A Frequency-Dependent Polarizable Force Field: ACKS2ω

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Frequency-dependent polarizabilities describe the density response of a system due to frequency-dependent (or time-dependent) external perturbations, determining properties of the system, e.g., absorption spectrum, long-range correlation energies, etc. They can be computed analytically with a high accuracy using quantum-mechanics-based (QM) methods with time-dependent extensions. Density functional theory (DFT) is a widely applied *ab initio* approach for simulating ground-state properties of molecules, clusters, and solids. To treat electronically excited states, time-dependent density functional theory (TD-DFT) is usually employed with a proper choice of exchange-correlation functional. In practice, those QM methods are still computationally expensive for extended systems. For such extended systems, a polarizable force field (PFF), which estimates response properties with empirical parameters, is still applicable due to its limited computational cost. While static PFFs are relatively wide-spread in the literature, only a few examples can be found of the frequency-dependent analogs (FD-PFF). Yet, such models are promising for modeling non-trivial long-range interactions in extended systems.

In this talk, a recently proposed static PFF, namely atom-condensed Kohn-Sham density functional theory approximated to second-order (ACKS2),[1,2] is used as a starting point. The merit of ACKS2 is that the electronic kinetic energy is included via Legendre transform as a correction for conventional PFFs. In addition, in the limit of a complete basis set in the ACKS2 model, the linear response properties of the underlying theory can be reproduced precisely. A frequency-dependent generalization of ACKS2, called ACKS2ω, can be derived similarly, by making use of the quasi-energy formalism.[3] Our method enables theoretical predictions for dynamical response properties of finite systems after an atoms-in-molecules partitioning of the frequency-dependent molecular response function. A numerical validation shows that spectra and dispersion coefficients can already be obtained with fluctuating monopoles and dipoles. These results confirm that ACKS2ω, as a FD-PFF candidate, offers a solid connection between the quantum-mechanical description of frequency-dependent response and computationally efficient force-field models.

References

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