Dynamics of Electron Transfer for a Nonsuperexchange Coherent Mechanism. 1

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In addition to mechanisms such as superexchange and a chemical intermediate mechanism for electron transfer from a donor D* to an acceptor A via a molecular bridge B, a third possibility occurs when the BA electronic coupling is very strong and the D*B and D^+B^- states have energies moderately close to each other. This mechanism is discussed here. Like superexchange, it is a coherent one, in contrast to the chemical intermediate mechanism, where the transfer is sequential and incoherent. The dynamics of the mechanism are discussed, particularly the maximum population of "B^-" and the question of whether an effective rate constant for its disappearance can be considerably larger than the maximum adiabatic rate constant. There are, as yet, no experimental data on the mechanism, though the synthesis of suitable D*BA's may permit its observation. In the treatment three collective nuclear coordinates are introduced, permitting independent reorganization energies for each reactive center. With certain approximations, namely, equal vibration frequencies and a nonadiabatic first step, the problem is reduced analytically to a one-coordinate one, which can be readily treated numerically. One rough but simple analytical result for the latter is also given.

I. Introduction

Electron transfers from a donor D* to an acceptor A via a bridge B may occur by one of several mechanisms. The most common one is that of superexchange, in which the transferring electron makes use of a virtual state, an orbital quite different in energy from that of the donor D* or the acceptor A. A second mechanism, which could occur when the relevant bridge orbital is close enough in energy to the D* one, is for the electron transfer to occur via a chemical intermediate B^-, whose presence could be detected experimentally. The kinetics of this transfer can be treated straightforwardly by using two consecutive steps.

A third possibility is considered in the present paper, one for which there are as yet no experiments but for which suitable D*BA systems might be synthesized. In this mechanism the relevant B orbital is readily accessible energetically, as in the second mechanism above, but B and A are so strongly coupled electronically that the entire transfer occurs coherently, rather than incoherently, in two successive steps.

One question that arises concerns the maximum population of "B^-" in this third mechanism. In the case of the second (sequential) mechanism this maximum population B^-_{max} is given by[1]

$$B^-_{max} = (k_1/k_2)^{k_2/(k_2-k_1)} \qquad (1.1)$$

where k_1 and k_2 are the rate constants of the D* → B and the B^- → A electron transfers, respectively. The question that arises is whether or not for the third mechanism eq 1.1 can still approximately represent the data but with a considerably enhanced value of k_2, a value substantially greater than the maximum k_2 for an adiabatic electron transfer. (In this case B^-_{max} would be much smaller than for a sequential mechanism.) The answer, as we shall see in a subsequent article on numerical results, is in the affirmative. Presumably, by a suitable choice of D*BA systems, e.g., a D* weakly coupled to B, a suitable choice of B with an energy level close to or far above that of D*, and a suitable choice of the electronic coupling between B and A (e.g., an aromatic or other appropriate group may provide strong coupling, a nonbornyl group relatively weaker coupling), it may be possible to construct a series of systems, different members of which proceed by one or the other of the three mechanisms.

In the present paper we set up a model for performing calculations of B^-_{max} and other properties. In this model there should preferably, for the purpose cited, be at least three collective coordinates,[2] each having its own reorganization parameter and each associated with an equilibrium vibrational displacement in a reactive center, D, B, and A. There should also be, in a quantum mechanical treatment of the dynamics of this coherent transfer, some mechanism for dissipation, at least toward the end of the transfer process, so that a wave packet describing the dynamics is not spuriously reflected back and forth. In practice, this dissipation is provided by the many coordinates in the actual system, which permit the reaction products to become thermalized before any reverse reaction occurs. (To design a theory that in one limit would yield two incoherently connected consecutive steps, a dissipative term accompanying the motion in the D^+B^-A stage would also be included, but for the present purpose of estimating a B^-_{max} we omit this additional feature here.)

Rather than solve the Schrödinger equation with these three collective coordinates purely numerically, although that would be useful, we introduce in the present paper some approximations such that the coherent problem can be reduced analytically from three coordinates to one. Then the latter can be treated either numerically (e.g., using a one-dimensional fast Fourier transform[3]) or, in a more approximate way, analytically. A rather rough analytical estimate is given in section V.

A coordinate system and the Hamiltonian are set up in section II, and an approximation is introduced (all three vibrational frequencies equal) which, when followed by a rotation of the coordinates, permits a reduction to a two-coordinate problem. In section III, the transfer from D* to the BA coupled system is treated nonadiabatically (Golden Rule). To calculate the time evolution of B^-, $B^-(t)$, the subsequent dynamics are investigated (section IV) in which the nonadiabatic step deposits a wave packet on the BA potential energy surface. This wave packet, continuously replenished from the decreasing concentration of D*, evolves in time on the BA surface and has a nuclear motion on BA which is seen in section IV to be separable. The treatment of the coherent dynamics has thereby been reduced to a one-coordinate problem. The energy partitioning and its effect on $B^-(t)$ are discussed in section V. Numerical results are given in the following paper.[4]

II. Coordinates and Hamiltonian

Diabatic electronic wave functions Ψ_i are introduced to describe the three electronic configurations D*BA, D^+B^-A, and D^+BA^-, corresponding to the transferring electron being on D (i = 1), B

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(1) Marcus, R. A. *Chem. Phys. Lett.* **1988**, *144*, 24.

(2) For example, in an electron transfer involving a hexacoordinated transition-metal cation, all six stretching vibrations of the ligands participate in the reorganization and their contribution to the reorganizational parameter λ can be described by the motion of a single collective coordinate—the normal coordinate involving the symmetric stretching vibration of the ligands.

