On the Three-State Approximation

We have shown in the above section that the TD2SA presents a largely simplified picture for studying complicated ET dynamics in proteins. If, however, a bridge state joins resonance with the donor and acceptor, the two-state picture may fail. Such a case invites an extra reduced state to describe the motion of the third resonant state.

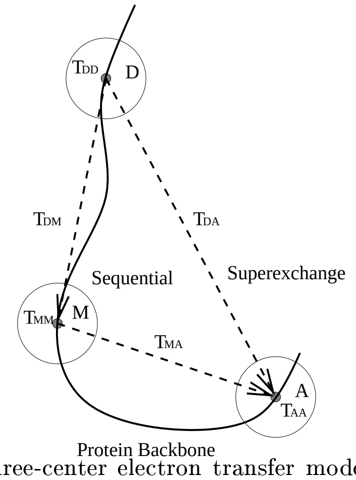

FIG. 1. Three-center electron transfer model. The redox center D is the origin(donor), M is the intermediate site (middle acceptor), and A is the destination(final acceptor).

We introduce here a general framework for the multistate reduction (MSR). Let us assume that we would like to do a n state reduction for a protein electronic structure which consists of N orbitals. The n orbitals are labeled as $p_1, p_2, \cdots, p_n$, while the remaining orbitals (the bridge) as $b_1, b_2, \cdots, b_{N-n} (N \gg n)$, the reduced matrix elements are given by using the projection technique

$$\mathcal{H}^E_{p_i p_j}(t) = H_{p_i p_j}(t) + T^E_{p_i p_j}(t) \tag{1}$$

$$T^E_{p_i p_j}(t) = \sum_{b_i, b_j} \left[ES_{p_i b_i}(t) - H_{p_i b_i}(t)\right] \times$$

$$\left\{\left[E\mathbf{S}^{\mathrm{br}}(t) - \mathbf{H}^{\mathrm{br}}(t)\right]^{-1}\right\}_{b_i b_j} \left[ES_{b_j p_j}(t) - H_{b_j p_j}(t)\right] \tag{2}$$

Similiar to the two-state reduction scheme, the final goal of the MSR is to approximate the ET dynamics of the real system with a reduced time-dependent Schrödinger equation in which the reduced Hamiltonian is given in the above projected form: $i\hbar\partial_t \Psi = \mathcal{H}^E \Psi$.

Let us study an ET system which has three redox centers, denoted by D, M, and A, respectively(Fig. 1). There are two possible types of ET reactions in a three-center system. The first one is the superexchange mechanism: $\mathrm{D}^* \cdots \mathrm{A} \longrightarrow \mathrm{D}^+ \cdots \mathrm{A}^-$. The second one is the sequential mechanism: $\mathrm{D}^* \cdots \mathrm{M} \cdots \mathrm{A} \longrightarrow \mathrm{D}^+ \cdots \mathrm{M}^- \cdots \mathrm{A} \longrightarrow \mathrm{D}^+ \cdots \mathrm{M} \cdots \mathrm{A}^-$. Three-center ET kinetics follows the superexchange pattern when the intermediate state M is off resonance with the donor and acceptor. In the resonance regime, the sequential pattern occurs where the intermediate site is also populated. For the same three-center system, the ET reaction should be much faster in the sequential channel than in the superexchange channel.

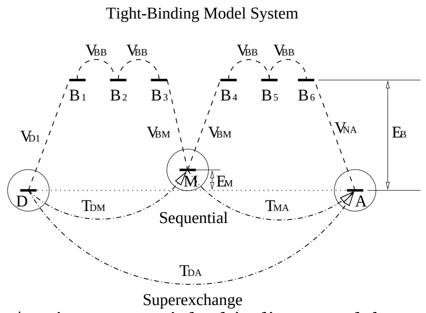

FIG. 2. A nine-state tight-binding model system. The site energies of all bridge states equal E_B, the energies of the donor and acceptor are zero, the intersite couplings are V_{BB} (bridge-bridge), V_{D1} (donor-bridge), V_{BM} (intermediate state-bridge), and V_{NA} (bridge-acceptor), non-nearest-neightbor interactions are neglected. The site energy of the intermediate site E_M is adjusted to drive the system into various transfer patterns.

In this Section, we shall discuss the three-center reduction with a simple tight-binding model (which is analogous to the Hückel model), since three-center ET reactions are relatively unfamiliar and we would like to establish a clear-cut picture before handling genuine systems.

Fig. 2 illustrates the tight-binding model for our study. For simplicity, we have chosen a homogenous system in which all the bridge sites have the same energy ($E_B = 4$, arbitrary unit) and all the intersite couplings are identical ($V_{D1} = V_{NA} = V_{BM} = V_{BB} = 1$), consequently the backscattering matrix elements for D and A are equal (this saves us efforts to tune them into resonance). Because of the difference of surroundings, the backscattering for the low-lying intermediate state differs from those for D and A. Therefore, the three-state resonance condition is not intuitively $E_D = E_M = E_A$. For a given static system, the transfer probilities from D to M and D to A oscillate with specific frequencies. The three-state resonance conditions can be found by computing the maximum electronic occupancy tunneled via the M site in several oscillation periods. Fig. 3 shows that $|E_M - E_D|$ for resonance increases when the couplings between M and its neighboring sites (V_{MB}) turn stronger. When $V_{MB} = 2$, this value is approximately 1.75, which is almost in the middle of the gap. This example demonstrates for a model three-state system the conspicuous dependence of the sequential resonance condition upon the electronic structure around the intermediate state.

