

TT 52: Electronic-Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - V (joint session DS, HL, MA, MM, O, TT, organized by O)

Time: Wednesday 15:00–18:15

Location: GER 38

TT 52.1 Wed 15:00 GER 38

First-principle Linear Response in Real Space — •HONGHUI SHANG¹, DANILO S. BRAMBILA¹, CHRISTIAN CARBOGNO¹, PATRICK RINKE², and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Aalto University, Helsinki, Finland

Density-functional perturbation theory (DFPT) has developed into an important computational tool for assessing the linear electronic response of crystalline solids to perturbations, e.g., from electric fields or nuclear displacements [1]. In this work we present a full real-space reformulation of DFPT and its implementation [2] in the all-electron, numeric atom-centered orbital electronic structure theory code FHI-aims. We discuss the specific contributions, e.g., relativistic effects and Pulay terms, that arise in such a formulation and validate our implementation by systematically comparing with the finite-difference approach for various extended systems. The computational efficiency is then analyzed via scaling and scalability tests on massively parallel architectures (CRAY and IBM x86 clusters). Finally, we show that this real-space formalism enables an arbitrarily dense sampling of the Brillouin zone by numerically cheap Fourier transformations, which in turn facilitates an efficient evaluation of the electron-phonon coupling matrix elements. We demonstrate the efficiency by computing the relaxation time of hot carriers in Si.

[1] X. Gonze and C. Lee, *Phys. Rev. B* **55**, 10355, (1997).

[2] H. Shang, *et al.*, *Comp. Phys. Comm.* (accepted), arXiv:1610.03756.

TT 52.2 Wed 15:15 GER 38

Anharmonic Vibrations in Solids: Why and When Going Beyond Perturbative Treatments is Necessary — •HAGEN-HENRIK KOWALSKI, MAJA-OLIVIA LENZ, CHRISTIAN CARBOGNO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

In *ab initio* theory, the nuclear motion is typically assessed using a truncated second order Taylor expansion for the potential energy (harmonic approximation). Recent computational and methodological advancements [1] allow to extend this expansion to the third order so to approximately treat also anharmonic effects. Little is known, however, about the role of higher order terms. In this contribution, we systematically compare how a third-order expansion performs with respect to techniques that are able to capture higher degrees of anharmonicity, e.g., the quasi-harmonic approximation and fully anharmonic molecular dynamics. For this purpose, anharmonic properties such as the thermal expansion and the Grüneisen parameters are computed for a set of materials with increasing degree of anharmonicity (Si, Mg₂Si, CuCl, and ZrO₂). This reveals that a third order expansion can still lead to quantitative and even qualitative errors at elevated temperatures and/or in highly anharmonic systems. Eventually, we discuss the impact of the chosen exchange-correlation functionals on these calculations and the implications of these findings for the computation of thermal conductivities [2].

[1] D. A. Broido, *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

[2] C. Carbogno, R. Ramprasad, and M. Scheffler, *ArXiv*: 1608.06917.

TT 52.3 Wed 15:30 GER 38

Anharmonic and Quantum Fluctuations in Molecular Crystals from Ab Initio Simulations — •MARIANA ROSSI¹ and MICHELE CERIOTTI² — ¹Fritz Haber Institute of the Max Planck Society, Berlin — ²École Polytechnique Fédérale de Lausanne, Switzerland

Molecular crystals often exist in multiple competing polymorphs which are challenging to be predicted computationally, but show significantly different physicochemical properties. This challenge is not due only to the combinatorial search space, but also to the complex interplay of subtle effects determine the relative stability of different structures. Here we estimate all contributions to the free energies of these systems with density-functional theory, including the oft-neglected anharmonic contributions and nuclear quantum effects, by using a series of different flavors of thermodynamic integration. As an example, for the two most stable forms of paracetamol we find that anharmonic contributions, different descriptions of van der Waals interactions, and nuclear quantum effects all matter to quantitatively determine the stability of

different phases [1]. Our studies indicate that anharmonic free energies could play an important role for molecular crystals composed by large molecules and opens the way for a systematic inclusion of these effects in order to obtain a predictive screening of structures. [1] Rossi, Gasparotto, Ceriotti, *PRL* **117**, 115702 (2016).