(3) (a) E.g.: Feit, M. D.; Fleck, Jr., J. A.; Steiger, A. *J. Comput. Phys.* **1982**, *47*, 412. Kosloff, D.; Kosloff, R. *J. Comput. Phys.* **1983**, *52*, 35. (b) Alvarellos, J.; Metiu, H. *J. Chem. Phys.* **1988**, *88*, 4957. Almeida, R. Ph.D. Thesis, University of California, Santa Barbara, 1987, Chapter 5.

(4) Almeida, R.; Marcus, R. A. *J. Phys. Chem.*, following paper in this issue.

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(i = 2), and A (i = 3). We let Φ_i denote the corresponding time-dependent nuclear wave functions, to be determined by solution of the Schrödinger equation. The electronic–nuclear wave function $\Psi(\tau)$ at time τ is now given by

$$\Psi(\tau) = \sum_{i=1}^{3} \Phi_i(\tau)\Psi_i \tag{2.1}$$

The Hamiltonian contains a nuclear kinetic energy operator K and several nuclear–electronic terms, H_{el}. Introduction of $\Psi(\tau)$ into the Schrödinger equation $H\Psi = i\hbar\, \partial\Psi/\partial\tau$, multiplication by Ψ_i^*, and integration over the electronic coordinates yields a standard result for the nuclear motion:

$$K\Phi_i + \sum_{j=1}^{3} H_{ij}\Phi_j = i\hbar\, \partial\Phi_i/\partial\tau \tag{2.2}$$

where H_{ij} denotes the matrix element

$$H_{ij} = \langle\Psi_i|H_{el}|\Psi_j\rangle \tag{2.3}$$

We next introduce three collective vibrational coordinates, $\bar{q}_1$, $\bar{q}_2$, $\bar{q}_3$, one collective vibration per center.[2] For simplicity, a common vibration frequency $\omega/2\pi$ is assumed for these vibrations ($\omega = (k_i/\mu_i)^{1/2}$, where k_i is the force constant and μ_i a reduced mass), and dimensionless coordinates $q_i = (\mu_i\omega/\hbar)^{1/2}\bar{q}_i$ are introduced. Equation 2.2 now becomes

$$-\frac{1}{2}\sum_j \frac{\partial^2}{\partial q_j^2}\Phi_i + \sum_j H_{ij}\Phi_j = i\frac{\partial\Phi_i}{\partial t} \tag{2.4}$$

where t is a dimensionless time variable $\omega\tau$ and H_{ij} denotes the H_{ij} in eq 2.2 divided by $\hbar\omega$. In actual fact, these three vibrational frequencies ω will not be equal, but we are more interested here in obtaining some insight into what magnitudes to expect for $B^-(t)$ for this mechanism rather than in an accurate numerical solution.

For each of the three electronic configurations D*BA, D^+B^-A, and D^+BA^-, a set of three equilibrium values of the q_i's is defined. When the electron is on D, namely, when Φ_1 is large, the equilibrium values of (q_1,q_2,q_3) are denoted by $(a_1,0,0)$, while when the electron is on B, they are taken to be $(0,a_2,0)$ and, when on A, $(0,0,a_3)$ (Figure 1). Thus, with this choice we have, for example, $q_1 = a_1$ at the equilibrium position for the vibration q_1 in the D* system and $q_1 = 0$ at the equilibrium position for q_1 when the D is in the form D^+. Using a harmonic approximation the diagonal matrix elements H_{ii} are now

$$\begin{aligned} H_{11} &= \tfrac{1}{2}(q_1 - a_1)^2 + \tfrac{1}{2}q_2^2 + \tfrac{1}{2}q_3^2 \\ H_{22} &= \tfrac{1}{2}q_1^2 + \tfrac{1}{2}(q_2 - a_2)^2 + \tfrac{1}{2}q_3^2 + \Delta E_{12} \\ H_{33} &= \tfrac{1}{2}q_1^2 + \tfrac{1}{2}q_2^2 + \tfrac{1}{2}(q_3 - a_3)^2 + \Delta E_{13} \end{aligned} \tag{2.5}$$

where the ΔE_{1i}'s denote the (equilibrium) energy differences of the first and the ith diabatic electronic configurations, divided by $\hbar\omega$. The off-diagonal H_{ij}'s will be taken to be independent of the q's.

To solve eqs 2.4–2.5, we first introduce a new Cartesian coordinate system (x,y,z) which permits a separation of the variable x from the (y,z) pair. The new axes are obtained by a rotation of the (q_1,q_2,q_3) axes, as in Figure 1. Customarily, three rotations are used for rotating the axes, as in the definition of the Euler angles.[5] However, for our purposes it suffices to introduce only two: The rotations are such that the final x axis is perpendicular to the $a_1a_2a_3$ plane and the final z axis is parallel to the a_2a_3 line.

We first rotate the axes through an angle Φ about the q_1 axis, such that the new q_3 coordinate (z in Figure 1) is parallel to the line a_2a_3, and then rotate the axes through an angle θ about this z axis, such that the new q_1 axis (x) is perpendicular to the plane $a_1a_2a_3$. We thus have

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Phi & \sin\Phi \\ 0 & -\sin\Phi & \cos\Phi \end{pmatrix}\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} \tag{2.6}$$

(5) E.g.: Goldstein, H. *Classical Mechanics*; Addison-Wesley: Reading, MA, 1959; pp 107–109.

