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Theory for Electron-Transfer Reactions in a Three-Component System: the "Degenerate" Regime

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Abstract

Theory for nonadiabatic electron-transfer reactions at high temperature is presented for a three-component system (a donor, an acceptor, and a bridging intermediate). Only the "degenerate" regime of triple energy-level crossing is considered assuming three Marcus parabolas cross at the same point and the direct free energy gap vanishes. Because the ordinary second-order perturbation theory fails, the nonperturbative stochastic Liouville approach of Zusman is used in deriving analytical expressions for the superexchange and the sequential electron-transfer rate constants.

1. Introduction

Most of the theoretical treatments of electron-transfer reactions since the pioneering study of Marcus,¹ have primarily focused on a two-component system with a donor and an acceptor. More recently there are some attempts²⁻⁹ to extend the theory to a three-component system in which an intermediate bridges a donor with a distant acceptor. In the approach of Mukamel et al.,^{5,6} the Padé approximation was assumed to include higher order terms of perturbation series for the degenerate case where the direct free energy gap vanishes and the second-order perturbation theory fails. In another simpler approach by Tang et al.,⁷⁻⁹ the nonperturbative approach of Zusman¹⁰ is used. In the Zusman's stochastic Liouville approach, the solvent motion is assumed to be overdamped and follows the classical description of Smoluchowski diffusion. In the more recent work,⁹ an analytical rate expression for both superexchange and sequential processes was derived. The derived formula for both sequential and superexchange electron-transfer rate constants bridges between the nonadiabatic and solvent-controlled adiabatic regimes. However, only the "nondegenerate" regime was considered there, assuming the direct free energy gap is much larger than the electronic couplings. As an extension to the previous reports, we will focus in this work on the "degenerate" case where the direct vertical energy gap between the donor and the intermediate vanishes and the three Marcus parabolas cross at the same point.

2. The stochastic Liouville theory and

In this work we consider a three-component system involving a donor, an intermediate, and an acceptor, represented by $|1\rangle$, $|2\rangle$, and $|3\rangle$, respectively. Here we shall assume a large separation between the donor and the acceptor. Although there is no direct electronic

coupling between them, they can interfere with each other in a superexchange manner through the intermediate state with the coupling to the donor (V_{12}) and to the acceptor (V_{23}). As shown in Fig. 1, each component is assigned a Marcus free-energy parabola $U_k(x)$ in the reaction coordinate

$$\begin{aligned} U_1(x) &= \frac{\lambda}{2} x^2 \\ U_2(x) &= \frac{\lambda}{2} (x - x_2)^2 - E_{g(12)} \\ U_3(x) &= \frac{\lambda}{2} (x - x_3)^2 - E_{g(13)} , \end{aligned} \tag{1}$$

where λ is the force constant; $E_{g(12)}$ (or $E_{g(13)}$) is the free-energy gap defined as the energy separation between the bottoms of the second parabola (or the third) and the first one. The bottom of the parabola $U_k(x)$ is assumed at x_k , and x_1 is at the origin. The reorganization energy $E_{r(ij)}$ can be related to these displacements x_i and x_j by

$$E_{r(ij)} = \frac{\lambda}{2} (x_i - x_j)^2 . \tag{2}$$

For the "degenerate" case treated here where all three parabolas cross at $x = 0$, one has $E_{r(ij)} = E_{g(ij)}$. The Zusman's stochastic Liouville equation for a three-component system can be described in the following Laplace transform⁹ with the variable s

