Extension of Hopfield's Electron Transfer Model to Accommodate Site-Site Correlation

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Abstract

Extension of the Förster analog for the ET rate constant (based on virtual intermediate electron detachment or attachment states) with inclusion of site-site correlation due to coulomb terms associated with solvent reorganization energy and the driving force, has been developed and illustrated for a simple 3-state 2-mode model. The model is applicable to charge separation (CS), recombination (CR), and shift (CSH) ET processes, with or without an intervening bridge. The model provides a unified perspective on the role of virtual intermediate states in accounting for the thermal Franck-Condon weighted density of states (FCWD), the gaps controlling superexchange coupling, and mean absolute redox potentials, with full accommodation of site-site coulomb interactions. Two types of correlation have been analyzed: aside from the site-site correlation due to coulomb interactions, we have emphasized the intrinsic 'nonorthogonality' which generally pertains to reaction coordinates (RCs) for different ET processes involving multiple electronic states, as may be expressed by suitably defined direction cosines ($\cos(\theta)$). A pair of RCs may be nonorthogonal even when the site-site coulomb correlations are absent. While different RCs are linearly independent in the mathematical sense for all $\theta \neq 0^\circ$, they are independent in the sense of being 'uncorrelated' only in the limit of orthogonality ($\theta=90^\circ$). Application to more than two coordinates is straightforward and may include both discrete and continuum contributions.

Key words:

resonant gaps| superexchange| nonorthogonality| absolute redox potential

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I. Introduction

By elegant analogy with the Förster¹ excitation energy transfer (EET) rate constant expression, Hopfield² derived the following rate constant expression for nonadiabatic electron transfer (ET) of the charge separation (CS) type, $DA \rightarrow D^+A^-$:

$$k_{ET} = (2\pi/\eta) (H_{DA})^2 \int_{-\infty}^{+\infty} P_D(\Delta) P_A(-\Delta) d\Delta, \quad (1)$$

where H_{DA} is the electronic coupling element linking the diabatic D and A states, localized primarily on the donor (D) and acceptor (A) sites, and $P_D(\Delta^d)$ and $P_A(\Delta^a)$ are taken as independent Gaussian thermal probability densities of the vertical gaps for, respectively, electron detachment (**d**) from site D and electron attachment (**a**) at site A, subject only to the constraint of resonance, $\Delta \equiv \Delta^d = -\Delta^a$ (in the present notation). The integral is the classical Franck-Condon weighted density of states (FCWD)³ in the form derived by Marcus⁴

$$\text{FCWD} = \exp\{-(\Delta G^0 + \lambda)^2/4k_B T\lambda\} / (4\pi k_B T\lambda)^{1/2} \quad (2)$$

where ΔG^0 and λ are, respectively, the standard free energy change and the reorganization free energy, and $(\Delta G^0 + \lambda)^2/4\lambda$ is the activation free energy, $\Delta G^\ddagger$.

This approach, an alternative route to the Marcus model,⁴ which yields the same form as Eq 2 (but with λ restricted to a sum of single-site terms, $\lambda_D + \lambda_A$, as would be suitable for molecular modes), has been useful for studies of long distance ET (*eg*, in proteins²), but for shorter D/A separations it cannot accommodate site-site correlations due to D/A coulomb terms arising in the solvent reorganization energy for polar media (or other baths dominated by low-frequency modes, which coherently couple the D and A sites) and the driving force ($-\Delta G^0$) for CS (or charge recombination (CR)).⁵⁻⁸

Here we extend the model to include the site-site terms, considering for illustration of our approach, the same 2-site/2-mode/3-state framework used by ref ², as introduced below, yielding i) generalized expressions for $\Delta G^\ddagger$ which include DA ‘cross terms’ as in the Marcus model ⁴ and ii) the resonant gap at the CS transition state (TS), Δ^{TS} , which provides an estimate for the mean redox potential of the DA system at the TS, as noted previously by Beratan and Hopfield.^{9,10} The same approach is also applied to a related process, bridge (B)-mediated CS ($DBA \rightarrow D^+B^-$ $A \rightarrow D^+BA^-$), where the corresponding resonant TS gap now controls the electron (**e**) or hole (**h**)

superexchange (se) coupling element ¹¹, H_{DA} (section VI). An example of the gap for a charge shift (CSh) ET process is also presented.

The analysis is based on total state energies, their equilibrium values, and the vertical gaps between them for a given configuration of the system coordinates. The initial, (virtual) intermediate, and final states forming the basis for the present model are depicted in Figure 1, which represents schematically a set of ground and vertically excited states for a typical configuration of system nuclear modes. The underlying electronic states can be thought in terms of orbital occupations, as displayed in Figure 1, but the details of the electronic states *per se* will not be dealt with here. The energy of the electron at infinity is taken as zero.

Figure 1. Depiction of vertical ET processes involving the initial state, DA (1) and final state, D⁺A⁻ (2), and a virtual intermediate state obtained from the initial state (1) by a) detachment (d) of an electron from D to infinity (state 3) or b) attachment (a) of an electron at A from infinity, the zero of energy (state 4). The d and a processes are denoted, respectively, by blue and red arrows. For schematic purposes, the energy levels (D and A) may be thought of as effective 1-

electron energies for a given set of system coordinates (negative *vertical* ionization potential (IP_D) or electron affinity (EA_A), in contrast to the *adiabatic* IP_D or EA_A which appear in the detailed expressions for the vertical gaps in section IV), where a single level is a) occupied (**da**) or b) empty (**ad**).

In the original model,¹¹ the detachment at D (**d**) and the attachment at A (**a**) were independent (uncorrelated), but in the extended model including site-site correlation, the results are found to depend on the order: detachment followed by attachment (**da**) as in Figure 1a or attachment followed by detachment (**ad**) as in Figure 1b). For the case of B-mediated CS, Δ^TS involves the virtual intermediate state based, respectively, on excitation of an electron to an unoccupied (**e**) or from an occupied (**h**) B level (see Figure 3 below).

With definitions of the system coordinates (section II), energies (section III), and vertical gaps (section IV) in hand, we develop the generalization of eq 1 in section V. After describing the application to DBA systems (section VI), and some ‘geometric’ aspects of reaction coordinates (section VII), we close with discussion and conclusions in section VIII and summary in section IX. As in previous work,^{8,12,13,14,15} we emphasize the need for a multidimensional (≥ 2) framework for treating reaction coordinates when multiple ET processes are involved. Various definitions of reaction ‘paths’ and ‘coordinates’ are considered below.

