

O 41: Ab-initio approaches to excitations in condensed matter I

Time: Wednesday 15:00–17:30

Location: SCH 251

O 41.1 Wed 15:00 SCH 251

Accurate van-der-Waals interactions from (semi)-local density functional theory — ●ALEXANDRE TKATCHENKO and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, Germany

Non-covalent forces, such as hydrogen bonding and van der Waals (vdW) interactions, are crucial for the formation, stability and function of molecules and materials. At present, vdW interactions can only be satisfactorily accounted for by high-level quantum-chemical wave function or by the Quantum Monte Carlo (QMC) method. In contrast, (semi)-local DFT and Hartree-Fock approximation fail for the description of vdW forces. We present a parameter-free method for describing the long-range vdW interaction in (semi)-local DFT. The leading C_6 coefficients are derived from the electron density of a molecule/solid and accurate reference values for the free atoms. The mean absolute error in the C_6 coefficients is 5.5% when compared to accurate experimental values for 1225 intermolecular pairs. We show that the C_6 coefficients depend strongly on the bonding type and geometry of molecules/solids. Finally, we analyze the vdW radii and the damping function in the C_6R^{-6} correction method for DFT calculations.

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Proton momentum distribution in hydrogen bonded systems — JOSEPH A. MORRONE, LIN LIN, and ●ROBERTO CAR — Princeton University, Princeton, USA

Recently the momentum distribution of the protons has been measured in neutron Compton scattering experiments: this property gives access to the local potential energy surface experienced by the protons in hydrogen bonded environments. Theoretically, the momentum distribution can be simulated using path integral Car-Parrinello molecular dynamics. In this talk recent results obtained with this approach for the proton momentum distribution in water and ice under standard thermodynamic conditions will be reviewed. Then, ice under very high pressure will be used to illustrate how the momentum distribution of the protons changes when the latter undergo quantum tunneling.

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O 41.3 Wed 15:30 SCH 251

Static Correlation in the Description of the Oxygen-Metal Interaction — ●CHRISTIAN CARBOGNO and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm,

The correct treatment of *static correlation*, i.e. the necessity to include multiple determinants to describe a wave function of a certain symmetry, is critical for the correct simulation of molecules, particularly if excited open-shell singlet states are addressed. Whereas these effects can be tackled unambiguously with CI, only an approximate description in terms of fractional occupation numbers is possible when solving the Kohn-Sham equations. For extended systems, where DFT methods are widely applied due to their numerical efficiency, such effects are typically negligible, especially if the interaction of a molecule with a metal surface is addressed. The thereby occurring *adiabatic* charge transfer, as described within the Born-Oppenheimer approximation, generally breaks the symmetry of the molecule: Thus one basic requirement for the manifestation of static correlation gets lost. For the oxygen chemistry on metal substrates, however, the Born-Oppenheimer approximation may fail under certain circumstances, as experimental [1] and theoretical [2] studies suggest. In such cases, the correct description of the molecule's excited states becomes of vital importance for the comprehension of the ongoing chemical processes. Accordingly, we will discuss the role of static correlation for this model system by comparing state-of-the-art MRCI and GGA-DFT calculations.

[1] R. Burgert *et al.*, Science **319**, 438 (2008).

[2] C. Carbogno *et al.*, Phys. Rev. Lett. **101**, 096104 (2008).

O 41.4 Wed 15:45 SCH 251

Implementation of the exact-exchange Kohn-Sham functional within the all-electron FLAPW method — ●MARKUS BETZINGER¹, CHRISTOPH FRIEDRICH¹, STEFAN BLÜGEL¹, and ANDREAS GÖRLING² — ¹Institut für Festkörperforschung and Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany

— ²Lehrstuhl für Theoretische Chemie, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

The success of density-functional theory (DFT) relies on the availability of accurate approximations for the exchange-correlation (xc) functional. Standard xc functionals, such as the local-density and the generalized-gradient approximation, suffer from several shortcomings: an unphysical electronic self-interaction, no discontinuity of the xc potential at integral particle numbers, wrong asymptotic behavior etc. Orbital-dependent functionals are a promising new generation of xc functionals. The simplest variant consistent with the Kohn-Sham theory requiring a local xc-potential is the exact-exchange (EXX) functional. It does not exhibit the above mentioned deficiencies. We implemented the EXX functional within the full-potential augmented-planewave (FLAPW) method using a specifically designed auxiliary basis set for the optimized effective potential (OEP) equation. We demonstrate that the auxiliary and FLAPW basis must be properly balanced to avoid spurious oscillations in the exact exchange potential and show first results for prototype semiconductors and insulators.

