

Parametrization of a heme-protein conductivity model by DFT and TDDFT

Luke Nambi Mohanam,[#] Rafael Umeda,^{*} Ruqian Wu,^{*} Sahar Sharifzadeh[#]
Department of Electrical and Computer Engineering, Boston University[#]
Department of Physics, University of California Irvine^{*}

Outer membrane cytochrome-C heme-protein polymers are bio-active electron transport chains for respiration, moving electrons outside of cells towards the final electron acceptor. This long-range electron transport occurs via electron transfer between heme group co-factors covalently attached to the protein. We present two approaches for incorporating density functional theory (DFT)-based parameters of heme pairs into a quantum Liouville charge carrier model for these protein polymers, which includes transient quantum charge carrier features that may be crucial for predictive charge carrier modelling. The first, which we term spin-flip diabatization, relies on the properties of unrestricted DFT to extract site energies and inter-site couplings from canonical orbitals. This approach preserves the single site-orbital picture of each heme, but leaves out relaxation of the electron density. A second approach relies on linear-response equations from time-dependent DFT (TDDFT) to calculate adiabatic charge transfer states, including electronic relaxations by calculating energy differences and couplings via the excitation vector. We contrast the formalism of these two approaches, and discuss the behavior of the Liouville charge carrier model in the electron-hopping regime of weak coupling and large site energy differences.