TT 28: Electronic-Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - III (joint session DS, HL, MA, MM, O, TT, organized by O)

Time: Tuesday 10:30–13:00   Location: GER 38

Invited Talk   TT 28.1   Tue 10:30   GER 38
Including spin effects in the strong-coupling limit of DFT —
●Paola Gori-Giorgi[1], Juri Grossi[1], Derk Pieter Kooi[1], Klaas
Giesbertz[1], Michael Seidl[1], Aron Cohen[2], and Paula Mori-
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Spain

The exact strong-coupling limit of density functional theory (DFT) re-
veals a different mathematical structure with respect to the one of tra-
ditional approximations for the exchange-correlation (xc) functional:
instead of the local density, local density gradients, or quantities re-
lated to the Kohn-Sham orbitals, some integrals of the density appear
in this limit. In the recent years, xc functionals directly inspired to
this mathematical structure have been constructed and implemented
in an efficient way. However, the leading terms (exact or approximate)
in the strong-coupling limit of DFT are intrinsically semiclassical and,
as such, do not incorporated the spin dependence. In this talk, I will
present the first study on the incorporation of the spin-dependence in
the exact strong-coupling limit in simple one-dimensional cases. I will
then discuss approximations for our findings and routes to the con-
struction of spin-dependent xc functionals for strong coupling. Com-
parison with exact calculations for the Hohenberg-Kohn functional in
the strong-coupling regime confirms the accuracy of our expressions
for the leading terms.

TT 28.2   Tue 11:00   GER 38
**Strong correlation from the Random Phase Approximation
and beyond** — ●Thomas Olsen and Kristian Thygesen — De-
partment of Physics, Technical University of Denmark

We assess the performance of the Random Phase Approximation
(RPA) for strongly correlated systems and discuss different routes to
venture beyond RPA. It is well-known that RPA reproduces the disso-
ciation curve of molecular H2 correctly and thus accurately captures
the strong static correlation inherent in the dissociation limit. It is thus
natural to ask whether RPA is able to describe the strongly correlated
Mott insulators as well. In particular, the accurate description of anti-
ferromagnetic systems is complicated by the fact that the magnetic
order often emerges from a detailed interplay between direct exchange
and super-exchange couplings, which are respectively exchange and
correlation effects. Whereas DFT+U, semi-local and hybrid function-
als are often capable of describing either exchange or super-exchange
accurately, RPA is shown to give an accurate account of both. We will
finally show that RPA can be improved by either including non-local
kernel in the framework of TDDFT or including electron-hole interac-
tions in the irreducible response function. Only the latter approach
improves the description of strong correlation, whereas the former ap-
proach improves atomization energies significantly compared to RPA.

TT 28.3   Tue 11:15   GER 38
**Surface and adsorption energy calculations within the ran-
dom phase approximation** — ●Per Schmidt and Kristian
Thygesen — Technical University of Denmark, DK-2800 Kongens
Lyngby, Denmark

The application of density functional theory (DFT) to the calculation
of adsorption and surface energies is ever increasing and as a theory,
it has the potential to e.g. guide experiments in the search of better
catalysts. However, a previous study[1] shows that with standardly
used semi-local functionals, DFT is not able to accurately predict sur-
face and adsorption energies simultaneously. By tuning the functional,
either the predicted surface or adsorption energies can be improved
at the expense of the other. For a few cases however, it has been
shown[1] that the many-body approach, the random phase approxi-
mation (RPA), yields both excellent surface and adsorption energies.
   In this work we expand the use of the RPA method to eight adsorp-
tion reactions over 20 transition metal surfaces using the electronic
structure code GPAW. We report the difference in surface and ad-
sorption energies compared with the standard DFT functionals: PBE,
RPBE and BEEF-vdW. We find that RPA does in general predict less
stable surfaces, in better agreement with experiments and the aver-
age change in adsorption energies varies between ± 0.5 eV. The RPA
values could be used to guide construction of new density-functionals

aimed at improving surface science calculations.
[1] L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F.
Mittendorfer, and G. Kresse, Nature Materials 9, 741 (2010).

