Application of Hybrid Density Functional Tight Binding (DFTB)-Molecular Mechanics Approach to Computing Optical Properties of Dyes on Nanoparticles

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The Density Functional based Tight Binding (DFTB) is promising for modeling of materials and interfaces for renewable energy applications, as it enables electronic structure-level modeling of larger and therefore more realistic systems than is routinely feasible with Density Functional Theory (DFT). This, in particular, concerns nanoparticles and molecule-nanoparticle systems used in solar cell applications and elsewhere. The CPU cost reduction in DFTB compared to DFT is achieved by the Slater-Koster (SK) pre-parameterization of the elements of the Hamiltonian matrix as well as the repulsion potential between all pairs of atoms. However, accurate parameterization for new systems in specific applications requires specialized manpower and computational resources. This hinders the application of DFTB to systems for which it was not parameterized. We previously introduced a DFTB-molecular mechanics (DFTB-MM) approach to expand the applicability of DFTB by modeling the interactions of the missing SK parameters with an interatomic interaction potential [1]. We showed that when interactions between the affected atoms do not critically affect key mechanisms of interaction, one obtains structures and partial densities of states with a similar accuracy to full DFTB. This allows for the use of DFTB in systems where not all pairs of atoms have been parameterized. Our preliminary exploration of applicability of the DFTB-MM approach to the computation of optical properties of molecular systems with TD (time-dependent) -DFTB showed that DFTB-MM can also be viable for optical property calculations [2]. TD-DFTB permits calculations that include a large number of excitations, which is required for systems with high densities of states, that would not be feasible with TD-DFT. Here, we further explore the capability of the DFTB-MM method to the calculation of optical properties of molecule-nanoparticles systems with TD-DFTB. We consider representative organic dyes with cyanoacrylic and silane-based anchoring groups adsorbed in different configurations on a titania nanoparticle and compare TD-DFT with TD-DFTB and TD-DFTB-MM. In the case of the cyanoacrylic group, direct comparison to full DFTB parameterization can be done while in the case of the silane group only the DFTB-MM parameterization could be used with the *matsci* or *tiorg* Slater-Koster parameters where Ti-Si parameters are missing [3]. We conclude that MM-based substitution of parameters for Ti-N or Ti-Si pairs has negligible effect on TD-DFTB spectra and therefore DFTB-MM can be recommended for optical property calculations when SK parameters for some atomic pairs are missing.

[1] J. Chem. Theory Comput., 19, 189-5198 (2023)

[2] R. Li, G. Budiutama, S. Manzhos, M. Ihara: Proceeding of 34th IUPAP Conference on Computational Physics (CCP2023), Springer Proceedings in Physics, in print.

[3] J. Phys. Chem. C, 113, 5730–5740 (2009)

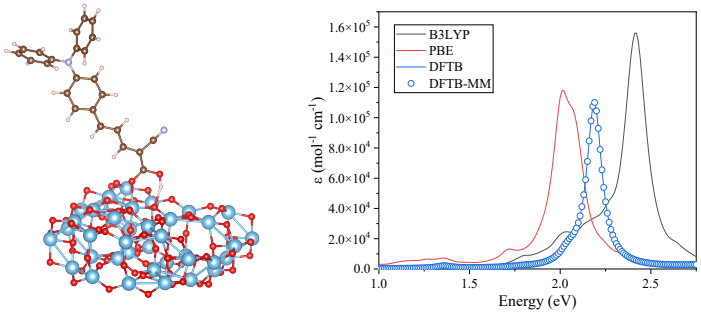

Figure 1. Left: representative dye-nanoparticle model. Right: Absorption spectra of a dye-nanoparticle model computed with different methods.