

CPP 10: Focus Session: Frontiers of Electronic-Structure Theory: Correlated Electron Materials I (joint session O/MM/DS/TT/ CPP)

Exploring, understanding, and describing materials with strong electronic Coulomb correlations remain among the big challenges of modern condensed matter physics. Correlated materials are characterized by an extreme sensitivity to external probes such as pressure or temperature, and slight changes in composition, constraints during the growth process (e.g. by heterostructuring) or off-stoichiometries can significantly alter their properties. While the invited lectures will have a focus on correlated electron materials, the symposium will cover the general field of computational materials science and electronic-structure theory.

Organizers: Silke Biermann, Ecole Polytechnique, Palaiseau cedex, France; Paul R. Kent, Oak Ridge National Laboratory, USA; Matthias Scheffler, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Time: Monday 10:30–13:00

Location: HL 001

CPP 10.1 Mon 10:30 HL 001

How Derivative Discontinuities in the Energy Yield Interatomic Steps in the Exact Kohn-Sham Potential of Density-Functional Theory — ●ELI KRAISLER¹, MATTHEW J. P. HODGSON¹, AXEL SCHILD², and EBERHARD K.U. GROSS^{1,3} — ¹Max-Planck-Institut für Mikrostrukturphysik, Halle (Saale), Germany — ²Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland — ³Fritz Haber Center for Molecular Dynamics, Institute of Chemistry, The Hebrew University of Jerusalem, Israel

Accurate density-functional calculations hinge on reliable approximations to the unknown exchange-correlation (xc) potential. The most popular approximations usually lack features of the exact xc potential that are important for an accurate prediction of the fundamental gap and the distribution of charge in complex systems. Two principal features in this regard are the spatially uniform shift in the potential, as the number of electrons infinitesimally surpasses an integer, and the spatial steps that form, e.g., between the atoms of stretched molecules. Although both aforementioned concepts are well-known, the exact relationship between them remained unclear. In this talk, we establish this relationship and introduce a new concept: the charge-transfer derivative discontinuity, Δ^{CT} . By numerically solving the many-electron Schrödinger equation, we extract the exact Kohn-Sham potential and directly observe its features, particularly the spatial interatomic steps. For the first time, spatial steps in the exact xc potential of a full configuration-interaction (FCI) calculation of a molecule are presented in three dimensions.

CPP 10.2 Mon 10:45 HL 001

Steps in the exact Kohn-Sham potential of ensemble density-functional theory for excited states and their relation to the derivative discontinuity — ●MATTHEW J. P. HODGSON¹, ELI KRAISLER¹, MICHAEL T. ENTWISTLE², AXEL SCHILD³, and EBERHARD K. U. GROSS^{1,4} — ¹MPI für Mikrostrukturphysik, D-06120 Halle, Germany — ²Dep. of Physics, Uni. of York, Heslington, YO10 5DD, UK — ³Lab. für Physikalische Chemie, ETH Zürich, 8093, Switzerland — ⁴Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem, 91904, Israel

An accurate approximation to the exchange-correlation (xc) part of the Kohn-Sham (KS) potential is essential for any density-functional calculation. Understanding the behaviour of the exact xc potential and developing improved approximations to it are crucial. The focus of calculations within density functional theory is usually on the ground state. However, knowledge of how the system responds to an excitation is important. In this talk we present the exact KS potential of an ensemble of the ground state and the first excited state of a 1D diatomic molecule. For this system, upon excitation, a small amount of charge transfers from one atom to the other. In the corresponding exact ensemble xc potential we find two plateaus: one that forms around the nucleus of the acceptor atom, associated with the derivative discontinuity of that atom, and another that forms around the donor atom and corresponds to a new phenomenon which we term the ‘charge-transfer derivative discontinuity’.

CPP 10.3 Mon 11:00 HL 001

Koopmans-compliant functionals: A reliable and efficient tool for the prediction of spectroscopic quantities — ●NICOLA COLONNA¹, NGOC LINH NGUYEN¹, ANDREA FERRETTI², and NICOLA MARZARI¹ — ¹THEOS and MARVEL, EPFL, Lausanne, Switzerland — ²Centro S3, CNR-Istituto Nanoscienze, Modena, Italy

Commonly used approximate density functionals produce total energies that do not exhibit the expected piecewise-linear behavior as a function of the particle number, leading to a discrepancy between total and partial electron removal/addition energies and poor predictive capabilities of ionization potentials. Koopmans-compliant functionals enforce a generalized criterion of piecewise linearity in the energy of any approximate density functional with respect to the partial removal/addition of an electron - i.e., with respect to charged excitations - from/to any orbital of the system. When used to purify approximate density functionals, Koopmans’ corrections lead to orbital-density dependent functionals and potentials that are able to deliver accurate spectroscopic properties. As an example, ionization potentials of a large set of molecules (the GW100 test set), photoemission spectra of organic donors and acceptors and band gaps of 35 semiconductors and insulators are presented, showing very good agreement with experiment or higher-order theories. Being this a functional framework, the straightforward advantages are that forces and other derivatives are also readily accessible, that the computational costs are much reduced, and the numerical parameters are those typical of DFT calculations.