II. Coordinates.

A. Discrete Nuclear Modes. The kinetic model developed below employs a discrete basis of nuclear coordinates denoted by the N -component vector $|X\rangle \equiv |X_p, p=1, N\rangle$, the equilibrium value $X_{p,eq}^j$ of each component p for electronic state j involved in the ET processes of interest (see Figure 1), and the shift in equilibrium values for each process $j \rightarrow k$ (denoted by the superscript jk), $\Delta X_{p,eq}^{jk}$. While the number of coordinates (N) is arbitrary, we restrict attention here for the purposes of illustration to two modes, using the following vector notation (see refs^{11,16} for more general treatments; in the remainder of the paper, the notation $|\dots\rangle$, $|\dots\rangle\langle\dots|$, and $\langle\dots|\dots|\dots\rangle$ denote discrete vectors and matrices, and their multiplication).

$$|X\rangle \equiv |X_\text{D}, X_\text{A}\rangle \quad (3)$$

$$|X_{\text{eq}}^j\rangle \equiv |X_{\text{D,eq}}^j, X_{\text{A,eq}}^j\rangle \quad (4)$$

$$|\Delta X_{\text{eq}}^{\text{jk}}\rangle \equiv |\Delta X_{\text{D,eq}}^{\text{k}}, \Delta X_{\text{A,eq}}^{\text{j}}\rangle \quad (5)$$

In ref ² these modes were taken as molecular modes. The 2-mode ($N=2$) expressions developed below can be adapted to solvent (*ie*, inertial continuum polarization) modes, and can also be extended to include dual sets, in which each site (D and A) has a solvent as well as a molecular mode.

When it comes to defining the equilibrium D and A coordinate values, we assume that $X_{\text{D,eq}}^j$ is independent of the oxidation state of site A (A or A⁻), and likewise, $X_{\text{A,eq}}^j$ is taken as independent of the oxidation state at D (D or D⁺), leading to

$$\Delta X_{\text{D}} \equiv \Delta X_{\text{D,eq}}^{\text{D} \rightarrow \text{D}^+} \quad (6a)$$

$$\Delta X_{\text{A}} \equiv \Delta X_{\text{A,eq}}^{\text{A} \rightarrow \text{A}^-} \quad (6b)$$

This approximation suppresses a certain degree of site-site correlation (*cf*, ref ⁸) but allows us to focus attention on the DA coulomb terms, which are expected to be the dominant source of correlation.

At this stage it is convenient to switch from the $|X\rangle$ basis to one defined in terms of dimensionless ‘progress parameters’ m_{D} and m_{A} , chosen to reflect progress, respectively, between the D and D⁺ oxidation state ($m_{\text{D}} = 0 \rightarrow 1$) and the A and A⁻ oxidation state ($m_{\text{A}} = 0 \rightarrow 1$).^{4,17,18} Thus for the CS process (**1** $\rightarrow$ **2**, as in Figure 2)

$$X_{\text{D}} - X_{\text{D,eq}}^{\text{1}} = m_{\text{D}}^{\text{12}} \Delta X_{\text{D,eq}}^{\text{12}} \quad (7a)$$

$$X_{\text{A}} - X_{\text{A,eq}}^{\text{1}} = m_{\text{A}}^{\text{12}} \Delta X_{\text{A,eq}}^{\text{12}} \quad (7b)$$

Throughout the paper, superscripts refer to electronic states (or the corresponding oxidation states (D, D⁺, A, or A⁻)) or the transitions between them (**1** $\rightarrow$ **2**, etc), and subscripts denote coordinate type (D or A). For convenience, we will in most cases suppress the ‘eq’ subscript.

Furthermore, for simplicity, we will use m_D^{12} and m_A^{12} together with ΔX_D and ΔX_A as defined in eq 6 in formulating the energetics for all of the other processes depicted in Figures 1 and 2 (**13**, **32**, **14**, and **42**) and will suppress the **12** superscript on m . The role of m_D and m_A in defining ‘reaction paths’ (as in Figure 2) will be discussed in section IVB.

Figure 2. Depiction of the five ET processes of interest, based on states **1-4**, plotted as vectors in the m_D and m_A plane, with 0 and 1 denoting the initial and final values of the progress parameters, corresponding to the respective equilibrium values of X_D and X_A (see the text, where notation $j \rightarrow k$ is shortened to jk). The color coding for the arrows is the same as in Figure 1.

B. Continuum Modes. Anticipating the case of a dielectric continuum dealt with below, we define the following continuum counterparts of the equilibrium coordinate shifts, X_D and X_A :¹¹

$$\Delta X_D \rightarrow \bar{\mathbf{D}}(\Delta \rho_D(\mathbf{r})) \quad (8a)$$

$$\Delta X_A \rightarrow \bar{\mathbf{D}}(\Delta \rho_A(\mathbf{r})) \quad (8b)$$

where $\vec{\mathbf{D}}$ is the electric displacement vector, ρ is an electronic charge density, $\mathbf{r}$ is the electronic coordinate variable in 3-dimensional space, and $\Delta\rho_{\text{D}}$ and $\Delta\rho_{\text{A}}$ are defined, respectively, as

$$\Delta\rho_{\text{D}} \equiv \rho^{\text{D}^+} - \rho^{\text{D}} \quad (9\text{a})$$

$$\Delta\rho_{\text{A}} \equiv \rho^{\text{A}^-} - \rho^{\text{A}} , \quad (9\text{b})$$

where in keeping with the above notation, the superscripts label the oxidation states of the diabatic charge densities localized primarily on the D and A sites. In the case of a dielectric continuum, we maintain a discrete 2-mode framework, but now each coordinate shift is a continuous function of 3-dimensional space *via* the density shifts $\Delta\rho_{\text{D}}$ and $\Delta\rho_{\text{A}}$.

III. State Energies

We first express the energy of state j ($j=1-4$, as in Figures 1 and 2) in general form, using the X coordinate basis:

$$V^j(|\mathbf{X}\rangle) = V^{j,0} + \langle \mathbf{X} - \mathbf{X}_{\text{eq}}^j | \mathbf{K} | \mathbf{X} - \mathbf{X}_{\text{eq}}^j \rangle / 2 \quad (10)$$

where $V^{j,0}$ is the equilibrium energy for state j , and $\mathbf{K}$ is a harmonic force constant matrix, non-diagonal in general (*ie*, representing site-site correlation), although for high-frequency modes it is often taken as diagonal (*eg*, single-site normal coordinates). In view of the global linear coupling assumed here, $\mathbf{K}$ is the same for all states j . In the case of symmetric exchange processes, where the reactant and product states are symmetry-equivalent, an effective $\mathbf{K}$ matrix averaged over initial and final states may be employed.^{19,20}

Following the approach summarized in Section II, Eq 10 is reexpressed for the 2-coordinate case in the $m_{\text{D}}, m_{\text{A}}$ representation as

$$V^1(m_{\text{D}}, m_{\text{A}}) = V^{1,0} + m_{\text{D}}^2 \lambda_{\text{D}} + m_{\text{A}}^2 \lambda_{\text{A}} + 2 m_{\text{D}} m_{\text{A}} \lambda_{\text{DA}} \quad (11\text{a})$$

$$V^2(m_{\text{D}}, m_{\text{A}}) = V^{2,0} + (m_{\text{D}}-1)^2 \lambda_{\text{D}} + (m_{\text{A}}-1)^2 \lambda_{\text{A}} + 2 (m_{\text{D}}-1) (m_{\text{A}}-1) \lambda_{\text{DA}} \quad (11\text{b})$$

$$V^3(m_{\text{D}}, m_{\text{A}}) = V^{3,0} + (m_{\text{D}}-1)^2 \lambda_{\text{D}} + m_{\text{A}}^2 \lambda_{\text{A}} + 2 (m_{\text{D}}-1) m_{\text{A}} \lambda_{\text{DA}} \quad (11\text{c})$$

$$V^4(m_{\text{D}}, m_{\text{A}}) = V^{4,0} + m_{\text{D}}^2 \lambda_{\text{D}} + (m_{\text{A}}-1)^2 \lambda_{\text{A}} + 2 m_{\text{D}} (m_{\text{A}}-1) \lambda_{\text{DA}} , \quad (11\text{d})$$

where the $V^{j,0}$ terms are expressed as

$$V^{2,0} - V^{1,0} = \text{IP}_D - \text{EA}_A - C_{DA} \quad (12a)$$

$$V^{3,0} - V^{1,0} = \text{IP}_D \quad (12b)$$

$$V^{4,0} - V^{1,0} = -\text{EA}_A \quad (12c)$$

with $V^{1,0}$ set to zero, and where IP_D and EA_A are, respectively, the adiabatic ionization potential of the neutral D species and electron affinity of the neutral A species, and $-C_{DA}$ is the negative coulomb interaction between D^+ and A^- sites. In liquid solution, IP_D , EA_A , and $-C_{DA}$ include solvation contributions.