TT 52.4 Wed 15:45 GER 38

Exact solutions and approximations in the exact factorization of the electron-nuclear wavefunction — •GRAEME GOSSEL and NEEPA MAITRA — Department of Physics and Astronomy, Hunter College of the City University of New York, 695 Park Avenue, New York, NY 10065.

"Recently it was shown how a molecular wavefunction may be written exactly as a single product of a nuclear and an electronic wavefunction, with a pair of corresponding equations of motion [1]. This exact factorization provides a new and rigorous starting point for developing intuitive and physical approximations to the exact coupled system. Strikingly, in this factorized picture the electronic Hamiltonian is not strictly Hermitian. Nevertheless, the norm is conserved so long as certain terms persist. This, and other constraints, inform the approximations we apply to make the process numerically feasible. In parallel we present numerical self-consistent solutions of the exact factorization equations devoid of approximations to assess accuracy and behaviour of different terms. Finally, we discuss how a well characterized and robust single-product-picture such as this may be used in TDDFT calculations.

[1] A Abedi, NT Maitra, and EKG Gross, *PRL* **105** (12), 123002, 2010

TT 52.5 Wed 16:00 GER 38

Insight into time-propagation TDDFT excitations via Kohn-Sham decomposition — •TUOMAS P. ROSSI¹, MIKAEL KUISMA^{2,3}, MARTTI J. PUSKA¹, RISTO M. NIEMINEN¹, and PAUL ERHART² — ¹Aalto University, Espoo, Finland — ²Chalmers University of Technology, Gothenburg, Sweden — ³University of Jyväskylä, Jyväskylä, Finland

The real-time-propagation formulation of time-dependent density-functional theory (RT-TDDFT) is an efficient method for calculating optical excitations of large molecules and nanoparticles. However, within RT-TDDFT, the analysis of the response is often limited to photoabsorption spectra and induced densities, in contrast to linear-response formulations of TDDFT, such as the Casida method, in which one can obtain further understanding on the basis of the Kohn-Sham electron-hole decomposition of the excitations.

In this work, we show that the Kohn-Sham decomposition can be equivalently obtained from RT-TDDFT calculations. We demonstrate the approach for the optical response of organic molecules and large metallic nanoparticles. The focus is especially on plasmonic applications, for which the method enables the analysis in terms of transition contribution maps [1]. By using the decomposition, we can shed light on the microscopic origin of plasmon resonances and their damping via plasmon-single-electron coupling, while retaining the favorable scaling of RT-TDDFT compared to linear-response formulations.

[1] S. Malola *et al.*, *ACS Nano* **7**, 10263 (2013).

TT 52.6 Wed 16:15 GER 38

Gauge-invariant Magnetic Properties from Time-Dependent Current-Density-Functional Theory — •NATHANIEL RAIMBAULT¹, PAUL DE BOEIJ³, PINA ROMANIELLO², and ARJAN BERGER¹ — ¹Laboratoire de Chimie et Physique Quantiques, IR-SAMC, Université Toulouse III - Paul Sabatier — ²Laboratoire de Physique Théorique, CNRS, IRSAMC, Université Toulouse III - Paul Sabatier — ³University of Twente, Faculty of Science and Technology, Physics of Interfaces and Nanomaterials

Standard formulations of magnetic response properties are often plagued by gauge dependencies, which can lead to unphysical results, and to a slow convergence with basis-set size. In this talk we present a novel method for obtaining magnetic properties from the current density [1]. This alternative scheme is fully gauge-invariant, numerically efficient, and can be applied to any method from which the current density can be obtained. To illustrate our method, we applied it to

time-dependent current-density-functional theory (TDCDFT). While different types of magnetic properties can be calculated in this way, we here emphasize the calculation of circular dichroism spectra, which are notably important in order to characterize secondary structures in biomolecules. The circular dichroism spectra we thus obtain for methyloxirane, dimethyloxirane and α -pinene are in good agreement with experiment [2]. [1] N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, PRL 114, 066404 (2015); [2] N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, JCTC 12, 3278 (2016)

TT 52.7 Wed 16:30 GER 38

Calculation of charge transfer integrals using constrained-DFT — ●TOBIAS LETTMANN and NIKOS DOLTSINIS — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Deutschland

For the investigation of charge transport properties of organic semiconductor materials, the fast and accurate calculation of charge transfer integrals (or transition matrix elements) is desirable. It has been suggested that the transfer integrals depend on a universal linear function of the corresponding wavefunction overlap, which can then be used to approximate the integral at a reduced computational cost¹.