CPP 10.4 Mon 11:15 HL 001

Selfconsistent density embedding - a new class of functionals for DFT — ●ULIANA MORDOVINA¹, TERESA E. REINHARD¹, HEIKO APPEL¹, and ANGEL RUBIO^{1,2,3} — ¹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ²Center for Computational Quantum Physics (CCQ), The Flatiron Institute, 162 Fifth Avenue, New York NY 10010, USA — ³Nano-bio Spectroscopy Group and ETSF, Departamento de Física de Materiales, Universidad del País Vasco UPV/EHU, San Sebastian, Spain

We propose a new technique to find functionals for 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.

The proposed density-embedding scheme serves as functional in DFT, which, unlike in usual DFT, can be systematically improved by increasing the size of the active space.

We show convergence toward exact results for 1D systems as well as results for 2D systems.

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

CPP 10.5 Mon 11:30 HL 001

Pressure dependence of the effective screened Coulomb interactions in transition metal monoxides — ●SWARUP KUMAR PANDA¹, HONG JIANG², and SILKE BIERMANN^{1,3} — ¹Centre de Physique Théorique, Ecole Polytechnique, France — ²College of Chemistry and Molecular Engineering, Peking University, China — ³Collège de France, Paris, France

In transition metal compounds, the magnitudes of the effective Coulomb interaction parameters (Hubbard U) and their pressure dependence are of utmost importance in any realistic many-body simulations for describing their pressure driven insulator-metal transition. One of the powerful methods for calculating the Hubbard U from first

principles is based on linear response theory within the constrained random-phase approximation (cRPA) [1], which provides the full U matrix including off-site elements and its frequency dependence. In this presentation, we apply this method (in its implementation into the Wien2k code [2]) to the transition metal monoxides (FeO, CoO, NiO, and CuO) [3]. Although the pressure induced changes in the bare Coulomb interactions are negligible, the effective screened U grows monotonically with increasing pressure for all of the above monoxides. Finally, I will argue that neither the pressure dependence nor the frequency dependence of U should be ignored in a reliable theoretical description of correlated oxides.

References: [1] Aryasetiawan et al., PRB 70, 195104 (2004) [2] Vaugier et al., PRB 86, 165105 (2012) [3] Panda et al., PRB 96, 045137 (2017)

CPP 10.6 Mon 11:45 HL 001

Self-Interaction Corrected SCAN for Molecules: All-Electron Implementation with Numerical Atom-Centered Basis Functions — ●SHENG BI, IGOR YING ZHANG, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

The self-interaction error (SIE) is a well-known problem in all semilocal density-functional approximations (DFAs), including the recently proposed "strongly constrained and appropriately normed" (SCAN) functional [1]. The so-called self-consistent Fermi-orbital SIC (FSIC) algorithm proposed by Pederson *et al.* [2] shows promising potential to eliminate the self-interaction error in semilocal approximations, which has been demonstrated for the local-spin-density approximation (LSDA) in a study of molecules.

We present an all-electron implementation of the self-consistent FSIC approach on the SCAN method [1]. Beside a systematic benchmark with respect to a selected molecular test set, we examine the performance of FSIC-SCAN in predicting the geometry of Pentacene, which is a well-documented challenge for standard semilocal DFAs [3]. Finally, we briefly discuss our ongoing work concerned with the implementation of the all-electron FSIC-SCAN approach for solids.

[1] J. Sun, A. Ruzsinszky, and J. P. Perdew, *Phys. Rev. Lett.* **115**, 036402 (2015).

[2] M. R. Pederson and T. Baruah, *Advances In Atomic, Molecular, and Optical Physics* **64**, 153 (2015).

[3] M. R. Pederson, T. Baruah, D. you Kao, and L. Basurto, *The Journal of Chemical Physics* **144**, 164117 (2016).