The reorganization energy terms, λ_{pq} (the elements of the λ matrix) are defined as¹⁶

$$\lambda_{pq} = \Delta X_{p,\text{eq}} K_{pq} \Delta X_{q,\text{eq}} / 2 \quad (13)$$

where $\lambda_{qp} = \lambda_{pq}$, with $p, q = D$ or A , and the subscripts for the two diagonal terms are shortened in the following to just D and A. For the CS process (12), the total reorganization energy is given by

$$\begin{aligned} \lambda^{12} &= \langle \Delta X_D, \Delta X_A | \mathbf{K} | \Delta X_D, \Delta X_A \rangle / 2 \\ &= \lambda_D + \lambda_A + 2\lambda_{DA} \end{aligned} \quad (14)$$

(for the 13 and 32 processes, where, respectively, the equilibrium X_A and X_D values do not change, we obtain $\lambda^{13} = \lambda_D$ and $\lambda^{32} = \lambda_A$, and similarly, $\lambda^{14} = \lambda_A$ and $\lambda^{42} = \lambda_D$).

For the case of continuum solvent modes (eq 8), λ^{12} becomes¹¹

$$\begin{aligned} \lambda^{12} &= (1/2)(P/4\pi) \left\{ \int d\mathbf{r} \bar{\mathbf{D}}(\Delta\rho_D(\mathbf{r})) \square \bar{\mathbf{D}}(\Delta\rho_D(\mathbf{r})) + \right. \\ &\quad \left. \int d\mathbf{r} \bar{\mathbf{D}}(\Delta\rho_A(\mathbf{r})) \square \bar{\mathbf{D}}(\Delta\rho_A(\mathbf{r})) + 2 \int d\mathbf{r} \bar{\mathbf{D}}(\Delta\rho_D(\mathbf{r})) \square \bar{\mathbf{D}}(\Delta\rho_A(\mathbf{r})) \right\} \end{aligned} \quad (15)$$

(using the notation introduced in section II and eqs 8 and 9), where the integration is over the region of space occupied by the solvent, and $\mathbf{K}$ is now a constant matrix (independent of p , q , and $\mathbf{r}$),

$$K_{pq} = (1/\epsilon_\infty - 1/\epsilon_0)/4\pi \quad (16)$$

for all p,q (D or A) In eq 16, the first factor is the Pekar factor²¹(in parentheses) denoted as P, and ϵ_∞ and ϵ_0 are the optical and static dielectric constants (the dependence of $\bar{D}$ on ϵ_∞ and ϵ_0 ('image effects' ^{22,23}) is neglected here). In comparison with eq 14, the solvent reorganization *energy* is seen to be an integral over the reorganization energy *density* in 3-dimensional space.

We can now identify the key correlation term in the case of solvent modes, $2\lambda_{DA}$ (absent in the model leading to eq 1²), which in the Marcus 2-sphere point-charge solvent model, for example, is the negative quantity⁴,

$$2\lambda_{DA} = -q^2 P / r_{DA}, \quad (17)$$

where q is the magnitude of the electronic charge, r_{DA} is the separation distance between the D and A sites (note that the negative sign is consistent with the signs in eqs 9 and 15). The other coulombic correlation term is C_{DA} , introduced in eq 12. The 2-sphere point-charge model⁴ is a useful approximation for illustrating the coulombic nature of λ_{DA} . For consistency with the dielectric continuum 2-sphere model, we can now express IP_D , EA_A , and C_{DA} (eq 12) as follows:

$$IP_D = IP_{vac} + q^2(1/\epsilon_0 - 1)/2r_D \quad (17a)$$

$$EA_A = EA_{vac} + q^2(1/\epsilon_0 - 1)/2r_A \quad (17b)$$

$$-C_{DA} = -q^2/\epsilon_0 r_{DA} \quad (17c)$$

where r_D and r_A are, respectively, the effective spherical radii of sites D and A

Of course, the continuum model (for an assigned set of point charge in spherical cavities) may be solved exactly, ensuring that the volume of the cavities is excluded from the integrals in eq 15, as reported, for example, by Najbar and Tachiya.¹³ Some sample studies of bridge-mediated ET by Liu and Newton²⁴ found that the simple Marcus-type point-charge 2-sphere model actually yielded results within a few percent of the exact continuum results. In the following, when solvent modes are involved, we will assume the simple form given by the 2-sphere point charge model (eq 14). Since the exact λ^{12} (and λ^{jk} in general) is intrinsically positive, and correspondingly, the matrix λ (eq 13) is positive definite, requiring $\lambda_D \lambda_A > \lambda_{DA}^2$, the use of the approximate eq 17 is clearly restricted to the case where r_{DA} is sufficiently large

relative to the effective spherical radii of the D and A sites. More general numerical treatments can accommodate solute cavities of arbitrary shape.²⁴

It should be noted that the diabatic energy surfaces $V^j(m_D, m_A)$ may in fact be considered as ‘constrained’ free energy surfaces employed as effective potential energy surfaces,²⁵ and the $V^{j,0}$ are similarly taken as equilibrium free energy values, so that ΔG^0 (eq 2) corresponds to $\Delta V^{12,0} \equiv V^{2,0} - V^{1,0}$ in the present treatment (eq 12a), and the free activation energy, $\Delta G^\ddagger$ (see eq 2) will be denoted as $\Delta V^{12,\ddagger}$ (here we do not consider the possible entropic content of $\Delta V^{12,\ddagger}$, which would distinguish the Arrhenius activation energy and the Marcus activation free energy, referring below to $\Delta V^{12,\ddagger}$ as simply the ‘activation energy’). The energy gaps ΔV are discussed in the next section. Strictly speaking, the fully relaxed free energy change, ΔG^0 (here, $\Delta V^{12,0}$), is distinct from its constrained value ($V^2(1,1) - V^1(0,0)$). In an atomistic path integral molecular dynamics (MD) study of an ET process involving ruthenium and cobalt complexes, Ungar *et al*²⁶ found a very minor difference (~ 0.001 eV).

IV. Vertical Energy Gaps

As a result of the linearity of the present model, all vertical gaps,

$$\Delta V^{jk}(m_D, m_A) = V^k(m_D, m_A) - V^j(m_D, m_A) \quad (18)$$

are linear functions of the coordinates (m_D, m_A) . Note that the three different sets of coordinates introduced here (X , m , and ΔV) are all linearly related.

