

O 37: Electronic-Structure Theory: General II

Time: Tuesday 14:00–16:15

Location: MA 141

Invited Talk

O 37.1 Tue 14:00 MA 141

Unraveling the structure and dynamics at solid-liquid interfaces by machine learning potentials — MATTI HELLSTRÖM¹, VANESSA QUARANTA², and JÖRG BEHLER¹ — ¹Theoretische Chemie, Universität Göttingen, Germany — ²Theoretische Chemie, Ruhr-Universität Bochum, Germany

Solid-liquid interfaces pose a significant challenge for atomistic simulations. The very different interactions and bonding situations in water and in solid surfaces are best described by electronic structure methods, which can also take into account the dissociation and recombination of water molecules at the interface. On the other hand, long simulations of large systems are required to obtain converged properties of the liquid phase, which is often computationally very demanding. Machine learning potentials offer a solution to this problem by combining a first principles quality description of the potential-energy surface with the efficiency of simple empirical potentials. In this talk, recent results for the interaction of water with metal and oxide surfaces will be presented, which have been obtained in molecular dynamics simulations employing high-dimensional neural network potentials (NNPs), a typical class of machine learning potentials. NNPs are reactive and thus allow to observe proton transfer processes at the interface, which also play an important role in highly concentrated electrolyte solutions.

O 37.2 Tue 14:30 MA 141

Representing energy landscapes by combining neural networks and the empirical valence bond method — SINJA KLEES¹, ECKHARD SPOHR², and JÖRG BEHLER^{1,3} — ¹Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany — ²Lehrstuhl für Theoretische Chemie, Universität Duisburg-Essen, D-45141 Essen, Germany — ³Theoretische Chemie, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany

Computer simulations of aqueous electrolyte solutions can be challenging for several reasons: (i) there can be huge variations in the ratio of solvent molecules and ions; (ii) large-scale simulations are needed to avoid artificial periodicity and (iii) reactive potentials are necessary to take omnipresent proton transfer reactions into account. Artificial neural networks (NNs) are a powerful method to construct reliable and unbiased interatomic potentials for a wide range of systems. However, the construction of NN potentials can become computationally very demanding due to the high dimensionality of the configuration space, which needs to be mapped. Combining NN potentials of different system fragments with the empirical valence bond (EVB) method offers a promising approach to derive the potential energy surface of complex systems with substantially reduced effort. Preliminary results will be discussed and compared to density functional theory data.

O 37.3 Tue 14:45 MA 141

Ultra long-range ab-initio calculations — TRISTAN MÜLLER¹, SANGEETA SHARMA^{1,2}, EBERHARD K.U. GROSS¹, and JOHN K. DEWHURST¹ — ¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — ²Department of Physics, Indian Institute of Technology-Roorkee, 247667 Uttarakhand, 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. Thus physical effects on the micron length scale, which nevertheless depend on details of the electronic structure can be computed exactly within density functional theory. As an example, we apply our method to solids subjected to spatially extended external electromagnetic fields.

15 min. break

O 37.4 Tue 15:15 MA 141

Optical Spectra from TDDFT with an Adiabatic GGA XC Kernel — NISHA SINGH^{1,2}, PETER ELLIOTT¹, J.K. DEWHURST¹, E.K.U. GROSS¹, and SANGEETA SHARMA^{1,2} — ¹Max-Planck Institute of Microstructure Physics, Halle, Germany — ²Indian Institute of Technology Roorkee, Roorkee, India

A complete understanding of a material requires both knowledge of the excited states, as well as the ground state. Time dependent den-

sity functional theory (TDDFT), within the linear response regime, has been a successful method to access these excited state properties. However, it suffers the drawback that the exchange-correlation (XC) kernel must be approximated. In this work, we climb up 'Jacob's ladder' of functionals and use an adiabatic generalized gradient approximation (AGGA) for the XC kernel, rather than the commonly used adiabatic local density approximation (ALDA). The performance of the AGGA kernel is assessed for simple solids by studying optical absorption spectra. We find better results, as compared to the ALDA kernel, when gradients of density are included in the XC kernel.