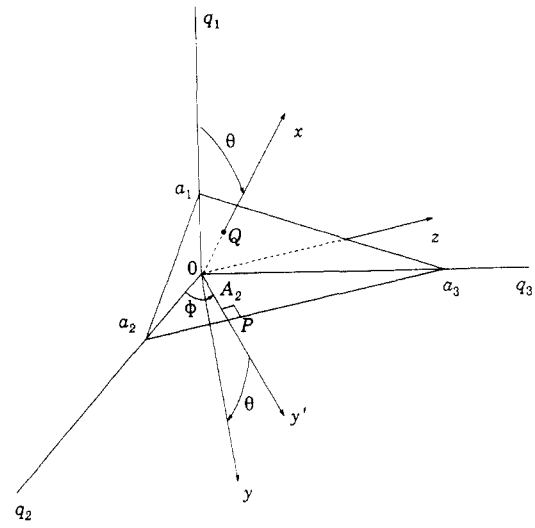

Figure 1. Original $(q_1q_2q_3)$ and rotated (xyz) coordinate axes. The x axis is perpendicular to the plane containing $a_1a_2a_3$ and intersects with it at Q. The z coordinate axis is parallel to the line a_2a_3 and serves as the reaction coordinate after the initial loss of the electron from D*. The y' axis is the result for the new q_2 axis, obtained after the rotation of an angle Φ about the q_1 axis, and the y axis results from $0y'$ after the rotation about $0z$ through an angle θ. P is the foot of the perpendicular from 0 to the line a_2a_3.

where in Figure 1 $\cos\Phi = 0P/a_2$, $\sin\Phi = 0P/a_3$, $\cos\theta = 0Q/a_1$, and $\sin\theta = 0Q/0P$. From the latter results we have $0P = A_2$ and $0Q = A_1$, where

$$A_1 = (\sum_{i=1}^{3} a_i^{-2})^{-1/2}, \quad A_2 = (a_2^{-2} + a_3^{-2})^{-1/2} \tag{2.7}$$

Upon multiplying the two matrices in eq 2.6 and taking the transpose so as to express the **q** column vector in terms of the **x** one, we have

$$\begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \begin{pmatrix} A_1/a_1 & -A_1/A_2 & 0 \\ A_1/a_2 & A_1A_2/a_1a_2 & -A_2/a_3 \\ A_1/a_3 & A_1A_2/a_1a_3 & A_2/a_2 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{2.8}$$

Applying this transformation to eqs 2.4–2.5, we have

$$-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Phi_i + \sum_j H_{ij}\phi_j = i\frac{\partial\Phi_i}{\partial t} \tag{2.9}$$

where

$$\begin{aligned} H_{11} &= (x - A_1)^2 + \tfrac{1}{2}(y + a_1A_1/A_2)^2 + \tfrac{1}{2}z^2 \\ H_{22} &= \tfrac{1}{2}(x - A_1)^2 + H_{22}(y) + H_{22}(z) \\ H_{33} &= \tfrac{1}{2}(x - A_1)^2 + H_{33}(y) + H_{33}(z) \end{aligned} \tag{2.10}$$

and[6]

$$\begin{aligned} H_{22}(y) = H_{33}(y) &= \tfrac{1}{2}(y - A_1A_2/a_1)^2 \\ H_{22}(z) &= \tfrac{1}{2}(z + a_2A_2/a_3)^2 + \Delta E_{12} \\ H_{33}(z) &= \tfrac{1}{2}(z - a_3A_2/a_2)^2 + \Delta E_{13} \end{aligned} \tag{2.11}$$

With the change of coordinates from (q_1,q_2,q_3) to (x,y,z), it is seen from eqs 2.9–2.11 that the x motion is identical for all H_{ii}'s and so is now separable from that of y and z, an anticipated result since the coordinate x was defined so as to be perpendicular to the plane containing all the geometrical changes. The calculation of the dynamics of the electron transfer starting from electronic configuration 1, i.e., from D*BA, now involves only the two coordinates y and z.

(6) This definition of the $H_{ii}(z)$'s was made (inclusion of the ΔE_{ii}'s in them instead of in the $H_{ii}(y)$'s) so as to simplify subsequent notation. E.g., in eq 4.10 $H_{22}^{xy} - H_{33}^{xy}$, which contains $\Delta E_{12} - \Delta E_{23}$, then reduces to $H_{22}(z) - H_{33}(z)$.

While eqs 2.10 and 2.11 follow from (2.5) and the coordinate transformation (2.8), the equilibrium values in the (x,y,z) system for the points a_1, a_2, a_3, evident from eqs 2.10–2.11, are also easily inferred from Figure 1.[7]

III. The Rate Constant

For the loss of the electron from D* we use a nonadiabatic description (weak interaction of D* with BA). A Golden Rule approximation can then be used for a first-order rate constant k_r for the disappearance of electronic configuration 1. For reactant from a particular vibrational state N_1 of D*, this k_r is given by[8,9]

$$k_r = 2\pi\omega H_{12}^2 \sum_{N_{23}} |\langle \Phi_{N_1}(y,z) | \Phi_{N_{23}}(y,z) \rangle|^2 \delta(E_{N_{23}} - E_{N_1}) \quad (3.1)$$

using the separability of the x from the (y,z) motion. In eq 3.1, H_{12} is the dimensionless H_{12} in (2.4) and E_{N_1} denotes the energy, divided by $\hbar\omega$, for a system whose electronic configuration is 1 and whose vibrational wave function is $\Phi_{N_1}(y,z)$. The vibrational wave function for the motion on a potential energy surface based on the pair of electronic configurations (2,3) is denoted by $\Phi_{N_{23}}(y,z)$, and the corresponding vibrational energy, divided by $\hbar\omega$, is $E_{N_{23}}$.

