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ELECTRON TRANSFER DRIVEN
BY CONFORMATIONAL VARIATIONS

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I. Introduction

Electron transitions are an important class of chemical and biological reactions. The theory of electron transfer (ET) reaction is the subject of persistent interest in chemical and biological physics[1-11]. Environmental effects on these reaction in complex dynamical systems, such as biomolecules, have drawn much interest in recent years[12-14]. It is by now well established that proteins at room temperature fluctuate around their average structure, and that these fluctuations have an important role in the proteins function[15]. It has been suggested that protein fluctuations open pathways for molecular motion, that are not available in the rigid proteins, by removing a steric hindrance or opening a gate[16]. Moreover, molecular dynamics simulations and temperature dependent 1H NMR spectra show that in porphyrin-quinon cyclophanes the conformational interconversions occur in solution[17]. Porphyrin serves as electron donor and one of several substituted quinones serves as electron acceptor in these systems[18]. The temperature and detection-wavelength dependence of the rates of the primary electron transfer reaction can reflect a distribution of reaction centers having differences in factors such as distances or orientations between cofactors[19]. For the elucidation of the mechanisms of electron transfer reactions in biological systems, the conformational variations must be incorporated into the model.

At present there are several published papers dealing with the problem of the ET driven by conformational variations. For example, the gating of electron transfer by conformational transitions was introduced in work[20]. The gating is supposed to take place in cytochrome oxidase[21], in the electron transfer between cytochrome *c* and special pair of bacteriochlorophylls in the reaction center of several photosynthetic bacteria[22]. The dynamic effect of donor-acceptor vibrations was displayed in the dependence of the nonadiabatic electron transfer probability on the medium friction in the work[23]. The influence of

dichotomically fluctuating tunneling coupling on long-range electron transfer was studied in the work[24].

In the present work a simple model of the conformational variations of the system was used to formulate electron transfer. We assume that there are only two conformational states possible which we denote as A and B and the localization of electron does not act on the dynamics of conformational variations. It means that we suppose that transfer of electron does not change significantly the force field in which the system execute its conformational dynamics. The ET is possible only in the state A and in the conformational state B the electron transfer reaction is completely interrupted. The conformational changes of the system are described as a classical telegraphic noise. Similar model was discussed in our previous papers[25,26] and in the work[27].

Our final aim is to get an analytical expression for the probability to find electron on donor at time t in the system where conformational variations are present. A functional integral techniques was used in the present paper to investigate how electron transport from donor to acceptor can be controlled by conformational variations of the system. The technical manipulations are similar to those advanced in the earlier works [28-33]. For simplicity, we consider the Hilbert space of the electron to consist of just those two states that are involved in the transfer. It is convenient to use the Pauli matrices for the operators in this space.

II. Theory

The Hamiltonian of the system that we shall study is

$$H(t) = \frac{1}{2} \Delta(c(t)) \sigma_x + \frac{1}{2} (\varepsilon_0 + \varepsilon(c(t))) \sigma_z \quad (1)$$

where $\Delta(c(t))$ is the electronic coupling parameter, $\varepsilon_0 + \varepsilon(c(t))$ is the bias (the reaction heat) between two equilibrium positions, Here, ε_0 is a static bias energy and $\varepsilon(c(t))$ is a part of the reaction heat which depends on the conformational state of the system. This time dependence

could arise, for example, from interaction of electron with molecules of medium. Further, the $\sigma_{x,z}$ are Pauli spin matrices and $c(t)$ representing random function of time. The electronic coupling parameter depends on the mutual orientation of the donor acceptor pair[34]. We suppose that this orientation is sensitive to the conformational changes of the system.