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &= i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + L_1 \hat{\rho}_{11} \\
s \hat{\rho}_{22} &= -i \frac{V_{12}}{\hbar} (\hat{\rho}_{12} - \hat{\rho}_{21}) + i \frac{V_{23}}{\hbar} (\hat{\rho}_{23} - \hat{\rho}_{32}) + L_2 \hat{\rho}_{22} \\
s \hat{\rho}_{33} &= -i \frac{V_{23}}{\hbar} (\hat{\rho}_{23} - \hat{\rho}_{32}) + L_3 \hat{\rho}_{33} \\
s \hat{\rho}_{12} &= -i \frac{U_{12}}{\hbar} \hat{\rho}_{12} + i \frac{V_{12}}{\hbar} (\hat{\rho}_{11} - \hat{\rho}_{22}) + i \frac{V_{23}}{\hbar} \hat{\rho}_{13} + L_{12} \hat{\rho}_{12} \\
s \hat{\rho}_{23} &= -i \frac{U_{23}}{\hbar} \hat{\rho}_{23} + i \frac{V_{23}}{\hbar} (\hat{\rho}_{22} - \hat{\rho}_{33}) - i \frac{V_{12}}{\hbar} \hat{\rho}_{13} + L_{23} \hat{\rho}_{23} \\
s \hat{\rho}_{13} &= -i \frac{U_{13}}{\hbar} \hat{\rho}_{13} - i \frac{V_{12}}{\hbar} \hat{\rho}_{23} + i \frac{V_{23}}{\hbar} \hat{\rho}_{12} + L_{13} \hat{\rho}_{13} \\
\hat{\rho}_{21} &= \hat{\rho}_{12}^* \\
\hat{\rho}_{32} &= \hat{\rho}_{23}^* \\
\hat{\rho}_{31} &= \hat{\rho}_{13}^* ,
\end{aligned} \tag{3}$$

The donor and the acceptor are assumed to be separated by a great distance and thus V_{13} vanishes. Here $U_{ij}(x)$ is defined as $U_i(x) - U_j(x)$. The Smoluchowski diffusion operator L_i is given by

$$L_i = \frac{1}{\tau_L} [1 + (x - x_p) \frac{\partial}{\partial x}] + \frac{k_B T}{\lambda \tau_L} \frac{\partial^2}{\partial x^2} \tag{4}$$

where τ_L known as the longitudinal relaxation time is a constant for a Debye solvent. The diffusion operator L_{ij} for the off-diagonal elements $\hat{\rho}_{12}$, $\hat{\rho}_{23}$, and $\hat{\rho}_{13}$ of the density matrix can be

neglected because of fast oscillation of these off-diagonal density-matrix elements.^{10,11} The subset of eq. (3) involving these off-diagonal elements can be given by

$$\begin{pmatrix} s + \frac{i}{\hbar} U_{12}(x) & 0 & -\frac{i}{\hbar} V_{23} \\ 0 & s + \frac{i}{\hbar} U_{23}(x) & \frac{i}{\hbar} V_{12} \\ -\frac{i}{\hbar} V_{23} & \frac{i}{\hbar} V_{12} & s + \frac{i}{\hbar} U_{13}(x) \end{pmatrix} \begin{pmatrix} \hat{\rho}_{12} \\ \hat{\rho}_{23} \\ \hat{\rho}_{13} \end{pmatrix} = \begin{pmatrix} \frac{i}{\hbar} V_{12}(\hat{\rho}_{11} - \hat{\rho}_{22}) \\ \frac{i}{\hbar} V_{23}(\hat{\rho}_{22} - \hat{\rho}_{33}) \\ 0 \end{pmatrix} \quad (5)$$

One can solve eq. (5) for $\hat{\rho}_{12}$ and $\hat{\rho}_{23}$ which are given by

$$\hat{\rho}_{12} = i \frac{V_{12}}{\hbar} \frac{(\hat{\rho}_{11} - \hat{\rho}_{22})[(s + i \frac{U_{13}}{\hbar})(s + i \frac{U_{23}}{\hbar}) + \frac{V_{12}^2}{\hbar^2}] + (\hat{\rho}_{22} - \hat{\rho}_{33}) \frac{V_{23}^2}{\hbar^2}}{D(s)}$$

$$\hat{\rho}_{23} = i \frac{V_{23}}{\hbar} \frac{(\hat{\rho}_{22} - \hat{\rho}_{33})[(s + i \frac{U_{13}}{\hbar})(s + i \frac{U_{12}}{\hbar}) + \frac{V_{23}^2}{\hbar^2}] + (\hat{\rho}_{11} - \hat{\rho}_{22}) \frac{V_{12}^2}{\hbar^2}}{D(s)} \quad (6)$$

$$D(s) = (s + i \frac{U_{12}}{\hbar})(s + i \frac{U_{23}}{\hbar})(s + i \frac{U_{13}}{\hbar}) + \frac{V_{12}^2}{\hbar^2}(s + i \frac{U_{12}}{\hbar}) + \frac{V_{23}^2}{\hbar^2}(s + i \frac{U_{23}}{\hbar}) .$$