TT 28.4   Tue 11:30   GER 38
**Large-scale cubic-scaling RPA correlation energy calculations
using a Gaussian basis** — ●Jan Wilhelm and Jürg Hutter —
University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzer-
land

The random phase approximation (RPA) for computing the electron
correlation energy has emerged as an accurate tool for predicting the
properties of molecules and condensed phase systems. RPA combines
a number of attractive features, most importantly that long-range van
der Waals interaction is included, in contrast to semilocal density func-
tionals. The drawback connected with RPA is the computational cost:
For canonical implementations of RPA, the numerical effort grows as
quickly as $O(N^4)$ with the system size N. We present an algorithm
for computing the RPA correlation energy in a Gaussian basis requir-
ing $O(N^3)$ operations and $O(N^2)$ memory. The cubic-scaling RPA
method is based on the resolution of the identity (RI) with the overlap
metric, a reformulation of RI-RPA in the Gaussian basis and imaginary
time as well as the use of sparse linear algebra. We report a massively
parallel implementation which is the key for the application to large
systems. As first benchmark of the method, we show the RPA correla-
tion energy of thousands of water molecules in a high-quality cc-TZVP
basis. For a comparison, the canonical RPA method is restricted to
500 water molecules using the whole Piz Daint supercomputer for two
hours. Our RPA algorithm enables the application of RPA to large
systems where van der Waals interactions play an important role, e.g.
for predicting the adsorption energy of large molecules on surfaces.

TT 28.5   Tue 11:45   GER 38
**Semi-local exchange functionals showing ultranonlocal re-
sponse: the hope to replace exact exchange** — ●Thilo Asche-
brock and Stephan Kümmel — Theoretical Physics IV, University
of Bayreuth, D-95440 Bayreuth, Germany

The widespread success of Density Functional Theory (DFT) is
based on a favorable ratio of accuracy to computinal cost, espe-
cially with semi-local approximations to the exchange-correlation en-
ergy. However, functionals such as the local density approxima-
tion (LDA), generalized-gradient approximations (GGA) or meta-
generalized-gradient approximations (meta-GGA), typically miss im-
portant exact exchange features related to the derivative discontinu-
ity. These are essential for accurately describing long-range charge
transfer processes. The electrical response of molecular chains, which
is dramatically overestimated by local and semi-local density func-
tionals, is a prime example. The key to its correct description is a
term in the Kohn-Sham exchange potential that counteracts the ex-
ternal field and has been named "ultranonlocal". We here present how
these field-counteracting properties can be incorporated into semi-local
DFT on the meta-GGA level. Thereby we show that by utilizing the
kinetic-energy-density, it is possible to model ultranonlocal effects in
the Kohn-Sham potential by virtue of a semi-local energy expression.

TT 28.6   Tue 12:00   GER 38
**(De)stabilizing dispersion interactions via external elec-
tric charges** — ●Andrii Kleshchonok[1] and Alexan-
dre Tkatchenko[1,2] — [1]Fritz-Haber-Institut der Max-Planck-
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Van der Waals (vdW) or dispersion interactions play a central role in
the structure, stability, and reaction mechanisms in large variety of
molecules and materials. However, in many situations of interest in
material science and biophysics, vdW interactions should account for
the coupling with external (in)homogeneous electric fields. In this work
we address the effect of external static charge field on long-range elec-
tron correlations. By using the quantum Drude oscillator model, we
derive analytical expressions of the charge induced dipole-quadrupole
dispersion energy, that is accounted neither in standard DFT methods,
nor in popular vdW correction schemes. Analysing the scaling laws of

this dispersion term, we conclude that positive charge stabilizes dispersion interactions, while a negative charge has an opposite effect. Benchmark over S22 molecular dataset estimates the induced dispersion to be in the range of 20-300 % of conventional electrostatic energy. Our findings could have broad potential implications, including exfoliation of 2D materials, chemical reaction rates in charged droplets, and biological membranes.