We have calculated transfer integrals for dimers of poly(3-hexylthiophene) (P3HT) and diperylene bisimide (DiPBI), which are used in organic solar cells, in a large variety of intra- and intermolecular conformations and polymer lengths using a constrained-DFT approach². Our results show, that there is indeed a universal relation between transfer integral and wavefunction overlap. However this relation is (i) nonlinear for large overlaps and (ii) only holds true if the transfer integral is rescaled by the number of electrons of the respective system.

¹ F. Gajdos et al.: *J. Chem. Theory Comput.*, 2014, **10**, 4653

² H. Oberhofer, J. Blumberger: *J. Chem. Phys.*, 2010, **133**, 244105

TT 52.8 Wed 16:45 GER 38

Towards ultra long-range ab-initio calculations — ●TRISTAN MÜLLER¹, SANGEETA SHARMA^{1,2}, EBERHARD K.U. GROSS¹, and JOHN K. DEWHURST¹ — ¹Max-Planck-Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — ²Department of physics, Indian Institute for Technology-Roorkee, 247997 Uttarkhand, India

We propose a generalization of the Bloch state which involves an additional sum over a finer grid in reciprocal space around each k-point. This allows for ab-initio calculations of ultra long-range modulations in the density which may involve millions of unit cells but with an efficiency rivaling that of a single unit cell. This is due to a new algorithm developed specifically for solving the particular eigenvalue problem that this ansatz requires. Thus physical effects on the micron length scale, which nevertheless depend on details of the electronic structure on nanometer length scales, can be computed exactly within density functional theory.

TT 52.9 Wed 17:00 GER 38

Local density fitting within a Gaussian and plane waves scheme for large-scale density functional theory calculations — ●DOROTHEA GOLZE^{1,2}, MARCELLA IANNUZZI¹, and JÜRIG HUTTER¹ — ¹Aalto University, Otakaari 1, 02150 Espoo, Finland — ²University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

A local resolution-of-identity (LRI) approach is introduced in the Gaussian and plane waves (GPW) scheme to enable large-scale Kohn-Sham (KS) density functional theory calculations. The construction of the KS matrix in GPW scales already linearly with respect to system size by using a plane wave expansion of the density for the evaluation of the Coulomb term in combination with a local basis. The intention is to retain the linear scaling of the GPW approach, while reducing the prefactor for computing the KS matrix. The locality of the density fitting ensures an $O(N)$ scaling and is implemented by approximating the atomic pair density by an expansion in one-center fit functions. The prefactor is smaller with LRI since the computational demands for the grid-based operations become negligible, while they are dominant in GPW. We observe a speed-up of the self-consistent field (SCF) procedure by a factor of up to 30 for periodic systems dependent on the symmetry of the simulation cell and the grid cutoff. The accuracy of LRIGPW is assessed for different systems and properties. Generally, total energies, reaction energies, intramolecular and intermolecular structure parameters are well reproduced. LRIGPW yields also high quality results for extended condensed phase systems such as liquid water, ice XV and molecular crystals.