From eq. (1) one can show $U_{ij}(x) = x/\xi_{ij}$ where $\xi_{ij} = 1/(2 \lambda E_{r(ij)})^{1/2}$. The roots for the determinant of the matrix in eq. (5), $D(s)$, can be solved by assuming a form of $-i\alpha_1 x/\hbar + \alpha_2$ for the root, and then determining α_1 and α_2 by their substitution in $D(s)$ while retaining the lowest order terms of x in the expansion. Three roots s_1 , s_2 and s_3 can be found accordingly and they are given by

$$s_1 = -i \frac{x}{\hbar \xi_0}$$

$$s_{2,3} = -i \frac{x}{\hbar \xi_s} \pm i \omega_s$$

$$\frac{1}{\xi_0} = \frac{V_{12}^2/\xi_{12} + V_{23}^2/\xi_{23}}{V_{12}^2 + V_{23}^2} \quad (7)$$

$$\frac{1}{\xi_s} = \frac{1}{2} \left(\frac{1}{\xi_{12}} + \frac{1}{\xi_{23}} + \frac{1}{\xi_{13}} - \frac{1}{\xi_0} \right)$$

$$\omega_s = \frac{1}{\hbar} \sqrt{V_{12}^2 + V_{23}^2}$$

One can expand $\hat{\rho}_{12}$ and $\hat{\rho}_{23}$ in eq. (6) about their poles which are the roots of $D(s)$ given in the above equation

$$\begin{aligned} \hat{\rho}_{12} = & i \frac{V_{12}}{\hbar} [(\hat{\rho}_{11} - \hat{\rho}_{22}) \frac{V_{12}^2}{\hbar^2 \omega_s^2} + (\hat{\rho}_{22} - \hat{\rho}_{33}) \frac{V_{23}^2}{\hbar^2 \omega_s^2}] \frac{1}{s + i \frac{x}{\hbar \xi_0}} \\ & + i \frac{V_{12}}{\hbar} (\hat{\rho}_{11} + \hat{\rho}_{33} - 2\hat{\rho}_{22}) \frac{V_{23}^2}{\hbar^2 \omega_s^2} \frac{1}{2} \left[\frac{1}{s + i \frac{x - x_s}{\hbar \xi_s}} + \frac{1}{s + i \frac{x + x_s}{\hbar \xi_s}} \right] \\ \hat{\rho}_{23} = & i \frac{V_{23}}{\hbar} [(\hat{\rho}_{11} - \hat{\rho}_{22}) \frac{V_{12}^2}{\hbar^2 \omega_s^2} + (\hat{\rho}_{22} - \hat{\rho}_{33}) \frac{V_{23}^2}{\hbar^2 \omega_s^2}] \frac{1}{s + i \frac{x}{\hbar \xi_0}} \\ & - i \frac{V_{23}}{\hbar} (\hat{\rho}_{11} + \hat{\rho}_{33} - 2\hat{\rho}_{22}) \frac{V_{12}^2}{\hbar^2 \omega_s^2} \frac{1}{2} \left[\frac{1}{s + i \frac{x - x_s}{\hbar \xi_s}} + \frac{1}{s + i \frac{x + x_s}{\hbar \xi_s}} \right] . \end{aligned} \quad (8)$$

