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Electron Transfer via Superexchange: A Time-Dependent Approach

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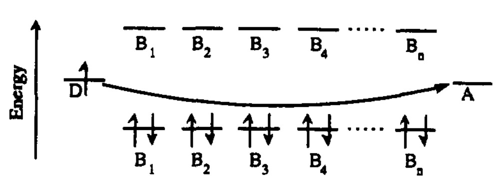
The superexchange model for the facilitation of electron transfer between donors and acceptors by means of intermediate bridges is recast in a time-dependent framework. We develop a model in which three electronic states (donor, bridge, and acceptor) are considered and vibronic levels are included on the donor and acceptor. An explicitly time-dependent formulation, in which the golden rule is rewritten in the form of an integral over a time-dependent correlation function, is used to calculate the rate. Simple example calculations for model three-site systems are given; inverted region behavior and reasonable values are obtained. The model is a general one and should be useful for interpretation of superexchange-assisted transfer based on experimental observations of frequencies and displacements (such as the information that can be obtained with Raman spectroscopy). The model can be generalized to include effects such as dephasing, relaxation, solvent dynamics, and anharmonicities, as well as breakdown of the Condon approximation.

I. Introduction

Electron transfer is one of the most important fundamental steps in chemistry, and interest in elucidation of electron-transfer rates in chemical reactions has recently made it the focus of numerous excellent treatments.[1] Specifically, the very attractive superexchange model, first introduced by McConnell,[2] has been carefully examined in the context of bridged, intramolecular charge transfer.[3,4] McConnell suggested that orbital sites intervening between donor and acceptor could facilitate the electron-transfer process. In the electron superexchange model, an electron is transferred between degenerate donor and acceptor orbitals, aided by the presence of high-lying (not necessarily degenerate) empty bridge orbitals (model 1). (A similar case exists for hole superexchange through low-lying fully occupied bridge orbitals.) The superexchange model differs from a "hopping" model (model 2) in that the electron does not actually occupy any of the bridge orbitals during the transfer event.



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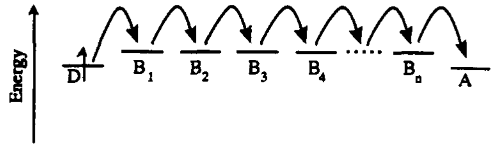

(2)

Following McConnell's original formulation, the coupling element between donor and acceptor is given by

$$T_{\mathrm{DA}}^{(n)} = \left(\frac{\beta_{\mathrm{DB_1}}\beta_{\mathrm{B}_n\mathrm{A}}}{E_{\mathrm{D,A}} - E_{\mathrm{B_1}}}\right)\left(\prod_{i=1}^{n-1}\frac{\beta_{i,i+1}}{E_{\mathrm{D,A}} - E_{\mathrm{B}_{i+1}}}\right) \qquad (3)$$

where β_{ij} is the tunneling integral between orbitals i and j, $E_{\mathrm{D,A}}$ is the (degenerate) energy of the donor and acceptor orbitals, E_i is the energy of the ith bridge orbital, and n is the number of bridge orbitals.

The McConnell superexchange model is simple to use for most cases of superexchange; however, it should be noted that this model is useful primarily for evaluating the electronic coupling. It is independent of both time and nuclear vibrations and requires that D and A be degenerate and energetically well removed from the bridge orbitals.

Perturbative methods for the calculation of electronic coupling in electron-transfer reactions have been offered by a number of groups.[2–7] It should be noted that these methods only yield the nonadiabatic coupling element between donor and acceptor, H_{DA}. This, in turn, may be used within a vibronic theory such as that of Jortner[8,9] or Fischer and Van Duyne.[10]

We present here a new approach to electron-transfer rate theory. It is based on an explicitly time-dependent rate expression for superexchange-assisted nonadiabatic electron transfer. This method is suggested by the very useful reformulation of such problems as optical line shapes,[11] resonance Raman spectra,[12] and solvated electron dynamics[13] in an explicitly time-dependent form. It describes thermal electron transfer and can be extended to include full vibrational behavior, frequency changes, anharmonicities, dephasing, and non-Condon terms; it can also be adopted to approximate discussions of slow gating modes and solvent relaxation. Further, since it does not require that the donor and acceptor states be degenerate, it generalizes the superexchange formalism in an important way. In section II, we describe a first-order version of our model, in which we use harmonic energy surfaces and the Condon approximation. In section III, we give the results of calculations on a model three-site system, consisting of a donor, a bridge, and an acceptor. Section IV offers some conclusions.

