

The Influence of Energy-Level Fluctuation and Acceptor Local Diffusion on Electron Transport in Biological Systems

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Abstract. The present work is a modification of nonadiabatic electron transfer theory for fixed electron exchanging groups. We attempt to account for the role of the relative motion of exchanging groups on electron transfer processes. We also show how the fluctuation of the potential surfaces of the initial and final states of solute molecules (here, the donor-acceptor pair) affect electron transfer.

Key words: Electron transport, Langevin equation, Brownian motion of acceptor, solvent effects.

1. Introduction

Many authors are interested in electron transitions from donor to acceptor. A characteristic feature of these reactions is that they may be activated at high temperatures and fall to almost constant values at low temperatures. The distance between the sites of electron localization in biological processes can be large, which leads to small tunneling matrix elements in comparison with vibronic energies. This has led to an idea that a majority of biological electron transfers are nonadiabatic. In an electron transfer reaction, the initial and final states were assumed to be at fixed intermolecular distances [1–10]. Nevertheless, we feel that the introduction of the relative motion of the donor to acceptor is unavoidable in order to understand the transport of electrons in biological systems. The present work is a modification of nonadiabatic electron transfer theory for fixed electron exchanging groups. We will assume that the distance is not fixed and can change during the reaction. For the sake of simplicity, we consider that the donor is fixed and the acceptor is free to move. The motion of the acceptor we describe as a motion of Brownian particles in the presence of the potential. We tried to provide a quantitative treatment of the influence of the acceptor motion on the transition probability. We assumed that the fluctuating medium acts on the system and results in a fluctuation of the Hamiltonian of the system. We also assumed that the motion of the acceptor is confined and

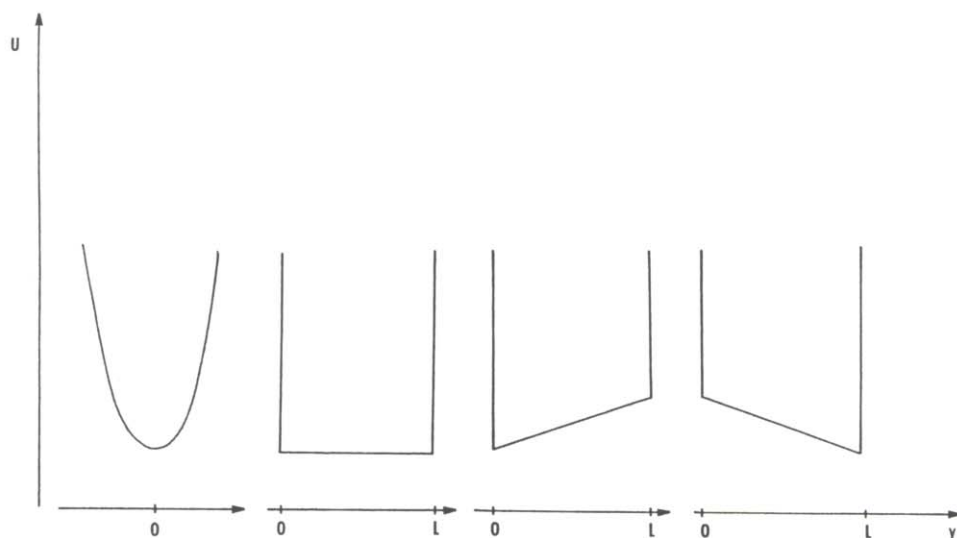


Fig. 1. Potential surfaces for acceptor motion. The first surface is a harmonic well, the second is a square-well potential, the third and fourth are a symmetric wells with opposite orientations. The donor is located at the point $-R_0 (R_0 > 0)$.

the potential in which the acceptor is moving is made up of surrounding molecules. We supposed that the acceptor is big enough to treat its motion classically and that the acceptor dynamics is governed by the Langevin equation of motion. The acceptor motion was treated in four different potentials (see Figure 1) and it was shown that the shape of the potential has a strong influence on the temperature dependence of the rate constant.

2. The Model of the System

We can write the Hamiltonian of the donor and acceptor molecules, which are surrounded by solvent molecules, as follows:

$$H(r, Q, R) = H_0(r, Q) + H_{\text{slv}}(R) + H_{\text{int}}(r, Q, R) + V(r, Q), \quad (2.1)$$

where H_0 , H_{slv} , H_{int} are, respectively, the Hamiltonians of the donor and acceptor molecules, the solvent, and the interaction between the solvent and the molecules of the donor and acceptor. 'V' is the Hamiltonian causing a transition of the electron from donor to acceptor. We will assume that the initial state is an eigenstate of H_0 and the transitions to other eigenstates of H_0 are induced by the term V . The initial and final states of a system are characterized in the Born–Openheimer approximation by the wavefunctions

$$\Psi_{\text{in}}(r, Q) = \Phi_i(r, Q) X_{\text{in}}(Q), \quad (2.2)$$

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$$\Psi_{\text{fm}}(r, Q) = \Phi_f(r, Q) X_{\text{fm}}(Q), \quad (2.3)$$

where Φ_i, Φ_f are the electronic wavefunctions of the donor and acceptor and $X_{\text{in}}, X_{\text{fm}}$ are the vibrational wavefunctions. The variables r, Q, R are the coordinates of the electron, the nucleus of the subsystem (donor and acceptor), and the coordinates of the position and orientation of the solvent molecules, respectively. We do not consider explicitly the role of vibrations in the solvent. This was explicitly done for a polar solvent in [11–15]. The distribution of the solvent molecules is not homogeneous and those motions are not in a steady state. Therefore, we will treat the solvent classically, with R changing with time t . $\Psi_{\text{in}}, \Psi_{\text{fm}}$ satisfy the Schrödinger equation

$$H_0 \Psi_{\text{in}} = E_{\text{in}} \Psi_{\text{in}}, \quad (2.4)$$

$$H_0 \Psi_{\text{fm}} = E_{\text{fm}} \Psi_{\text{fm}}. \quad (2.5)$$

Under the harmonic approximation for the molecular vibration around the adiabatic potential minimum, the total energy is

$$E_{l\nu} = E_l^0 + (\nu + \frac{1}{2})\hbar\omega, \quad (2.6)$$

where E_l^0, ω, ν are the total energy at potential minimum, the frequency, and the quantum number of a typical intramolecular vibrational mode in the l th electronic state. We will be working in the approximation of the one accepting mode. $X_{\text{in}}, X_{\text{fm}}$ are the harmonic wavefunctions of vibration

$$X_{\text{in}} = \left(\frac{\beta}{\pi^{1/2} 2^n n!} \right)^{1/2} H_n(\beta Q) \exp(-\beta^2 Q^2 / 2), \quad (2.7)$$

$$X_{\text{fm}} = \left(\frac{\beta}{\pi^{1/2} 2^m m!} \right)^{1/2} H_m(\beta(Q - \Delta Q)) \exp(-\beta^2(Q - \Delta Q)^2 / 2), \quad (2.8)$$

where ΔQ denotes the shift of the origin and H_r is Hermitean polynomial of order r , $\beta = (\mu\omega/\hbar)^{1/2}$, where μ is the effective mass of intramolecular vibrational mode. We consider that the system is at time $t = 0$ in state Ψ_{in} . We intend to find the transition probability that at time t , the system will be in state Ψ_{fm} . This transition probability can be expressed in the form

$$W_{\text{in}}^{\text{fm}} = |\langle \Psi_{\text{fm}} | U(t, 0) | \Psi_{\text{in}} \rangle|^2, \quad (2.9)$$

where $U(t, 0)$ is the evolution operator which can be displayed within the framework of first-order time-dependent theory

$$U(t, 0) = \exp \left(-\frac{i}{\hbar} \int_0^t \hat{H}(\tau) d\tau \right) \times \left(1 - \frac{i}{\hbar} \int_0^t \exp \left[\frac{i}{\hbar} \int_0^{\tau'} \hat{H}(\tau) d\tau \right] V(\tau') \exp \left[-\frac{i}{\hbar} \int_0^{\tau'} \hat{H}(\tau) d\tau \right] d\tau' \right), \quad (2.10)$$