where $x_s = \hbar\omega_s\xi_s$. The above equation indicates that although these parabolas $U_1(x)$, $U_2(x)$ and $U_3(x)$ cross at $x = 0$, however, because of their interactions, the actual effective crossing points are now at $x = 0$, $-x_s$ and x_s . By combining the above equation with eq. (3) and with the approximation of $2s/(\hbar^2s^2 + x^2/\xi_0^2)$ by a δ -function $2\pi\xi_0\delta(x)/\hbar$ and $2s/(\hbar^2s^2 + (x \pm x_s)^2/\xi_s^2)$ by $2\pi\xi_s\delta(x \pm x_s)/\hbar$, one can show

$$\begin{aligned}
s \hat{\rho}_{11} - \rho_{11}(0) &= -\frac{2\pi}{\hbar}\delta(x)\xi_0[W_{12}^2(\hat{\rho}_{11} - \hat{\rho}_{22}) + W_s^2(\hat{\rho}_{22} - \hat{\rho}_{33})] \\
&\quad - \frac{2\pi}{\hbar}[\delta(x-x_s) + \delta(x+x_s)]\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11} + \hat{\rho}_{33} - 2\hat{\rho}_{22}) + L_1\hat{\rho}_{11} \\
s \hat{\rho}_{22} &= \frac{2\pi}{\hbar}\delta(x)\xi_0[W_{12}^2(\hat{\rho}_{11} - \hat{\rho}_{22}) + W_s^2(\hat{\rho}_{22} - \hat{\rho}_{33})] \\
&\quad - \frac{2\pi}{\hbar}\delta(x)\xi_0[W_s^2(\hat{\rho}_{11} - \hat{\rho}_{22}) + W_{23}^2(\hat{\rho}_{22} - \hat{\rho}_{33})] \\
&\quad + \frac{2\pi}{\hbar}[\delta(x-x_s) + \delta(x+x_s)]\xi_s W_s^2(\hat{\rho}_{11} + \hat{\rho}_{33} - 2\hat{\rho}_{22}) + L_2\hat{\rho}_{22} \\
s \hat{\rho}_{33} &= \frac{2\pi}{\hbar}\delta(x)\xi_0[W_s^2(\hat{\rho}_{11} - \hat{\rho}_{22}) + W_{23}^2(\hat{\rho}_{22} - \hat{\rho}_{33})] \\
&\quad - \frac{2\pi}{\hbar}[\delta(x-x_s) + \delta(x+x_s)]\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11} + \hat{\rho}_{33} - 2\hat{\rho}_{22}) + L_3\hat{\rho}_{33} ,
\end{aligned} \tag{9}$$

where we have used the following notation for the effective coupling constants:

$$\begin{aligned}
W_{12} &= \frac{V_{12}^2}{\sqrt{V_{12}^2 + V_{23}^2}} \\
W_{23} &= \frac{V_{23}^2}{\sqrt{V_{12}^2 + V_{23}^2}} \\
W_s &= \frac{V_{12} V_{23}}{\sqrt{V_{12}^2 + V_{23}^2}} .
\end{aligned}
\tag{10}$$

In the "nondegenerate" case with a large direct free energy gap, the sequential and the superexchange reactions occur through a different pathway, i.e., the transition occurs at a different crossing point for a different mechanism.⁹ However, in this "degenerate" case, both the sequential and the superexchange transition can occur at all three effective crossing points 0, $-x_1$ and x_1 .

Eq. (9) can be solved by the Green's function method.^{9,11} The Laplace transform of the Green's function satisfies the following Smoluchowski equation