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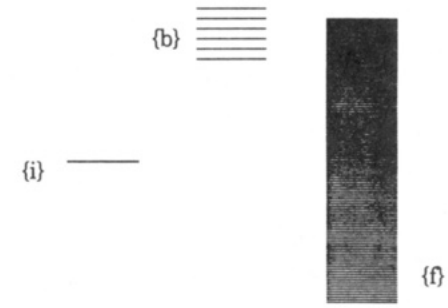

Figure 1. Initial (I), bridge (B), and final (F) electronic states and associated vibrational levels ({i}, {b}, and {f}, respectively) for the transition described in the text, for $T = 0$.

II. A Time-Dependent Superexchange Model

Even though we are ultimately interested in a time-dependent formulation of the electron-transfer rate, it is convenient to begin with a time-independent formulation. For simplicity, we consider a system of three electronic states: an initial state I, a bridge state B, and a final state F. We further ignore direct electronic coupling between the initial and final states, so $V_{IF} = V_{FI} = 0$. In what follows, $\sum_S$ refers to a summation over vibrational levels belonging to the electronic state S (= I, B, and F). We take $\hbar = 1$.

We first consider the transition out of a particular state i, referring to the model in Figure 1. The transition rate is associated with the imaginary part of the self-energy $S_i(E)$ (at $E = E_i$), defined by

$$G_{ii}(E) = \frac{1}{E - E_i - S_i(E_1)} \tag{4}$$

where $G_{ii}(E)$ is Green's function element $\langle i|(E - H + i\epsilon)^{-1}|i\rangle$ ($\epsilon \to 0$). For the present model, $G_{ii}(E)$ is calculated by using the Dyson equation $G = G_0 + G_0VG$ to obtain a set of closed coupled equations:

$$G_{ii} = G_{ii}^0 + G_{ii}^0 \sum_b V_{ib} G_{bi} \tag{5}$$

$$G_{bi} = G_{bb}^0 V_{bi} G_{ii} + G_{bb}^0 \sum_f V_{bf} G_{fi} \tag{6}$$

$$G_{fi} = G_{ff}^0 \sum_b V_{fb} G_{bi} \tag{7}$$

Here, $G_{jj}^0 = (E - E_j + i\epsilon)^{-1}$. Inserting (7) and (6) leads to a set of equations (one for each b) of the form

$$G_{bi} = G_{bb}^0 V_{bi} G_{ii} + G_{bb}^0 \sum_f V_{bf} G_{ff}^0 \sum_{b'} V_{fb'} G_{b'i} \tag{8}$$

Multiplying this equation by V_{fb} followed by a summation over b yields the following result (for $x \equiv \sum_b V_{fb} G_{bi}$):

$$x = \frac{U_{fi}}{1 - \alpha} G_{ii} \tag{9a}$$

where

$$U_{fi} = \sum_b \frac{V_{fb} V_{bi}}{E - E_b} \tag{9b}$$

$$\alpha = \sum_b \sum_f \frac{V_{fb} V_{bf}}{(E - E_b)(E - E_f + i\epsilon)} \tag{9c}$$

Inserting (9a) into (8) yields

$$G_{bi} = \frac{V_{bi}}{E - E_b} G_{ii} + \frac{1}{E - E_b} \sum_f \frac{V_{bf} U_{fi}}{(E - E_f + i\epsilon)} \frac{G_{ii}}{1 - \alpha} \tag{10}$$

Inserting this result in (5) finally yields (4) with

$$S_i(E) = \sum_b \frac{V_{ib} V_{bi}}{E - E_b} + \frac{1}{1 - \alpha} \sum_f \frac{U_{if} U_{fi}}{E - E_f + i\epsilon} \tag{11}$$

Since $S_i(E)$ is to be evaluated at $E = E_i$, we keep the small imaginary term $i\epsilon$ in the denominator which may otherwise vanish (since $E_f \cong E_i$). Similarly, we take $\alpha \ll 1$, since it is the quotient of the energy width of the final state divided by the electronic excitation gap.