where

$$\hat{H} = H_0 + H_{\text{slv}} + H_{\text{int}} . \quad (2.11)$$

Here we assume that V is dependent on time. We will compute the transition probability

$$W_{\text{in}}^{\text{fm}} = \frac{1}{\hbar^2} \left| \int_0^t \exp \left[\frac{i}{\hbar} \int_0^{t'} (\hat{E}_{\text{fm}}(\tau) - \hat{E}_{\text{in}}(\tau)) d\tau \right] \times \right. \\ \left. \times \langle \Psi_{\text{fm}} | V(t') | \Psi_{\text{in}} \rangle dt' \right|^2 , \quad (2.12)$$

where

$$\hat{E}_{\text{in}} = E_{\text{in}} + h_i(R(t)) , \quad (2.13)$$

$$\hat{E}_{\text{fm}} = E_{\text{fm}} + h_f(R(t)) . \quad (2.14)$$

Here

$$h_i(R) = \langle \Phi_i | H_{\text{slv}} + H_{\text{int}} | \Phi_i \rangle , \quad (2.15)$$

$$h_f(R) = \langle \Phi_f | H_{\text{slv}} + H_{\text{int}} | \Phi_f \rangle . \quad (2.16)$$

$H_{\text{slv}} + H_{\text{int}}$ plays the role of fluctuating the electronic state of the molecules of the subsystem. We consider that

$$\langle \Psi_{\text{fm}} | V(t') | \Psi_{\text{in}} \rangle \gg \langle \Psi_{\text{fm}} | H_{\text{slv}} + H_{\text{int}} | \Psi_{\text{in}} \rangle . \quad (2.17)$$

This means that we assume the transition is mainly caused by the Hamiltonian V and the influence of the electron-solvent interaction on the transition of electrons can be neglected. The effects of solvent on Ψ_{in} , Ψ_{fm} are omitted. Then we adopt only the diagonal terms of Hamiltonian \hat{H} . We consider that the diagonal matrix elements of V are small and can be neglected. We will assume that the Q dependence of H_{int} is very small and we will use

$$H_{\text{int}}(r, Q, R) = H_{\text{int}}(r, Q_0, R) ,$$

where Q_0 is the equilibrium coordinate of vibration. As was stated above, we will treat the solvent classically, with R changing with time t . Thus, we can rewrite $h_i(R)$, $h_f(R)$ as follows [16]:

$$h_i(t) = \varepsilon_i^0 + W_i(t) , \quad (2.18)$$

$$h_f(t) = \varepsilon_f^0 + W_f(t) , \quad (2.19)$$

where ε_i^0 and ε_f^0 are constant. $W_i(t)$ and $W_f(t)$ are the fluctuating fields given to the potential surfaces of the final and initial states of the solute molecules. $W_i(t)$ and $W_f(t)$ satisfy

$$\langle W_i(t) \rangle_{\text{slv}} = \langle W_f(t) \rangle_{\text{slv}} = 0, \quad (2.19a)$$

where $\langle \rangle_{\text{slv}}$ is the ensemble average over the solvent motion. Under these treatments, the transition probability reduces to

$$W_{\text{in}}^{\text{fm}} = \frac{1}{\hbar^2} \left| \int_0^t \exp \left(-\frac{i}{\hbar} \int_0^{t'} (\varepsilon_{\text{in,fm}} + \varepsilon(\tau)) d\tau \right) \times \right. \\ \left. \times V_{\text{fm,in}}(t') dt' \right|^2, \quad (2.20)$$

where

$$\varepsilon_{\text{in,fm}} = E_{\text{in}} + \varepsilon_i^0 - (E_{\text{fm}} + \varepsilon_f^0), \quad (2.21)$$

$$\varepsilon(t) = W_i(t) - W_f(t), \quad (2.22)$$

$$V_{\text{fm,in}}(t) = \langle \Psi_{\text{fm}} | V(t) | \Psi_{\text{in}} \rangle. \quad (2.22a)$$

We will consider only the nonadiabatic processes and since the electron transition rate is considerably slower than the rate of vibrational relaxation, the distribution of the vibrational energy level may be regarded as being in equilibrium. The transfer rate for reaction can be given by

$$R_{if} = \sum_{m,n} \rho_n W_{\text{in}}^{\text{fm}}, \quad (2.23)$$

where

$$\rho_n = \exp(-E_{\text{in}}/kT) / \sum_{m=0}^{\infty} \exp(-E_{\text{im}}/kT). \quad (2.24)$$

We rewrite the expression for the transfer rate in the following form

$$R_{if} = \frac{2}{\hbar^2} \sum_{m,n} \rho_n \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} \exp \left(-\frac{i}{\hbar} \int_{t_1}^{t_2} (\varepsilon(\tau)) d\tau \right) \times \\ \times V_{\text{fm,in}}(t_2) V_{\text{in,fm}}(t_1) \times \\ \times \exp \left(-\frac{i}{\hbar} [(n+1)\hbar\omega - (m+1)\hbar\omega + \varepsilon_0] (t_2 - t_1) \right) dt_1, \quad (2.25)$$

where

$$\varepsilon_0 = E_i^0 + \varepsilon_i^0 - E_f^0 - \varepsilon_f^0. \quad (2.26)$$

We will now carry out an ensemble average over the solvent motion. Assuming the Gauss processes for the fluctuations of the solvent, we have [17]

$$\begin{aligned} & \left\langle \exp \left(-\frac{i}{\hbar} \int_{t_1}^{t_2} (\varepsilon(\tau)) d\tau \right) \right\rangle_{\text{slv}} \\ &= \exp \left(-\frac{1}{2\hbar^2} \int_{t_1}^{t_2} \int_{t_1}^{t_2} \langle \varepsilon(t_3) \varepsilon(t_4) \rangle_{\text{slv}} dt_3 dt_4 \right) \end{aligned} \quad (2.27)$$

and we obtain the transition rate in the form

$$\begin{aligned} R_{if} &= \frac{2}{\hbar^2} \sum_{m,n} \rho_n \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} \xi(t_2 - t_1) \times \\ & \quad \times V_{\text{fm,in}}(t_2) V_{\text{in,fm}}(t_1) \times \\ & \quad \times \exp \left(-\frac{i}{\hbar} [(n+1)\hbar\omega - (m+1)\hbar\omega + \varepsilon_0] (t_2 - t_1) \right) dt_1, \end{aligned} \quad (2.28)$$

where

$$\xi(t_2 - t_1) = \exp \left(-\frac{1}{2\hbar^2} \int_{t_1}^{t_2} \int_{t_1}^{t_2} \langle \varepsilon(t_3) \varepsilon(t_4) \rangle_{\text{slv}} dt_3 dt_4 \right). \quad (2.29)$$

We have assumed that the process is stationary with a vanishing mean value

$$\langle \varepsilon(t) \rangle_{\text{slv}} = 0 \quad (2.30)$$

and the correlation function given by

$$\langle \varepsilon(t_3) \varepsilon(t_4) \rangle_{\text{slv}} = \langle \varepsilon^2 \rangle_{\text{slv}} \exp \left(-|t_3 - t_4|/\tau_e \right). \quad (2.30a)$$

Integrating with t_3 and t_4 in Equation (2.29), we can obtain

$$\begin{aligned} & \xi(t_2 - t_1) \\ &= \exp \left[-\Gamma_e (t_2 - t_1 - \tau_e (1 - \exp(-(t_2 - t_1)/\tau_e))) \right], \end{aligned} \quad (2.31)$$

where

$$\Gamma_e = \frac{1}{\hbar^2} \langle \varepsilon^2 \rangle_{\text{slv}} \tau_e. \quad (2.32)$$

3. Definition of Acceptor Motion

In this section we define the motion of the acceptor. While doing so, we make some assumptions. We suppose that we can use the Condon approximation according to which $V_{fm,in}$ can be factorized.