A. Detachment and attachment gaps. In extending eq 1, a particular focus is the vertical gaps for the **da** sequence (ΔV^{13} , ΔV^{32}) and the alternative **ad** sequence (ΔV^{14} , ΔV^{42}).

Straightforward use of eq 11 yields the following expressions (see Appendix A for further details) relating m_D and m_A to the gaps,

- **da (13, 32):**

$$\langle m_D, m_A | = -(1/2) \langle \Delta V^{13} + Z^{13}, \Delta V^{32} + Z^{32} | \begin{pmatrix} \lambda_A & -\lambda_{DA} \\ -\lambda_{DA} & \lambda_D \end{pmatrix} / (\lambda_D \lambda_A - \lambda_{DA}^2) \quad (19a)$$

- **ad (14, 42):**

$$\langle m_D, m_A | = (1/2) \langle \Delta V^{14} + Z^{14}, \Delta V^{42} + Z^{42} | \begin{pmatrix} \lambda_{DA} & -\lambda_D \\ -\lambda_A & \lambda_{DA} \end{pmatrix} / (\lambda_D \lambda_A - \lambda_{DA}^2) \quad (19b)$$

where the ‘constant’ vector terms are $Z^{13} = -IP_D - \lambda_D$; $Z^{32} = EA_A + C_{DA} - \lambda_A - 2\lambda_{DA}$; $Z^{14} = EA_A - \lambda_A$; and $Z^{42} = -(IP_D - C_{DA}) - \lambda_D - 2\lambda_{DA}$. We see that a given pair of gap values (ΔV^{13} , ΔV^{32} or ΔV^{14} , ΔV^{42}) defines a ‘hypersurface’ (a straight line in the present 2-coordinate m_D , m_A space). In the following, ‘hypersurface’ is understood to refer to this straight line.

B. The CS gap ($V^{12}(m_D, m_A)$), the Reaction Coordinate, and the Transition State (TS).

Since our ultimate goal is to model the CS rate constant (see Section I), the ΔV^{12} gap must also be considered, and we find

$$\Delta V^{12}(m_D, m_A) = \Delta V^{12,0} + (1-2m_D) \lambda_D + (1-2m_A) \lambda_A + 2(1-m_D - m_A) \lambda_{DA} \quad (20)$$

This gap is commonly taken as the reaction coordinate, RC.²⁷⁻³⁰ For a particular value, $\Delta V^{12} = \eta$, minimization of V^1 (or V^2) subject to the constraint of $\Delta V^{12} = \eta$ (imposed by use of a LaGrange multiplier) yields the minimum energy RC ‘path’,

$$(RC)_{\min} = \Delta V^{12,0} + (1-2m_{\min}(\eta)) \lambda^{12} \quad (21)$$

where $m_D = m_A = m_{\min}(\eta)$, the linear **12** path in Figure 2 (the vector $|m_{\min}, m_{\min}\rangle$). For the **12** process, the minimum energy RC path (eq 21) is simply a shifted, scaled version of the $m_{\min}(\eta)$ path.

The transition state (TS) is given by the point on the $(RC)_{\min}$ path where $\eta = 0$ and

$$m_{\min}(0) = m^\dagger = (\Delta V^{12,0} + \lambda^{12})/2 \lambda^{12}. \quad (22)$$

We find (by inserting $m^\dagger$ in eq 19) that the TS is also a point on the hypersurface where the detachment and attachment gaps are ‘resonant’ (*ie*, equal in magnitude and opposite in sign, as discussed below in section V). For the **da** sequence,

$$\begin{aligned} \Delta V^{\mathbf{da}(\text{TS})} &= \Delta V^{13} = -\Delta V^{32} = \\ &= \{IP_D (\lambda_A + \lambda_{DA}) + (EA_A + C_{DA})(\lambda_D + \lambda_{DA})\} / (\lambda_D + \lambda_A + 2\lambda_{DA}) - \lambda_{DA} \end{aligned} \quad (23a)$$

For the **ad** sequence, a similar but distinct result is obtained,

$$\begin{aligned} \Delta V^{\mathbf{ad}(\text{TS})} &= -\Delta V^{14} = \Delta V^{42} = \\ &= \{(IP_D - C_{DA})(\lambda_A + \lambda_{DA}) + EA_A(\lambda_D + \lambda_{DA})\} / (\lambda_D + \lambda_A + 2\lambda_{DA}) + \lambda_{DA}. \end{aligned} \quad (23b)$$

(the denominator in the first terms of eqs 23a and 23b is just λ^{12} ; see eqs 14 (discrete) and 15 (continuum)), and we find,

$$\Delta V^{\text{ad(TS)}} - \Delta V^{\text{da(TS)}} = 2 \lambda_{\text{DA}} - C_{\text{DA}} = -q^2/\epsilon_{\infty} r_{\text{DA}} \quad (24)$$

The last equality results from eqs 17 and 17c. The fact that the two TS gaps are not equal is simply a manifestation of the role of the site-site coulomb interactions, the same factor which prevents the detachment at site D and the attachment at site A from being independent processes.

The sign convention in the definition of the $\Delta V^{(\text{TS})}$ gaps (eqs 23a and 23b) corresponds to the positive energy gap for removal of an electron from D (referred to here as ‘detachment’) or from A (the reversal of the ‘attachment’ process). The role of $\Delta V^{\text{da(TS)}}$ and $\Delta V^{\text{ad(TS)}}$ in the ET (CS) rate constant is pursued in the next section. While eq 23 is derived for a 2-coordinate system, we note that in typical applications, λ_{D} and λ_{A} may each be taken as the sum of a molecular and a solvent contribution.¹¹ Furthermore, as noted above, the equilibrium (adiabatic) quantities IP_{D} , EA_{A} , and C_{DA} may include solvation terms (see eqs 17a-c).

The $m_{\text{min}}(\eta)$ path presented above for the **12** process can be defined similarly for the other processes shown in Figure 2: *ie*, **13**, **32**, **14**, and **42**, where the respective counterparts of $|m, m\rangle$ are given by the vectors $|m_{\text{D}}, m_{\text{A}}\rangle = |m, 0\rangle$, $|1, m\rangle$, $|0, m\rangle$, and $|m, 1\rangle$ for an arbitrary value of the variable m . The direction cosine of each of these vectors with respect to the **12** vector $|m, m\rangle$, when shifted to a common origin, corresponds to $\pm 45^\circ$ (as in Figure 2). Further discussion of direction cosines involving the ΔV^{jk} minimum energy RCs are given in section VII.