The transition rate out of state i is associated with the imaginary part of $S_i(E_i)$:

$$\Gamma_i = 2\pi \sum_f |U_{if}|^2 \delta(E_i - E_f) \tag{12}$$

which is the usual golden rule with the renormalized i–f coupling (eq 9b). In what follows, we assume for simplicity that $V_{fb} \equiv V_{FB}$ and $V_{bi} \equiv V_{BI}$ are independent of the individual vibronic level (this assumption may be relaxed in a somewhat more involved treatment), whereupon

$$U_{if} = \langle i|U|f\rangle \tag{13}$$

with the operator U defined by

$$U = V_{IB} V_{BF} \frac{1}{H_I - H_B} \tag{14}$$

Here H_S (A = I, B, F) is the nuclear Hamiltonian associated with the electronic state S. Finally, using the fact that the kinetic energy parts of H_I and H_B are the same, (14) is rewritten in the form

$$U = \frac{V_{IB} V_{BF}}{V_I(X) - V_B(X)} \tag{14a}$$

where $V_S(X)$ is the potential surface for the nuclear motion in electronic state S.

The rate (eq 12) can be expressed as the Fourier transform of the time correlation function

$$\Gamma_i = \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{-i\Delta E t} \langle i|e^{iH_I t} U e^{-iH_F t} U|i\rangle \tag{15}$$

where $\Delta E = E_I^0 - E_F^0$ is the difference between the origins of the electronic states F and I and where H_I and H_F are the nuclear Hamiltonians associated with these states. Finally, the thermally averaged rate is

$$\Gamma_I = \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{-i\Delta E t} C(t) \tag{16}$$

where

$$C(t) = \langle i|e^{iH_I t} U e^{-iH_F t} U|i\rangle_T = \sum_i \frac{e^{-\beta E_i}}{Q} \langle i|e^{iH_I t} U e^{-iH_F t} U|i\rangle \tag{17}$$

and

$$Q = \sum_i e^{-\beta E_i} \tag{18}$$

Following Neria et al.,[13] we now make a semiclassical approximation by replacing $|i\rangle$ in (17) by Gaussian wavepackets centered about the classical position and momenta of the atomic nuclei moving on the I potential surface. The thermal average is implemented by sampling these positions and momenta from a Boltzmann distribution.

The time evolution $\exp(iH_It)|i\rangle$ is implemented with the frozen Gaussian[11] approximation which is valid if $C(t)$ decays to zero before the wavepacket distorts appreciably. In this approximation, the time evolutions $\exp(iH_It)|t\rangle$ and $\exp(iH_Ft)|i\rangle$ are obtained by moving the mean position and momentum of the Gaussian according to the classical equations of motion on the corresponding potential surfaces.

Consider now the operation $U|i\rangle$ encountered in (17), where $|i\rangle$ is now a Gaussian wavepacket associated with the classical position $X^i(0)$ and momentum $P^i(0)$ and a corresponding classical energy $E_I = H_I^{(cl)}(X^i(0),P^i(0))$ (where $H_I^{(cl)}$ is the classical nuclear Hamiltonian on electronic state I). In this case, $U|i\rangle$ may be approximated by

$$U|i\rangle = \frac{V_{IB}V_{BF}}{V_I(X^i(0)) - V_B(X^i(0))}|i\rangle \qquad (19a)$$

$$U|i\rangle \simeq \frac{V_{IB}V_{BF}}{V_I^{(cl)}(X^i(0)) - V_B^{(cl)}(X^i(0))}|i\rangle \qquad (19b)$$

where $V_S^{(cl)}(X)$ is the (classical) nuclear potential (electronic energy as a function of nuclear position) in state S (=I, B).