$$\langle \Psi_{fm}|V|\Psi_{in} \rangle = \langle \Phi_f|V|\Phi_i \rangle \langle X_{fm}|X_{in} \rangle, \quad (3.1)$$

$\langle \Phi_f|V|\Phi_i \rangle$ is taken at nuclear coordinates where its value is maximum [18]. We will assume that the electron is tunneling from donor to acceptor and the electron matrix elements have the form

$$\langle \Phi_f|V|\Phi_i \rangle = J \exp(-\lambda x), \quad (3.2)$$

where $x(t)$ is the distance between the donor and acceptor, which is time-dependent and λ is the damp coefficient. Now the transfer rate can be written as

$$\begin{aligned} R_{if} = & \frac{2J^2}{\hbar^2} \sum_{m,n} \rho_n F_{mn} \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} dt_1 \times \\ & \times \xi(t_2 - t_1) \exp[-\lambda(x(t_1) + x(t_2))] \times \\ & \times \exp\left(-\frac{i}{\hbar} [(n + 1/2)\hbar\omega - (m + 1/2)\hbar\omega + \varepsilon_0] (t_2 - t_1)\right), \end{aligned} \quad (3.3)$$

where $F_{mn} = |\langle X_{fm}|X_{in} \rangle|^2$. Now we use the relation [19]

$$\begin{aligned} Z(s, q) = & \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} s^n q^m F_{mn} \\ = & [(1 - s^2)(1 - q^2) + (s - q)^2]^{-1/2} \times \\ & \times \exp\left(-\frac{\Delta^2(1 - s)(1 - q)}{(1 + s)(1 - q) + (1 - s)(1 + q)}\right), \end{aligned} \quad (3.4)$$

where $\Delta^2 = m\omega(\Delta Q)^2/\hbar$ is dimensionless shift of the origin of the potential surfaces. For the transfer rate, we get

$$\begin{aligned} R_{if} = & \frac{2}{\hbar^2} J^2 \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} dt_1 \xi(t_2 - t_1) \exp[-\lambda(x(t_1) + x(t_2))] K(t_2 - t_1) \times \\ & \times \exp\left(-\frac{i}{\hbar} \varepsilon_0(t_2 - t_1)\right) dt_1, \end{aligned} \quad (3.5)$$

where

$$K(\tau) = \exp[-\Delta^2(\bar{n} + 1/2)] \exp\left(\frac{\Delta^2}{2} [(\bar{n} + 1)e^{i\omega\tau} + \bar{n}e^{-i\omega\tau}]\right), \quad (3.6)$$

with $\bar{n} = [\exp(\hbar\omega/k_B T) - 1]^{-1}$. We describe the motion of the acceptor classically and in one dimension. Without any loss of generality, we assume that the coordinate of the donor is $-R_0$ ($R_0 > 0$) and the coordinate of the acceptor is $y(t)$. The distance between the donor and acceptor is $x = |y(t) + R_0|$. We suppose that the variables $y(t)$ obey the Langevin equation

$$M_a \frac{d^2}{dt^2} y + \gamma \frac{d}{dt} y + \frac{d}{dy} U(y) = f(t). \quad (3.7)$$

This means that the motion of the acceptor can be described as a Brownian motion of particles in the presence of the potential. Here M_a is the mass of the acceptor, γ the friction coefficient, $U(y)$ is the potential, and $f(t)$ is the random force.

$$\langle f(t) f(t') \rangle = 2k_B T \gamma \delta(t - t'), \quad (3.8)$$

$$\langle f(t) \rangle = 0. \quad (3.9)$$

Now we will carry out an ensemble average over the acceptor motion and compute the transfer rate

$$R_{if} = \frac{2}{\hbar^2} J^2 \operatorname{Re} \int_0^t dt_2 \int_0^{t_2} \xi(t_2 - t_1) \langle \exp[-\lambda(x(t_1) + x(t_2))] \rangle_y \times \\ \times K(t_2 - t_1) \exp\left(-\frac{i}{\hbar} \varepsilon_0(t_2 - t_1)\right) dt_1 \quad (3.10)$$

$\langle \rangle_y$ is an ensemble average over the acceptor motion, $x(t) = |y(t) + R_0|$. We assume that this process is stationary, so

$$\langle \exp[-\lambda(x(t_1) + x(t_2))] \rangle_y = \eta(t_2 - t_1). \quad (3.11)$$

Supposing that $\Gamma_e t \gg 1$, we can write the rate constant in the form

$$k_{if} = \frac{2J^2}{\hbar^2} \operatorname{Re} \int_0^\infty \xi(\tau) \eta(\tau) K(\tau) \exp\left(-\frac{i}{\hbar} \varepsilon_0 \tau\right) d\tau. \quad (3.12)$$

Now we will derive the rate constant for several cases.

4. The Derivation of the Rate Constant

4.1. HARMONIC POTENTIAL

In this section, we suppose that the potential is harmonic, $U = \frac{1}{2} M_a \omega_0^2 y^2$ and $M_a \omega_0^2 R_0^2 \gg k_B T$. The second condition means that there is a very small probability to find the acceptor very close to the donor. In this limit, we have

$$\eta(\tau) = \exp\left(\lambda^2[a(\tau) + a(0)]\right) \exp(-2\lambda R_0), \quad (4.1)$$

where $a(\tau) = \langle y(0)y(\tau) \rangle$ is the correlation function. In the case of harmonic potential, we have [19]

$$a(\tau) = \frac{k_B T}{M_a(\omega_1 - \omega_2)} \left(\frac{e^{i\omega_1\tau}}{\omega_1} - \frac{e^{i\omega_2\tau}}{\omega_2} \right), \quad (4.2)$$

where

$$\omega_{1/2} = i \frac{\gamma}{2M_a} \pm (\omega_0^2 - \gamma^2/4M_a^2)^{1/2}. \quad (4.3)$$

In the limiting cases $\omega_0 \gg \gamma/2M_a$ and $\omega_0 \ll \gamma/2M_a$, we have

$$a(\tau) = \frac{k_B T}{M_a\omega_0^2} \exp\left(-\frac{\gamma}{2M_a}\tau\right) \cos \omega_0\tau, \quad (4.4)$$

$$a(\tau) = \frac{k_B T}{M_a\omega_0^2} \exp\left(-\frac{M_a\omega_0^2}{\gamma}\tau\right). \quad (4.5)$$

4.1.1. Overdamped Limit $\omega_0 \ll \gamma/2M_a$

We will compute the rate constant when the correlation function $a(\tau)$ is given by Equation (4.5)

$$\begin{aligned} k_{if} = & \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \operatorname{Re} \int_0^\infty \exp\left(\frac{\lambda^2 k_B T}{M_a\omega_0^2} \left[\exp\left(-\frac{M_a\omega_0^2}{\gamma}\tau\right) + 1 \right] - \right. \\ & \left. -\Gamma_e[\tau - \tau_e(1 - e^{-\tau/\tau_e})] \right) \exp\left(-\frac{i}{\hbar}\varepsilon_0\tau\right) \times \\ & \times \exp[-\Delta^2(\bar{n} + \frac{1}{2})] \exp\left(\frac{\Delta^2}{2} [(\bar{n} + 1)e^{i\omega\tau} + \bar{n}e^{-i\omega\tau}]\right) d\tau. \quad (4.6) \end{aligned}$$

