atoms. However, one is often faced with the problem of computing polarizabilities for large systems with thousands of atoms. We present a parameter-free computationally efficient approach to calculate accurate static and frequency dependent polarizabilities for molecules and non-metallic solids. Specifically, we link the TS-vdW [1] method, which accurately treats hybridization effects, with the self-consistent screening equation from classical electrodynamics [2]. Using only the electron density and reference data for the free atoms, we obtain an accuracy of about 7% for both static polarizabilities and van der Waals coefficients for a wide variety of systems. We illustrate the interplay of hybridization and long-range electrostatic screening effects for the polarizability of large proteins and condensed-matter systems. [1] A. Tkatchenko and M. Scheffler, PRL **102**, 073005 (2009); [2] B. U. Felderhof, Physica **76**, 486 (1974).