From the Heisenberg representation,

$$Ue^{-H_It}|i\rangle = U|i(t)\rangle \qquad (20)$$

where $i(t)$ is a Gaussian wavepacket centered at $\{X^i(t),P^i(t)\}$ (the classical positions and momenta obtained by propagating the initial classical state $X^i(0),P^i(0)$ with the classical Hamiltonian $H_I^{(cl)}$ associated with electronic state I). Therefore,

$$Ue^{-iH_It}|i\rangle = \frac{V_{IB}V_{BF}}{V_I^{(cl)}(X^i(t)) - V_B^{(cl)}(X^i(t))}e^{-iH_It}|i\rangle \qquad (21)$$

Equation 17 then becomes

$$C(t) = |V_{IB}V_{BF}|^2\left\langle\left[\frac{1}{V_I^{(cl)}(X^i(0)) - V_B^{(cl)}(X^i(0))}\right] \times \left[\frac{1}{V_I^{(cl)}(X^i(t)) - V_B^{(cl)}(X^i(t))}\right]J(t)\right\rangle_T \qquad (22)$$

with

$$J(t) = \langle X(0)P(0)|e^{iH_It}e^{-iH_Ft}|X(0)P(0)\rangle \qquad (23)$$

where $\langle\cdots\rangle_T$ in (22) denotes the classical thermal average over the initial positions and momenta. Here, $\exp(-iH_St)|X(0)P(0)\rangle$ (S = I, B) denotes the time-dependent frozen Gaussian wavepacket

$$e^{-iH_St}|X(0)P(0)\rangle = |X^S(t)P^S(t)\rangle = \exp[i\alpha(X - X^S(t))^2 + iP^S(t)(X - X^S(t)) + i\gamma(t)] \qquad (24)$$

where

$$\alpha = \frac{im\omega}{2} \qquad (25)$$

and

$$\gamma(t) = -\frac{1}{4}i \log\left(\frac{m\omega}{\pi}\right) - \frac{1}{2}\omega t + \varphi(t) \qquad (26)$$

The phase term is

$$\varphi(t) = \int_{x^S(0)}^{x^S(t)} P(X)\,dX - Et \qquad (27)$$

where $P(X)$ is the classical momentum at X for total energy E.

Equations 16–22 represent a semiclassical, time-dependent wavepacket approach to the calculation of electron-transfer rate constants. The actual calculation proceeds by propagating the packets on the initial and final states, computing the overlap integral, and thermally averaging over the initial state distribution to obtain $C(t)$.

We now apply this treatment to a model system.

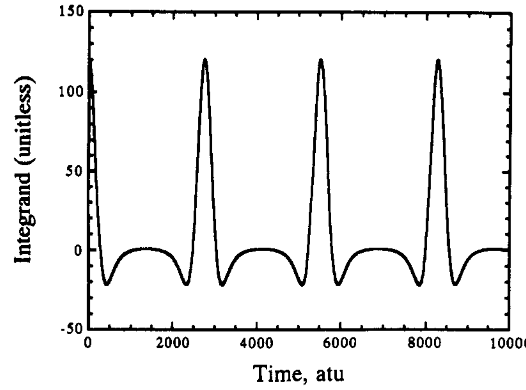

Figure 2. Integrand of eq 16, as described in the text. Relevant parameters for the one-mode case shown are as follows: $\hbar\omega = 500$ cm^{-1}; $\Delta E_{bi} = \Delta E_{bf} = 20\,000$ cm^{-1} (i and f are degenerate); $V_{IB} = V_{BF} = V_{BI} = V_{FB} = 4000$ cm^{-1}; location of minima (unitless): $\tilde{X}_{0,I} = -1.15$, $\tilde{X}_{0,B} = 0.00$, $\tilde{X}_{0,F} = +1.15$. 1 atu (atomic time unit) = 2.4189×10^{-17} s. Note the effects of the phase factor, defined in eq 27, seen here as secondary peaks in the integrand. Note also that in the absence of irreversible processes such as damping, slow gating, dephasing, or dissociation, we observe recurrence, and no rate can be defined.