The electronic state associated with the $|+1\rangle$ eigenstate of σ_x (with eigenvalue $+1$) shall be designated as the donor electronic state. The other electronic base state is the acceptor state. We examine the dynamics of an electron which is at time $t=0$ localized on the donor. At a later time t the system is then found again on the donor with probability $W(t)$

$$W(t) = \left\langle \left| \bar{T} \exp\left[-\frac{i}{\hbar} \int_0^t H(\tau) d\tau\right] |+1 \right\rangle_{md} \right|^2 \quad (2)$$

\bar{T} is a time ordering operator ordering later times to the left. The bracket $\langle \rangle_{md}$ is the ensemble average over all possible realizations of $c(t)$. Now we define the molecular dynamics of the system. We assume that there exist two conformational states A and B with free energies E_a and E_b . The transfer between these two states is characterized by the random function $c(t)$ that take on any of two values which we denote a,b. This process is defined by the differential equation for conditional probabilities

$$\partial_t P(a, t|y, t_0) = -\lambda P(a, t|y, t_0) + \mu P(b, t|y, t_0) \quad (3a)$$

$$\partial_t P(b, t|y, t_0) = -\mu P(b, t|y, t_0) + \lambda P(a, t|y, t_0) \quad (3b)$$

with the normalization condition

$$P(a, t|x, t_0) + P(b, t|x, t_0) = 1$$

and initial conditions

$$P(x, t_0|y, t_0) = \delta_{x,y}$$

Here, λ is the transition rate from state A to state B and μ is the transition rate from state B to state A. We suppose that these two parameters do not depend on the localization of the

electrons. The stationary solutions of the equations (3) are

$$P(a) = \mu / (\lambda + \mu) \quad , \quad P(b) = \lambda / (\lambda + \mu) \quad (4)$$

The stationary solutions must fulfill Boltzmann condition

$$P(a) / P(b) = \exp[-\beta(E_a - E_b)] = \mu / \lambda \quad (5)$$

where $\beta = 1 / k_B T$. From equations (4) and (5) we get

$$P(a) = \frac{e^{-\beta E_a}}{e^{-\beta E_a} + e^{-\beta E_b}} \quad , \quad P(b) = \frac{e^{-\beta E_b}}{e^{-\beta E_a} + e^{-\beta E_b}} \quad (6)$$

Now we write general expression for $W(t)$ as a power series in $\Delta(c(t))$ [35]

$$W(t) = \left\langle 1 + \sum_{n=1}^{\infty} (-1)^n \int_0^t dt_{2n} \frac{\Delta(t_{2n})}{2\hbar} \int_0^{t_{2n-1}} dt_{2n-1} \frac{\Delta(t_{2n-1})}{2\hbar} \dots \int_0^{t_2} dt_1 \frac{\Delta(t_1)}{2\hbar} F(t_1, t_2, \dots, t_{2n}) \right\rangle_{md} \quad (7a)$$

where

$$F = \sum_{\{\xi_j = \pm 1\}} \sum_{\{\chi_j = \pm 1\}} \exp \left\{ \sum_{j=1}^n i \frac{\xi_j}{\hbar} [\varepsilon_0(t_{2j} - t_{2j-1}) + \int_{t_{2j-1}}^{t_{2j}} \varepsilon(\tau) d\tau] \right\} \quad (7b)$$

Now we sum over the possible values of the χ_j ($j=1,2,\dots,n-1$) and take the average over all realization of $c(t)$. We get

$$W(t) = 1 + \sum_{n=1}^{\infty} (-1)^n \left(\frac{J}{2\hbar} \right)^{2n} 2^{n-1} \int_0^t dt_{2n} \dots \int_0^{t_2} dt_1 K_1\{t_m\} K_2\{t_m\} \quad (8a)$$

where was assumed similarly as in work [36] that $\Delta(a) = J$, $\Delta(b) = 0$. It was considered that electron transfer reaction can be completely interrupted by the fluctuations of electronic coupling. It results in the so called gated reaction since the electronic coupling fluctuates between 0 (gate is closed) and J (gate is open), and thus drives the electron transfer.

