Effect of the molecular dynamics of exchanging groups on electron transport. Stochastic Liouville equation approach

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Abstract

We developed a theory of nonadiabatic electron transfer reactions in the systems where conformational variations are present. This is done with the use of the stochastic Liouville equation approach. The conformational changes of the system are described as a two-state jump Markov process. Limiting regime analytic results for rate constants are presented for high and slow Markovian modulation.

1. Introduction

In a previous Letter [1] we developed a simple theory for electron transport in a fluctuating medium. In this Letter we treat the problem from a somewhat different point of view. The stochastic Liouville equation approach will be used [2,3]. A correct expression for the electron transfer rate will be derived.

Electron transfer in porphyrin–quinone cyclophanes has been treated [4]. Porphyrin serves as electron donor and one of several substituted quinones serves as electron acceptor in these systems. Temperature-dependent ^{1}H NMR spectra show that conformational interconversions occur in solution. Molecular dynamics simulations also show that there exist two conformational states of the system, where the mutual donor–acceptor orientation is different [5]. The electronic interaction matrix elements between initial and final electronic states depend on the mutual orientation of the donor–acceptor pair [6–8]. X-ray analysis of the photosynthetic reaction center revealed an arrangement of prosthetic groups that act as electron donors and acceptors in the sequence of primary charge separation reactions [9–11]. These studies provided a static structure for the molecules, but conformational variations are always present. The temperature and detection-wavelength dependence of the rates of the primary electron transfer reaction that was measured in Ref. [12] can reflect a distribution of reaction centers having differences in factors such as distances or orientations between cofactors. It was showed [13] that biological electron transfer reaction may be controlled by conformational transitions in electron transfer complexes. Molecular dynamics effects on electron transfer are important and deserve our attention in the context of electron transfer theory.

2. Theory

Generally, the development of the density matrix of any statistical system is believed to be determined by the Liouville equation

$$i\frac{\partial}{\partial t}\rho(t) = \frac{1}{\hbar}[H(c(t)), \rho],\tag{1}$$

with H being the Hamiltonian operator and $c(t)$ representing a random function of time. Our system is characterized by the Hamiltonian H which is divided into two parts

$$H = H_0 + V,\tag{2}$$

where

$$H_0 = [H_i(\boldsymbol{R}) + E_i + V_i(c(t))]a_i^+ a_i + [H_f(\boldsymbol{R}) + E_f + V_f(c(t))]a_f^+ a_f,\tag{3}$$

$$V = J(c(t))[a_i^+ a_f + a_f^+ a_i].\tag{4}$$

We assume that the total statistical system described by the density matrix ρ consists of a system of interest (electrons) and a bath (molecules of the environment). $J(c(t))$ is the nondiagonal part of a perturbation causing a transition between the eigenstates of H_0. $V_n(c(t))$ are diagonal elements of the perturbation. The E_n and a_n^+ (a_n) are the site energy and the creation (annihilation) operator of the electron at site n ($n = $ i, f), respectively. We denote the solvent Hamiltonian when the electron is at site n by $H_n(\boldsymbol{R})$. $\boldsymbol{R}$ denotes the coordinates of the position and orientation of the solvent molecules. We assume that

$$H_i(\boldsymbol{R}) - H_f(\boldsymbol{R}) = \Delta + W(t).\tag{5}$$

$W(t)$ is taken to be a Gaussian–Markovian process with zero mean, and correlation function

$$\langle W(t_1)W(t_2)\rangle = \langle \xi^2\rangle_{\text{slv}} \exp(-|t_1 - t_2|/\tau_e).\tag{6}$$

We start from the stochastic Liouville equation and designate

$$\rho_I(c(t), t) = \left[\vec{T}\exp\left(\frac{i}{\hbar}\int_0^t H_0(\tau)\,d\tau\right)\right]\rho(c(t))\left[\overleftarrow{T}\exp\left(-\frac{i}{\hbar}\int_0^t H_0(\tau)\,d\tau\right)\right],\tag{7a}$$

$$V_I(c(t), t) = \left[\vec{T}\exp\left(\frac{i}{\hbar}\int_0^t H_0(\tau)\,d\tau\right)\right]V(c(t))\left[\overleftarrow{T}\exp\left(-\frac{i}{\hbar}\int_0^t H_0(\tau)\,d\tau\right)\right],\tag{7b}$$

