Implementation of Modified-Redfield Theory into *ab Initio* Excited-State Dynamics

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ABSTRACT

Understanding photo-induced biological processes, such as photosynthesis, and controlling materials development for opto-electronic applications, such as photovoltaics, both fundamentally rely on the manipulation of charge-carriers to result in interfacial charge-transfer. For describing electron transfer rates there are two limiting scenarios: when changes to the charge-carriers dielectric environment are 'weak', as described by Redfield theory, or 'strong', as described by Marcus theory. Marcus theory predicts that electron transfer processes depend on the donor-acceptor energy difference and the reorganization energy of the dielectric environment. Redfield theory treats the reorganization energy perturbativity and predicts that rates are linear with reorganization energy while Marcus theory describes a non-linear dependence giving the empirically observed 'inverted regime'. The perturbative treatment of reorganization energy in Redfield theory can result vastly overestimating charge-transfer rates[1] and providing qualitatively wrong trends for atomistic simulations. So called modified-Redfield[2] remedies this situation by including the diagonal elements of the electron-phonon interaction, which describes nuclear reorganization, into the explicit Hamiltonian while still treating the off-diagonal elements perturbatively. Here we implement modified-Redfield into *ab Initio* atomistic simulations to model photo-induced charge-transfer. Initial test systems are donor-acceptor molecules which result in intra-molecular charge-transfer after photo-excitation.

1. Landry, B. R.; Subotnik, J. E., Surface Hopping Outperforms Secular Redfield Theory When Reorganization Energies Range from Small to Moderate (and Nuclei Are Classical). *The Journal of Chemical Physics* **2015**, *142*, 104102.

2. Zhang, W. M.; Meier, T.; Chemyak, V.; Mukamel, S., Exciton-Migration and Three-Pulse Femtosecond Optical Spectroscopies of Photosynthetic Antenna Complexes. *Journal of Chemical Physics* **1998**, *108*, 7763-7774.