Dr. Joe Subotnik – University of Pennsylvania

The initial and final states of electron and energy transfer processes.

Abstract

For a system which undergoes electron or energy transfer in a polar solvent, we will give a practical way to define the diabatic states, that is the initial and final states of the system, before and after the nonequilibrium transfer process. We will consider two models for the system-solvent interactions: A solvent that is linearly polarized in space and a solvent that responds linearly to the system. From these models, we will derive two new schemes for obtaining diabatic states from ab initio calculations of the isolated system in the absence of solvent. Interestingly, these algorithms will resemble standard approaches for orbital localization, namely, the Boys and Edmiston–Ruedenberg formalisms. We will show that Boys localization is appropriate for describing electron transfer, while the ER describes both electron and energy transfer. To prove the meaning of our diabatic state definitions, we will apply Marcus theory to the pioneering photochemical Closs experiments of the late 1980's, and will demonstrate that Marcus theory yields accurate triplet-triplet energy transfer rates.