The stationary-state Schrödinger equation for Φ_{N_1}, obtained from (2.9)–(2.11), is

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + \tfrac{1}{2}(y + a_1A_1/A_2)^2 + \tfrac{1}{2}z^2 \right] \Phi_{N_1}(y,z) = E_{N_1}\Phi_{N_1}(y,z) \quad (3.2)$$

Equation 3.2 is separable, and we have

$$\Phi_{N_1}(y,z) = \Phi_n(y)\,\Phi_m(z), \quad E_{N_1} = E_n + E_m \quad (3.3)$$

where n and m are the respective quantum numbers for the y and z vibrational motions in electronic configuration 1, N_1 thus denoting the pair (n,m). $\Phi_n(y)$ and $\Phi_m(z)$ are the corresponding wave functions.

When the eigenfunctions $\Phi_{N_{23}}(y,z)$ in eq 3.1 are approximated by being taken to be the solutions of the diabatic equation

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + H_{22}(y) + H_{22}(z) \right) \Phi_{N_{23}}(y,z) = E_{N_{23}}\Phi_{N_{23}}(y,z) \quad (3.4)$$

$\Phi_{N_{23}}(y,z)$ becomes

$$\Phi_{N_{23}}(y,z) = \Phi_{n'}^{(2)}(y)\,\Phi_{m'}(z), \quad E_{N_{23}} = E_{n'} + E_{m'} \quad (3.5)$$

where

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \tfrac{1}{2}(y - A_1A_2/a_1)^2 \right] \Phi_{n'}^{(2)}(y) \equiv H_y'\Phi_{n'}^{(2)}(y) = E_{n'}\Phi_{n'}^{(2)}(y) \quad (3.6)$$

and

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial z^2} + H_{22}(z) \right] \Phi_{m'}(z) = E_{m'}\Phi_{m'}(z) \quad (3.7)$$

where $H_{22}(z)$ is defined in (2.11). The first half of eq 3.6 defines H_y'.

To obtain a thermally averaged rate constant, eq 3.1 is multiplied by the Boltzmann factor $\exp(-\beta' E_{N_1})/Qxy$ and summed over N_1. Here, β' denotes $\hbar\omega/k_BT$, k_B being Boltzmann's constant and T the temperature, and Q_{yz} is the yz vibrational partition function when the electronic configuration is that of 1. Since the y and z vibrations for the initial electronic configuration 1 are treated as harmonic, Q_{yz} is given by a standard expression. When the y motion is that of a harmonic oscillator in the diabatic electronic states 1 and 2, and when the harmonic $H_{22}(z)$ potential is used instead of an adiabatic potential $E_-(z)$ discussed later, eq 3.1 yields the standard result for the thermally averaged rate constant $k_r(T)$[10]

$$k_r(T) = \langle k_r \rangle = 2\pi\omega|H_{12}|^2(\exp[-\lambda_{12}\coth(\beta'/2) + \beta' p/2])I_p[\lambda_{12}\operatorname{cosech}(\beta'/2)] \quad (3.8)$$

where $I_p(u)$ is a modified Bessel function of order p and argument u, and where

$$p = -\Delta E_{12}, \quad \lambda_{12} = \tfrac{1}{2}(a_1^2 + a_2^2) \quad (3.9)$$

λ_{12} is the usual "reorganization" term in electron transfers, divided by $\hbar\omega$, namely, in the present case the value of $H_{22}(z) - H_{11}(z) - \Delta E_{12}$, at the equilibrium z position for the $H_{11}(z)$ potential.[11] All the quantities in (3.1) and (3.9), apart from ω, are dimensionless.

In arriving at eqs 3.8–3.9 from (3.1), using a set of z-mode acceptor states (Hamiltonian $H_{22}(z)$), we assumed a coupling of this mode to the many other coordinates in the system. Each z-mode acceptor state was thereby broadened. The sum over N_{23} in (3.1) can then be replaced by an integral containing the density $(\hbar\omega)^{-1}$ of z-mode states. The condition $E_{N_1} - E_{N_{23}} = 0$ in the delta function would be satisfied by having a maximal number of vibrational quanta $p\hbar\omega$ going into the z mode, with the residual energy imbalance being supplied from a coupling of other modes of the system to a state. Thereby, the p in (3.9) is the integer nearest $-\Delta E_{12}$ (with $-\Delta E_{12}$ expressed in units of $\hbar\omega$). In practice, eqs 3.8–3.9 will be treated as being interpolative, i.e., with p not being restricted to be an integer but rather equal to $-\Delta E_{12}$. The agreement of the various results in part 2, e.g., a comparison of (3.8) at 0 K with a numerical solution for k_r, provides some support for this approach.

IV. Population of B^-

When B^- is formed as an intermediate in an incoherent (hopping) mechanism, its time-dependent population can be calculated by standard chemical kinetics in terms of rate constants k_1 and k_2 of the two successive steps. However, when electronic configurations 2 and 3 are strongly coupled electronically, the wave packet representing the system can, on reaching the B^- region of the (2,3) pair of surfaces, move rapidly downhill. It is the dynamics on this (2,3) pair of surfaces that is treated next, the packet being steadily resupplied by the nonadiabatic transition from the decaying electronic configuration 1.

