Computer Simulation of Electron Transfer

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Abstract
This lecture reviews our recent work on simulating the aqueous ferrous-ferric electron transfer. The calculations involve potential modeling, non-Boltzmann sampling procedures, quantum Monte Carlo and also classical dynamics. We demonstrate that the spin-boson model – the Hamiltonian that underlies the Marcus theory of electron transfer – is essentially correct.

This paper outlines my lecture discussing some of our recent work simulating electron transfer in an aqueous environment. The work is well described in the current and forthcoming literature [1–3], so this review is appropriately brief.

A qualitative mechanism for electron transfer was proposed long ago by Marcus [4, 5]. In subsequent time, virtually all intelligent research on electron transfer has been guided by Marcus’ theory. The underlying model in Marcus’ picture is the so-called ‘spin-boson’ Hamiltonian. The most important predictions of Marcus’ theory are all consequences of this very simple model – a two-state quantum system linearly coupled to a harmonic (i.e. bosonic) bath. A primary purpose in our computer simulation work was to examine the validity of this model.

Our first effort was the laborious task of creating potential energy models to mimic the Fe^{3+}–Fe^{2+} exchange in water. The elementary constituents we considered were water molecules, ferric ions (i.e. two structureless Fe^{3+} particles), and a quanta electron. To model water, we picked the SPC potential [6] on the basis of simplicity and its dielectric properties. Watanabe and Klein [7] have shown, through the calculation of the Kirkwood factor, that the zero frequency dielectric constant, \( \epsilon_{\text{spc}} \), is approximately 70. Further, on examining the effects of long-ranged interactions, we have shown [1], in effect, that the nuclear dielectric response (1/\( \epsilon_c \) – 1/\( \epsilon_{\text{spec}} \)) is approximately 1/2.

For the H_2O–e^- pseudopotential, we have used the Coulomb interactions between the e^- and the partial charges of the SPC model. Laria [8] has shown that this simple model is consistent with the experimental chemical potential of the solvated electron. For the Fe^{3+}–e^- pseudopotential, we used the single parameter Shaw potential [9] adjusted to reproduce the experimental ionization potential for Fe^{3+} → Fe^{2+} + e^-, IP \( \approx 30 \) eV. Finally, to create a potential for Fe^{2+}–H_2O, we supplemented the Coulomb interactions with a spherical ion–oxygen repulsion. The strength and power law of that repulsion was adjusted so that the solvated ligand structure for (Fe^{2+})_6(H_2O)_6 was in accord with experiment.

After those adjustments were made, with no further alterations, an e^- was added to the Fe^{3+} in water. The resulting solvated ferrous ion, Fe^{2+}, exhibited in our simulation much the same structure as observed experimentally in nature. The model we have created thus appears to be a reasonably realistic caricature of the aqueous Fe^{3+}–Fe^{2+} system.

Were it not for the electron dynamics, which we treat by path integral quantum Monte Carlo, the system we have created would evolve by classical trajectories. Thus, except for the actual transfer event, all the simulations we have performed involve classical dynamics only. Considerable care was taken to ensure that our results were not unduly influenced by the finite size of our system (430 water molecules) and the finite distances at which we truncate intermolecular potentials.

On examining the model, we convinced ourselves that at reasonable energies – both for natural thermally stimulated electron transfer and for photochemically stimulated electron transfer – the two-state or tight-binding model of the quantum mechanics is quantitatively accurate. Further, from basis set calculations we determined that the coupling (i.e. half the tunnel splitting) between the two redox states is about (1.1 kcal/mol) exp\[-(R - 5 \text{ Å})/0.43 \text{ Å}\] where \( R \) is the distance between the two iron ions. The energy and length scale for this coupling are similar to those found by Logan and Newton [10].

To compute the free energy of activation for electron transfer, we have used the so-called procedure of ‘umbrella sampling’ [11]. The biasing potential we adopt exploits the accuracy of the tight-binding approximation. In particular, as a ‘reaction coordinate’, we use \( \Delta \theta \) the potential energy difference felt by the electron at the two redox sites. When the sites are degenerate, the electron resonates and electron transfer can take place. Thus, as first noted by Marcus [4], this point of degeneracy is the transition state. An umbrella sampling scheme much like the one the we have employed has also been used by Warshel [12]. One should note that, in effect, the scheme we use drags the centroid of the electron quantum path reversibly from a stable state to the midpoint between the two redox sites. As such, the method is closely tied to Gillan’s quantum transition state theory [13].

The activation free energy we have computed is about 20 kcal/mol, essentially the same as that observed in nature by experiment. One somewhat surprising fact we have uncovered is that nearly all of this free energy is due to solvent and ligand rearrangement. Dielectric continuum estimates had incorrectly suggested that only about half or two thirds were due to these rearrangements.

The most important fact, however, is the remarkable parabolic nature of the free energy function \( \Delta F(\Delta \theta) \). According to the spin-boson model and the implied Marcus relations, this function should be parabolic. And it is! Figure 1 illustrates this fact.
Fig. 1. Diabatic free energy, \( \Delta F \), for interionic separation of 5.5 Å, as a function of the energy gap, \( \Delta E \). The free energy was computed by umbrella sampling and reported in ref. [1]. Due to symmetry, the two diabatic states are reflections of one another, so calculations were performed for only one state, and the results for the second state shown above are produced by reflection from the first. The statistical uncertainties are small as illustrated in the figure by showing \( \Delta F \) obtained from three entirely uncorrelated runs. For perfect parabolic behavior, \( \Delta F \) at the activated state – the intersection of the two diabatic states – is \( |\Delta E|/4 \) for \( \Delta E \) at one of the minima. This condition holds within the statistical uncertainties of the calculation.

We have analyzed the adiabaticity parameter [14] in the region of the transition state. Its value is about 0.1 implying that the dynamics across the transition state is highly non-adiabatic. Since the corresponding splitting between adiabatic states is \( \gtrsim k_B T \), the small adiabaticity parameter implies that the adiabatic surfaces are very sharp near the transition state. This fact implies that nuclear tunneling can be important and worthy of future investigations employing quantum dynamics.

To further examine the validity of the spin-boson model, we have performed a simulation of fast photochemically induced electron transfer. Here, after equilibrating the system to the Fe\(^{2+}\)–Fe\(^{3+}\) state, the electron is placed instantaneously on the opposite iron thus forming a non-equilibrium Fe\(^{3+}\)–Fe\(^{2+}\) state with approximately 4 eV excess energy. We then analyzed the subsequent dynamics in much the same way as recently done for an analogous system by Maroncelli and Fleming [15]. Our analysis of the subsequent dynamics shows: (1) the surrounding water adjusts on a femtosecond time scale (i.e., very fast); (2) the process is so rapid that there is little leakage into other diabatic state; and (3) the relaxation follows that of the equilibrium linear response functions to a remarkable degree. This fact is illustrated in Fig. 2. Since the harmonic bosonic bath exhibits no nonlinear response, the spin-boson model would predict perfect agreement between the non-equilibrium experiment and the linear response functions. Since the two agree closely in our simulations, our analysis provides further evidence of the essential correctness of the Marcus picture of electron transfer.

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### References

5. For a recent review, see Marcus, R. A. and Sutin, N., Biochimica et Biophysica Acta 811, 265 (1985).
16. See, for example, chap. 8 of Chandler, D. (ref. [11]).