

Non-adiabatic QM/MM Simulations of Fast Charge Transfer in *E. coli* DNA Photolyase

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In this work, we study the photo-activation process in *E. coli* DNA photolyase, involving long-range electron transport along a conserved chain of Trp residues between the protein surface and the FAD cofactor. Fully coupled non-adiabatic (Ehrenfest) QM/MM simulations allow us to follow the time evolution of charge distributions over the natural time scale of multiple charge transfer events and conduct rigorous statistical analysis. Charge transfer rates in excellent agreement with experimental data are obtained without the need for any system-specific parameterization. The simulations are shown to provide a more detailed picture of electron transfer than a classical analysis of Marcus parameters. The protein and solvent both strongly influence the localization and transport properties of a positive charge, but the directionality of the process is mainly caused by solvent polarization. The time scales of charge movement, delocalization, protein relaxation and solvent reorganization overlap and lead to nonequilibrium reaction conditions. All these contributions are explicitly considered and fully resolved in the model used and provide an intricate picture of multi-step biochemical electron transfer in a flexible, heterogeneous environment.