At zero time the system is in some zeroth-order vibrational eigenstate $\Phi_{nm}(y,z) = \Phi_n(y)\,\Phi_m(z)$ of electronic configuration 1. If one uses the type of perturbation theory associated with exponential decay phenomena,[8] the subsequent time evolution of $\Phi_{nm}(y,z,t)$ in electronic configuration 1 is given by[8]

$$\Phi_{nm}(y,z,t) = e^{-k_rt/2 - iE_{nm}t}\Phi_{nm}(y,z) \quad (4.1)$$

where the rate constant k_r is given by eq 3.1 and E_{nm} is the vibrational energy for the (n,m) vibrational state in electronic configuration 1.

(7) E.g., a_1, a_2, and a_3 all have an x equal to $0Q$, and $0Q$ equals A_1. Further, $z = 0$ describes the plane containing q_1, 0, y', and y, and so the point a_1 in Figure 1 has $z = 0$. The z's for a_2 and a_3 are seen as follows: The z for a_3 is Pa_3 in Figure 1, which equals $a_3 \cos\Phi = a_3(0P/a_3) = a_3A_2/a_2$. The z for a_2 is $-Pa_2$, which equals $-a_2 \sin\Phi = -a_2A_2/a_3$. The y for points a_2 and a_3 is $A_2 \cos\theta = A_2A_1/a_1$, and the y for a_1 is $-a_1 \sin\theta = -a_1A_1/A_2$. All of these values agree with the minima in (2.10)–(2.11), which are the points a_1, a_2, and a_3 in the new coordinate system.

(8) E.g.: Merzbacher, E. *Quantum Mechanics*: Wiley: New York, 1970; Chapter 18.

(9) This bra–ket notation is used for matrix elements involving the vibrational wave functions, indicating also by a (y,z) or (y), as in (3.1) and (4.9), the domain of those vibrational states to avoid confusion. The bra–ket notation is also used to label electronic states later in the article, as in eqs 4.2–4.8. In eq 4.8, a ket notation is also used to indicate an electronic–vibrational state, $|\Psi(y,z,t)\rangle$.

(10) E.g.: Levich, V. G.; Dogonadze, R. R. *Collect. Czech. Chem. Commun.* **1961**, *26*, 193 (Translated by O. Boshko, University of Ottawa). Levich, V. G. In *Physical Chemistry; An Advanced Treatise*; Eyring, H.; Henderson, D., Jost, W., Eds.; Academic Press: New York, 1970; Vol. 9B, p 985. Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. Pagitsas, H.; Freed, K. *Chem. Phys.* **1977**, *23*, 387.

(11) E.g.: Marcus, R. A.; Sutin, N. *Comments Inorg. Chem.* **1986**, *5*, 119.

The wave function from electronic state 1 is continuously deposited on the (2,3) pair of surfaces as a result of the nonadiabatic transition. In the perturbation theory[8] used to obtain eqs 3.1 and 4.1, the deposited wave function is $|\Psi_2\rangle H_{12}\Phi_{nm}(y,z,t)$. The latter then moves in time on the coupled (2,3) pair of surfaces, evolving under the influence of the electronic–nuclear Hamiltonian H_{yz} given below. The electronic–nuclear wave function $\Psi(y,z,t)$ is now given by the convolution expression[12]

$$|\Psi(y,z,t)\rangle = -i\int_0^t d\theta\, e^{-iH_{yz}(t-\theta)}|\Psi_2\rangle H_{12}\Phi_{nm}(y,z,\theta) \quad (4.2)$$

where $\Phi_{nm}(y,z,\theta)$ is given by eq 4.1. It is assumed for simplicity in eqs 4.2 and 3.1 that because of the large separation distance the electronic matrix element H_{13} directly coupling state Ψ_1 to Ψ_3 can, in the first approximation, be neglected. In terms of a bra–ket notation for the diabatic electronic wave functions Ψ_i's, the H_{yz} in eq 4.2 can be written as

$$H_{yz} = H_y + H_z \quad (4.3)$$

where, without loss of generality, the definition of H_z includes the H_{23} term:

$$H_z = \sum_{i=2}^{3}\sum_{j=2}^{3}|\Psi_i\rangle\left(-\frac{1}{2}\frac{\partial^2}{\partial z^2}\delta_{ij} + H_{ij}(z)\right)\langle\Psi_j| \quad (4.4)$$

and, using the fact from eq 2.11 that $H_{22}(y) = H_{33}(y)$

$$H_y = \sum_{i=2}^{3}\sum_{j=2}^{3}|\Psi_i\rangle\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2} + H_{22}(y)\right)\delta_{ij}\langle\Psi_j| = H_y'I \quad (4.5)$$

Here, I denotes the identity operator $\sum_{i=2}^{3}|\Psi_i\rangle\langle\Psi_i|$ in the (Ψ_2,Ψ_3) subspace, and H_y' is defined in the first half of (3.6): H_y is seen from eq 4.5 to induce no transitions in the (Ψ_2,Ψ_3) subspace, as expected.