C. Estimates of absolute redox potentials. The quantities $\Delta V^{\text{da(TS)}}$ and $\Delta V^{\text{ad(TS)}}$ provide estimates of the mean absolute redox potential ($E^{0'}$) for the CS process at the TS ($E^{0'} = \Delta V^{\text{da(TS)}}/q$ or $\Delta V^{\text{ad(TS)}}/q$), but due to the site-site correlation *via* coulombic terms, the estimates from the **da** and **ad** sequences may be appreciably different in magnitude (for the point-charge model,⁴ a difference of $-q^2/\epsilon_{\infty} r_{\text{DA}}$ is found (eq 24)). One compromise would be to take the mean value of the two TS gaps. With neglect of λ_{DA} and C_{DA} , the two gaps become identical and correspond directly to average TS redox potential which Beratan and Hopfield^{9,10} obtained relative to the normal hydrogen electrode (NHE) in the uncorrelated case. Note that the mean $E^{0'}$ estimates with inclusion of correlation terms (eq 23) are not simple weighted means of IP_{D} and EA_{A} , in contrast to the models based on eq 1.^{9,10}

V. Rate Constant

In the present treatment, considering first the **da** sequence, the FCWD based on independent densities of nuclear states (P_D and P_A in eq 1) is generalized as,

$$\text{FCWD} = \int_{-\infty}^{+\infty} P^1(\Delta V^{13}, \Delta V^{32}) \delta(\Delta V^{13} + \Delta V^{32}) d(\Delta V^{13}) d(\Delta V^{32}) \quad (25)$$

where

$$P^1 = N \exp(-V^1(m_D, m_A)/k_B T), \quad (26)$$

with $m_D(\Delta V^{13}, \Delta V^{32})$ and $m_A(\Delta V^{13}, \Delta V^{32})$ given in turn by eq 19a, and N is a normalization constant such that

$$\begin{aligned} & \int_{-\infty}^{+\infty} P^1(\Delta V^{13}, \Delta V^{32}) d(\Delta V^{13}) d(\Delta V^{32}) = \\ & N \int_{-\infty}^{+\infty} \exp\{-<\Delta V^{13} + Z^{13}, \Delta V^{32} + Z^{32} | \lambda' | \Delta V^{13} + Z^{13}, \Delta V^{32} + Z^{32} > / 4k_B T (\lambda_D \lambda_A - \lambda_{DA}^2)\} d(\Delta V^{13}) d(\Delta V^{32}) \\ & = 1, \end{aligned} \quad (27)$$

where λ' is obtained from λ (eq 13) by interchanging the diagonal elements and replacing λ_{DA} with $-\lambda_{DA}$. Using the unitary transformation which diagonalizes λ' (see Appendix B), we find $N = 1/4\pi k_B T (\lambda_D \lambda_A - \lambda_{DA}^2)^{1/2}$.

Eq 25 is now reexpressed as

$$\text{FCWD} = N \int_{-\infty}^{+\infty} \exp(-\alpha <\Delta V^{\text{res}} + Z^{13}, \Delta V^{\text{res}} + Z^{32} | \lambda' | \Delta V^{\text{res}} + Z^{13}, \Delta V^{\text{res}} + Z^{32} >) d(\Delta V^{\text{res}}), \quad (28)$$

where $\alpha = 1/4k_B T (\lambda_D \lambda_A - \lambda_{DA}^2)$ and the Z terms are given after eq 19b in section IV. As a result of the delta function in eq 25, the gaps become resonant, and we relabel the gap variable, $\Delta V^{\text{res}} \equiv \Delta V^{13} = -\Delta V^{32}$, yielding the resonant hypersurface noted in section IVB. Finally, we recast the exponent in eq 28, yielding,

$$\text{FCWD} = (N \int_{-\infty}^{+\infty} \exp\{-\alpha \lambda^{12} (\Delta V^{\text{res}} - \Delta V^{\text{da(TS)}})^2\} d(\Delta V^{\text{res}})) (\exp\{-(\Delta V^{12} + \lambda^{12})^2 / 4k_B T \lambda^{12}\}) \quad (29)$$

After carrying out the integration, we finally obtain the Marcus FCWD (eq 2), which includes the site-site correlating coulomb terms (it turns out that the **ad** sequence gives an identical result for the FCWD). Some details of the integration are given in Appendix B. We see that the exponential argument in the second factor in eq 29 is $-1/k_B T$ times the Marcus activation energy, $\Delta V^{12,\dagger}$ in the present notation. While virtual intermediate states are at the heart of the procedure leading up to eq 29, we see that explicit reference to these states is absent in eq 29, as a result of integration over the Gaussian distribution. It is also emphasized that while the integrals in eqs 27-29 formally include ‘resonances’ between the D and A states and the virtual intermediate states, this would only occur in the exponential tails of the integrands, and hence does not pose a significant quantitative issue.

VI. Superexchange Gaps. The preceding model can be easily applied to bridge (B)-mediated CS, $\text{DBA} \rightarrow \text{D}^+\text{B}^-\text{A} \rightarrow \text{D}^+\text{BA}^-$ or $\text{DBA} \rightarrow \text{DB}^+\text{A}^- \rightarrow \text{D}^+\text{BA}^-$, yielding, respectively, the vertical gaps controlling electron (**e**) and hole (**h**) superexchange (se) coupling (H_{DA}).¹¹ We continue in the 3-state framework, illustrated in Figure 3, the counterpart of Figure 1, where the analogous virtual states are denoted, respectively, as **3'** and **4'**, and the **e** and **h** processes are the analogs of the **da** and **ad** sequences introduced above.

Figure 3. Schematic levels analogous to those in Figure 1, with the electron level at infinity

replaced by a virtual B^- (B_{lumo}) or B^+ (B_{homo}) state, involved, respectively, in electron (**e**) and (**h**) superexchange (se); B_{lumo} and B_{homo} correspond, respectively to the negative *vertical* electron affinity (EA_B) or ionization potential (IP_B) of the bridge for a given set of system coordinates (in contrast to the *adiabatic* IP_B or EA_B which appear in the detailed expressions for the vertical gaps in section VI). States **3'** and **4'** are the counterparts of states **3** and **4** in Figure 1.

Maintaining the 2-mode model, we assume that B is fixed at its equilibrium geometry, but new reorganization terms associated with the vertical excitations arise. In analogy to the TS gaps in eq 23, we obtain,

$$\Delta V^{\text{e(TS)}} = \Delta V^{13'} = -\Delta V^{3'2} = - (EA_B + C_{DB}) + (\lambda_B^{\text{e}} + \lambda_{DB}^{\text{e}} + \lambda_{BA}^{\text{e}}) + \quad (30a)$$

$$\{IP_D (\lambda_A + \lambda_{DA} - \lambda_{DB}^{\text{e}} + \lambda_{BA}^{\text{e}}) + (EA_A + C_{DA})(\lambda_D + \lambda_{DA} + \lambda_{DB}^{\text{e}} - \lambda_{BA}^{\text{e}})\} / (\lambda_D + \lambda_A + 2\lambda_{DA}) - \lambda_{DA}.$$

In addition to IP_D , EA_A , and C_{DA} , the equilibrium energies $V^{j,0}$ now also include IP_B , EA_B , C_{DB} , and C_{BA} , and reorganization terms λ_B^{e} , λ_{DB}^{e} , and λ_{BA}^{e} also appear.. Eq 30a is seen to include all the terms in eq 23a plus the new terms involving B, and similarly, we obtain eq 30b for hole transfer, the counterpart of $\Delta V^{\text{ad(TS)}}$ (eq 23b), but with a different assignment of signs, as discussed below.

$$\Delta V^{\text{h(TS)}} = \Delta V^{14'} = -\Delta V^{4'2} = (IP_B - C_{BA}) + (\lambda_B^{\text{h}} + \lambda_{DB}^{\text{h}} + \lambda_{BA}^{\text{h}}) - \quad (30b)$$

$$\{(IP_D - C_{DA}) (\lambda_A + \lambda_{DA} - \lambda_{DB}^{\text{h}} + \lambda_{BA}^{\text{h}}) + EA_A (\lambda_D + \lambda_{DA} + \lambda_{DB}^{\text{h}} - \lambda_{BA}^{\text{h}})\} / (\lambda_D + \lambda_A + 2\lambda_{DA}) - \lambda_{DA}.$$

The superscripts **e** and **h** denote λ values involving the B site, where the equilibrium coordinate shifts (analogous to eq 6; see also eq 13) correspond to $B \rightarrow B^-$ (for **e**) and $B \rightarrow B^+$ (for **h**).

