TT 106: Frontiers of Electronic Structure Theory: Many-Body Effects, Methods (organized by O)

Time: Thursday 15:00–18:30   Location: MA 004

Invited Talk   TT 106.1   Thu 15:00   MA 004

Natural orbital functional theory with higher-order occupation probabilities — •Ralph Gebauer[1], Roberto Car[2], and Morrel Cohen[2,3] — [1]International Centre for Theoretical Physics (ICTP), Trieste, Italy — [2]Department of Chemistry, Princeton University, Princeton, USA — [3]Department of Physics and Astronomy, Rutgers University, USA

We introduce a novel energy functional for ground-state electronic-structure calculations. Its fundamental variables are the natural spin-orbitals of the implied singlet many-body wave function and their joint occupation probabilities. The functional derives from a sequence of controlled approximations to the two-particle density matrix. Algebraic scaling of computational cost with electron number is obtainable in general, and Hartree-Fock scaling in the seniority-zero version of the theory. Results obtained with the latter version for saturated small molecular systems are compared with those of highly-accurate quantum-chemical computations. The numerical results are variational, capturing most of the correlation energy from equilibrium to dissociation. Their accuracy is considerably greater than that obtainable with current density-functional theory approximations and with current functionals of the one-particle density matrix only.

TT 106.2   Thu 15:30   MA 004

Electronic Properties of Surfaces and Interfaces with Self-Consistent Interatomic van der Waals Density Functional — •Nicola Ferri[1], Robert A. Distasio Jr.[2], Alberto Ambrosetti[1], Roberto Car[2], Matthias Scheffler[1], and Alexandre Tkatchenko[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Princeton University, USA

Ubiquitous long-range van der Waals (vdW) interactions play a fundamental role in the structure and stability of a wide range of systems. Within the DFT framework, the vdW energy represents a crucial, but tiny part (0.001%) of the total energy, hence its influence on the electronic density, $n(\mathbf{r})$, and derived electronic properties is typically assumed to be rather small. Here, we address this question via a fully self-consistent (SC) implementation of the interatomic Tkatchenko-Scheffler vdW functional [1] and its extension to surfaces [2]. For several transition metal surfaces, self-consistency increases their dipole moments and induces non-trivial electron density rearrangements. As a consequence, we observed changes of up to 0.3 eV in the surface work-functions, with vdW self-consistency improving the agreement with experiments. Similar behavior is observed for molecules adsorbed on metals, where vdW contributions influence both Pauli push-back and charge transfer, the two phenomena that determine interface work-functions. [1] A. Tkatchenko and M. Scheffler, PRL (2009). [2] V. G. Ruiz, W. Liu, E. Zojer, M. Scheffler, and A. Tkatchenko, PRL (2012).

TT 106.3   Thu 15:45   MA 004

Exact functionals for a lattice model — •Tanja Dimitrov[1], Heiko Appel[1,3], and Angel Rubio[1,2,3] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Nano-bio Spectroscopy Group/ETSF Scientific Development Centre, Universidad del Pais Vasco UPV/EHU, San Sebastian — [3]MPI for the Structure and Dynamics of Matter, Hamburg

Standard local exchange-correlation and semi-local functionals in ground-state density functional theory are known for their shortcomings in describing correct charge transfer, dissociation energies of molecular ions, and barriers of chemical reactions [1,2]. To understand the failures of approximate functionals, to gain insight into the behavior of the exact functional, and to devise new approximations, we investigate the exact solution of the many-body Schrödinger equation in Fock space for a lattice model with a softened Coulomb interaction term. Using quadratic optimization with quadratic constraints, or alternatively exact diagonalization, we explicitly construct the *exact* density-to-potential and density-to-wave-function map. We discuss the behavior of functionals in the low-density limit.

[1] A. J. Cohen et al. Science **321**, 792 (2008).
[2] P. Mori-Sanchez et al., Phys. Rev. Lett. **100**, 146401 (2008).

TT 106.4   Thu 16:00   MA 004

Many-body dispersion meets non-local density functionals:

A unified approach for van der Waals correlations — •Jan Hermann, Matthias Scheffler, and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

It is an ongoing challenge to develop an efficient method for van der Waals (vdW) non-local correlation within DFT which would be both accurate and broadly applicable. Current approaches can be loosely divided into the fragment-based ones, two-point density functionals and methods based on the density-density response function. The fragment-based models utilize parameters not derivable from the electron density. Two-point approaches are explicit density functionals, but difficult to generalize to include many-body correlations.