Since H_y and H_z commute, the time evolution operator $\exp(-iH_{yz}\tau)$ in eq 4.2 can be written as $\exp(-iH_y\tau)\exp(-iH_z\tau)$. Further, using (4.5) we have

$$\exp(-iH_y\tau)|\Psi_2\rangle\Phi_n(y) = |\Psi_2\rangle\exp(-iH_y'\tau)\Phi_n(y) \quad (4.6)$$

With a change of variable $t - \theta \rightarrow \theta$, eq 4.2 now becomes

$$|\Psi(y,z,t)\rangle = -iH_{12}e^{-(k_r/2+iE_{nm})t}\int_0^t d\theta\, e^{(k_r/2+iE_{nm})\theta}[e^{-iH_y'\theta}\Phi_n(y)] \times [e^{-iH_z\theta}|\Psi_2\rangle\Phi_m(z)] \quad (4.7)$$

which is the desired final expression.

The "population" $B^-(t)$ of the intermediate electronic configuration 2 is obtained by projecting $|\Psi(y,z,t)\rangle$ onto the diabatic electronic state $|\Psi_2\rangle$ and integrating over the nuclear coordinates:

$$B^-(t) = \int\int dy\, dz\, |\langle\Psi_2|\Psi(y,z,t)\rangle|^2 \quad (4.8)$$

Strictly speaking, B^- does not actually exist in this mechanism, and it would be more rigorous to treat an observable, such as the absorption spectrum in the B spectral region, rather than defining a $B^-(t)$ via eq 4.8. Use of eq 4.8 for B^- presumes that the quantity so defined adequately describes this depletion in the spectral region of B.

The $\exp(-iH_y'\theta)\Phi_n(y)$ term in eq 4.7 can be written as

$$e^{-iH_y'\theta}\Phi_n(y) = \sum_{n'}\langle\Phi_{n'}^{(2)}(y)|\Phi_n(y)\rangle e^{-iE_{n'}\theta}\Phi_{n'}(y) \quad (4.9)$$

where $\Phi_{n'}^{(2)}(y)$ is the n'th eigenfunction of the Hamiltonian H_y', defined in eq 3.6, $E_{n'}$ is the corresponding eigenvalue, and $\langle\Phi_{n'}^{(2)}(y)|\Phi_n(y)\rangle$ is a Franck–Condon factor. Each of the quantities in eq 4.9 is well-known[13] for the present case where H_y' is a harmonic oscillator Hamiltonian, eq 3.6. The z-dependent term in (4.7), $\exp(-iH_z(\theta)|\Psi_2\rangle\Phi_m(z)$, can be calculated by using a fast Fourier transform (FFT) method.[3] In the procedure some mechanism is prescribed for the dissipation of the wave packet after reaching the $H_{33}(z)$ surface, for example, by adding an imaginary term $-i\Gamma$ to $H_{33}(z)$ in eq 4.4 or by modifying $H_{33}(z)$ and then introducing an absorbing boundary.[4]

In ref 4, for comparison with some of the numerical results for eqs 4.7–4.8, we have also made some calculations with $H_{22}(y) + H_{22}(z)$ in eq 3.4 replaced by an adiabatic surface $E_-(y,z)$. From a comparison of the two sets of calculations information is obtained on the reflection, if any, of the wave packet during its passage through the H_{22} and H_{33} intersection region. $E_-(y,z)$ is the lower of the two adiabatic potentials constructed from H_{22} and H_{33} and is given by

$$E_-(y,z) = \tfrac{1}{2}\{H_{22}^{yz} + H_{33}^{yz} - [(H_{22}^{yz} - H_{33}^{yz})^2 + 4H_{23}^2]^{1/2}\} \quad (4.10)$$

where H_{ii}^{yz} is $H_{ii}(y) + H_{ii}(z)$, defined in (2.10)–(2.11).

Inasmuch as $H_{22}^{yz} - H_{33}^{yz}$ depends only on z (cf. eq 2.11) the adiabatic potential $E_-(y,z)$ given by (4.10) is seen to be the sum of two terms

$$E_-(y,z) = \tfrac{1}{2}(y - A_1A_2/a_1)^2 + E_-(z) \quad (4.11)$$

where

$$E_-(z) = \tfrac{1}{2}\{[H_{22}(z) + H_{33}(z)] - \{[H_{22}(z) - H_{33}(z)]^2 + 4H_{23}^2\}^{1/2}\} \quad (4.12)$$

V. Energy Partitioning among the y and z Modes

When the wave packet from state 1, given in (4.2), is deposited on the (2,3) surface, the population $B^-(t)$ estimated in (4.8) depends on the partitioning of the excess energy among the y and z modes. To obtain some insight into numerical results[4] for this partitioning, and later into an effective rate constant k_2, it is useful to introduce here a quite rough but analytic estimate.

The intersection of the $H_{11}(y,z)$ and $H_{22}(y,z)$ potential energy surfaces has some lowest point $(y_{12}^\ddagger, z_{12}^\ddagger)$. If we use the arguments given in Appendix A, the excess energy E_y in the y mode, measured relative to the energy at the lowest point y_2^0 of the curve $H_{22}(y)$, is

$$E_y = n + \tfrac{1}{2} + (\Delta E_{12}/\lambda_{12})(\lambda_2^2/\lambda_{23}) - \Delta E_{12} \equiv n' + \tfrac{1}{2} \quad (5.1)$$

where this n' so defined is predicted to be a dominant term in eq 4.9 or an average, $\sum_{n'} n'|\langle\Phi_{n'}^{(2)}|\Phi_n\rangle|^2$, of the terms there. Subtracting this E_y from the approximate total energy after the $\Psi_1 \rightarrow \Psi_2$ transition, $m + n + 1 - \Delta E_{12}$, the average z-mode energy E_z for motion on the (2,3) pair of surfaces is estimated to be

$$E_z = m + \tfrac{1}{2} - (\Delta E_{12}/\lambda_{12})(\lambda_2^2/\lambda_{23}) \quad (5.2)$$

In the three-state dynamics the system is initially deposited from state 1 onto the $H_{22}(y,z)$ surface, since $H_{13} \simeq 0$. However, because of the strong coupling of the (2,3) pair, it may quickly settle down to a motion largely on the $E_-(y,z)$ surface.

