

Dynamics of open quantum systems: Electron transfer in a mixed-valence compound

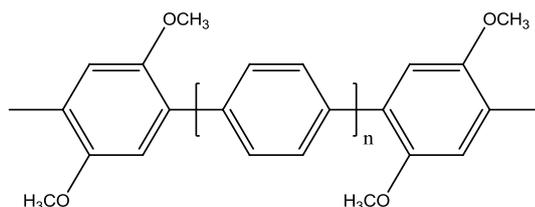
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Quantum coherences have been found to be important in excitation or electron transfer processes despite the extremely large system size, for instance, in photosynthetic proteins or conducting polymers. A deep understanding of those transfers in the presence of nuclear motion is of fundamental importance.

Here we study the electron transfer in an organic mixed-valence compound with one charge. It consists of two dimethoxy-methyl-phenyl units separated by a bridge of p-phenylene. We describe the system with a two-level system spin-boson model. All the *ab initio* data are computed by the new constrained DFT method [1] allowing us to enforce electronic localization on one redox side and therefore to obtain diabatic states and their coupling [2,3].



In order to take into account the nuclear motion, we use a method of dissipative quantum mechanics developed by Meier and Tannor [4,5]. We adopt a non-markovian master equation for the evolution of the density matrix of the quantum system coupled to a dissipative thermal bath. This approach is perturbative in the system-bath coupling but it has the advantage of being valid for any timescales that occur in the system dynamics or in the bath relaxation. It leads to a coupled equation system between the system density matrix and auxiliary matrices that depend on the setting of the correlation function of the bath of oscillators. The bath is entirely described by its spectral density, that we calculate here from the displacements of each normal mode of the molecule [6] in reference to their position in the neutral molecule.

We study the coherence properties of the transfer dynamics. One of the challenges is to determine the importance of nuclear motions which substantially affect the transfer mechanism.

References:

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