Here, we show that these seemingly contrasting approaches can be unified within a single framework based on the adiabatic-connection formalism in the random-phase approximation. We use a local response-function model from the VV09 functional [1] together with the many-body dispersion approach to create an atom-based model with no external parameters. We introduce a consistent correlation-functional-based coupling of the short- and long-range correlation energy. We show that this unification provides new insights into the different approaches, naturally deals with the partitioning of ionic and delocalized states and paves path towards self-consistent description of many-body vdW correlations.

[1] O. A. Vydrov, T. Van Voorhis, Phys. Rev. Lett. 103, 063004

TT 106.5   Thu 16:15   MA 004

Reduced Density-Matrix Functional Theory: correlation and spectroscopy — Stefano Di Sabatino[1], Jan A. Berger[2], Lucia Reining[3], and •Pina Romaniello[1] — [1]Laboratoire de Physique Théorique, CNRS, IRSAMC, Université Toulouse III - Paul Sabatier, Toulouse, France and ETSF — [2]Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Toulouse III - Paul Sabatier, CNRS, Toulouse, France and ETSF — [3]Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, Palaiseau, France and ETSF

We study the performance of approximations to electron correlation in reduced density-matrix functional theory (RDMFT) and of approximations to the observables calculated within this theory [1]. We use the exactly solvable Hubbard molecule as test case. In particular we focus on the atomic limit and we explore how degeneracies and spin-symmetry breaking are treated in RDMFT. We find that, within the used approximations, RDMFT is not able to describe the signature of strong correlation in the spin-singlet ground state, whereas it give the exact result for the spin-symmetry broken case. [1] S. Di Sabatino, J.A. Berger, L. Reining, and P. Romaniello, submitted

TT 106.6   Thu 16:30   MA 004

Does GW obey the straight-line condition? — Matthias Dauth[1,3], Fabio Caruso[2], Stephan Kuemmel[1], and •Patrick Rinke[3] — [1]University of Bayreuth, Germany — [2]University of Oxford, England — [3]Aalto University, Helsinki, Finland

Many-body theory in the GW approach has become the method of choice for calculating charged excitations in solids. Recently, it is also increasingly being applied to molecules, but fundamental questions regarding its accuracy remain. One such fundamental theorem requires that the total energy changes linearly with gradual (i.e. fractional) ionisation of the molecule. In this work we investigate, if GW is piecewise linear or if it exhibits a derivation of the straight line error (DSLE). Since the derivative of the total energy with respect to the electron number gives the ionisation energy, we quantify the DSLE by taking the difference between the energy of the highest occupied state of the neutral and the lowest unoccupied state of the singly ionised molecule (which would be equal in the DSLE-free case). We find for a subset of molecules from the quantum chemical G2 benchmark set, that the DSLE in self-consistent GW amounts to 1.1 eV on average. This DSLE can be mitigated in perturbative G_0W_0 by varying the starting point. We use density-functional theory as starting point and vary the amount of exact exchange α in the Perdew-Burke-Ernzerhof hybrid functional (PBEh). G_0W_0 becomes DSLE-free for $\alpha \approx 0.4$. The average deviation from the experimental IPs is then very close to that of self-consistent GW and amounts to ~ 0.25 eV.

TT 106.7   Thu 16:45   MA 004

Green's Function embedding for Advanced Electronic Structure Methods based on Dynamical Mean-Field Theory — •Wael Chibani[1], Xinguo Ren[2], Matthias Scheffler[1], and Patrick Rinke[3] — [1]*Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany* — [2]*Key Laboratory of Quantum Information, USTC, Hefei, China* — [3]*Aalto University, Helsinki, Finland*