Using the multinomial expansion of $K(\tau)$, see Appendix A, we can rewrite Equation (4.6) as

$$\begin{aligned} k_{if} = & \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{q/2} I_q\left(2S[\bar{n}(\bar{n} + 1)]^{1/2}\right) \times \\ & \times \exp\left(\frac{\lambda^2 k_B T}{M_a\omega_0^2} + \Gamma_e\tau_e - S(2\bar{n} + 1)\right) \times \end{aligned}$$

$$\begin{aligned} & \times \int_0^{\infty} \exp\left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp\left(-\frac{M_a \omega_0^2}{\gamma} \tau\right) - \Gamma_e [\tau + \tau_e e^{-\tau/\tau_e}]\right) \times \\ & \times \cos\left[\left(\frac{\varepsilon_0}{\hbar \omega} - q\right) \omega \tau\right] d\tau, \end{aligned} \quad (4.7)$$

where $S = \Delta^2/2$, I_q is the modified Bessel function. When $\Gamma_e \ll \omega$, we can write Equation (4.7) in the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{p/2} I_p\left(2S[\bar{n}(\bar{n} + 1)]^{1/2}\right) \times \\ & \times \exp\left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} + \Gamma_e \tau_e - S(2\bar{n} + 1)\right) \times \\ & \times \int_0^{\infty} \exp\left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp\left(-\frac{M_a \omega_0^2}{\gamma} \tau\right) - \Gamma_e [\tau + \tau_e e^{-\tau/\tau_e}]\right) d\tau, \end{aligned} \quad (4.8)$$

where $p = \varepsilon_0/\hbar\omega$. A useful expression for k_{if} may be derived in terms of the confluent hypergeometric function, see Appendix B

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{p/2} \times \\ & \times I_p\left(2S[\bar{n}(\bar{n} + 1)]^{1/2}\right) \exp\left(\frac{T}{T_c} - S(2\bar{n} + 1)\right) \times \\ & \times \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c}\right)^n \frac{1}{1 + n\xi} M(1, n\xi\alpha + \alpha + 1, \alpha), \end{aligned} \quad (4.9)$$

where

$$\xi = \frac{M_a \omega_0^2}{\gamma \Gamma_e}, \quad \alpha = \Gamma_e \tau_e, \quad \frac{1}{T_c} = \frac{\lambda^2 k_B}{M_a \omega_0^2}$$

and $M(a, b, x)$ is the confluent hypergeometric function. The numerical results are given in Figures 2 and 3. Now we consider several limiting cases. If parameter $\xi \ll 1$, we can rewrite the rate constant in the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{p/2} I_p\left(2S[\bar{n}(\bar{n} + 1)]^{1/2}\right) \times \\ & \times \exp\left(\frac{2T}{T_c} - S(2\bar{n} + 1)\right) M(1, \alpha + 1, \alpha). \end{aligned} \quad (4.10)$$

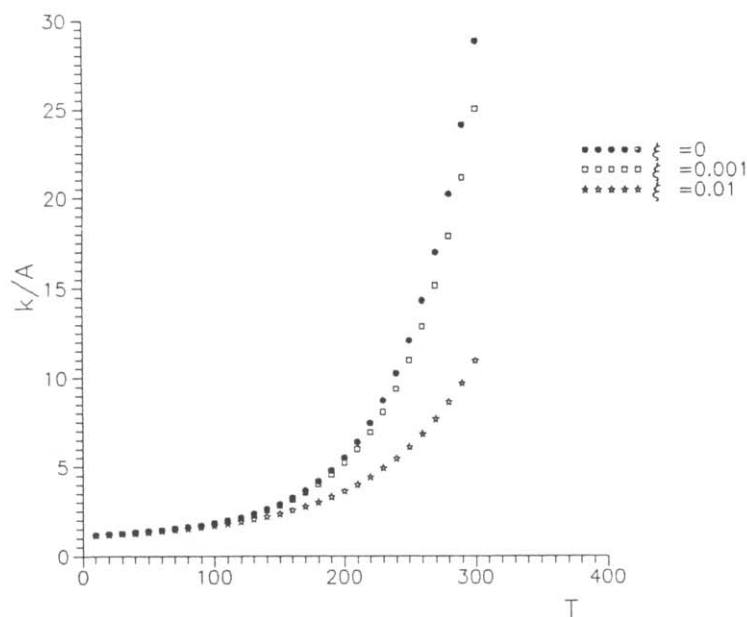


Fig. 2. Ratio k/A versus temperature T in K . k is the rate constant and $A = 2J^2 \exp(-2\lambda R_0)/\hbar^2 \Gamma_e$. The activationless regime parameters are $p = S = 20$. The vibrational mode frequency $\omega = 6 \times 10^{13} \text{ s}^{-1}$. The other parameters are $T_c = 700 \text{ K}$, $\alpha = 100$. Here $T_c = M_a \omega_0^2 / \lambda^2 k_B$, $\alpha = \Gamma_e \tau_e$, and $\xi = M_a \omega_0^2 / \gamma \Gamma_e$. Harmonic well.

In this case, the dynamics of the Brownian motion of the acceptor is slow and does not display in the rate constants. When $T_c \gg T$ we obtain the rate constant in the form

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) \times \\ \times M(1, \alpha + 1, \alpha). \quad (4.11)$$

Our result was reduced to the case where the distance between the donor and acceptor is fixed and the distribution of the acceptor is $\delta(y)$. The confluent hypergeometric function $M(1, \alpha + 1, \alpha)$ can be approximated with an asymptotic expression [20]

$$M(1, \alpha + 1, \alpha) \alpha \frac{1}{2} (2\pi\alpha)^{1/2}, \quad \alpha \gg 1, \quad (4.12)$$

$$M(1, \alpha + 1, \alpha) \alpha 1, \quad \alpha \ll 1. \quad (4.13)$$

In the limit of short correlation time of the solvent when parameter $\alpha \ll 1$, by using expression (4.13), we get

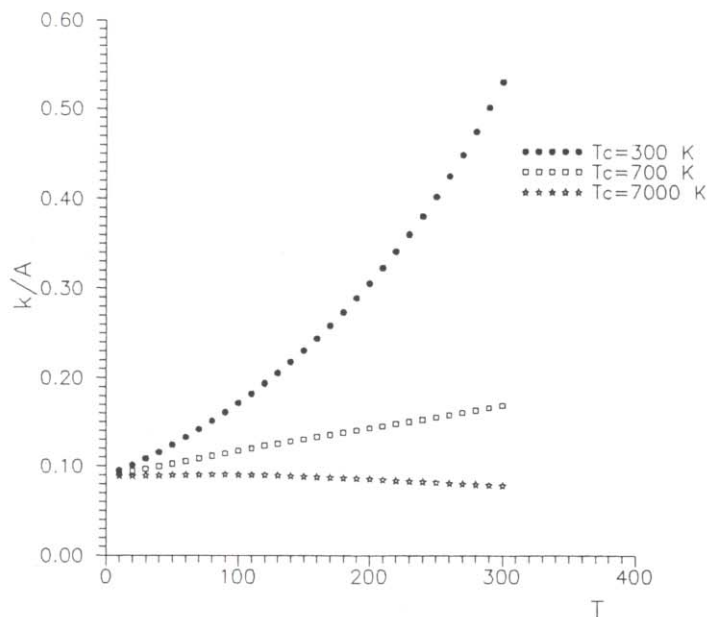


Fig. 3. Ratio k/A versus temperature T in K. The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{ s}^{-1}$, $\xi = 0$, $\alpha = 0$. Here $T_c = M_a \omega_0^2 / \lambda^2 k_B$, $\alpha = \Gamma_e \tau_e$, and $\xi = M_a \omega_0^2 / \gamma \Gamma_e$. Harmonic well.

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) . \quad (4.14)$$

At a long correlation time of the solvent when $\alpha \gg 1$, by using expression (4.12), we obtain

$$k_{if} = \frac{V^2}{\hbar} \left(\frac{2\pi}{\langle \varepsilon^2 \rangle_{\text{slv}}} \right)^{1/2} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \times \exp(-S(2\bar{n} + 1)) , \quad (4.15)$$

where $V^2 = J^2 \exp(-2\lambda R_0)$. We can see that at a long time approximation, the rate constant does not depend on the solvent correlation time τ_e .