O 37.5 Tue 15:30 MA 141

First Principles Simulations of Small Polarons in Ionic Crystals — MARIA DRAGOMI, SEBASTIAN KOKOTT, SERGEY LEVCHENCO, IGOR YING ZHANG, and MATTHIAS SCHEFFLER — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

A small polaron can be modeled by a supercell with a hole or an electron in periodic boundary conditions. In order to correctly cover long-range contribution, very large supercells are often needed, which makes advanced first principles simulations prohibitively expensive to run. In this work, we propose a force-field corrected model to efficiently describe the lattice distortion due to the long range contribution in a reasonably small supercell model [1]. In this approach the electronic structure close to the center is treated accurately, on the theoretical levels of semilocal PBE, hybrid HSE06, and second-order Møller-Plesset perturbation theory, but taking into account the contribution of elastic distortion of the distant atoms by an appropriate model hamiltonian. The convergence behavior of long-range contribution in this hybrid strategy is examined and we apply this method to study the geometry distortion of the small polaron in MgO. The results are compared to other calculations using standard supercell models and to available experimental data.

[1] M. Scheffler, J.P. Vigneron, and G. B. Bachlelet, Phys. Rev. B 31, 6541 (1985).

[2] S. Kokott, S. V Levchenko, P. Rincke, and M. Scheffler, Submitted, arxiv:1710.03722 (2017).

O 37.6 Tue 15:45 MA 141

Vibrational Anharmonic Raman Spectra of Polymorphic Crystals from Density-Functional-Perturbation Theory — NATHANIEL RAIMBAULT, HONGHUI SHANG, and MARIANA ROSSI — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Vibrational Raman spectroscopy is widely used for characterizing different molecular-crystal polymorphs and their phase transitions. Few theoretical studies take anharmonic effects into account, despite their acknowledged importance in particular in organic and flexible compounds. In this work we compute anharmonic Raman spectra through the calculation of polarizability autocorrelation functions in thermodynamic equilibrium, obtaining polarizability tensors from our recent implementation of Density Functional Perturbation Theory (DFPT) in the all-electron FHI-aims code [1,2]. We focus here on different polymorphic forms of the paracetamol and aspirin crystals. Our anharmonic calculations show important effects in the low-frequency range of these spectra which prove essential for obtaining agreement with experimental data. Furthermore, in order to reduce the cost of DFPT simulations we use Kernel Ridge Regression (KRR) to obtain DFPT-level polarizabilities at a reduced cost. Training our model on a few thousand points, we can reproduce Raman spectra that would typically take the calculation of hundreds of thousands of points. [1] H. Shang *et al.*, CPC **215**, 26 (2017) [2] H. Shang, N. Raimbault, *et al.*, submitted (2017)

O 37.7 Tue 16:00 MA 141

Engineering one-body density-matrix functionals — CARLOS L. BENAVIDES-RIVEROS¹, NEKTARIOS LATHIOTAKIS², and MIGUEL A. L. MARQUES¹ — ¹Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, GR-11635 Athens, Greece

The problem of computing ground states of systems of many electrons is at the very heart of many-body quantum physics. This problem is so challenging that a major goal in electronic modelling is to reduce

that hardness much more below the one of the wave function. Density and reduced-density-matrix functional theories achieve a maximal reduction by using, respectively, the electronic density and the one-body reduced density matrix (1RDM) as the basic variables. In the literature there are several functionals of the 1RDM for closed shell systems. Based on recent progress on fermionic exchange symmetry, we produce

a family of functionals for systems with odd numbers of active electrons. Since the general structure of the functionals is derived from general pure representability considerations, our approach suggests a systematic way to produce functionals within reduced density matrix functional theory.