O 41.5 Wed 16:00 SCH 251

Towards a low-dimensional Lieb-Oxford bound — ●CÉSAR R. PROETTO^{1,2}, KLAUS CAPELLE³, STEFANO PITTALIS¹, and ESA RÄSÄNEN⁴ — ¹Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany and European Theoretical Spectroscopy Facility (ETSF) — ²Centro Atómico Bariloche and Instituto Balseiro, 8400 S. C. de Bariloche, Río Negro, Argentina — ³Departamento de Física e Informática, Instituto de Física de São Carlos, Universidade de São Paulo, São Paulo, 13560-970, Brazil — ⁴Nanoscience Center, Department of Physics, P. O. Box 35 FIN-40014 University of Jyväskylä, Finland

Exact constraints on the unknown exchange-correlation (xc) energy functional are of fundamental importance in density-functional theory (DFT): One main and successful strategy in the never-ending challenge for the building of more accurate xc functionals consist of satisfying as many exact constraints as possible. The Lieb-Oxford bound (LOB) for three-dimensional (3D) systems is one of such exact constraints, and in its more useful version within the context of DFT is given as a lower bound on the correlation energy, in terms of a power of the particle density. For the bound to be useful, it should be as tight as possible. In this talk, we will provide the construction of the equivalent of the 3D LOB, but for the low-dimensional cases. In particular, by using scaling analysis and exploiting the fact that for some low-dimensional systems we know the ground-state xc energy and density, we have computed the expression for the bound in the 1D and 2D cases, and analyzed in detail the dimensionality crossover in between.

O 41.6 Wed 16:15 SCH 251

Exploring the random phase approximation: application to CO adsorption, bulk metals, and weakly bonded molecules — ●XINGUO REN¹, PATRICK RINKE^{1,2}, and MATTHIAS SCHEFFLER^{1,2} — ¹Fritz-Haber-Institut der MPG, D-14195 Berlin, Germany — ²Materials Dept., UC Santa Barbara, CA 93106, USA

Density-functional theory (DFT) within the generalized gradient approximation (GGA) has been immensely successful in describing the ground state properties of a diverse range of materials. However, inherent strong self-interaction effects and the absence of van der Waals (vdW) interactions are two prominent examples of GGA's failures. These severely affect the description of (bio)molecules and in certain cases (e.g. CO) their adsorption on (transition)metal surfaces. Many-body perturbation theory in the random phase approximation (RPA) presents a promising way to go beyond GGA since it is expected to perform well for molecular, metallic and vdW systems alike. However, despite the recent interest the RPA has generated, a comprehensive assessment of its performance is not available. Using CO@Cu(111), a selection of bulk metals, and the benzene dimer, a prototypical π -conjugated system, as examples, we demonstrate the performance of the RPA for different types of systems. We show that the potential-energy surface of CO adsorbed on Cu(111) can be correctly described within RPA at a quantitative level. The binding energy of the benzene dimer, on the other hand, is considerably underestimated. We further show that these RPA results are not sensitive to the DFT functional chosen for the description of the unperturbed system.