$$(s - L_k) \hat{G}_k(x, x') = \delta(x - x') , \quad k = 1, 2, 3 . \tag{11}$$

One can express eq. (9) in terms of the Green's function

$$\begin{aligned}
\hat{\rho}_{11}(\mathbf{x}) &= \frac{1}{s} \rho_{11,\text{eq}}(\mathbf{x}) - \frac{2\pi}{\hbar} \hat{G}_1(\mathbf{x}, 0) \xi_0 [W_{12}^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_s^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar} \hat{G}_1(\mathbf{x}, -\mathbf{x}_s) \frac{\xi_s}{2} W_s^2(\hat{\rho}_{11}(-\mathbf{x}_s) + \hat{\rho}_{33}(-\mathbf{x}_s) - 2\hat{\rho}_{22}(-\mathbf{x}_s)) \\
&\quad - \frac{2\pi}{\hbar} \hat{G}_1(\mathbf{x}, \mathbf{x}_s) \frac{\xi_s}{2} W_s^2(\hat{\rho}_{11}(\mathbf{x}_s) + \hat{\rho}_{33}(\mathbf{x}_s) - 2\hat{\rho}_{22}(\mathbf{x}_s)) \\
\hat{\rho}_{22}(\mathbf{x}) &= \frac{2\pi}{\hbar} \hat{G}_2(\mathbf{x}, 0) \xi_0 [W_{12}^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_s^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar} \hat{G}_2(\mathbf{x}, 0) \xi_0 [W_s^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_{23}^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad + \frac{2\pi}{\hbar} \hat{G}_2(\mathbf{x}, -\mathbf{x}_s) \xi_s W_s^2(\hat{\rho}_{11}(-\mathbf{x}_s) + \hat{\rho}_{33}(-\mathbf{x}_s) - 2\hat{\rho}_{22}(-\mathbf{x}_s)) \\
&\quad + \frac{2\pi}{\hbar} \hat{G}_2(\mathbf{x}, \mathbf{x}_s) \xi_s W_s^2(\hat{\rho}_{11}(\mathbf{x}_s) + \hat{\rho}_{33}(\mathbf{x}_s) - 2\hat{\rho}_{22}(\mathbf{x}_s)) \\
\hat{\rho}_{33}(\mathbf{x}) &= \frac{2\pi}{\hbar} \hat{G}_3(\mathbf{x}, 0) \xi_0 [W_s^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_{23}^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar} \hat{G}_3(\mathbf{x}, -\mathbf{x}_s) \frac{\xi_s}{2} W_s^2(\hat{\rho}_{11}(-\mathbf{x}_s) + \hat{\rho}_{33}(-\mathbf{x}_s) - 2\hat{\rho}_{22}(-\mathbf{x}_s)) \\
&\quad - \frac{2\pi}{\hbar} \hat{G}_3(\mathbf{x}, \mathbf{x}_s) \frac{\xi_s}{2} W_s^2(\hat{\rho}_{11}(\mathbf{x}_s) + \hat{\rho}_{33}(\mathbf{x}_s) - 2\hat{\rho}_{22}(\mathbf{x}_s)) .
\end{aligned} \tag{12}$$

We shall now define $\hat{\sigma}_1(s)$, $\hat{\sigma}_2(s)$ and $\hat{\sigma}_3(s)$ as the populations on each surface, i.e., $\int d\mathbf{x} \hat{\rho}_{kk}(\mathbf{x})$ (for $k=1, 2, 3$). By integrating $\hat{\rho}_{kk}(\mathbf{x})$ in eq. (12) over $\mathbf{x}$, one can show

$$\begin{aligned}
s\hat{\sigma}_1(s) - 1 &= -\frac{2\pi}{\hbar}\xi_0[W_{12}^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_s^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar}\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11}(-x_s) + \hat{\rho}_{33}(-x_s) - 2\hat{\rho}_{22}(-x_s)) \\
&\quad - \frac{2\pi}{\hbar}\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11}(x_s) + \hat{\rho}_{33}(x_s) - 2\hat{\rho}_{22}(x_s)) \\
s\hat{\sigma}_{22}(s) &= \frac{2\pi}{\hbar}\xi_0[W_{12}^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_s^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar}\xi_0[W_s^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_{23}^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad + \frac{2\pi}{\hbar}\xi_s W_s^2(\hat{\rho}_{11}(-x_s) + \hat{\rho}_{33}(-x_s) - 2\hat{\rho}_{22}(-x_s)) \\
&\quad + \frac{2\pi}{\hbar}\xi_s W_s^2(\hat{\rho}_{11}(x_s) + \hat{\rho}_{33}(x_s) - 2\hat{\rho}_{22}(x_s)) \\
s\hat{\sigma}_{33}(s) &= \frac{2\pi}{\hbar}\xi_0[W_s^2(\hat{\rho}_{11}(0) - \hat{\rho}_{22}(0)) + W_{23}^2(\hat{\rho}_{22}(0) - \hat{\rho}_{33}(0))] \\
&\quad - \frac{2\pi}{\hbar}\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11}(-x_s) + \hat{\rho}_{33}(-x_s) - 2\hat{\rho}_{22}(-x_s)) \\
&\quad - \frac{2\pi}{\hbar}\frac{\xi_s}{2}W_s^2(\hat{\rho}_{11}(x_s) + \hat{\rho}_{33}(x_s) - 2\hat{\rho}_{22}(x_s)) .
\end{aligned} \tag{13}$$