CPP 10.7 Mon 12:00 HL 001

Progress in Fermi-Löwdin orbital self-interaction correction to DFT — ●TORSTEN HAHN¹, SEBASTIAN SCHWALBE¹, SIMON LIEBING¹, MARK PEDERSON², and JENS KORTUS¹ — ¹TU Freiberg, Institute for Theoretical Physics, Germany — ²Johns Hopkins University, Department of Chemistry, USA

The accuracy of density functional theory (DFT) calculations is limited by the so called self-interaction error [1]. The recently proposed Fermi-Löwdin orbital based method [2,3,4] for self-interaction correction (FLO-SIC) is a unitary invariant and size extensive approach to overcome this error. We present the current state of the method and discuss the performance of FLO-SIC DFT applied to atoms and molecules in combination with different exchange-correlation functionals. In addition, this method delivers a description of the chemical bonding as intuitive as Lewis theory that may bridge the gap between DFT and chemical intuition.

[1] J. P. Perdew, A. Zunger, *Phys. Rev. B* **23**, 5048 (1981)

[2] M. R. Pederson et al., *J. Chem. Phys.*, vol. 140, 121103 (2014)

[3] M. R. Pederson, *J. Chem. Phys.*, vol. 142, 064112 (2015)

[4] T. Hahn et. al., *J. Chem. Phys.*, vol- 143, 224104 (2015)

CPP 10.8 Mon 12:15 HL 001

First-principles modeling of mixed-valence compounds from extended Hubbard-corrected functionals — ●MATTEO COCCIONI and NICOLA MARZARI — Theory and Simulations of Materials and MARVEL, EPFL, Lausanne, Switzerland

Modeling the electronic properties of mixed valence compounds is cen-

tral to developing many materials of technological relevance. Unfortunately, most approximate implementations of density functional theory (DFT) fail in capturing the localization of valence electrons on low dispersion states (e.g., of d or f kind) and mis-represent many properties of these systems. Quantitatively predictive first-principles calculations thus require, for these systems, the use of corrective functionals able to improve the description of electronic localization. Using the results of a recent study on materials for cathodes of Li-ion batteries this work shows how an extended Hubbard correction to DFT functionals, including on-site (U) and inter-site (V) interactions (named DFT+ $U+V$) improves considerably on simpler approximations for electronic, magnetic and structural properties and correctly describes localized states even in presence of significant inter-site hybridization. The work also demonstrates that evaluating the effective interaction parameters (U and V) consistently with the electronic and crystal structures, and treating them as material-specific quantities, improves the prediction of thermodynamic quantities and of average voltages. Finally, a novel method to compute these interactions from density-functional perturbation theory is shown to guarantee unprecedented efficiency, accuracy and convergence control.

CPP 10.9 Mon 12:30 HL 001

A Kohn-Sham type construction on a lattice with the exact kinetic energy density — ●IRIS THEOPHILOU¹, MICHAEL RUGGENTHALER¹, FLORIAN BUCHHOLZ¹, FLORIAN EICH¹, 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

In this presentation we explore a possible formulation of ground state Density Functional Theory by introducing the kinetic energy density as basic quantity in addition to the density. We presently restrict this formulation to the lattice case, and show that for a few site Hubbard interacting model it is numerically feasible to find an equivalent non-interacting system that yields the same density and kinetic energy density. By finding such a non-interacting system we mean here finding the local/on site potential and the non-local site dependent hopping that will give the target density and kinetic energy density. Our hope is that by including the kinetic energy density we will facilitate the functional construction and also put into grounds already existing approximations based on this quantity.

CPP 10.10 Mon 12:45 HL 001

Small-Polaron Formation in Polymorphs of Ga₂O₃ and TiO₂ — ●SEBASTIAN KOKOTT, SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin 14195, Germany

Transparent oxides are key materials for new devices in photovoltaics and electronics. One important factor influencing the behavior of charge carriers in these materials is the interaction with polar phonon modes. We focus on materials with strong electron-phonon coupling, where small polarons are formed. Although, density-functional theory (DFT) is often used for calculating polaron properties, there are two challenges: Sensitivity of the calculated properties to the errors in exchange-correlation treatment, and finite-size effects in supercell calculations. We have developed an approach [1] to address these issues. The polaron properties are obtained using a modified neutral potential-energy surface from DFT [2]. Based on Pekar's model [3], we correct for the proper elastic long-range behavior of the polaron in a supercell. With this approach, the influence of the crystal structure on the polaron properties is investigated for rutile and anatase TiO₂, and for the monoclinic β - and orthorhombic ϵ -Ga₂O₃. We find that in rutile TiO₂ only small electron polarons are stable, while only small hole polarons are found in anatase. On the contrary, small hole polarons exist in both Ga₂O₃ polymorphs but have significantly different binding energies.

[1] S. Kokott, arXiv:1710.03722 (2017)

[2] B. Sadigh et al., *Phys. Rev. B* **92**, 75202 (2015)

[3] S. I. Pekar, *Zh. Eksp. Teor. Fiz.* **16** 335 (1946)