$$K_1\{t_m\} = \sum_{\{\xi_j\}} \exp \left\{ \sum_{j=1}^n i \xi_j \frac{\varepsilon_0}{\hbar} (t_{2j} - t_{2j-1}) \right\} \prod_{j=1}^n K_{\xi_j}(a, t_{2j} | a, t_{2j-1}) \quad (8b)$$

$$K_2\{t_m\} = \sum_{x=a,b} P(x, t | a, t_{2n}) \prod_{j=1}^{n-1} P(a, t_{2j+1} | a, t_{2j}) \sum_{y=a,b} P(a, t_1 | y, 0) P(y) \quad (8c)$$

where we introduce

$$K_{\xi_j}(a, t_{2j} | a, t_{2j-1}) = \left\langle \exp \left[\frac{i \xi_j}{\hbar} \int_{t_{2j-1}}^{t_{2j}} \varepsilon(\tau) d\tau \right] \right\rangle_{a,a} \quad (9)$$

This is the expectation of $\exp[i(\xi_j / \hbar) \int_{t_{2j-1}}^{t_{2j}} \varepsilon(\tau) d\tau]$ under the condition that the system is at

time t_{2j-1} in conformational state A and finds itself in conformational state A at time t_{2j} . By

using the relations

$$\sum_{y=a,b} P(a, t_1 | y, 0) P(y) = P(a) \quad , \quad \sum_{x=a,b} P(x, t | a, \tau) = 1$$

we obtain

$$K_2\{t_m\} = P(a) \prod_{j=1}^{n-1} P(a, t_{2j+1} | a, t_{2j}) \quad (10)$$

where[26]

$$P(a, t | a, \tau) = P(a) + P(b) e^{-(\lambda + \mu)(t - \tau)} \quad (11)$$

Generally the expression for the $K_{\xi_j}(a, t | a, \tau)$ is cumbersome and so we present some limited

cases. In these cases we assume without loss of generalization that $\varepsilon(a) \geq \varepsilon(b)$ and $\lambda \geq \mu$.

III. High-modulation limit

We first examine the high-modulation limit. In this limit we assume that

$\lambda + \mu \gg [\varepsilon(a) - \varepsilon(b)] / \hbar$. In this case we have[26]

$$K_{\xi_j}(a, t_{2j} | a, t_{2j-1}) = e^{i \xi_j \varepsilon_m (t_{2j} - t_{2j-1})} \left\{ P(b) e^{-(\lambda + \mu)(t_{2j} - t_{2j-1})} + P(a) e^{-\Theta(t_{2j} - t_{2j-1})} \right\} \quad (12)$$

where $\varpi = [\varepsilon(a) + \varepsilon(b)] / 2\hbar$ and $\Theta = \frac{[\varepsilon(a) - \varepsilon(b)]^2}{\hbar^2(\lambda + \mu)} P(a)P(b)$. After summing over the

possible values ± 1 of the ξ_j ($j=1,2,\dots,n$) in Eq.(8b) we get

$$K_1\{t_m\} = \prod_{j=1}^n 2 \cos[\Omega(t_{2j} - t_{2j-1})] \{P(a)e^{-\Theta(t_{2j}-t_{2j-1})} + P(b)e^{-(\lambda+\mu)(t_{2j}-t_{2j-1})}\} \quad (13)$$

where $\Omega = \varepsilon_0 / \hbar + \varpi$. Now we apply the Laplace transform to $W(t)$. Defining

$$\tilde{W}(p) = \int_0^\infty e^{-pt} W(t) dt \quad (14)$$

we get

$$\begin{aligned} \tilde{W}(p) &= \frac{1}{p} + \frac{P(a)}{2} \sum_{n=1}^{\infty} (-1)^n \left(\frac{J^2}{\hbar^2}\right)^n \frac{1}{p} f(p)^n g(p)^{n-1} \frac{1}{p} \\ &= \frac{1}{p} - \frac{P(a) J^2 f(p)}{2 \hbar^2 p^2} \frac{1}{1 + \frac{J^2}{\hbar^2} f(p)g(p)} \end{aligned} \quad (15)$$