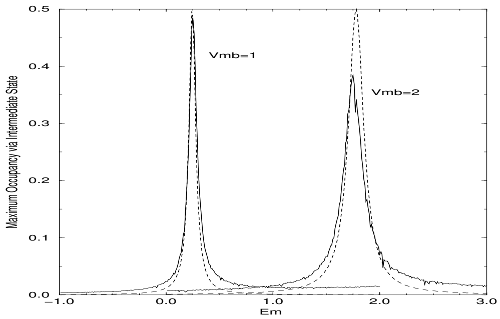

FIG. 3. Maximum occupancy transfered via the dynamically populated intermediate state as a function of its energy. Three-state resonance associated with sequential tunneling mechanism occurs around $E_M \approx 0.25$ when $V_{MB} = 1$ and $E_M \approx 1.75$ when $V_{MB} = 2$. Tunneling energy was chosen as -0.35 for the former case and -0.19 for the latter. Full lines represent the exact results; Dashed lines represent those of the 3SA(eq.(3)).

The 2SA cannot depict precisely the ET dynamics via an intervening state when the system enters the sequential transfer regime where a large part of occupancy goes through the middle state. A three-state approximation(3SA) has to be introduced

$$i\hbar \frac{d}{dt} \begin{bmatrix} \Psi_D(t) \\ \Psi_M(t) \\ \Psi_A(t) \end{bmatrix} = \begin{bmatrix} \mathcal{H}^E_{DD} & \mathcal{H}^E_{DM} & \mathcal{H}^E_{DA} \\ \mathcal{H}^E_{MD} & \mathcal{H}^E_{MM} & \mathcal{H}^E_{MA} \\ \mathcal{H}^E_{AD} & \mathcal{H}^E_{AM} & \mathcal{H}^E_{AA} \end{bmatrix} \begin{bmatrix} \Psi_D(t) \\ \Psi_M(t) \\ \Psi_A(t) \end{bmatrix} \tag{3}$$

where the effective three-state Hamiltonian matrix elements are obtained by using eqs.(1) and (2).

Fig. 4(a) shows that the 3SA can reproduce the exact dynamics perfectly when $E_M = 0.2$. One can see that in this case the 2SA can somewhat describe the transfer dynamics between D and A with a slightly different tunneling energy, since the transfer dynamics between D and A still resembles the sinusoidal behavior. But when E_M is increased to 0.24, resemblance to sinusoidal behavior vanishes, as is shown in Fig. 4(b). The time evolution cannot be attributed to a two-state mode. By comparison, the 3SA does much better, albeit its performance is not as impressive as shown in Fig. 4(a). In Fig. 3, we also show that the maximum population transfered through the middle site M versus E_M can be approximately reproduced by the three-state model. As expected, the 3SA deteriorates when the localization of M weakens (V_{BM} becomes greater).

The above analysis is not merely for improving the 2SA. As was pointed out by Ulstrup and coworkers[1], some of the most exciting chemical and biomolecular ET systems involve more than two reaction centers. Multistep ET and dynamically populated intermediate states ("hot" electronic states) in such systems has become central concepts in the new areas of ultrafast(femtosecond) processes. Our MSR approach provides, from rigorous electronic structure point of view, an effective multicenter picture for such type of multi-channel ET reactions.

(a)

(b)

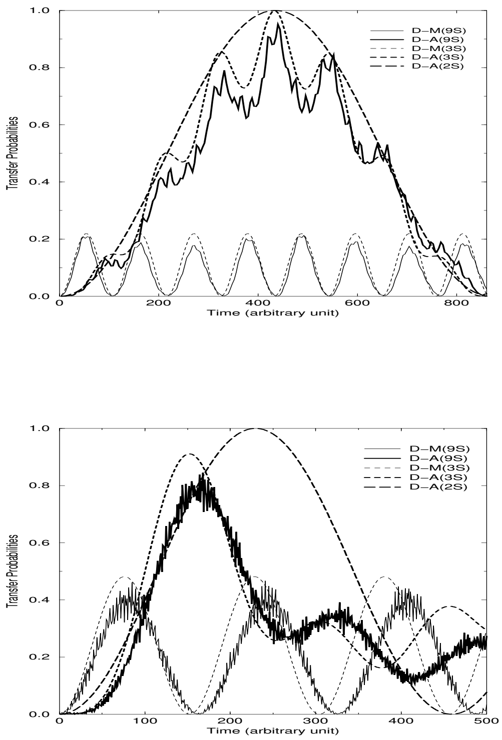

FIG. 4. Comparison of electronic propogation results produced by the exact, 2SA and 3SA methods for the tight-binding model system in the sequential transfer regime. (a)$E_M = 0.2, E^{2s}_{tun} = -0.34, E^{3s}_{tun} = -0.35$; (b)$E_M = 0.24, E^{2s}_{tun} = -0.285, E^{3s}_{tun} = -0.28$.

[1] G. Iversen, Y. I. Kharkats, A. M. Kuznetsov, and J. Ulstrup, Adv. Chem. Phys. **106**, 453 (1999)