For nonadiabatic process, $G_k(x, x')$ can be approximated by $\rho_{kk,eq}(x)/s$.¹¹ With this approximation of $G_k(x, x')$ substituted in eq. (12), one can evaluate $\hat{\rho}_{kk}(x)$ at the crossing point x_c . It can be shown from eqs. (12) and (13) that $\hat{\rho}_{kk}(x_c) = \rho_{kk,eq}(x_c)\hat{\sigma}_k(s)$, where $x_c = 0, -x_s$ or x_s . One may transform eq. (13) into the following kinetic equation involving only $\hat{\sigma}_k(s)$ if one replaces $\hat{\rho}_{kk}(x_c)$ in eq. (13) with $\rho_{kk,eq}(x_c)\hat{\sigma}_k(s)$

$$\begin{aligned}
s\hat{\sigma}_1(s) - 1 &= -(k_{12}+k_{13})\hat{\sigma}_1(s) + k_{21}\hat{\sigma}_2(s) + k_{31}\hat{\sigma}_3(s) \\
s\hat{\sigma}_2(s) &= k_{12}\hat{\sigma}_1(s) - (k_{21}+k_{23})\hat{\sigma}_2(s) + k_{32}\hat{\sigma}_3(s) \\
s\hat{\sigma}_3(s) &= k_{13}\hat{\sigma}_1(s) + k_{23}\hat{\sigma}_2(s) - (k_{31}+k_{32})\hat{\sigma}_3(s) .
\end{aligned} \tag{14}$$

The sequential (k_{12} , k_{21} , k_{23} , k_{32}) and the superexchange (k_{13} , k_{31}) rate constants in the above equation are defined as

$$\begin{aligned}
k_{12} &= \frac{2\pi}{\hbar}(W_{12}^2 - W_S^2)\xi_0 \rho_{11,eq}(0) + \frac{2\pi}{\hbar}W_S^2\xi_s [\rho_{11,eq}(x_s) + \rho_{11,eq}(-x_s)] \\
k_{23} &= \frac{2\pi}{\hbar}(W_{23}^2 - W_S^2)\xi_0 \rho_{22,eq}(0) + \frac{2\pi}{\hbar}W_S^2\xi_s [\rho_{22,eq}(x_s) + \rho_{22,eq}(-x_s)] \\
k_{13} &= \frac{2\pi}{\hbar}W_S^2\xi_0 \rho_{11,eq}(0) - \frac{2\pi}{\hbar}W_S^2\frac{\xi_s}{2} [\rho_{11,eq}(x_s) + \rho_{11,eq}(-x_s)] \\
k_{21} &= \frac{2\pi}{\hbar}(W_{12}^2 - W_S^2)\xi_0 \rho_{22,eq}(0) + \frac{2\pi}{\hbar}W_S^2\xi_s [\rho_{22,eq}(x_s) + \rho_{22,eq}(-x_s)] \\
k_{32} &= \frac{2\pi}{\hbar}(W_{23}^2 - W_S^2)\xi_0 \rho_{33,eq}(0) + \frac{2\pi}{\hbar}W_S^2\xi_s [\rho_{33,eq}(x_s) + \rho_{33,eq}(-x_s)] \\
k_{31} &= \frac{2\pi}{\hbar}W_S^2\xi_0 \rho_{33,eq}(0) - \frac{2\pi}{\hbar}W_S^2\frac{\xi_s}{2} [\rho_{33,eq}(x_s) + \rho_{33,eq}(-x_s)] .
\end{aligned} \tag{15}$$