Extension to bridge-mediated charge recombination (CR) and charge shift (CSh) is straightforward. For CR, only the sign of $\Delta V^{12,0}$ changes. For CSh, taking the ‘electron’ (**e**) se case (eg, $D^- BA \rightarrow DB^- A \rightarrow DBA^-$), the result is

$$\Delta V^{\text{e(TS)}} = \Delta V^{13''} = -\Delta V^{3''2} = - IP_B + (\lambda_B^{\text{e}} + \lambda_{DB}^{\text{e}} + \lambda_{BA}^{\text{e}}) + \quad (30c)$$

$$\{EA_D (\lambda_A + \lambda_{DA}^e - \lambda_{DB}^e + \lambda_{BA}^e) + EA_A (\lambda_D^e + \lambda_{DA}^e + \lambda_{DB}^e - \lambda_{BA}^e)\} / (\lambda_D^e + \lambda_A + 2\lambda_{DA}^e) - \lambda_{DA}^e,$$

quite similar in form to that for the CS **e** case (eq 30a), with state **3''** the counterpart of state **3'**, IP_D replaced by EA_D (equivalent to the IP of D^-), and the B-type coulomb terms C absent. Here, the λ terms involving D have a superscript **e**, corresponding to the $D \rightarrow D^-$ process. The analogous $\Delta V^{\mathbf{h}}(\text{TS})$ CSh gap is easily generated. For example, the $DBA^+ \rightarrow DB^{+-}A \rightarrow D^+BA$ process yields the variant of eq 30c in which EA_A is replaced by IP_A (or equivalently, EA_{A^+}), and superscript **e**, by **h** (including terms involving A , corresponding to the $A^+ \rightarrow A$ process). The gaps obtained here in a 2-dimensional framework can be compared with alternative results based on effective 1-dimensional models.^{8,31,32}

The apparent complexity of the expressions for these TS gaps (eqs 23 and 30a-c) is in part a consequence of the multidimensional (here 2) nature of the space containing the various reaction coordinates: *ie*, the RCs involving the virtual intermediate states are neither collinear (fully correlated) nor orthogonal (fully uncorrelated) to the RC for the CS process (**12**), as noted in section IVB and discussed further in the next section. Here we use the term ‘correlation’ in a sense different from that due to coulombic site-site correlation.

For perturbative se theory to be valid, the vertical gaps must be sufficiently large in magnitude relative to the DB and BA electronic coupling magnitudes^{31,33}. These gaps (taken here at the TS for thermal ET, where the D and A levels are resonant) are generally positive. Accordingly, in the CS **e** case (eqs 30a and 30c), EA_B must either be negative (corresponding to an intermediate resonance state, not a bound state), or if positive, then sufficiently less than IP_D and EA_A in magnitude. On the other hand, for **h** se (eq 30b), IP_D and EA_A must be sufficiently smaller than IP_B . Including also the CSh **e** and **h** cases, the qualitative energy relationships must conform to the inequality, $IP_B > IP_D$, EA_A , EA_D , $IP_A > EA_B$.

In the foregoing, we have considered the virtual se gap for a system with a single bridge site. In the more general case of n sites (DB_nA), the gap at each site will vary according to the relevant DB and BA distances involved in the coulomb terms (λ_{DB} , λ_{BA} , C_{DB} , and C_{BA}). For n bridge sites in the limit of large DB and AB gaps relative to DB and BA coupling elements, the McConnell tight binding model³⁴ gives as the leading ($n+1$ order) perturbation term, the nearest

neighbor se pathway from D to A.³¹ Further discussion regarding the effective coupling controlling H_{DA} in multi bridge site situations is given in section VIII.

More general nonperurbative se models, applicable as long as the D and A levels lie outside of the band of the bridge sites, has been reported by Evenson and Karplus³³ and by Ratner.³⁵ As **e** and **h** gaps begin to approach the order of magnitude of the λ terms, H_{DA} values will become increasingly sensitive to medium fluctuations (*eg*, as in the case of hole transfer in DNA³⁶).

In contrast to the foregoing, we note a recently reported rate constant expression, designated ‘the flickering resonance model’,³⁷ which superficially resembles the superexchange tunneling model in yielding exponential falloff with D/A separation, but in fact involves no virtual states, but rather real states which may be brought into quasi resonance due to molecular fluctuaations.

VII. Geometrical Features

A. Reaction Paths and Coordinates. We have already discussed reaction ‘paths’ and ‘coordinates’ in terms, respectively, of progress parameters (sections II and IV) and vertical gaps (sections II and IV-VI). To explore some additional geometrical aspects, we take the example of the CS (**12**) and detachment (**13**) processes, displaying ΔV^{13} as (see sections II-IV),

$$\Delta V^{13}(|\mathbf{X}\rangle) = \Delta V^{13,0} - \langle \mathbf{X} - \mathbf{X}_{eq}^1 | \mathbf{K} | \Delta \mathbf{X}^{13} \rangle + \lambda_D. \quad (31)$$

In the case of interest here, the **12** CS process, where the minimum energy RC path (eq 21) can be expressed as $|\mathbf{X}\rangle = m_{\min}(\eta) |\Delta \mathbf{X}^{12}\rangle$, eq 31 becomes

$$\begin{aligned} \Delta V^{13}(|\mathbf{X}\rangle) &= \Delta V^{13,0} - m_{\min}(\eta) \langle \Delta \mathbf{X}^{12} | \mathbf{K} | \Delta \mathbf{X}^{13} \rangle + \lambda_D \\ &= \Delta V^{13,0} - 2m_{\min}(\eta) \lambda^{12,13} + \lambda_D, \end{aligned} \quad (32)$$

where we have introduced the generalized reorganization energy¹¹, $\lambda^{12,13}$, which provides a measure of the correlation between the **12** and **13** coordinates (distinct from the coulombic correlation, as noted in section VI). For the present 2-mode model, we find,¹¹

$$\lambda^{12,13} = \langle \Delta \mathbf{X}^{12} | \mathbf{K} | \Delta \mathbf{X}^{13} \rangle / 2 = (\lambda^{12} + \lambda^{13} - \lambda^{23}) / 2 \quad (33)$$

(in ref ¹¹, using somewhat different notation, $\lambda^{12,13}$ is found for both DA and DBA systems to be positive for typical reorganization energy terms).