TT 28.7 Tue 12:15 GER 38

An optimisability proof for self-consistent constrained DFT, and its implications for constraint-based self-interaction error correction — Glenn Moynihan[1], Gilberto Teobaldi[2,3], and •David D. O'Regan[1] — [1]School of Physics, CRANN and AMBER, Trinity College Dublin, Ireland. — [2]Stephenson Institute for Renewable Energy and Department of Chemistry, The University of Liverpool, U.K. — [3]Beijing Computational Science Research Center, China.

We develop the connection between constrained DFT energy derivatives and response functions, providing a rigorous assessment of the uniqueness and character of cDFT stationary points while accounting for electronic interactions and screening [1]. In particular, we provide a non-perturbative proof that stable stationary points of linear density constraints occur only at energy maxima with respect to their Lagrange multipliers, generalizing the proof of Ref. [2]. We demonstrate that multiple solutions, hysteresis, and energy discontinuities may occur in cDFT, and we provide necessary conditions for the optimizability of multi-constraint cDFT. We show that the applicability of cDFT in automating symmetry-preserving self-interaction error corrections is limited by a fundamental incompatibility with non-linear constraints. We circumvent this by utilizing separate linear and quadratic correction terms, which may be interpreted either as distinct constraints, each with its own Hubbard U type Lagrange multiplier, or as the components of a generalized, two-parameter DFT+U functional [3]. [1] Phys. Rev. B **94**, 035159 (2016). [2] Phys. Rev. A **72**, 024502 (2005). [3] Phys. Rev. B Rapid Comms., Accepted (2016), arXiv:1608.07320.

TT 28.8 Tue 12:30 GER 38

Density-based local hybrid functional for interfaces — •Pedro Borlido[1], Silvana Botti[1], and Miguel Marques[2] — [1]Institu für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743, Jena, Germany — [2]Instiut für Physik, Martin-Luther-Universität Halle Wittenberg, D-06099 Halle, Germany

Hybrid functionals in density functional theory have become the state-of-the-art for the calculation of electronic properties of solids. The key to their performance is how and in which amount a part of Fock exchange is mixed with semi-local exchange-correlation functionals. We propose here a material dependent and local mixing parameter which is a functional of the electron density alone, through an estimator of the local dielectric function inspired by the work done in *Phys. Rev. B* 83, 035119 (2011). This new functional is by construction an approximation of the GW self-energy and it enables therefore calculations of quasiparticle energy levels of comparable quality as GW, but at the reduced cost of a hybrid density functional. In contrast with other recent self-consistent schemes for the mixing parameter, our approach does not require to calculate the dielectric function and leads to a negligible increase of the computation time.

TT 28.9 Tue 12:45 GER 38

On the hunt for better functionals in DFT: a new quantum embedding scheme — •Uliana Mordovina[1], Teresa E. Reinhard[1], Heiko Appel[1], and Angel Rubio[1,2] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — [2]Nano-bio Spectroscopy Group and ETSF, Departamento de Fisica de Materiales, Universidad del Pais Vasco UPV/EHU, San Sebastian, Spain

We propose a new systematic technique to derive functionals for standard density functional theory (DFT) in an ab-initio fashion. This technique origins in the recently developed density-matrix embedding theory (DMET) [1]. DMET is a quantum-in-quantum embedding method, which is based on finding a projection between the high-dimensional wave function of the full system and a lower-dimensional wavefunction living in the active space of the embedded system, which is then solved exactly. In the original DMET scope, the projection is improved via optimization of the reduced one-body density matrix. We replace this optimization by a density inversion, exploiting the one-to-one mapping between electronic density and Kohn-Sham potential.

Not only the DMET scheme is improved by the uniqueness of the density-potential mapping, the proposed density-embedding also allows for finding accurate Kohn-Sham potentials. Moreover, unlike in usual DFT, we can systematically improve the description by increasing the size of the active space.

We show benchmark results of our method for molecules in 1D.

[1] G. Knizia, G. K.-L Chan, Phys. Rev. Lett 109, 186404, (2012)