$$L(t) = \frac{1}{\hbar}[V_I(c(t), t), \ldots].\tag{8}$$

$\overleftarrow{T}$ $(\vec{T})$ is a time ordering operator ordering later times to the left (right). The stochastic Liouville equation for the density matrix in the interaction picture reads

$$\partial_t \rho_I(c(t), t) = -iL(t)\rho_I(c(t), t),\tag{9}$$

and using standard projection techniques [14] we get

$$\partial_t D\rho_I(c(t), t) = -iDL(t)D\rho_I(c(t), t) - iDL(t)(1 - D)\rho_I(c(t), t),\tag{10}$$

$$\partial_t(1 - D)\rho_I(c(t), t) = -i(1 - D)L(t)(1 - D)\rho_I(c(t), t) \\ -i(1 - D)L(t)D\rho_I(c(t), t),\tag{11}$$

Here D is a projection operator. Solving the last equation and introducing the result into (10) yields

$$\partial_t D\rho_I(c(t), t) = -iDL(t)D\rho_I(c(t), t) \\ -DL(t)\int_0^t\left[\overleftarrow{T}\exp\left(-i(1 - D)\int_\tau^t L(\tau_1)\,d\tau_1\right)\right](1 - D)L(\tau)D\rho_I(\tau)\,d\tau,\tag{12}$$

where it is assumed that the initial condition is

$$(1 - D)\rho_1(q(0), 0) = 0. \tag{13}$$

We will work to second order of perturbation theory. In this approximation we have

$$\partial_t D\rho_1(c(t), t) = -iDL(t)D\rho_1(c(t), t) - DL(t)\int_0^t (1 - D)L(\tau)D\rho_1(c(\tau), \tau)\, d\tau. \tag{14}$$

Now we will use the projector in the form

$$(DA)_{mn} = \delta_{m,n}\langle A_{mm}\rangle_B. \tag{15}$$

The bracket $\langle\ \rangle_B$ is the ensemble average over the solvent and conformational motion. We use the identity

$$DL(t)D = 0 \tag{16}$$

and from (14) we get

$$\partial_t D\rho_1(c(t), t) = -DL(t)\int_0^t L(\tau)D\rho_1(c(\tau), \tau)\, d\tau. \tag{17}$$

For Eq. (17) we take the matrix elements $\langle m|\ldots|m\rangle, |m = i, f\rangle$ are the eigenstates of H_0. We get

$$\frac{\partial P_i(t)}{\partial t} = -\int_0^t w_{if}(t, \tau)P_i(\tau)\, d\tau + \int_0^t w_{fi}(t, \tau)P_f(\tau)\, d\tau, \tag{18a}$$

$$\frac{\partial P_f(t)}{\partial t} = \int_0^t w_{if}(t, \tau)P_i(\tau)\, d\tau - \int_0^t w_{fi}(t, \tau)P_f(\tau)\, d\tau. \tag{18b}$$

Here $P_m(t) = \langle\rho_{mm}(t)\rangle_B$ and

$$w_{if}(t, \tau) = \frac{2}{\hbar^2}\text{Re}\exp\left(-\frac{i}{\hbar}\varepsilon_0(t - \tau)\right)\langle Q^+(t, \tau)\rangle_{md}\,\xi(t - \tau), \tag{19a}$$

$$w_{fi}(t, \tau) = \frac{2}{\hbar^2}\text{Re}\exp\left(\frac{i}{\hbar}\varepsilon_0(t - \tau)\right)\langle Q^+(t, \tau)\rangle_{md}\,\xi(t - \tau), \tag{19b}$$

where $\varepsilon_0 = E_i - E_f + \Delta$ and $\xi(t) = \exp(-\Gamma_e\{t - \tau_e[1 - \exp(-t/\tau_e)]\})$. Here $\Gamma_e = \langle\xi^2\rangle_{slv}\tau_e/\hbar^2$. The bracket $\langle\ \rangle_{md}$ is the ensemble average over all possible realisations of $c(t)$ and

$$Q^\pm(t, \tau) = J(c(t))\exp\left(\pm\frac{i}{\hbar}\int_\tau^t \varepsilon(c(\tau_1))\, d\tau_1\right)J(c(\tau)), \tag{20}$$

where $\varepsilon(c(t)) = V_i(c(t)) - V_f(c(t))$.

