

Abstract Submitted
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A Molecularly-Based Theory for Electron Transfer in Polar Solvents¹ BILIN ZHUANG, ZHEN-GANG WANG, Cal Inst of Tech (Caltech)
— Using field-theoretic methods, we develop a mean-field theory for charge solvation in equilibrium and nonequilibrium conditions, and apply it to study electron transfer reactions. The resulting dipolar mean-field theory (DMFT) considers the effects of solvent dipole moments and polarizabilities, and consists of simple sets of equations for the equilibrium and nonequilibrium conditions as well as an analytical expression for the free energy. With no adjustable parameters, the DMFT predicts the activation and the reorganization energies in good agreement with previous data. We have shown that, as DMFT is able to describe the solvent properties in the immediate vicinity of the charges, it is unnecessary to distinguish the inner-sphere and the outer-sphere solvent molecules in the calculation of reorganization energy. Furthermore, we examine the nonequilibrium free energy surfaces of electron transfer, and find that the parabolic approximation is not applicable for reactions with a large free energy change. In the case of solvent mixtures, we show that there are three classes of solvent structures around the ions, and the solvent structure is a key factor determining how the activation energy of electron transfer in a solvent mixture compares to those in the pure solvent components.

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