III. A Model System

As a first test of the time-dependent calculation, we choose to sample some parameters of a real intramolecular electron-transfer system, $[(H_3N)_5Ru^{II}$–4,4′-bipy–$Ru^{III}(NH_3)_5]^{5+}$ (here 4,4′-bipy is 4,4′-bipyridine), a symmetric, mixed valent dimer, which has been the focus of a number of experimental studies.[14,15] With the understanding that the electron-transfer process involves many vibrational degrees of freedom, we choose the most significant vibration, ≈500 cm^{-1}, corresponding to the asymmetric ruthenium–ammonia breathing mode (in which Ru–N distances are increased about one ruthenium center and simultaneously decreased about the other), and use it in a one-dimensional application of our method. We obtain unitless equilibrium displacements[16] of the initial (−1.15), bridge (0.00), and final (+1.15) states from crystal structures of the bis(ruthenium pentaammine)–pyrazine 4+ (Ru^{II}–Ru^{II}) and 6+ (Ru^{III}–Ru^{III}) dimers.[17] These displacements are based on the difference of the average Ru–NH_3 distances between the Ru^{II} and Ru^{III} centers. (The bridge-localized state corresponds to $[(H_3N)_5Ru^{III}$–4,4′-bipy$^-$–$Ru^{III}(NH_3)_5]^{5+}$, in which both rutheniums are identical and the odd electron is localized on the bridge.) V_{IB} and V_{BF} for this system are assumed to be equal and are taken to be 4000 cm^{-1}.[18] As vibrational levels are very closely spaced on the bridge state relative to the separation between the initial and the bridge states (20 000 cm^{-1}), vibronic states are ignored on the bridge.

Figure 2 shows the integrand term of (16) for the one-dimensional, harmonic system described above, with degenerate donor and acceptor electronic states, at the $T = 0$ K limit.[19] At $t = 0$, the system is prepared by assigning the ground-state Gaussian (with zero momentum) on the initial surface. The final state Gaussian is assigned the same position and momentum, such that

$$X^i(0) = X^f(0)$$

$$P^i(0) = P^f(0) = 0 \qquad (28)$$

The Gaussians are then allowed to propagate classically, and the real part of $\langle f(t)|i(t)\rangle$ is calculated analytically.

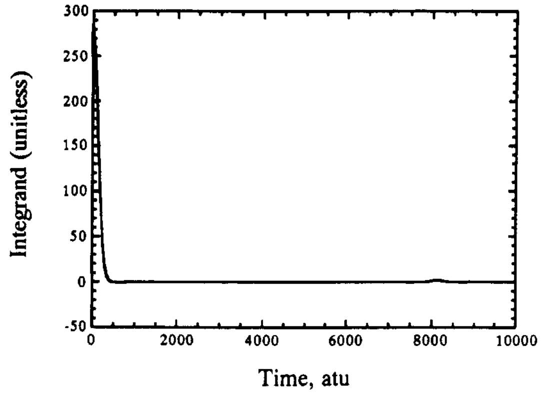

Figure 3. Integrand of eq 16, as described in the text. Relevant parameters for the three-mode case shown are as follows: $\hbar\omega_1 = 500$ cm^{-1}; $\hbar\omega_2 = 1$ cm^{-1}; $\hbar\omega_3 = 170$ cm^{-1}; $\Delta E_{bi} = 20\,000$ cm^{-1}; $\Delta E_{if} = 7000$ cm^{-1} (this is the crossing point shown in Figure 4b; note the absence of "phase" effects as seen in Figure 2); $V_{IB} = V_{BF} = V_{BI} = V_{FB} = 4000$ cm^{-1}. 1 atu (atomic time unit) = 2.4189×10^{-17} s. Note that addition of two solvent modes (with positions noted in the text) removes recurrence, and a rate can be defined. The rate for the system described is 1.68×10^{13} s^{-1}.