3. Molecular dynamics

Let us assume a system with two conformational states A and B, with free energies E_a and E_b. The stochastic function $c(t)$ can take on any of two values, which we denote a, b. This process is defined by the differential equation for conditional probabilities

$$\partial_t P(a, t\,|\, y, t_0) = -\lambda P(a, t\,|\, y, t_0) + \mu P(b, t\,|\, y, t_0), \tag{21a}$$

$$\partial_t P(b, t\,|\, y, t_0) = \lambda P(a, t\,|\, y, t_0) - \mu P(b, t\,|\, y, t_0), \tag{21b}$$

with the normalization condition

$$P(a, t\,|\, x, t_0) + P(b, t\,|\, x, t_0) = 1. \tag{22}$$

The conditional probabilities reduce for $t - t_0 = 0$ to

$$P(y, t \mid x, t_0) = \delta_{y,x}. \tag{23}$$

Here μ is the transition rate from state B to state A and λ is the transition rate from state A to state B. We can see that the stationary solutions of Eqs. (21) with conditions (22) and (23) are

$$P(a) = \exp(-E_a/k_\mathrm{B}T)/[\exp(-E_a/k_\mathrm{B}T) + \exp(-E_b/k_\mathrm{B}T)] = \mu/(\mu + \lambda), \tag{24a}$$

$$P(b) = \exp(-E_b/k_\mathrm{B}T)/[\exp(-E_a/k_\mathrm{B}T) + \exp(-E_b/k_\mathrm{B}T)] = \lambda/(\mu + \lambda). \tag{24b}$$

Now we compute the quantity $\langle Q^-(t, \tau)\rangle_\mathrm{md}$ for the stochastic process $c(t)$, which was described above.

$$\langle Q^-(t, \tau)\rangle_\mathrm{md} = \sum_{x=a,b} \sum_{y=a,b} J(x)K^-(x, t \mid y, \tau)J(y)P(y), \tag{25}$$

where we introduce

$$K^-(x, t \mid y, \tau) = \left\langle \exp\left(-\frac{\mathrm{i}}{\hbar} \int_\tau^t \varepsilon(\tau_1)\, \mathrm{d}\tau_1\right)\right\rangle_{x,y}. \tag{26}$$

This is the expectation of $\exp[-(\mathrm{i}/\hbar)\int_\tau^t \varepsilon(\tau_1)\, \mathrm{d}\tau_1]$ under the condition that the system is at time τ in conformational state y and finds itself in conformational state x at time t. This satisfies the equation [15]

$$K^-(x, t+h \mid y, t_1) = K^-(x, t+h \mid a, t)K^-(a, t \mid y, t_1) + K^-(x, t+h \mid b, t)K^-(b, t \mid y, t_1). \tag{27}$$

Now we have from (21) for small h

$$K^-(a, t+h \mid a, t) = 1 - \mathrm{i}\varepsilon(a)h - \lambda h, \qquad K^-(a, t+h \mid b, t) = \mu h, \tag{28a}$$

$$K^-(b, t+h \mid b, t) = 1 - \mathrm{i}\varepsilon(b)h - \mu h, \qquad K^-(b, t+h \mid a, t) = \lambda h. \tag{28b}$$

From relations (27) and (28) one obtains

$$\partial_t K^-(a, t \mid y, t_1) = -\left(\frac{\mathrm{i}}{\hbar}\varepsilon(a) + \lambda\right)K^-(a, t \mid y, t_1) + \mu K^-(b, t \mid y, t_1), \tag{29a}$$

$$\partial_t K^-(b, t \mid y, t_1) = -\left(\frac{\mathrm{i}}{\hbar}\varepsilon(b) + \mu\right)K^-(b, t \mid y, t_1) + \lambda K^-(a, t \mid y, t_1), \tag{29b}$$

with initial conditions

$$K^-(x, t_1 \mid y, t_1) = \delta_{x,y}. \tag{30}$$

From Eqs. (29) and (30) we get

$$K^-(a, t \mid a, t_1) = \frac{\mu\lambda}{O^2 + \mu\lambda}\exp[-\mathrm{i}\omega_1(t - t_1)] + \frac{O^2}{O^2 + \mu\lambda}\exp[-\mathrm{i}\omega_2(t - t_1)], \tag{31a}$$

$$K^-(b, t \mid a, t_1) = \frac{\lambda O}{O^2 + \mu\lambda}\{-\exp[-\mathrm{i}\omega_1(t - t_1)] + \exp[-\mathrm{i}\omega_2(t - t_1)]\}, \tag{31b}$$