O 41.7 Wed 16:30 SCH 251

Exact Kohn-Sham potential of strongly correlated finite systems — ●NICOLE HELBIG, ILYA TOKATLY, and ANGEL RUBIO — Nano-Bio Spectroscopy group and ETSF, Dpto. de Física de Materiales, Universidad del País Vasco and Centro Mixto CSIC-UPV/EHU, San Sebastián, Spain

The description of strongly correlated systems within density functional theory has proven very difficult in the past. The dissociation of molecules, even the most simple hydrogen molecule, cannot be described accurately with any of the presently available density functionals. These problems have led to a discussion of what properties the local Kohn-Sham potential has to satisfy in order to correctly describe strongly correlated systems. We use a one-dimensional, two electron model system to investigate the behavior of the exact Kohn-Sham potential, which can be calculated easily for this system. We present an analytic expression for the potential at the dissociation limit and show that the numerical calculations indeed approach and reach this limit as we dissociate the system. It is shown that the functional form of the Kohn-Sham potential is independent of the details of the system under consideration making the results easily transferable to other systems. We use this knowledge to calculate the exact Kohn-Sham potential of the hydrogen molecule in the dissociation limit.

O 41.8 Wed 16:45 SCH 251

Discontinuity of chemical potential in reduced density matrix functional theory: open shell formulation — ●N.N. LATHIOTAKIS^{1,2,4}, N. HELBIG^{2,3,4}, and E.K.U. GROSS^{2,4} — ¹TPCI, NHRF, Vass. Constantinou 48, Athens, Greece — ²Institut für Theoretische Physik, FU Berlin, Arnimallee 14, D14195 Berlin, Germany — ³Nano-Bio Spectroscopy group, Dpto. de Física de Materiales, Universidad del País Vasco UPV/EHU and Centro Mixto CSIC-UPV/EHU, San Sebastián, Spain — ⁴European Theoretical Spectroscopy Facility

In reduced-density-matrix-functional theory, approximations of the total energy as a functional of the one-body-reduced-density matrix are minimized. In an open-shell treatment, this minimization involves two Lagrange multipliers that ensure the conservation of the number of particles separately for each spin. We prove that these Lagrange multipliers are the chemical potentials, i.e. the derivatives of the total energy with respect to the numbers of spin up and spin down electrons. For the exact functional, these Lagrange multipliers show a discontinuity at integer values of the spin-resolved particle numbers which equals the fundamental gap. We test present-day RDMFT functionals for this property and find that many of them reproduce a step-like behavior, in resemblance to the exact theory. This behavior is improved in the

open-shell treatment i.e. when all fractional electrons are added to the same spin. The obtained discontinuities are in very good agreement with the gaps of the studied finite systems. These promising results are a motivation for the application of RDMFT to problems like the band gaps of solids where DFT results deviate from experiments.

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Reduced Density Matrix Functional for Many-Electron Systems — SANGEETA SHARMA^{1,2,3}, ●KAY DEWHURST^{1,2,3}, NEKTARIOS LATHIOTAKIS^{4,3}, and E. K. U. GROSS^{2,3} — ¹Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany. — ²Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany — ³European Theoretical Spectroscopy Facility (ETSF) — ⁴Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, Vass. Constantinou 48, 11635 Athens, Greece

We explore the performance of reduced-density-matrix-functional theory (RDMFT) for solids, in particular, for strongly correlated solids. To this end, we introduce a novel exchange-correlation functional of RDMFT based on a fractional power of the one-body density matrix. We show that, compared to other functionals, this new functional produces more accurate total energies as a function of particle number. Moreover, it captures the correct band gap behavior for conventional semiconductors as well as strongly correlated Mott insulators, where a gap is obtained in absence of any magnetic ordering.

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Stroboscopic wavepacket description of non-equilibrium many-electron problems — ●PETER BOKES — Dept. of Physics, Slovak University of Technology FEI STU, Bratislava, Slovakia

We introduce the construction of a orthogonal wavepacket basis set, using the concept of stroboscopic time propagation, tailored to the efficient description of non-equilibrium extended electronic systems. Thanks to three desirable properties of this basis, significant insight is provided into non-equilibrium processes (both time-dependent and steady-state), and reliable physical estimates of various many-electron quantities such as density, current and spin polarization can be obtained. The use of this novel tool is demonstrated for time-dependent switching-on of the bias in quantum transport, and new results are obtained for current-induced spin accumulation at the edge of a 2D doped semiconductor caused by edge-induced spin-orbit interaction.

[1] P. Bokes, F. Corsetti, and R. W. Godby, Phys. Rev. Lett. 101, 046402 (2008)