TT 52.10 Wed 17:15 GER 38

From the Electron Localization Function to a Coalescent-Pair Locator — ●STEFANO PITTALIS¹, DANIELE VARSANO¹, ALAIN DELGADO^{2,3}, and CARLO ANDREA ROZZI¹ — ¹Istituto Nanoscienze, Consiglio Nazionale delle Ricerche, Via Campi 213a, 41125 Modena, Italy — ²Department of Physics, University of Ottawa, Ottawa, ON K1N 6N5, Canada — ³Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear, Calle 30 # 502, 11300 La Habana, Cuba

The Electron Localization Function (ELF), as proposed originally by Becke and Edgecombe, uses the information on the distribution of pairs of electrons with parallel spins. The ELF has been widely adopted as a descriptor of atomic shells and covalent bonds, but it is not useful to visualize the bond in H₂ – the simplest neutral molecule in the universe. Here we propose a complementary descriptor which also works for H₂ by exploiting the information on pairs of electrons with opposite spins. Remarkably, only quantities derived from occupied single-particle orbitals are required in the calculations. If time allows, implications for developing improved approximate density functionals will also be discussed.

TT 52.11 Wed 17:30 GER 38

Band structure interpolation via maximally localized Wannier functions implemented in LAPW+lo basis — ●SEBASTIAN TILLACK, ANDRIS GULANS, and CLAUDIA DRAXL — Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin

The band structure is one of the most fundamental quantities of any solid that carries a lot of information about the material's properties. Obtaining a smooth dispersion from density-functional theory (DFT) and especially from the *GW* approximation of many-body perturbation theory may be very expensive. To this extent, we have implemented a method for generating maximally localized Wannier functions (WF) [1] from Kohn-Sham wavefunctions in the full-potential all-electron code *exciting* [2] using a (linearized) augmented plane-waves plus local-orbitals basis. These WF are used for interpolating wavefunctions and corresponding eigenenergies for arbitrary *k*-points in a computationally cheap post-processing step. The interpolated Kohn-Sham and *GW* bands of conventional and two-dimensional semiconductors and insulators are also used as an input to calculations of optical-excitation spectra.

[1] N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997)

[2] A. Gulans, et al. *J. Phys.: Condens. Matter* **26**, 363202 (2014)

TT 52.12 Wed 17:45 GER 38

Chemical insight from Fermi-Löwdin orbitals — ●TORSTEN HAHN¹, SEBASTIAN SCHWALBE¹, SIMON LIEBING¹, JENS KORTUS¹, and MARK PEDERSON² — ¹Institute for Theoretical Physics, TU Freiberg, Germany — ²Department of Chemistry, Johns Hopkins University, Baltimore Maryland (MD), US

The recently developed Fermi-Löwdin orbital based method for correcting the self-interaction error in Density Functional Theory (FLO-SIC DFT) [1,2,3] is briefly introduced. Contrary to standard DFT approaches, where only auxiliary Kohn-Sham orbitals are available, FLO-SIC DFT delivers a set of well-defined, localised Fermi-Löwdin orbitals. These localised orbitals together with their optimised reference positions yield an inherently ‘chemical’ representation of bonding details in molecules that resembles remarkably well Lewis concept of lone and binding electron pairs. For complex examples, the method provides detailed insights into the bonding situation in terms of multi-center many-electron bonds in a natural, chemically-intuitive fashion.

[1] M. R. Pederson et al., JCP 140, 121103 (2014).

[2] M. R. Pederson, JCP 142, 064112 (2015).

[3] T. Hahn et al., JCP 143, 224104 (2015).

TT 52.13 Wed 18:00 GER 38

Conditions for describing triplet states in reduced density matrix functional theory — IRIS THEOPHILOU¹, NEKTARIOS N. LATHIOTAKIS², and ●NICOLE HELBIG³ — ¹Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48, GR-11635 Athens, Greece — ³Peter-Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich, D-52425 Jülich, Germany

We consider necessary conditions for the one body-reduced density ma-

trix (1RDM) to correspond to a triplet wave-function of a two electron system. The conditions concern the occupation numbers and are different for the high spin projections, $S_z = \pm 1$, and the $S_z = 0$ projection. Hence, they can be used to test if an approximate 1RDM functional yields the same energies for both projections. We employ these conditions in reduced density matrix functional theory calculations for the

triplet excitations of two electron systems. In addition, we propose that these conditions can be used in the calculation of triplet states of systems with more than two electrons by restricting the active space. We assess this procedure in calculations for a few atomic and molecular systems. We show that the quality of the optimal 1RDMs improves by applying the conditions in all the cases we studied.