$$K^-(a, t \mid b, t_1) = \frac{\mu O}{O^2 + \mu\lambda}\{-\exp[-\mathrm{i}\omega_1(t - t_1)] + \exp[-\mathrm{i}\omega_2(t - t_1)]\}, \tag{32a}$$

$$K^-(b, t \mid b, t_1) = \frac{O^2}{O^2 + \mu\lambda}\exp[-\mathrm{i}\omega_1(t - t_1)] + \frac{\mu\lambda}{O^2 + \mu\lambda}\exp[-\mathrm{i}\omega_2(t - t_1)], \tag{32b}$$

where

$$\omega_{1,2} = \varpi - \tfrac{1}{2}\mathrm{i}(\lambda + \mu) \pm \tfrac{1}{2}\Big[\delta\omega^2 - 2\mathrm{i}\delta\omega(\lambda - \mu) - (\lambda + \mu)^2\Big]^{1/2},$$

$$O = -\tfrac{1}{2}\mathrm{i}\delta\omega + \tfrac{1}{2}(\mu - \lambda) + \tfrac{1}{2}\mathrm{i}\Big[\delta\omega^2 - 2\mathrm{i}\delta\omega(\lambda - \mu) - (\lambda + \mu)^2\Big]^{1/2},$$

$$\varpi = \frac{1}{2\hbar}\big[\varepsilon(a) + \varepsilon(b)\big], \qquad \delta\omega = \frac{1}{\hbar}\big[\varepsilon(a) - \varepsilon(b)\big].$$

By using expressions (31) and (32) in (25) we get

$$\langle Q^-(t, \tau)\rangle_{\mathrm{md}} = A_1 \exp\big[-\mathrm{i}\omega_1(t - \tau)\big] + A_2 \exp\big[-\mathrm{i}\omega_2(t - \tau)\big]. \tag{33}$$

Here

$$A_1 = \frac{1}{O^2 + \mu\lambda}\Big[\mu\lambda J(a)^2 P(a) - \mu O J(a) J(b) P(b) - \lambda O J(a) J(b) P(a) + O^2 J(b)^2 P(b)\Big],$$

$$A_2 = \frac{1}{O^2 + \mu\lambda}\Big[O^2 J(a)^2 P(a) + \mu O J(a) J(b) P(b) + \lambda O J(a) J(b) P(a) + \mu\lambda J(b)^2 P(b)\Big].$$

4. Computation of the rate constant

In this section we compute the rate constant. According to our aim, we perform the Markovian approximation

$$\frac{\partial P_{\mathrm{i}}(t)}{\partial t} = -k_{\mathrm{if}} P_{\mathrm{i}}(t) + k_{\mathrm{fi}} P_{\mathrm{f}}(t), \tag{34}$$

$$\frac{\partial P_{\mathrm{f}}(t)}{\partial t} = k_{\mathrm{if}} P_{\mathrm{i}}(t) - k_{\mathrm{fi}} P_{\mathrm{f}}(t), \tag{35}$$

where we introduce the rate constants k_{if} and k_{fi} in the form

$$k_{\mathrm{if}} = \int_0^\infty w_{\mathrm{if}}(\tau)\,\mathrm{d}\tau, \qquad k_{\mathrm{if}} = \int_0^\infty w_{\mathrm{if}}(\tau)\,\mathrm{d}\tau. \tag{36}$$

Generally the expressions for the rate constant are cumbersome and so we present some limited cases. In these cases we assume without loss of generalisation that $\varepsilon(a) \geqslant \varepsilon(b)$ and $\lambda \geqslant \mu$.

4.1. Slow-modulation limit

In this limit we assume that $\lambda + \mu \ll \delta\omega$. In this case we have

$$\langle Q^-(\tau)\rangle_{\mathrm{md}} = P(a) J(a)^2 \exp[(\mathrm{i}/\hbar)\epsilon(a)\tau - \lambda\tau] + P(b) J(b)^2 \exp[(\mathrm{i}/\hbar)\epsilon(b)\tau - \mu\tau].$$