4.1.2. Underdamped Limit $\gamma \ll 2M_a \omega_0$

In this case, the formula for the rate constant has the form

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \exp \left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} + \Gamma_e \tau_e - S(2\bar{n} + 1) \right) \times$$

$$\begin{aligned} & \times \operatorname{Re} \int_0^{\infty} \exp \left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp \left(-\frac{\gamma}{2M_a} \tau \right) \cos(\omega_0 \tau) - \Gamma_e [\tau + \tau_e e^{-\tau/\tau_e}] \right) \\ & \times \exp \left(-\frac{i}{\hbar} \varepsilon_0 \tau \right) \exp \left(\frac{\Delta^2}{2} [(\bar{n} + 1) e^{i\omega\tau} + \bar{n} e^{-i\omega\tau}] \right) d\tau. \end{aligned} \quad (4.16)$$

We can rewrite this equation, in a way similar to the case of high friction in the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \times \\ & \times \exp \left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} + \Gamma_e \tau_e - S(2\bar{n} + 1) \right) \times \\ & \times \int_0^{\infty} \exp \left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp \left(-\frac{\gamma}{2M_a} \tau \right) \cos(\omega_0 \tau) - \Gamma_e [\tau + \tau_e e^{-\tau/\tau_e}] \right) d\tau. \end{aligned} \quad (4.17)$$

We compute integral in Equation (4.17) in several limiting cases.

(4.1.2a). $\Gamma_e \gg \omega_0$

In this case, we can rewrite the integral to the form

$$I = \int_0^{\infty} \exp \left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp \left(-\frac{\gamma}{2M_a} \tau \right) - \Gamma_e (\tau + \tau_e e^{-\tau/\tau_e}) \right) d\tau$$

and the rate constants have the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp \left(\frac{T}{T_c} - S(2\bar{n} + 1) \right) \times \\ & \times \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c} \right)^n \frac{1}{1 + n\theta} M(1, n\theta\alpha + \alpha + 1, \alpha), \end{aligned} \quad (4.18)$$

where

$$\theta = \frac{\gamma}{2M_a \Gamma_e}, \quad \alpha = \Gamma_e \tau_e, \quad \frac{1}{T_c} = \frac{\lambda^2 k_B}{M_a \omega_0^2}.$$

In this limit, practically $\theta \Rightarrow 0$ and so the rate constants have the same form as in Equation (4.10).

(4.1.2b). $\omega_0 \gg \Gamma_e$

Using the multinomial expansion of

$$\exp\left(\frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp\left(-\frac{\gamma}{2M_a} \tau\right) \cos(\omega_0 \tau)\right)$$

in (4.17), we get for the rate constant

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} I_p\left(2S[\bar{n}(\bar{n}+1)]^{1/2}\right) \times \\ &\times \exp\left(\frac{T}{T_c} + \Gamma_e \tau_e - S(2\bar{n}+1)\right) \times \\ &\times \int_0^\infty \left[\sum_{n=1}^\infty 2 I_n\left(\frac{T}{T_c} \exp(-\tau/\tau_c)\right) \cos(n\omega_0 \tau) + I_0\left(\frac{T}{T_c} \exp(-\tau/\tau_c)\right) \right] \times \\ &\times \exp\left(-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]\right) d\tau, \end{aligned} \quad (4.19)$$

where $\tau_c = 2M_a/\gamma$.

Because $\omega_0 \gg \Gamma_e$, we adopt only the element with I_0 and for the rate constant, we have

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} I_p\left(2S[\bar{n}(\bar{n}+1)]^{1/2}\right) \times \\ &\times \exp\left(\frac{T}{T_c} + \Gamma_e \tau_e - S(2\bar{n}+1)\right) \times \\ &\times \int_0^\infty I_0\left(\frac{T}{T_c} \exp(-\tau/\tau_c)\right) \exp\left(-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]\right) d\tau. \end{aligned} \quad (4.20)$$

Now we use

$$I_0(z) = \sum_{n=0}^\infty \frac{(z/2)^{2n}}{(n!)^2}$$

and we can express the rate constant in the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{p/2} I_p\left(2S[\bar{n}(\bar{n}+1)]^{1/2}\right) \times \\ &\times \exp\left(\frac{T}{T_c} - S(2\bar{n}+1)\right) \sum_{n=0}^\infty \frac{1}{(n!)^2} \left(\frac{T^2}{4T_c^2}\right)^n \times \end{aligned}$$

$$\times \frac{1}{1+n\beta_a} M(1, n\alpha\beta_a + \alpha + 1, \alpha), \quad (4.21)$$

where

$$\beta_a = \frac{\gamma}{M_a \Gamma_e}, \quad \alpha = \Gamma_e \tau_e.$$

For $T_c \gg T$, we get the result (4.11). The condition $\gamma \ll 2M_a\omega_0$ is not fulfilled in biological objects [19].

4.2. SQUARE-WELL POTENTIAL

In this section, we will consider the simple one-dimensional problem of an acceptor moving under the influence of a square-well potential of an infinite well. The probability density $P(y, t)$ associated with Langevin equation (3.7) satisfies the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial y^2} + \frac{D}{k_B T} \frac{\partial}{\partial y} \left(P \frac{\partial U}{\partial y} \right), \quad (4.23)$$

here $D = k_B T / \gamma$ is a diffusion coefficient. In our case, $U(y)$ have the form

$$U = 0, \quad 0 < y < L,$$

$$U = \infty, \quad y \leq 0 \text{ or } y \geq L. \quad (4.24)$$

Equation (4.23) will be solved with the boundary conditions

$$\frac{\partial}{\partial y} P + \frac{1}{k_B T} P \frac{\partial U}{\partial y} \Big|_{0,L} = 0. \quad (4.25)$$

This corresponds to the reflection condition on the boundaries. We will compute the joint probability and so we assume that the particle is initially at y_0 .

$$P(y, t = t_0) = \delta(y - y_0), \quad 0 < y_0 < L. \quad (4.26)$$

$P(y, t)$ is normalized

$$\int_0^L P(y, t) dy = 1, \quad (4.27)$$

It is a straightforward calculation to carry out the joint probability in this case. We have

$$\begin{aligned} & P(y, t | y_0, t_0) \\ &= \frac{1}{L} \left(\sum_{n=1}^{\infty} 2 \cos\left(\frac{\pi n}{L} y\right) \cos\left(\frac{\pi n}{L} y_0\right) \exp\left[-\frac{\pi^2 n^2 D}{L^2} (t - t_0)\right] + 1 \right). \end{aligned} \quad (4.28)$$

Now we must compute an ensemble average over the acceptor motion. In this case, we have $x(t) = y(t) + R_0$ and

$$\begin{aligned} & \langle \exp[-\lambda(x(t_1) + x(t_2))] \rangle_y \\ &= \exp(-2\lambda R_0) \langle \exp[-\lambda(y(t_1) + y(t_2))] \rangle_y, \end{aligned} \quad (4.29)$$

where

$$\begin{aligned} & \langle \exp[-\lambda(y(t_1) + y(t_2))] \rangle_y \\ &= \int_0^L \int_0^L \int_0^L \exp(-\lambda(y_1 + y_2)) \times \\ & \quad \times P(y_2, t_2 | y_1, t_1) P(y_1, t_1 | y_0, t_0) P(y_0) dy_0 dy_1 dy_2. \end{aligned} \quad (4.30)$$

Here, $P(y_0)$ is the initial distribution of the acceptor. For the ensemble average, we obtain

$$\begin{aligned} & \langle \exp[-\lambda(y(t_1) + y(t_2))] \rangle_y \\ &= \left(\frac{1 - \exp(-\lambda L)}{\lambda L} \right)^2 + 2(\lambda L)^2 \times \\ & \quad \times \sum_{n=1}^{\infty} A_n \exp\left(-\pi^2 n^2 \frac{D}{L^2} (t_2 - t_1)\right), \end{aligned} \quad (4.31)$$

where

$$A_n = \left(\frac{1 - (-1)^n \exp(-\lambda L)}{(\lambda L)^2 + \pi^2 n^2} \right)^2.$$

Substituting (4.31) into Equation (3.10) and using the same procedure as in the case of the harmonic well, the rate constant k_{if} is obtained.