We introduce an embedding scheme for periodic systems that facilitates a self-consistent treatment of the physically important part of a system with electronic structure methods, that are computationally too expensive for periodic systems. We use dynamical mean-field theory [1] (DMFT) to couple to the rest of the system, which is treated with less demanding approaches such as Kohn-Sham density functional theory. In contrast to the original DMFT formulation for correlated model Hamiltonians, we consider here the unit cell as local embedded cluster in an *ab initio* way, that includes all electronic degrees of freedom. The performance of our scheme is demonstrated by treating the embedded region with hybrid and GW self-energies (scGW) for simple bulk systems. The total energy and the density of states converge rapidly with respect to the computational parameters and approach their bulk limit with increasing cluster size. For non self-consistent GW calculations we observe Plasmon satellites for Si – in good agreement with periodic G_0W_0 calculations [2] – that vanish at self-consistency. Our scGW gap of ~ 0.9 eV for a two atom unit cell agrees well with previous G_0W_0 calculations and experiment. [1] A.Georges *et al.*, Rev.Mod.Phys.(2006), [2] M.Guzzo *et al.*, PRL(2011)

TT 106.8   Thu 17:00   MA 004
Improved Ground State Electronic Structure and Optical Dielectric Constants With a Semi-Local Exchange Functional — •Vojtěch Vlček[1], Gerd Steinle-Neumann[1], Linn Leppert[1], Rickard Armiento[2], and Stephan Kümmel[1] — [1]University of Bayreuth, Germany — [2]Linköping University, Sweden

For a set of solids, we explore a recently developed generalized gradient exchange functional (AK13) that has two characteristic features: its enhancement factor diverges for large reduced density gradients s as $s \ln(s)$ and its potential changes discontinuously at integer electron numbers. We apply the functional to semiconductors, Mott insulators, and ionic crystals and compare results for band structure and dielectric constants with a standard GGA. The AK13 functional provides a better description of the KS orbitals and we observe a qualitative improvement both in the bandgaps and in the optical dielectric constants, especially for the small gap semiconductors we explore (Ge, α-Sn, and CdO)

TT 106.9   Thu 17:15   MA 004
Accurate, efficient localized resolution of identity of the Coulomb operator across the periodic table — •Arvid Ihrig[1], Jürgen Wieferink[1], Igor Ying Zhang[1], Patrick Rinke[1,2], Volker Blum[1,3], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Aalto University, Helsinki, Finland — [3]Duke University, Durham, USA

A key component of advanced electronic structure methods is the explicit evaluation of the Coulomb operator. The corresponding four-center integrals can be solved with a "resolution of identity" (RI) approach for numeric atom-centered orbitals, as they are used in, e.g., FHI-aims [1]. In RI, basis function products are expanded in an auxiliary basis. The complete auxiliary basis is used for "RI-V", the most accurate and most commonly used RI. We developed a localized RI ("RI-LVL"), which expands the products only in the subset of those auxiliary functions centered on the same atoms as the basis functions. This approach yields a superior scaling with system size, both in terms of computational time and memory requirements. At the same time it also retains the accuracy of the RI-V, as we have shown for HF, MP2, PBE0 and RPA calculations. The systems we investigated include weakly interacting molecular dimers (S22 test set) as well as TiO_2, Cu, and Au clusters. In all test cases we found that RI-LVL reproduces RI-V very accurately. Even for RPA-calculations of gold with very large basis sets the deviation to RI-V is only ~1.5 meV per atom. [1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009).

TT 106.10   Thu 17:30   MA 004
Explicitly correlated self consistent field theory — •Christian Lasar and Thorsten Klüner — Carl von Ossietzky Universität, Oldenburg, Germany

There is a variety of methods available which aim to describe molecules and molecular reactions with chemical accuracy. The two main classes of these methods are density functional theory (DFT) and electron correlation approaches. DFT achieves great accuracy for many molecules and is applicable to quite large molecules. Unfortunately, DFT is not systematically improvable since the exact form of the exchange correlation functional remains unknown. Correlation methods do not suffer from this lack of systematic improvement. Unfortunately, they often require too much computational resources for large molecules. Additionally, they show a very slow convergence with the size of the basis set. Explicitly correlated methods are known to be able to solve this convergence problem. In these methods, the wavefunction is augmented with a function f_{ij} which explicitly depends on two electronic coordinates. Combining the advantages of low computational resources and the ability for systematic improvement, one ends up in the following ansatz for the wavefunction $\Psi = (1 + \sum_{ij} f_{ij})\Phi$, where Φ is one slater determinant. With this ansatz the long determinant expansion is avoided. Additionally, there will be a fast convergence with the basis set size. We currently investigate the derivation of the working equations and their implementation for different functions f_{ij}. Some results for small molecules have already been obtained and will be presented in this contribution.