A geometrical perspective comes from recognizing $\lambda^{12,13}$ as an inner vector product by defining ‘rotated’ coordinate shifts,

$$|\Delta \mathbf{X}'\rangle = |\mathbf{K}^{1/2} \Delta \mathbf{X}\rangle, \quad (34)$$

thus allowing $\lambda^{12,13}$ to be recast in terms of the direction cosine linking the **12** and **13** coordinate shifts, $\cos \theta^{12,13}$,

$$\begin{aligned} \lambda^{12,13} &= \langle \Delta \mathbf{X}'^{12} | \Delta \mathbf{X}'^{13} \rangle / 2 \\ &= \{ \cos \theta^{12,13} (\langle \Delta \mathbf{X}'^{12} | \Delta \mathbf{X}'^{12} \rangle \langle \Delta \mathbf{X}'^{13} | \Delta \mathbf{X}'^{13} \rangle)^{1/2} \} / 2 \\ &= \cos \theta^{12,13} \{ (\lambda_D + \lambda_A + 2\lambda_{DA})(\lambda_D) \}^{1/2}. \end{aligned} \quad (35)$$

Hence for the present 2-mode model we have (*via* eqs 33 and 35),

$$\cos \theta^{12,13} = (\lambda_D + \lambda_{DA}) / \{ (\lambda_D + \lambda_A + 2\lambda_{DA})(\lambda_D) \}^{1/2}. \quad (36)$$

In the analogs of eqs 35 and 36 for se gaps, state 3 is replaced by state 3' or 4' (see section VI). For e-type se, $\lambda^{13'}$ and $\lambda^{23'}$ are given, respectively, by $\lambda_D + \lambda_B + 2\lambda_{DB}$ and $\lambda_A + \lambda_B + 2\lambda_{BA}$ (see comments in section III following eq 17 regarding the use of the 2-sphere point-charge approximation for λ terms).

Results essentially equivalent to eqs 33-36 for other 2-mode 3-state systems, but obtained by different routes, have been reported by Tachiya and coworkers,^{13,15} Tang and Norris,⁸ and Cho and Silbey.¹⁴ The results in ref ¹⁵ involved diagonalization of a reorganization energy matrix (in a basis of *jk* processes) distinct from the matrix defined in eq 13

In general, the angle $\theta^{12,13}$ lies between 0° and 90°. For the limiting case, $\lambda_D = \lambda_A$ and $\lambda_{DA} = 0$, $\theta^{12,13} = 45^\circ$ (the same as is exhibited by the **12** and **13** paths in Figure 2 based on the m_D and m_A coordinates). These geometrical results manifest a type of ‘correlation’ (*ie*, $\theta^{12,13} \neq 90^\circ$) between different ET processes which is independent of the coulomb terms (*ie*, it is present even when $\lambda_{DA} = 0$). Within the present 2-dimensional framework, the fully correlated limit ($\theta^{12,13} = 0$) is not accessible, since it corresponds to $\lambda_D \lambda_A = \lambda_{DA}^2$, in violation of the positive definite requirement for λ^{12} (see section III).

Cases in which multiple ET processes in DBA and other systems, constrained to be fully correlated (*ie*, 1-dimensional models with all $\theta = 0^\circ$), are found to place physically unreasonable restrictions on λ parameters, with better results obtained when a moderate degree of correlation ($0^\circ < \theta < 90^\circ$) is incorporated into the models.^{8,12,13}

B. Angle between the 12 reaction path and the resonant hypersurface. Another geometrical feature is that the hypersurface associated with the resonant **13** and **32** gaps is not in general perpendicular to the CS minimum energy path ($m_{\min}(\eta) = m_D = m_A$, as in eq 21). The direction cosine of the angle of intersection (θ^{int}) is (see Appendix D),

$$\cos \theta^{int} = \{1 - (\lambda_D + \lambda_{DA})/(\lambda_A + \lambda_{DA})\} / \sqrt{2(1 + \{(\lambda_D + \lambda_{DA})/(\lambda_A + \lambda_{DA})\}^2)^{1/2}}. \quad (37)$$

Thus an angle of 90° is found only in the limit when $\lambda_D = \lambda_A$ and $\lambda_{DA} = 0$.

VIII. Discussion and Conclusions.

A. The FCWD and Prefactors. The foregoing sections have shown how the classical FCWD factor in the ET rate constant can be expressed in terms of the vertical gaps for detachment and attachment of an electron in a DA system. The corresponding gaps involving bridge-mediated DBA systems are an essential component in perturbative expressions for coupling elements, H_{DA} , where the coupling occurs *via se*. In the nonadiabatic limit (eq 1), the prefactor is proportional to $(H_{DA})^2$, but this can be generalized within the transition state theory (TST) framework by, for example, the Landau-Zener model.^{8,19,38,39}

The relationship between the classical FCWD (eq 2) and the vertical gaps is explicitly displayed in eq 29 as the product of a Gaussian integral over the entire resonant ‘hypersurface’, ΔV^{res} (where $\Delta V^{\text{da(TS)}}$ is the value of ΔV^{res} at the TS, and N and α are given following, respectively, eqs 27 and 28) and the Marcus form of the activation factor, with full inclusion of coulombic site-site correlation terms. In other words, aside from the activation factor after the integral, eq 29 yields the denominator of eq 2, which serves as the normalization factor for the nuclear modes density of states.

The classical FCWD can be extended to account for nuclear quantum effects. Corrections for nuclear tunneling when nuclear frequencies are comparable to or greater than $k_B T/h$ can be estimated by use of stationary phase methods.^{3,40} The one employed in ref ² is restricted to the vicinity of

activationless ET (*ie*, where $m^\dagger$ is near 0). Alternatives have been explored for the case of normal or inverted ET kinetics.^{40,41}

B. Solvent polarity. For the limiting case of complete CS ($DA \rightarrow D^+A^-$), the vertical **13** gap at the initial state equilibrium ($\Delta V^{12}(0,0) = \lambda^{12} + \Delta V^{12,0}$) is known on the basis of dielectric continuum models to be independent of solvent polarity (*ie*, the static dielectric constant, ϵ_0), due to cancellation of terms in λ^{12} and $\Delta V^{12,0}$, thus leading to the well known weakness of solvatochromism in optical CS absorption spectra.⁴² The dependence on ϵ_∞ remains, but ϵ_∞ is similar in magnitude for most common solvents. Note, however, that the denominator (λ^{12}) in the CS activation energy $\Delta V^{12,\dagger}$ (see eq 29 and the following discussion) still depends on ϵ_0 via the Pekar factor (see eq 16). The cancellation for CS does not, of course, pertain to CR *absorption*, but rather for *emission*.

C. Energy Profiles and Reaction Coordinates. We have already emphasized the central importance of the vertical gaps at the TS (the crossing point of V^1 and V^2 on the **12** $m_{\min}(\eta)$ path, $m^\dagger$, where $\eta=0$ (see eqs 21 and 22). Taking the example of ΔV^{13} , we find that the TS gap ($\Delta V^{13(TS)}$) is appreciably less than that at the initial state equilibrium ($\Delta V^{13,0} + \lambda_D$), with the precise value related to the directions of the (generally nonorthogonal) **12** and **13** minimum energy paths in the m_D, m_A space (section VII). Some perspective is offered in Figure 4, where the V^1 , V^2 , and V^3 profiles (in red) along the **12** minimum energy path are superposed on the V^3 profile (in blue) along the **13** minimum energy path.