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(\Gamma_e \tau_e - S(2\bar{n} + 1)) \times \\ & \quad \times \left[\left(\frac{1 - e^{-\lambda L}}{\lambda L} \right)^2 \int_0^{\infty} \exp(-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]) d\tau + \right. \\ & \quad \left. + 2(\lambda L)^2 \sum_{n=1}^{\infty} A_n \int_0^{\infty} \exp\left(-\pi^2 n^2 \frac{D}{L^2} \tau - \Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]\right) d\tau \right]. \end{aligned} \quad (4.32)$$

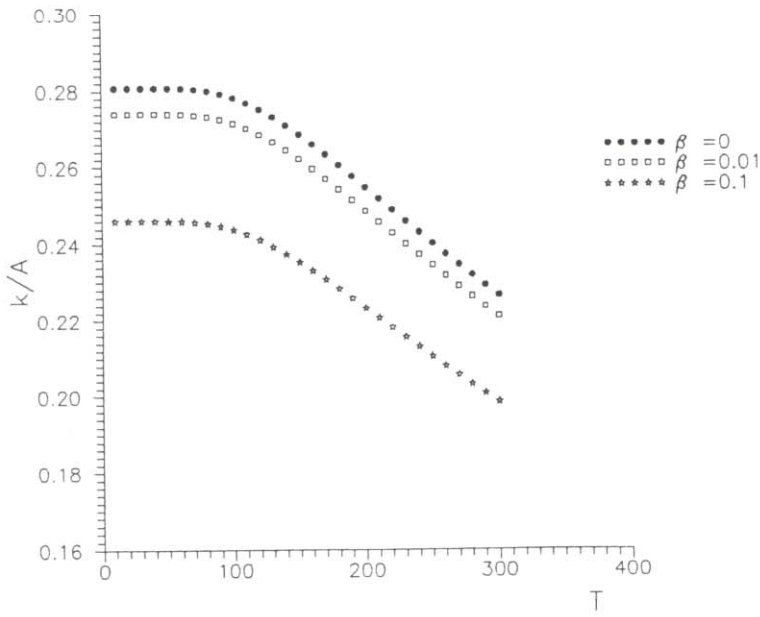


Fig. 4. Ratio k/A versus temperature T . The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{ s}^{-1}$, $\alpha = 100$, $\lambda L = 2$. Here $\alpha = \Gamma_e \tau_e$, $\beta = \pi^2 D / L^2 \Gamma_e$. Square well.

Computing the integral in Equation (4.32), we get the rate constant in the form

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) \times \\ \times \left[A_0 M(1, \alpha + 1, \alpha) + 2(\lambda L)^2 \sum_{n=1}^{\infty} \frac{A_n}{1 + n^2 \beta} M(1, n^2 \beta \alpha + \alpha + 1, \alpha) \right], \quad (4.33)$$

where

$$\beta = \frac{\pi^2 D}{L^2 \Gamma_e} \quad \text{and} \quad A_0 = \left(\frac{1 - e^{-\lambda L}}{\lambda L} \right)^2.$$

The numerical results are given in Figure 4. If $\beta \Rightarrow 0$, for the rate constant we obtain

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(-2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) \times \\ \times \left[A_0 + 2(\lambda L)^2 \sum_{n=1}^{\infty} A_n \right] M(1, \alpha + 1, \alpha). \quad (4.34)$$

This is the case, when the dynamics of the Brownian motion can be neglected and the influence on the temperature dependence of the rate constant depends only on the stationary distribution of the acceptor. For $\lambda L \Rightarrow 0$, we obtain the same result as in (4.11). In this limit, we obtain the expression for the nonadiabatic electron transfer when the exchanging groups are fixed.

4.3. ASYMMETRIC WELL

In this section we will consider that the acceptor is moving in an asymmetric well. We have two possibilities for the orientation of the well. One possibility is that it is deeper on the side of the donor. The second possibility is the opposite. We will consider the well in the simplest form. We want to add the effects which are due to the change of the mean distance between the donor and acceptor, when the temperature is changed. These changes are not revealed in the symmetric well.

4.3.1. Asymmetric Well with the Minimum in Zero

We will assume that the well has the form which is illustrated in Figure 1, case three.

$$U = \infty, \quad L \leq y, \quad \text{or} \quad y \leq 0,$$

$$U = -\varepsilon + \frac{\varepsilon}{L} y, \quad 0 < y < L. \quad (4.35)$$

We will compute the joint probability which obeys Equation (4.23) with the same initial and boundary conditions as in the case of the square-well potential. P is also normalized to 1. In this case, the joint probability has the form

$$\begin{aligned} P(y, t | y_0, t_0) &= \frac{1}{L} \left(\sum_{n=1}^{\infty} \frac{2\pi^2 n^2}{\lambda_n} \left(\cos \frac{\pi n}{L} y - \frac{\sigma}{2\pi n} \sin \frac{\pi n}{L} y \right) \times \right. \\ &\quad \times \left(\cos \frac{\pi n}{L} y_0 - \frac{\sigma}{2\pi n} \sin \frac{\pi n}{L} y_0 \right) \times \\ &\quad \times \exp \left(- \left[\frac{\sigma}{2L} (y - y_0) + \lambda_n \frac{D}{L^2} (t - t_0) \right] \right) + \\ &\quad \left. + a_0 \exp(-\sigma y/L) \right), \quad (4.36) \end{aligned}$$

where

$$\sigma = \varepsilon/k_B T, \quad \lambda_n = \pi^2 n^2 + (\sigma/2)^2, \quad a_0 = \sigma/(1 - \exp(-\sigma))$$

and we compute the ensemble average over the acceptor motion in a similar way as for the square well potential. We obtain

$$\begin{aligned} & \langle \exp[-\lambda(x(t_1) + x(t_2))] \rangle_y \\ &= \exp(-2\lambda R_0) \times \left[A_0 + 2a_0(\lambda L)^2 \sum_{n=1}^{\infty} A_n \exp\left(-\lambda_n \frac{D}{L^2} (t_2 - t_1)\right) \right]. \end{aligned} \quad (4.37)$$

Here

$$A_0 = \left[\frac{\sigma}{\sigma + \lambda L} \frac{1 - e^{-(\lambda L + \sigma)}}{1 - e^{-\sigma}} \right]^2,$$

$$A_n = \left[\frac{1 - (-1)^n e^{-(\lambda L + \sigma/2)}}{(\sigma/2 + \lambda L)^2 + \pi^2 n^2} \right]^2 \frac{\pi^2 n^2}{\lambda_n}.$$

The rate constant can be expressed as

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(\Gamma_e \tau_e - S(2\bar{n} + 1)) \times \\ & \times \left[A_0 \int_0^{\infty} \exp(-\Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]) d\tau + \right. \\ & \left. + 2a_0(\lambda L)^2 \sum_{n=1}^{\infty} A_n \int_0^{\infty} \exp\left(-\lambda_n \frac{D}{L^2} \tau - \Gamma_e[\tau + \tau_e e^{-\tau/\tau_e}]\right) d\tau \right]. \end{aligned} \quad (4.38)$$

After computing the integral in (4.38), we obtain the rate constant in the form

$$\begin{aligned} k_{if} &= \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) \times \\ & \times \left[A_0 M(1, \alpha + 1, \alpha) + 2a_0(\lambda L)^2 \sum_{n=1}^{\infty} \frac{A_n}{1 + \beta_n} M(1, \beta_n \alpha + \alpha + 1, \alpha) \right], \end{aligned} \quad (4.39)$$

where

$$\beta_n = \frac{\lambda_n D}{L^2 \Gamma_e}.$$

The numerical results are given in Figures 5 and 6. We used the designations $\zeta = D/L^2 \Gamma_e$ and $T_a = \varepsilon/K_B$.