If $\Gamma_\mathrm{e}\tau_\mathrm{e} \ll 1$, we get the rate constant in the form

$$k_{\mathrm{if}} = P(a)\frac{2J(a)^2}{\hbar^2}\frac{\Gamma_\mathrm{e} + \lambda}{\omega_a^2 + (\Gamma_\mathrm{e} + \lambda)^2} + P(b)\frac{2J(b)^2}{\hbar^2}\frac{\Gamma_\mathrm{e} + \mu}{\omega_b^2 + (\Gamma_\mathrm{e} + \mu)^2}, \tag{37}$$

where $\omega_a = [\varepsilon_0 + \varepsilon(a)]/\hbar$ and $\omega_b = [\varepsilon_0 + \varepsilon(b)]/\hbar$. When $\Gamma_e \tau_e \gg 1$ we have

$$k_{if} = \theta \int_{-\infty}^{+\infty} d\omega \left(\frac{P(a)J(a)^2 \lambda/\pi}{(\omega_a - \omega)^2 + \lambda^2} + \frac{P(b)J(b)^2 \mu/\pi}{(\omega_b - \omega)^2 + \mu^2} \right) \exp(-\hbar^2 \omega^2/2\langle \xi^2 \rangle_{slv}), \tag{38}$$

where $\theta = (2\pi/\langle \xi^2 \rangle_{slv} \hbar^2)^{1/2}$.

4.2. High-modulation limit

In this limit we assume that $\lambda + \mu \gg \delta\omega$. In this case we have

$$\langle Q^-(\tau) \rangle_{md} = [P(a)J(a) + P(b)J(b)]^2 \exp(-i\overline{\omega}\tau - \Omega\tau)$$
$$+ P(a)P(b)[J(a) - J(b)]^2 \exp[-i\varpi\tau - (\lambda + \mu)\tau],$$

where

$$\Omega = \frac{\delta\omega^2}{4(\lambda + \mu)} \left[1 - \left(\frac{\lambda - \mu}{\lambda + \mu} \right)^2 \right].$$

In this limit when $\Gamma_e \tau_e \ll 1$ we get

$$k_{if} = \frac{2}{\hbar^2} [P(a)J(a) + P(b)J(b)]^2 \frac{\Gamma_e + \Omega}{(\varepsilon_0/\hbar + \varpi)^2 + (\Gamma_e + \Omega)^2}$$
$$+ \frac{2}{\hbar^2} P(a)P(b)[J(a) - J(b)] \frac{\Gamma_e + \lambda + \mu}{(\varepsilon_0/\hbar + \varpi)^2 + (\Gamma_e + \lambda + \mu)^2}. \tag{39}$$

When $\Gamma_e \tau_e \gg 1$ we get

$$k_{if} = \theta \int_{-\infty}^{+\infty} d\omega \left(\frac{[P(a)J(a) + P(b)J(b)]^2 \Omega/\pi}{(\varepsilon_0/\hbar + \varpi - \omega)^2 + \Omega^2} \right.$$
$$\left. + \frac{P(a)P(b)[J(a) - J(b)]^2 (\lambda + \mu)/\pi}{(\varepsilon_0/\hbar + \varpi - \omega)^2 + (\lambda + \mu)^2} \right) \exp(-\hbar^2 \omega^2/2\langle \xi^2 \rangle_{slv}). \tag{40}$$

5. Conclusion

We have derived a formula for the electron transfer rate k_{if}. We obtained formally similar results as in the theory of dynamic nuclear magnetic resonance spectroscopy [16]. In the slow-modulation limit we expressed the rate constant as a sum of the rates in the conformation states A and B multiplied by the corresponding Boltzmann factors of these states. In the high-modulated limit we obtained the rate constant as in the case where the energy gap between donor and acceptor is $\varepsilon_0 + \hbar\varpi$ and the Hamiltonian causing the transition is $P(a)J(a) + P(b)J(b)$. We have the same results as in Ref. [1] for the case where $\varepsilon(a) = \varepsilon(b)$. When $\varepsilon(a) \neq \varepsilon(b)$, the results of Ref. [1] are incorrect. This is caused by the incorrect derivation of equations for the quantity $K(x, t \mid y, \tau)$ in Ref. [1]. The derivation that was used in Ref. [1] cannot be applied for stochastic processes with discrete state space. We estimated also the parameter $\alpha = \Gamma_e \tau_e$. $\alpha \gg 1$ for electron transfer reaction in polar liquids. In the case of non-polar and non-viscous solvents, where the reorganisation energy is small [4,17] and the correlation time τ_e is also small [18], the parameter α can be smaller than 1.

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