The Boltzmann distribution $\rho_{kk,eq}(x_c)$ at the crossing x_c on the k -th surface is given by $(\lambda/2\pi k_B T)^{1/2} \exp(-\lambda(x_c - x_e)^2/2k_B T)$. The kinetic equation we have derived here describes nonadiabatic electron transfer among the states $|1\rangle$, $|2\rangle$, and $|3\rangle$ with the sequential transition rate constants given by k_{12} , k_{23} and the superexchange transition rate constant given by

k_{13} . It can be shown that the forward and the backward transition rate constants, k_{ij} and k_{ji} , in eq. (15) satisfy the detailed balance principle. By substitution of ξ_0 , ξ_s , x_s and W_{ij} as defined earlier, these rate constants in eq. (15) can be expressed in terms of V_{12} , V_{23} and the reorganization energy $E_{r(ij)}$. In particular, one can show

$$k_{13} = \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi k_B T}} \frac{V_{12}^2 V_{23}^2}{V_{12}^2 + V_{23}^2} \left[\frac{V_{12}^2 + V_{23}^2}{V_{12}^2 \sqrt{E_{r(12)}} + V_{23}^2 \sqrt{E_{r(23)}}} \right. \\ \left. - \frac{2 \exp\left[- \frac{V_{12}^2 + V_{23}^2}{k_B T (\sqrt{E_{r(12)}} + \sqrt{E_{r(23)}} + \sqrt{E_{r(13)}} - (V_{12}^2 \sqrt{E_{r(12)}} + V_{23}^2 \sqrt{E_{r(23)}}) / (V_{12}^2 + V_{23}^2))} \right]}{\sqrt{E_{r(12)}} + \sqrt{E_{r(23)}} + \sqrt{E_{r(13)}} - (V_{12}^2 \sqrt{E_{r(12)}} + V_{23}^2 \sqrt{E_{r(23)}}) / (V_{12}^2 + V_{23}^2)} \right]. \quad (16)$$

The second term in the above equation can be neglected if the couplings V_{12} and V_{23} are so strong that the exponent is much larger than one. On the other hand, for weak coupling three effective crossing points are very close and $\rho_{kk,eq}(\pm x_s)$ in eq. (15) can be approximated by $\rho_{kk,eq}(0)$. In this limit one has the following simple relation

$$k_{12} = \frac{2\pi}{\hbar} [W_{12}^2 \xi_0 + W_s^2 (2\xi_s - \xi_0)] \rho_{11,eq}(0) \\ k_{23} = \frac{2\pi}{\hbar} [W_{23}^2 \xi_0 + W_s^2 (2\xi_s - \xi_0)] \rho_{22,eq}(0) \\ k_{13} = \frac{2\pi}{\hbar} W_s^2 (\xi_0 - \xi_s) \rho_{11,eq}(0). \quad (17)$$

3. Conclusions

We have applied the stochastic Liouville equation of Zusman to investigate the electron-transfer reactions for a three-component system involving a donor, a distant acceptor and a bridging intermediate. We have focused here the "degenerate" regime where the direct vertical energy gap vanishes and three Marcus parabolas cross at the same point. Although the ordinary second-order perturbation theory is invalid in this case, the non-perturbative approach of Zusman allows us to derive analytical expressions for the rate constants for both the sequential and the superexchange pathways. In this report, only the nonadiabatic limit is considered. Extension of this work to the more complicate adiabatic limit and the "quasi-degenerate" regime, where the direct free energy gap and the coupling strength are of the same order of magnitude, is now under investigation and will be reported elsewhere.

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Figure Captions

Fig. 1. Schematic representation of the Marcus free-energy profiles in the reaction coordinate for the donor (U_1), the intermediate (U_2), and the acceptor (U_3) in a three-component system. $E_{g(12)}$ and $E_{g(13)}$ are the corresponding free-energy gaps. In this "degenerate" regime, all three parabolas are assumed to cross at $x = 0$.

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