If the diffusion coefficient $D \Rightarrow 0$,

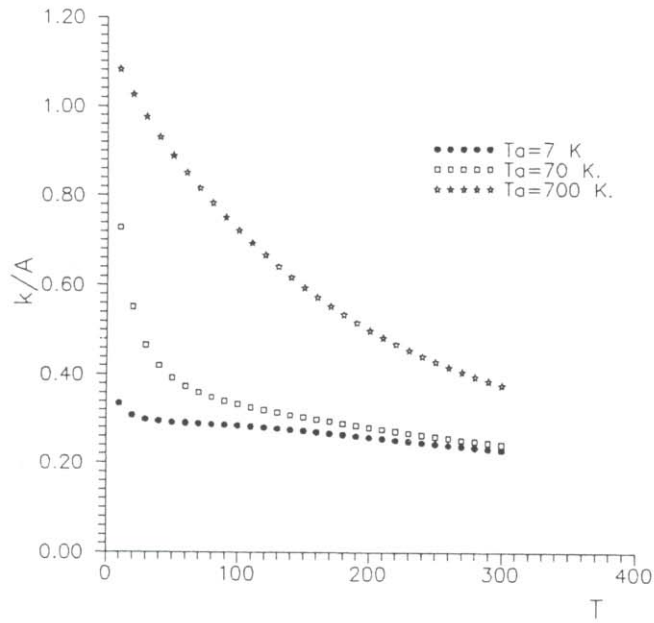


Fig. 5. Ratio k/A versus temperature T . The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{s}^{-1}$, $\alpha = 100$, $\lambda L = 2$, $\zeta = 0$. Here $\alpha = \Gamma_e \tau_e$, $\zeta = D/L^2 \Gamma_e$, and $T_a = \varepsilon/k_B$. Asymmetric well with the minimum at zero.

$$k_{if} = \frac{2J^2 e^{-2\lambda R_0}}{\hbar^2 \Gamma_e} \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{p/2} I_p \left(2S[\bar{n}(\bar{n} + 1)]^{1/2} \right) \exp(-S(2\bar{n} + 1)) \times \\ \times \left[A_0 + 2(\lambda L)^2 \sum_{n=1}^{\infty} A_n \right] M(1, \alpha + 1, \alpha). \quad (4.40)$$

For $\lambda L \Rightarrow 0$, we obtain the same expression for the rate constant as in (4.11).

4.3.2. Asymmetric Well with the Minimum at the Point L

In this case, the well has the form

$$U = \infty, \quad L \leq y \text{ or } y \leq 0,$$

$$U = -\frac{\varepsilon}{L} y, \quad 0 < y < L.$$

Here we get the same formulae for the rate constant as in the last case. Only in this case a_0, A_n are different

$$A_0 = \left[\frac{\sigma}{\sigma - \lambda L} \frac{e^{\sigma - \lambda L} - 1}{e^{\sigma} - 1} \right]^2,$$

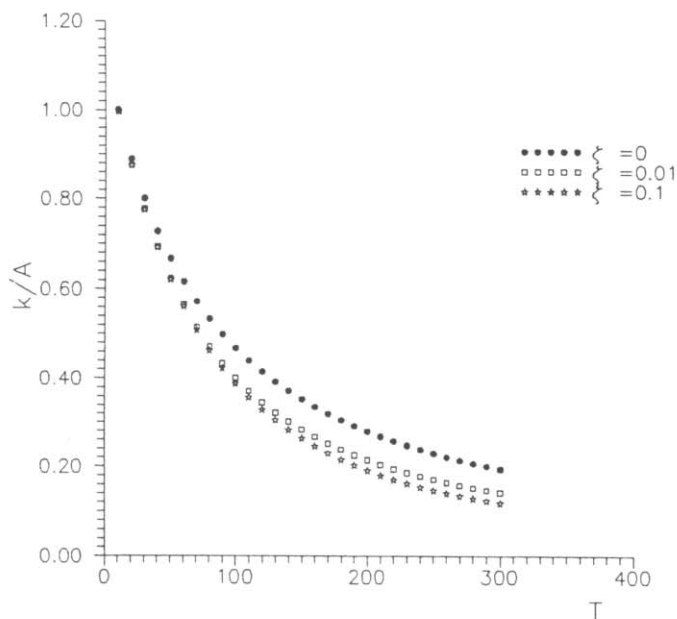


Fig. 6. Ratio k/A versus temperature T . The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{ s}^{-1}$, $\alpha = 100$, $T_a = 700 \text{ K}$, $\lambda L = 5$. Here $\alpha = \Gamma_e \tau_e$, $\zeta = D/L^2 \Gamma_e$, and $T_a = \varepsilon/k_B$. Asymmetric well with the minimum in zero.

$$A_n = \left[\frac{1 - (-1)^n e^{-(\lambda L - \sigma/2)}}{(\sigma/2 - \lambda L)^2 + \pi^2 n^2} \right]^2 \frac{\pi^2 n^2}{\lambda_n}, \quad n = 1, 2, \dots,$$

$$a_0 = \sigma / (\exp(\sigma) - 1).$$

The numerical results are given in Figures 7 and 8. On the plots, the designations $T_a = \varepsilon/k_B$ and $\zeta = D/L^2 \Gamma_e$ were used.

5. Discussion

The main goal of this theory was to describe the influence of a Brownian motion of the acceptor on the temperature dependence of the rate constant. The results are presented as plots of k/A versus temperature. Here k is the rate constant and $A = 2J^2 \exp(-2\lambda R_0) / \hbar^2 \Gamma_e$. The rate constants were obtained and analyzed for four potentials $U(y)$ and expressed as products of an electronic coupling term, a nuclear Frank–Condon factor, and a diffusion factor. Numerical results are done in the activationless regime, where the influence of the electron-vibronical coupling on the temperature-dependence of the rate constant is minimal and the contribution of the Brownian motion of the acceptor towards the temperature dependence of the rate constant is more evident. The calculations of an ensemble average of the

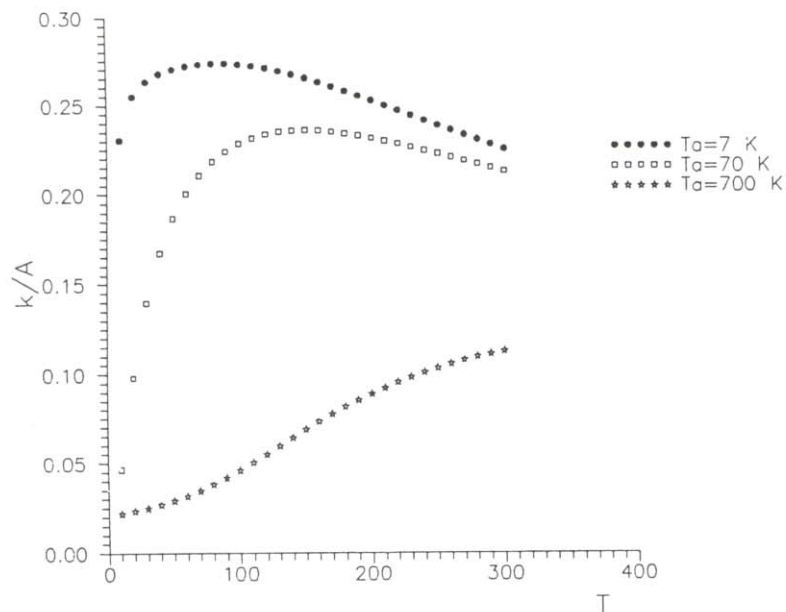


Fig. 7. Ratio k/A versus temperature T . The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{ s}^{-1}$, $\alpha = 100$, $\lambda L = 2$, $\zeta = 0$. Here $\alpha = \Gamma_e \tau_e$, $\zeta = D/L^2 \Gamma_e$, and $T_a = \varepsilon/k_B$. Asymmetric well with the minimum at the point L .

acceptor motion were made for the case that the initial distribution $P(y_0)$ of the acceptor is given by a stationary one within the potential U . When the potential U depends on the localization of the electron, we can prepare an initial distribution different from the stationary one [21,22] and the results will be different. If the stationary distribution depends on the temperature, our approximation at low temperatures is not correct because the diffusion coefficient D approaches zero and we cannot reach the stationary distribution at these low temperatures. This means that the contribution of the acceptor's local diffusion to the rate constant at a low temperature T_0 is the same for all temperatures $T \leq T_0$.

