Density Matrix Propagation for Modeling Time-dependent Phenomena in Nanoscopic Systems:

Application to Solar Energy Harvesting

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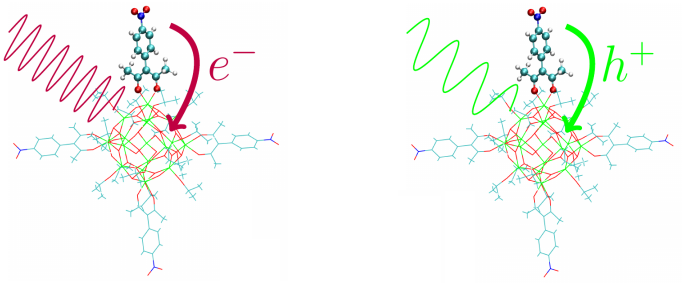
Quantum dynamics simulation based on the density matrix formalism can address several questions about non-equilibrium phenomena occurring at nanoscale dimensions. In particular it can provide a detailed description of the time-dependent photoinjection process occurring in Dye Sensitized Solar Cells (DSSC)[1]. The simulations are performed by integrating the Liouville-von Neumann equation to get the time-dependent evolution for the density matrix ρ and with it, the evolution of any expectation value of interest. In order to describe the electronic structure of the systems we employ a Self-Consistent Tight-Binding method based on Density Functional Theory (DFTB)[2].



When applied to simulate the absorption spectra of organic molecules, this method leads to a remarkable agreement with experimental results[3]. Moreover, it is able to depict subtle differences between the mechanisms underlying the photoinjection process in DSSCs. Recently, this method was used to study the photoinjection dynamics occurring in crystallographically resolved 4-nitrophenyl-acetylacetonate sensitized $Ti_{17}O_{24}$ nano-clusters[4]. Unexpectedly, a hole injection phenomenon was predicted upon excitation with long wavelengths. Subsequent photoelectrochemical measurements on thin layers of functionalized $Ti_{17}O_{24}$ deposited on FTO working electrodes lead to the observation of a negative photocurrents when illuminating the sample with visible light. This experimental result confirmed the computationally predicted hole injection mechanism occurring in sensitized $Ti_{17}O_{24}$ nano-clusters. The set of results here exposed show that quantum dynamics based on the density matrix formalism is suitable for describing as well as predicting non-equilibrium processes occurring in DSSCs.

References

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