In that case there is a larger energy available at (y_2^0, z_2^0), larger than (5.1)–(5.2) and distributed between the y and z motions. The additional amount of energy shared between those coordinates is estimated in Appendix A to be $H_{22}(z_2^0) - E_-(z_2^0)$ and thereby that $E_y + E_z$ is given by

$$E_y + E_z = m + n + 1 - \Delta E_{12} + [\tfrac{1}{4}(\lambda_{23} + \Delta E_{23})^2 + H_{23}^2]^{1/2} - \tfrac{1}{2}(\lambda_{23} + \Delta E_{23}) \quad (5.3)$$

instead of $m + n + 1 - \Delta E_{12}$.

To interpret some of the numerical results for $B^-(t)$ and for B^-_{max} given in part 2 and provide an approximate indication of what might be expected for other values of the various parameters, we obtain below a rather rough classical estimate of the time spent by the system in the "B^- region" and for an effective rate constant k_2. For this purpose we approximate the length of this region by the z interval between $z_{12}^\ddagger$ and the intersection $z_{23}^\ddagger$ of the $H_{22}(z)$

(12) Cf.: Loudon, R. *The Quantum Theory of Light*; Clarendon: Oxford, 1973: p 279.

(13) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*: McGraw-Hill: New York, 1979; pp 112–115.

(14) Child, M. S. In *Semiclassical Methods in Molecular Scattering and Spectroscopy*. *NATO ASI Ser., Ser. C.* **1979**, *53*, 127.

(15) Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21. Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

and $H_{33}(z)$ surfaces. The point $z_{23}^{\ddagger}$ is given by equations analogous to eqs A3 and A4

$$z_{23}^{\ddagger} = z_2^0 + M(z_2^0 - z_3^0) \tag{5.4}$$

where M satisfies

$$-(2M + 1)\lambda_{23} = \Delta E_{23} \tag{5.5}$$

Thereby, the value of $z_{23}^{\ddagger} - z_{12}^{\ddagger}$, obtained as the difference, $z_{23}^{\ddagger} - z_2^0 - (z_{12}^{\ddagger} - z_2^0)$, is found, using eqs A3 and A4 for $z_{12}^{\ddagger}$, to be

$$z_{23}^{\ddagger} - z_{12}^{\ddagger} = [(\Delta E_{23} + \lambda_{23}) + (\Delta E_{12} - \lambda_{12})(\lambda_2/\lambda_{12})]/(2\lambda_{23})^{1/2} \tag{5.6}$$

When the wave packet undergoes negligible reflection in the region near $z_{23}^{\ddagger}$, a condition we denote by setting the $2 \rightarrow 3$ transition probability, w_{23}, to be approximately unity, the time τ_2 spent by the system in the B^- region is then, classically

$$\tau_2 \sim \int_{z_{12}^{\ddagger}}^{z_{23}^{\ddagger}} dz/v_z \quad (\text{when } w_{23} \sim 1) \tag{5.7}$$

where v_z is the local z component of velocity. In the case of the $H_{22}(z)$ curve v_z is $[2\{E_z - H_{22}(z) + H_{22}(z_2^0)\}]^{1/2}$, and in the case of the $E_-(z)$, curve v_z would be somewhat larger. Equation 5.7 can be written in terms of some averaged velocity, $\bar{v}_z$, $\tau_2 = (z_{23}^{\ddagger} - z_{12}^{\ddagger})/\bar{v}_z$.

If τ_2 is regarded as the reciprocal of an effective rate constant k_2, then eq 1.1 still applies approximately for the maximum population of B^-, but now with the k_2 given by

$$k_2 \sim \bar{v}_z/|z_{23}^{\ddagger} - z_{12}^{\ddagger}| \quad (\text{when } w_{23} \sim 1) \tag{5.8}$$

A few examples of $B_{-\max}$ calculated from eqs 1.1 and 5.8 are given in part 2 and indicate that eq 5.8 is correct to roughly a factor of about 2 when w_{23} is approximately unity. Further, a comparison is also made there with the full $B^-(t)$ vs t curve using this effective k_2. This k_2 becomes large when the z interval in the denominator of eq 5.8 becomes small (but not too small, if the expression is to have some validity) and if at the same time $w_{23} \sim 1$.

In several respects a recent article[16] by Lin on a donor–bridge–acceptor electron transfer is complementary to the present one: the case when the B^- orbital is close to D^* is included there, and the overall $D^* \rightarrow A$ transfer is assumed to be coherent. There are several differences: a steady-state (Golden Rule) perturbative type treatment was used in ref 16 for the entire process, $D^* \rightarrow A$, so that the time evolution for the formation of A^- was described by a single exponential. The electronic matrix elements are presumably assumed to be small in ref 16, so that the perturbative treatment can be used throughout. In the present treatment a highly nonexponential formation of A^- may occur (e.g., Figure 3 in part 2), and a large H_{23} matrix element is permitted. One focus in the present article, unlike that in ref 16, is on the maximum "B^-" population. Another treatment akin to that in ref 16 is that of Kharkats et al.,[17] who used for simplicity a one-coordinate treatment. Other studies include one by Friesner and Wertheimer,[18] who assumed a strong vibronic (nonperturbative) coupling in a photosynthetic system: They employed vibrational frequencies that nearly matched the assumed electronic energy gaps and so caused, thereby, a strong electronic interstate mixing. Coherent electron transfer in a two-level system has been discussed by Jortner.[19]

Applications of the present formalism are made in part 2.