5.1. HARMONIC WELL

Although the Brownian motion of an acceptor in biological objects has an overdamped character, we believe that the underdamped limit is of considerable physical interest. The different features of the dependence of the rate constant on the friction coefficient γ encountered in these two limits can be summarized as follows: in an overdamped limit with increasing γ , the rate constant increases, while in the underdamped limit with increasing γ , the rate constant decreases. Another parameter which acts on the rate constant is $k_B T / M_a \omega_0^2$ – the mean-square displacement of the acceptor from the equilibrium position at temperature T . The rate constant in-

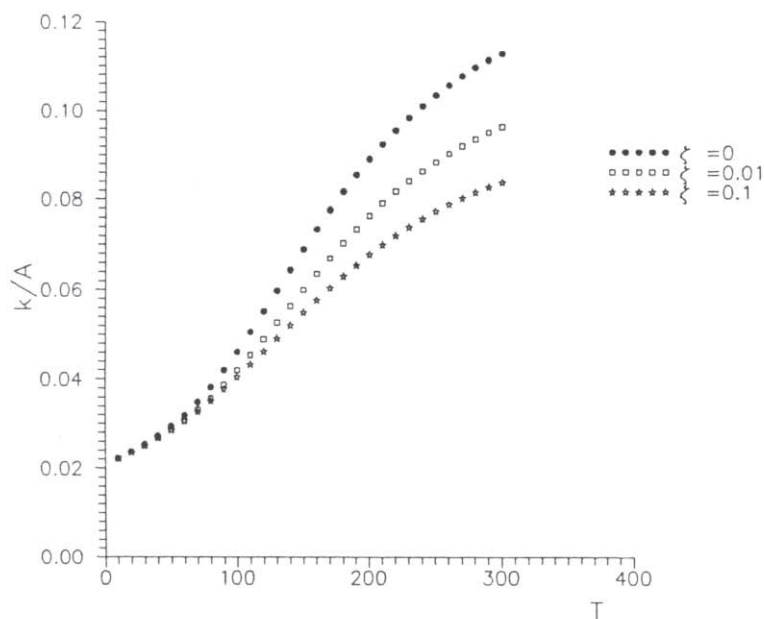


Fig. 8. Ratio k/A versus temperature T . The following parameters are used: $p = S = 20$, $\omega = 6 \times 10^{13} \text{s}^{-1}$, $\alpha = 100$, $\lambda L = 2$, $T_a = 700$. Here $\alpha = \Gamma_e \tau_e$, $\zeta = D/L^2 \Gamma_e$, and $T_a = \varepsilon/k_B$. Asymmetric well with the minimum at the point L .

creases with this parameter. If the condition $\lambda^2 k_B T / M_a \omega_0^2 \ll 1$ is fulfilled, we get the expression for the nonadiabatic electron transfer when the exchanging groups are fixed.

5.2. SQUARE AND ASYMMETRIC WELLS

In these cases, we have done a computation of the rate constant for an overdamped limit of the Brownian motion of an acceptor. In this limit with increasing diffusion coefficient D , the rate constant decreases. When the acceptor is moving in the square well, the temperature-dependence of the rate constant is not strongly influenced by this motion because the distribution of the acceptor is temperature-independent. The motion of the acceptor is mainly displayed in the rate constant by the friction coefficient γ . The distribution of an acceptor depends on the temperature when it is moving in an asymmetric well. For an asymmetric well deeper at the point L , this distribution is more appropriate for the transport of an electron at higher temperatures in spite of the case when the acceptor is moving in an asymmetric well deeper in zero and so, in the first case, the rate constant increases with the temperature and decreases in the second one.

In the present work, it was shown that the molecular dynamic of exchanging groups acted on the electron transport. The molecular dynamics is governed by the

surroundings of the exchanging groups and so the structure of the protein can also act on the electron transport.

6. Conclusions

The theory developed in this article is a generalization of the nonadiabatic electron transition for fixed exchanging groups. We incorporated the dynamic effects of the acceptor (donor) motion to the nonadiabatic electron-transport theory and we believe that the inclusion of the relative motion of exchanging groups to the nonadiabatic electron-transport theory can help in the elucidation of anomalous effects in the transport of the electrons in photosynthetic reaction centers [23]. We also showed how the fluctuation of the potential surfaces of the final and initial states of the solute molecules influence the electron transport. The main accomplishments of the present study can be summarized as follows:

6.1. SOLVENT DYNAMICS

Equation (4.11) allow us to predict the variation of the nonadiabatic rate with τ_e . Consider a system with short τ_e , when $\alpha \ll 1$. In this case, the rate will decrease as τ_e^{-1} . When τ_e is increased and parameter α becomes large, the nonadiabatic rate reaches a plateau and becomes independent of τ_e .

6.2. DYNAMICS OF EXCHANGING GROUPS

At an overdamped limit, the main effect of the Brownian motion of the acceptor is to slow the rate process. This probably arises since the motion of the molecules is diffusive in this limit and it hinders the electrons effectively providing the energy to vibrational degrees of freedom. At an underdamped limit, the rate constant grows with a decrease in the friction coefficient γ . In this limit, the motion of the acceptor is more regular and helps to provide electron energy in the solute molecules.

Appendix A

In this appendix we do a multinomial expansion of $K(\tau)$

$$K(\tau) = \exp[-\Delta^2(\bar{n} + 1/2)] \exp\left(\frac{\Delta^2}{2} [(\bar{n} + 1) e^{i\omega\tau} + \bar{n} e^{-i\omega\tau}]\right). \quad (\text{A1})$$

Using the multinomial expansion, Equation (A1) becomes

$$K(\tau) = \exp[-\Delta^2(\bar{n} + 1/2)] \times \\ \times \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \frac{[S(\bar{n} + 1)]^\alpha [S\bar{n}]^\beta}{\alpha!\beta!} \exp[i\omega(\alpha - \beta)\tau]. \quad (\text{A2})$$

Equation (A2) can be recast in the form

$$K(\tau) = \exp[-\Delta^2(\bar{n} + 1/2)] \times \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n} + 1}{\bar{n}}\right)^{q/2} I_q \left(2S[\bar{n}(\bar{n} + 1)]^{1/2}\right) \exp(i\omega q \tau). \quad (\text{A3})$$

Appendix B

We consider the integral

$$I = \int_0^{\infty} \exp\left(\frac{T}{T_c} \exp(-M_a \omega_0^2 / \gamma \tau) - \Gamma_e[\tau - \tau_e(1 - e^{-\tau/\tau_e})]\right) d\tau. \quad (\text{B1})$$

Using the expansion of the exponential

$$\exp\left(\frac{T}{T_c} \exp(-M_a \omega_0^2 / \gamma \tau)\right) = 1 + \frac{\lambda^2 k_B T}{M_a \omega_0^2} \exp(-M_a \omega_0^2 / \gamma \tau) + \dots,$$

we find that

$$I = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c}\right)^n \int_0^{\infty} \exp\left(-n M_a \omega_0^2 / \gamma \tau - \Gamma_e[\tau - \tau_e(1 - e^{-\tau/\tau_e})]\right) d\tau. \quad (\text{B2})$$

Upon changing the integration variable to

$$y = 1 - \exp(-\tau/\tau_e),$$

we get

$$I = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c}\right)^n \tau_e \int_0^1 \exp(\alpha y) (1 - y)^{n\xi\alpha + \alpha - 1} dy \quad (\text{B3})$$

and we can rewrite I in the form

$$I = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c}\right)^n \frac{\Gamma(1) \Gamma(c_n - 1)}{\Gamma(c_n)} \tau_e M(1, c_n, \alpha), \quad (\text{B4})$$

where

$$c_n = n\xi\alpha + \alpha + 1, \quad \alpha = \Gamma_e \tau_e,$$

$\Gamma(z)$ is the gamma function and $M(a, b, c)$ is the confluent hypergeometric function [20]. By using the relations

$$\Gamma(z + 1) = z\Gamma(z), \quad (\text{B5})$$

$$\Gamma(1) = 1, \quad (\text{B6})$$

we get

$$I = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{T}{T_c}\right)^n \frac{1}{\Gamma_e(n\xi + 1)} M(1, c_n, \alpha). \quad (\text{B7})$$

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