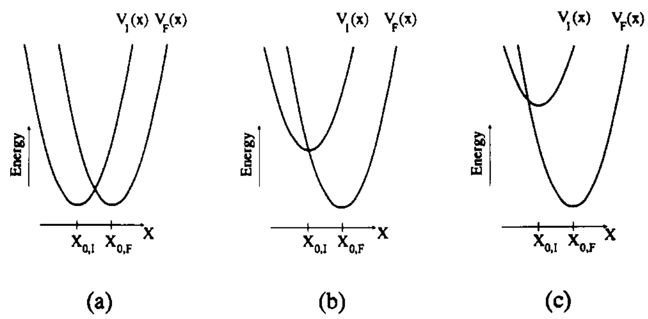

Figure 4. Harmonic, one-dimensional initial and final state potential surfaces. (a) Shows the system in the "normal" regime, (b) shows the crossing point, at which the rate is maximum, and (c) shows the "inverted" region.

Without damping, slow gating, dissociation, dephasing, or some such irreversible process, recurrence is inevitable, as is shown in Figure 2. In reality, one cannot assign a rate for a process exhibiting such undamped recurrences. The addition of more degrees of freedom, especially solvent modes (both high- and low-frequency modes with substantial displacements), increases the recurrence time until it becomes unreasonable to sample any but the initial decay shown in Figure 2. Figure 3 shows, for a similar time scale, a three-mode system, including the 500-cm^{-1} metal–ligand mode and two solvent modes. The two solvent modes, with frequencies 1 and 170 cm^{-1} and unitless changes in equilibrium displacement ± 58 and ± 6.2, respectively, were defined according to the method of Siders and Marcus,[20] in which they used a two-frequency quantum description of the interaction of water with an electron-transfer system. The addition of these two modes, as shown, removes the recurrence, and thus a rate can be defined. For the system shown, calculated at the crossing point to the inverted region (see Figure 4b and text, below), the calculated rate is 1.69×10^{13} s^{-1}.[21]

As the initial state surface is raised from being degenerate with the final state, the activation energy decreases, until the minimum on the initial state surface crosses the final state surface, at which point the activation energy is effectively zero (Figure 4). If the initial state surface is raised further, the activation energy begins to increase again, and the system enters the so-called inverted or abnormal region described by Marcus.[22] Inverted region effects for the single-mode system described above (integrated over the first decay only)[19] are shown in Figure 5. A number of discussions have appeared dealing with inverted region effects on rates, including those by Marcus,[22] Van Duyne and Fischer,[10] Wasielewski,[23] Closs and Miller,[24] and others.[25] We observe the expected increase and decrease in rate; further, we see nonquadratic behavior, as expected for a multimode energy gap.

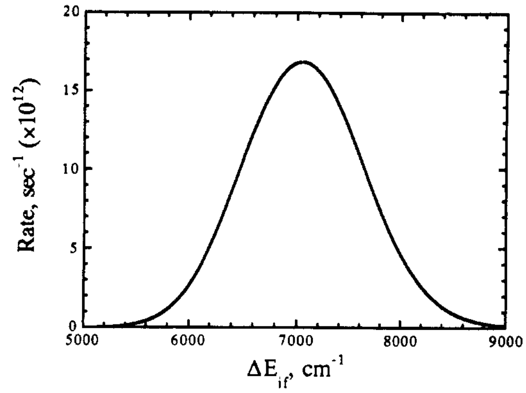

Figure 5. Variance of rate with ΔE_{if} for the three-mode system. The maximum occurs at the point where the minimum of the surface I crosses surface F and the system crosses into the inverted region (see text and Figure 4b). Other relevant parameters are as described in Figure 3.