Figure 4. Energy profiles $V^1(m, m)$, $V^2(m, m)$, and $V^3(m, m)$ along the **12** minimum energy reaction path (red curves), where m is the variable value of $m_{\min}$ (a function of η ; see eq 21), and also V^3 (blue curve) along the **13** minimum energy path (variable m_D , with $m_A = 0$, as in Figure 2). The curves are schematic, but correspond approximately to the parameter values $\lambda_D = \lambda_A$, $\lambda_{DA} = -0.25 \lambda_D$, $\Delta V^{12,0} = -0.25 \lambda_D$, and $\Delta V^{13,0} = 3 \lambda_D$. When constrained to follow the **12** reaction path ($m_{\min}(\eta)$), the minimum energy point of V^3 lies $\sim 0.75 \lambda_D$ above its global minimum at $m_D=1$ and $m_A=0$.

The explicit relationship between the ΔV^{13} gap and $\theta^{12,13}$ along the **12** minimum energy path, $m_{\min}(\eta)$, is given by,

$$\Delta V^{13}(m_{\min}, m_{\min}) - \Delta V^{13}(0) = -2 m_{\min} \cos \theta^{12,13} (\lambda^{12} \lambda^{13})^{1/2}. \quad (38)$$

Eq 38 shows that $\Delta V^{13}(m_{\min})$ decreases monotonically with $m_{\min}$ since $\cos \theta^{12,13}$ (as defined in eq 36), or equivalently, $\lambda^{12,13}$, is positive for typical system parameters¹¹ (see also, comments following eq 17). A similar situation pertains to the se analogs (section VI).

D. Optical ET. The present study deals with thermal ET processes occurring at the TS, where the initial and final levels are resonant. We note, however, that the corresponding optical ET processes, based on the initial state equilibrium structure ($m_D = m_A = 0$, where of course, $\Delta V^{13'} \neq \Delta V^{23'}$, taking the **e**-type se process as an example (see section VI)), may be used as a means of estimating H_{DA} . The coupling obtained in this manner³¹ may be employed in modeling the thermal rate constant if the Condon approximation⁴³ is assumed (*ie*, invariant coupling magnitude along the reaction coordinate). The optically-derived H_{DA} can be expressed in terms of an effective energy gap, ΔV_{eff} , whose form depends on the number of bridge sites in the case of **se**. For example, for a single site, $\Delta V_{\text{eff}} ; 2 \{1/\Delta V^{13'}(0,0) + 1/\Delta V^{23'}(0,0)\}^{-1}$.³¹ While the details depend on all the parameters appearing in the gap expressions (eqs 18 and 23), ΔV_{eff} is typically found to be smaller than not only $\Delta V^{13'}(0,0)$, but also $\Delta V^{13'}(\text{TS})$.^{11,44}

IX. Summary

1) extension of the Förster analog for the ET rate constant (based on virtual intermediate electron detachment or attachment states) with inclusion of site-site correlation due to coulomb terms

associated with solvent reorganization energy and the driving force, has been developed and illustrated for a simple 3-state 2-mode model; **2)** the model is applicable to CS, CR, and CSh ET processes, with or without an intervening bridge; **3)** The model provides a unified perspective on the role of virtual intermediate states in accounting for the thermal Franck-Condon weighted density of states (FCWD), the gaps controlling superexchange coupling, and mean absolute redox potentials, with full accommodation of site-site coulomb interactions. **4)** two types of correlation have been analyzed: aside from the site-site correlation due to coulomb interactions, we have emphasized the intrinsic ‘nonorthogonality’ which generally pertains to RCs for different ET processes involving multiple electronic states. A pair of RCs may be nonorthogonal even when the site-site coulomb correlations are absent (*eg*, as shown for the case of $\theta^{12,13}$ in section VII). While different RCs are linearly independent in the mathematical sense, for $\theta \neq 0^\circ$, they are independent in the sense of being ‘uncorrelated’ only in the limit of orthogonality ($\theta=90^\circ$); **5)** application to more than two coordinates is straightforward, having been discussed earlier in ref ¹¹, and may include both discrete and continuum contributions.

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Appendix A

From eqs 11 and 18 we obtain by straightforward algebra,

$$\langle \Delta V^{13} + Z^{13}, \Delta V^{32} + Z^{32} \rangle = -2 \langle m_D, m_A \rangle \begin{pmatrix} \lambda_D & \lambda_{DA} \\ \lambda_{DA} & \lambda_A \end{pmatrix} \quad (\text{A1})$$

$$\langle \Delta V^{14} + Z^{14}, \Delta V^{42} + Z^{42} \rangle = -2 \langle m_D, m_A \rangle \begin{pmatrix} \lambda_{DA} & \lambda_D \\ \lambda_A & \lambda_{DA} \end{pmatrix} \quad (\text{A2})$$

where the constant terms are $Z^{13} = -\mathbf{IP}_D - \lambda_D$; $Z^{32} = \mathbf{EA}_A + \mathbf{C}_{DA} - \lambda_A - 2\lambda_{DA}$; $Z^{14} = \mathbf{EA}_A - \lambda_A$; and $Z^{42} = -(\mathbf{IP}_D - \mathbf{C}_{DA}) - \lambda_D - 2\lambda_{DA}$. Inverting Eqs. A1 and A2 yields,

$$\langle m_D, m_A | = - (1/2) \langle \Delta V^{13} + Z^{13}, \Delta V^{32} + Z^{32} | \begin{pmatrix} \lambda_A & -\lambda_{DA} \\ -\lambda_{DA} & \lambda_D \end{pmatrix} / (\lambda_D \lambda_A - \lambda_{DA}^2) \quad (\text{A3})$$

$$\langle m_D, m_A | = (1/2) \langle \Delta V^{14} + Z^{14}, \Delta V^{42} + Z^{42} | \begin{pmatrix} \lambda_{DA} & -\lambda_D \\ -\lambda_A & \lambda_{DA} \end{pmatrix} / (\lambda_D \lambda_A - \lambda_{DA}^2) . \quad (\text{A4})$$

Appendix B

A simple way to carry out the integration in eq 28 is to reexpress the exponential argument as

$$\langle \dots | \boldsymbol{\lambda}' | \dots \rangle = \langle \dots | \mathbf{U} (\mathbf{U}^\dagger \boldsymbol{\lambda}' \mathbf{U}) \mathbf{U}^\dagger | \dots \rangle \quad (\text{B1})$$

where the unitary matrix $\mathbf{U}$ diagonalizes the matrix $\boldsymbol{\lambda}'$, allowing the double integral to be separated as the product of two 1-dimensional Gaussian integrals. Because $\mathbf{U}$ is unitary, the relevant Jacobian factor is unity. Furthermore, the quantity $\lambda_D \lambda_A - \lambda_{DA}^2$ is found to be the product of the two eigenvalues of $\boldsymbol{\lambda}'$.

Appendix C.

Eq 36 is based on the following definition for the two relevant vectors, with origin

at the TS (eq 22): the CS (**12**) vector,

$$|t \hat{m}_D, t \hat{m}_A \rangle,$$

and the vector associated with the resonant **13** and **32** gaps,

$$|t \hat{m}_D, -t \{(\lambda_D + \lambda_{DA}) / (\lambda_A + \lambda_{DA})\} \hat{m}_A \rangle,$$

where $\hat{m}$ denotes a unit vector along the X_D or X_A axis and t is an arbitrary variable. The slope of the second vector in the m plane is derived from eq A1 by setting $\Delta V^{32} = -\Delta V^{13}$.

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