

MM 29: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - III

Time: Tuesday 10:30–13:00

Location: GER 38

Invited Talk

MM 29.1 Tue 10:30 GER 38

Including spin effects in the strong-coupling limit of DFT — ●PAOLA GORI-GIORGI¹, JURI GROSSI¹, DERK PIETER KOOI¹, KLAAS GIESBERTZ¹, MICHAEL SEIDL¹, ARON COHEN², and PAULA MORI-SANCHEZ³ — ¹Vrije Universiteit Amsterdam, The Netherlands — ²University of Cambridge, UK — ³Universidad Autonoma de Madrid, Spain

The exact strong-coupling limit of density functional theory (DFT) reveals a different mathematical structure with respect to the one of traditional approximations for the exchange-correlation (xc) functional: instead of the local density, local density gradients, or quantities related 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 incorporate 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 construction of spin-dependent xc functionals for strong coupling. Comparison with exact calculations for the Hohenberg-Kohn functional in the strong-coupling regime confirms the accuracy of our expressions for the leading terms.

MM 29.2 Tue 11:00 GER 38

Strong correlation from the Random Phase Approximation and beyond — ●THOMAS OLSEN and KRISTIAN THYGESEN — Department 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 dissociation 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 functionals 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 interactions in the irreducible response function. Only the latter approach improves the description of strong correlation, whereas the former approach improves atomization energies significantly compared to RPA.

MM 29.3 Tue 11:15 GER 38

Surface and adsorption energy calculations within the random 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 surface 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 approximation (RPA), yields both excellent surface and adsorption energies.

In this work we expand the use of the RPA method to eight adsorption reactions over 20 transition metal surfaces using the electronic structure code GPAW. We report the difference in surface and adsorption 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 average 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).

MM 29.4 Tue 11:30 GER 38

Large-scale cubic-scaling RPA correlation energy calculations using a Gaussian basis — ●JAN WILHELM and JÜRGEN HUTTER — University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

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 functionals. 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 requiring $O(N^3)$ 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 correlation 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.

MM 29.5 Tue 11:45 GER 38

Semi-local exchange functionals showing ultranonical response: the hope to replace exact exchange — ●THILO ASCHEBROCK 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 computational cost, especially with semi-local approximations to the exchange-correlation energy. However, functionals such as the local density approximation (LDA), generalized-gradient approximations (GGA) or meta-generalized-gradient approximations (meta-GGA), typically miss important exact exchange features related to the derivative discontinuity. 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 functionals, is a prime example. The key to its correct description is a term in the Kohn-Sham exchange potential that counteracts the external field and has been named "ultranonical". 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 ultranonical effects in the Kohn-Sham potential by virtue of a semi-local energy expression.

MM 29.6 Tue 12:00 GER 38

(De)stabilizing dispersion interactions via external electric charges — ●ANDRII KLESHCHONOK¹ and ALEXANDRE TKATCHENKO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Physics and Materials Science Research Unit, University of Luxembourg, L-1511 Luxembourg

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 electron 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.

MM 29.7 Tue 12:15 GER 38

An optimisability proof for self-consistent constrained DFT, and its implications for constraint-based self-interaction error correction — GLENN MOYNIHAN¹, GILBERTO TEOBALDI^{2,3}, and DAVID D. O'REGAN¹ — ¹School of Physics, CRANN and AMBER, Trinity College Dublin, Ireland. — ²Stephenson Institute for Renewable Energy and Department of Chemistry, The University of Liverpool, U.K. — ³Beijing 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.

MM 29.8 Tue 12:30 GER 38

Density-based local hybrid functional for interfaces — PEDRO BORLIDO¹, SILVANA BOTTI¹, and MIGUEL MARQUES² — ¹Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743, Jena, Germany — ²Institut 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.

MM 29.9 Tue 12:45 GER 38

On the hunt for better functionals in DFT: a new quantum embedding scheme — ULIANA MORDOVINA¹, TERESA E. REINHARD¹, HEIKO APPEL¹, and ANGEL RUBIO^{1,2} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ²Nano-bio Spectroscopy Group and ETSF, Departamento de Física de Materiales, Universidad del País 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 originates 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)