TT 106.11   Thu 17:45   MA 004
Comparison of two self-consistent GW schemes — •Peter Koval[1], Dietrich Foerster[2], and Daniel Sanchez-Portal[1,3] — [1]Donostia International Physics Center, San Sebastián, Spain — [2]Laboratoire Ondes et Matiére d'Aquitaine, Bordeaux, France — [3]Material Physics Center, San Sebastián, Spain

GW approximation (GWA) as a competitor of DFT provides a better description of electronic structure in several respects. However, a GW calculation is more expensive than similar DFT calculation. This fact contributed to a wide usage of simpler calculations based on GWA (SEX, COSEX, plasmon-pole approximations etc.) This manyfold of approximations hampers a non-biased evaluation of merits of GWA to describe the electronic correlations. We produced a rigorous GW implementation where the only approximation is the use of localized orbitals [1]. The usage of spectral functions allowed us to realize two self-consistent GW schemes: scGW [2] and qsGW [3] in one code [4]. Furthermore, we used all-electron Gaussian basis sets that allows for a coherent comparison with quantum chemistry methods. We use coupled-cluster methods CCSD and CCSD(T) as reference and compare ionization potentials of 15 molecules. The calculations show trends in scGW and qsGW and give hints on possible sources of discrepancies/directions towards improving GWA. [1] D. Foerster, P. Koval, D. Sánchez-Portal, *J. Chem. Phys.* **135**, 074105 (2011); [2] L. Hedin, *J. Phys. Cond. Mat.* **11**, R489 (1999); [3] S. V. Faleev, M. van Schilfgaarde, T. Kotani, *Phys. Rev. Lett.* **93**, 126406 (2004); [2] P. Koval, D. Foerster, D. Sánchez-Portal, *Phys. Rev.* B **89**, 155417 (2014).

TT 106.12   Thu 18:00   MA 004
Quasiparticle Self-Consistent GW for Molecules — •Ferdnand Kaplan[1,2,3], Michiel van Setten[1,2,5], Florian Weigend[1,3], and Ferdinand Evers[1,2,3,4] — [1]Institute of Nanotechnology (INT) — [2]Institute for Theoretical Condensed Matter Physics (TKM) — [3]Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany — [4]Universität Regensburg, D-93040 Regensburg, Germany — [5]Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium

One of the most used approaches for the computational study of nanoscale systems and molecules is the density functional theory (DFT). However, DFT calculations of single particle excitation spectra, e.g. ionization potentials, often suffer from method-inherent difficulties. To systematically improve the estimation of quasi-particle energies for molecular system, we have implemented the GW method. The approach represents a perturbative expansion of the many-body Green's function with respect to the screened Coulomb interaction, W.

On G_0W_0 level the GW-self energy is calculated with the Kohn-Sham Green's function of the underlying DFT. Hence, one finds a strong dependence of the excitation energies on the reference system, i.e. DFT functionals. To overcome this problem, we implemented a self-consistent cycle which takes into account the deviations of the quasiparicle(qp)-wavefunctions from their Kohn-Sham parents.

We find that this procedure converges to a fixed point solution which is independent of the reference system. For the testset of molecules anlyzed by us so far, the results for ionization-energy and electron-affinity improve upon G_0W_0, when comparing to experimental data.

TT 106.13   Thu 18:15   MA 004

Pure state N-representability conditions: Should they be taken into account in Reduced density matrix functional theory? — •Iris Theophilou[1], Nektarios Lathiotakis[2,3], and Nicole Helbig[1] — [1]Peter Grünberg Institut (PGI-1), Forschungszentrum Jülich, Jülich, Gernany — [2]Theoretical and Physical Chemistry Institute (TPCI), National Hellenic Research Foundation , Athens, Greece — [3]Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

In Reduced Density Matrix Functional Theory (RDMFT) the natural occupation numbers are minimized under the ensemble N-representability conditions, i.e they are restricted to be between zero and one and sum to the number of electrons. Recently, the pure state N-representability problem for the one-body reduced density matrix has been solved [M. Altunbulak and A. Klyachko, Commun. Math. Phys. 282, 287 (2008)]. In this talk we discuss to which extend these pure state conditions are satisfied without being enforced in 3 electron systems using some standard RDMFT functionals. Our aim is to impose those pure state conditions that are not automatically satisfied and check whether this improves RDMFT results.