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(18) Friesner, R.; Wertheimer, R. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *79*, 2138.
(19) Jortner, J. *Philos. Mag.* **1979**, *B40*, 317.

Appendix A: Energy Partitioning among the x and y Modes

The average distribution of the excess energy in each of the y and z modes after a $1 \rightarrow (2,3)$ transition is estimated in this Appendix. When a matrix element $\langle \Phi_{N_1}(y,z)|\Phi_{N_{23}}(y,z)\rangle$ in eq 3.1 is treated semiclassically,[14] it has a stationary-phase point which lies on the intersection surface of $H_{11}(y,z)$ and a second surface, $H_{22}(y,z)$ or $E_-(y,z)$, depending on the approximate $\Phi_{N_{23}}(y,z)$ used for the stationary-phase condition: The stationary-phase point occurs where there is no change in the y and z components of momentum and so occurs on the above intersection surface (Franck–Condon principle). In the classical limit, the dominant semiclassical matrix elements provide information on an ensemble of classical trajectories from state 1 to state (2,3). This ensemble, in their crossing from the $H_{11}(y,z)$ surface to the second surface, is centered around the lowest point $(y_{12}^{\ddagger},z_{12}^{\ddagger})$ on the intersection surface.

If the y-mode and z-mode energies before and just after the transition are E_n and E_m, respectively, in the notation of eq 3.3, the y-mode *kinetic energy* at $(y_{12}^{\ddagger},z_{12}^{\ddagger})$ is $E_n - {}^1/_2(y_{12}^{\ddagger} - y_1^0)^2$, where (y_1^0,z_1^0) specifies the minimum of the $H_{11}(y,z)$ surface. The potential energy for the y mode on the $H_{22}(y,z)$ surface, relative to what it would be at the point y_2^0 is ${}^1/_2(y_{12}^{\ddagger} - y_2^0)^2$, where (y_2^0,z_2^0) specifies the minimum of $H_{22}(y,z)$. Thus, E_y, the y-mode energy in excess of the potential energy $H_{22}(y_2^0)$ after the $1 \rightarrow (2,3)$ transition, is

$$E_y = n + {}^1/_2 - {}^1/_2(y_{12}^{\ddagger} - y_1^0)^2 + {}^1/_2(y_{12}^{\ddagger} - y_2^0)^2 \tag{A1}$$

We define the corresponding z-mode energy E_z as its value relative to that at z_2^0. Thereby

$$E_z = m + {}^1/_2 - {}^1/_2(z_{12}^{\ddagger} - z_1^0)^2 + {}^1/_2(z_{12}^{\ddagger} - z_2^0)^2 \quad (H_{22} \text{ surface}) \tag{A2}$$

The dominant n' term in eq 4.9 is the one whose energy, $n' + {}^1/_2$, in units of $\hbar\omega$, most closely approximates the energy E_y given by (A1).

By use of concepts employed for intersecting parabolic surfaces,[15] the point $(y_{12}^{\ddagger},z_{12}^{\ddagger})$ lying on the intersection of $H_{11}(y,z)$ and $H_{22}(y,z)$ surfaces and having the least potential energy is given by

$$y_{12}^{\ddagger} = y_1^0 + M(y_1^0 - y_2^0), \quad z_{12}^{\ddagger} = z_1^0 + M(z_1^0 - z_2^0) \tag{A3}$$

where M satisfies the equation[15]

$$-(2M + 1)\lambda_{12} = \Delta E_{12} \tag{A4}$$

Equations A1–A5 then yield the energy partitioning expressions, eqs 5.1–5.2.

If the system after the $1 \rightarrow 3$ transition is better described near z_2^0 as residing on the $E_-(y,z)$ surface rather than on the $H_{22}(y,z)$ one, then there is available for distribution among the y and z motions some extra energy (extra when $H_{22} > H_-$), namely, $H_{22}(z_2^0) - E_-(z_2^0)$. Using eqs 4.12 and 2.11, this additional energy term is found to be given by eq 5.3.

Appendix B: Landau–Zener Transmission Probability near $z_{23}^{\ddagger}$

In a Landau–Zener treatment the probability w_{23} of remaining on the potential energy curve $E_-(z)$ after a single passage through $z_{23}^{\ddagger}$ is given by[14]

$$w_{23} = 1 - e^{-2\pi H_{23}^2/v_z|\Delta s|} \tag{B1}$$

when $z_{23}^{\ddagger}$ is real. Here, v_z is the velocity at the crossing point and Δs is the difference of slopes of the intersecting diabatic potential energy curves there. If we set $v_z^2 = N$ in dimensionless units (which defines N) and if we introduce the value[1] for $|\Delta s|$, namely, $(z_3^0 - z_2^0)$ in dimensionless units, one finds that

$$w_{23} = 1 - e^{-2\pi H_{23}^2/(\lambda_{23}/N)^{1/2}} \tag{B2}$$

For example, if the z energy in the vicinity of $z_{23}^{\ddagger}$ is approximately the zero-point energy, then $N \simeq 1$. Employing eq B2 when H_{23} becomes very large may, however, be questionable.