

MM 14: Computational Materials Modelling - Methods I

Time: Monday 15:45–16:45

Location: IFW D

MM 14.1 Mon 15:45 IFW D

Accuracy vs. efficiency? Towards ACKS2-based polarization in force fields — ●PATRICK GÜTLEIN¹, KARSTEN REUTER¹, HARALD OBERHOFER¹, and JOCHEN BLUMBERGER² — ¹Technische Universität München, Germany — ²University College London, UK

Electronic polarization poses a minor energy contribution compared to the formation and arrangement of covalent bonds, yet it crucially influences both geometric and electronic properties of soft condensed matter and molecular crystals. Frequently, effective force field techniques employed to sample the phase space of such systems insufficiently cover the complex dielectric response to external perturbations. Here, the recently proposed atom-condensed Kohn-Sham density functional theory approximated to second order (ACKS2) approach promises to be a computationally undemanding, still accurate electronic polarization extension to conventional force field methods. It rests on an atom-centered basis set expansion of the linear responses of both the electron density and the Kohn-Sham potential.

In order to provide a generally applicable ACKS2 extension to force fields, we develop a new and efficient Gaussian type basis set representation. We demonstrate the efficacy of ACKS2 with the new basis set for a range of molecular model systems, which are relevant building blocks in common organic semiconductors and biotic materials. Furthermore, we formulate a fragmentation scheme to improve both computational scaling with system size and evaluation of the condensed response parameters. This marks important first steps to employ ACKS2 as polarization correction in force fields.

MM 14.2 Mon 16:00 IFW D

Modified Becke-Johnson calculations using pseudopotential plane-wave approach: Systematic analysis — ●HAZEM ABU-FARSAKH¹, MOHAMMAD ABU-JAFAR², and ABDALLAH QTEISH³ — ¹Dept. of General Sciences, Prince Sultan University, Riyadh, Saudi Arabia — ²Dept. of Physics, An-Najah National University, Nablus, Palestine — ³Dept. of Physics, Yarmouk University, Irbid, Jordan

The modified Becke-Johnson exchange potential (mBJ) has been promising for providing accurate band gaps for various types of solids at low cost. The optimization of the mBJ potential was done using the all-electron (AE) electronic structure technique and it is usually tested within the AE method (mBJ@AE). On the other hand, the performance of the mBJ with the pseudopotential approach (mBJ@PP) is not well explored. We therefore present systematic investigation of the electronic structure of different semiconductors and insulators employing the mBJ@PP approach. mBJ@AE and screened hybrid functional YS-PBE0 calculations are also performed for comparison. It is found that using typical PP's the mBJ@PP calculations lead to bandgaps that are significantly smaller than in the mBJ@AE approach. The best agreement with the mBJ@AE band gaps is obtained by including the outer core *p* electrons as valence in the cation PPs. For the considered systems, apart from Cu₂O and ScF₃, the obtained bandgaps are in very good agreement with those of YS-PBE0, G₀W₀, and experiment. We also investigate the calculated binding energies of the

semicore *d* electrons, upper valence bandwidths, and electron effective masses. Explanations of the mBJL@PP results are provided.

MM 14.3 Mon 16:15 IFW D

Optimized effective potentials to increase the accuracy of approximate proton transfer energy calculations in the excited state — ●POUYA PARTOVI-AZAR and DANIEL SEBASTIANI — Institute for Chemistry, MLU Halle-Wittenberg

In various systems, acidic properties emerge when the system is electronically excited. Although the time scale attributed to the dynamics of the electrons is usually on the order of femtoseconds, the electronic excitations can in general trigger much slower processes.

Here, we propose and benchmark a novel approximate first-principles molecular dynamics simulation idea for increasing the computational efficiency of density functional theory-based calculations of the excited states. We focus on obtaining proton transfer energy at the S₁ excited state through actual density functional theory calculations at the T₁ state with additional optimized effective potentials. The potentials are optimized such as to reproduce the time-dependent density functional theory energy surface, but can be generalized to other more accurate quantum chemical methods. We demonstrate the applicability of this method for two prototypical photoacids, namely phenol and 7-hydroxyquinoline. We show that after optimizing the additional effective potentials for carbon, nitrogen, oxygen, and the acidic hydrogens, both thermodynamics and kinetics of proton dissociation reaction can be well reproduced as compared to reference excited-state calculations. It is found that a good agreement can be reached by only optimizing two effective potential parameters per each species in the photoacids.

MM 14.4 Mon 16:30 IFW D

Assessing the accuracy of screened range-separated hybrids for bulk properties of semiconductors — ●STEFAN ALOIS SEIDL, BERNHARD KRETZ, and DAVID ALEXANDER EGGER — Department of Physics, Technical University of Munich, 85748 Garching, Germany

While conventional semilocal and hybrid functionals in density functional theory (DFT) are known to predict structural properties of semiconductors accurately, they fail to quantitatively describe electronic-structure and optical properties of these materials. Screened range-separated hybrid (SRSH) functionals were recently shown to provide highly accurate electronic-structure and optical properties of prototypical semiconductors [1]. In the SRSH approach, a single empirical parameter is used to fit the SRSH band gap such that it reproduces the GW band gap, by tuning the range-separation parameter while maintaining 25% exact exchange in the short-range [1]. Here, we assess the accuracy of the SRSH approach in computing bulk properties (e.g., lattice constants, bulk moduli, atomization energies etc.) of several prototypical semiconductors. To this end, results from the SRSH method are compared to experimental data as well as to computational results obtained when using conventional semilocal and hybrid DFT functionals.

[1] D. Wing et al, Phys. Rev. Materials 3, 064603 (2019)