As a means of comparison, we used the formula derived by Jortner[9,26] from the low-temperature limit of a polaron treatment to estimate the rate for the electron transfer at $T = 0$:

$$k_{T\to 0}^{(\max)} = \frac{|T_{DA}|^2}{\omega}\left(\frac{2\pi}{S}\right)^{1/2} \qquad (29)$$

where T_{DA} is the effective superexchange electronic-transfer matrix element, ω is the oscillator frequency, and $S = \lambda/\omega$ (λ is the reorganization energy). As this is a maximum rate for a one-mode (single-frequency) system, it is appropriate to compare it to our single-mode system at the crossing point to the inverted region (see Figure 4b). Using the parameters outlined above for the ruthenium dimer system and making use of eq 3 ($\beta_{DA} = \beta_{BA} = 4000$ cm^{-1}, $n = 1$) to give $T_{DA} = 800$ cm^{-1}, we obtained a rate of 2.2×10^{13} s^{-1} using Jortner's treatment. If we integrate over the first peak only in the single-mode system, we obtain a (maximum) rate of 1.69×10^{13} s^{-1}.

IV. Remarks

We have demonstrated a new electron-transfer model based on an explicitly time-dependent reformation of the superexchange-assisted nonadiabatic electron-transfer process. As such, it offers several important extensions to the degenerate, purely electronic superexchange model of McConnell. As it is time-dependent, it is able to explicitly include vibronics, and temperature can be included to allow for a distribution of initial and final vibronic states. It is not limited to degenerate donor and acceptor states. Both theoretical (normal mode analysis routines) and experimental (near- and at-resonance Raman)[14e,26] methods can be used to generate unitless equilibrium displacements and frequencies, which can be put directly into our model to generate electron-transfer rates for molecular systems.

The current formulation is semiclassical in two senses: first, the quantum vibrational states are represented as frozen Gaussian wavepackets; second, the Hamiltonian operators in the propagator (14) are replaced by the potentials in (19). Both of these semiclassical approximations can break down in specific cases (such as an excited state that is very anharmonic and weakly bound), but for most vibrations of stable molecules, we expect them to hold reasonably generally.

In the absence of damping or dephasing processes, we observe, for the $T = 0$, one-mode system, the expected recurrences (Figure 2). Inclusion of solvent modes increases the recurrence time to the point that calculation of a rate becomes possible (Figure 3), and an examination of rate vs ΔE_{if} indicates the expected inverted region effects (Figure 5).

Future discussions of this model will include both electronic and vibronic dephasing, temperature dependence, unfreezing of the Gaussian wavepackets, inclusion of vibronic levels on the bridge, removal of the Condon approximation, and anharmonicities.

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(16) To simplify the propagation of the wavepackets, we use unitless coordinates and momenta. Conversion from standard units is as follows: $\hat{X} = X[(m\omega)/\hbar]^{1/2}$ and $\hat{P} = P[1/(m\omega\hbar)]^{1/2}$, where $\hat{X}$ and $\hat{P}$ are unitless versions of the coordinate X and the momentum P, respectively, and m is the reduced mass appropriate for the vibration of frequency ω. The Hamiltonian is then $H = [(\hbar\omega)/2]\ (\hat{X}^2 + \hat{P}^2)$, and the equations of motion are $\dot{\hat{X}} = \omega\hat{P}$ and $\dot{\hat{P}} = -\omega\hat{X}$. The coordinate $\hat{X}$ for the Ru–NH_3 asymmetric breathing mode is given by the following: $\hat{X} = (1/10^{1/2})(\sum\hat{R}^{L}_{Ru-NH_3} - \sum\hat{R}^{R}_{Ru-NH_3})$, where $\sum\hat{R}^{x}_{Ru-NH_3}$ is the unitless (relative to $[(m\omega)/\hbar]^{1/2}$) distance between the x ruthenium (x = L and R for left and right, respectively) and each of five ammonias. Substitution of crystallographic Ru–N distances (see ref 17) yields $\hat{X}_0$, which is the coordinate of the minimum corresponding to electron localization on the left ($\hat{X}_0 > 0$) or right ($\hat{X}_0 < 0$) ruthenium. For this system, $|\hat{X}_0| = 1.15$.

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