where

$$\begin{aligned} f(p) &= \int_0^\infty e^{-pt} \cos \Omega t \{P(a)e^{-\Theta t} + P(b)e^{-(\lambda+\mu)t}\} dt \\ &= P(a) \frac{p + \Theta}{(p + \Theta)^2 + \Omega^2} + P(b) \frac{p + \lambda + \mu}{(p + \lambda + \mu)^2 + \Omega^2} \end{aligned} \quad (16)$$

$$g(p) = \int_0^\infty e^{-pt} \{P(a) + P(b)e^{-(\lambda+\mu)t}\} dt = \frac{p + \mu}{p(p + \lambda + \mu)} \quad (17)$$

In this section we calculate $W(t)$ for the case of zero bias ($\Omega=0$) and assume that $\varepsilon(a)=\varepsilon(b)$. In

this limit $f(p)=g(p)$ and we have

$$\tilde{W}(p) = \frac{1}{p} - \frac{P(a) J^2}{2p \hbar^2} \frac{(p + \mu)(p + \lambda + \mu)}{p^2(p + \lambda + \mu)^2 + \frac{J^2}{\hbar^2}(p + \mu)^2} \quad (18)$$

The expressions for the kinetics of the electron transfer are given by the inverse Laplace transformation of Eq.(18). The inverse Laplace transform is represented by a set of simple poles of $\tilde{W}(p)$. Evaluating it we obtain

$$W(t) = 1 - \frac{P(a) J^2}{2 \hbar^2} \{a_0 + \sum_{j=1}^4 a_j e^{p_j t}\} \quad (19)$$

with the amplitudes (a_1, a_2, a_3, a_4 cycl.)

$$a_1 = \frac{(p_1 + \mu)(p_1 + \lambda + \mu)}{p_1(p_1 - p_2)(p_1 - p_3)(p_1 - p_4)}, \quad a_0 = \frac{\hbar^2}{P(a)J^2} \quad (20)$$

where

$$p_1 = -\frac{1}{2}(\lambda + \mu - u) - \frac{i}{2}(J/\hbar - v), \quad p_2 = -\frac{1}{2}(\lambda + \mu + u) - \frac{i}{2}(J/\hbar + v)$$

$$p_3 = -\frac{1}{2}(\lambda + \mu + u) + \frac{i}{2}(J/\hbar + v), \quad p_4 = -\frac{1}{2}(\lambda + \mu - u) + \frac{i}{2}(J/\hbar - v)$$

$$u = \left(\frac{1}{2} \left[(\lambda + \mu)^2 - \frac{J^2}{\hbar^2} + \sqrt{\left((\lambda + \mu)^2 - \frac{J^2}{\hbar^2} \right)^2 + 4 \frac{J^2}{\hbar^2} (\lambda - \mu)^2} \right] \right)^{1/2}$$

$$v = \left(\frac{1}{2} \left[-(\lambda + \mu)^2 + \frac{J^2}{\hbar^2} + \sqrt{\left((\lambda + \mu)^2 - \frac{J^2}{\hbar^2} \right)^2 + 4 \frac{J^2}{\hbar^2} (\lambda - \mu)^2} \right] \right)^{1/2}$$

In the nonadiabatic approximation we assume that $J/\hbar \ll \lambda + \mu$. From Eq.(19) we get

$$W(t) = \frac{1}{2} + \frac{1}{2} \cos \left[\frac{J}{\hbar} P(a)t \right] e^{-\frac{J^2 P(a)P(b)}{\hbar^2(\lambda + \mu)} t} \quad (21)$$

This describes damped coherent oscillations at a frequency $\omega = P(a)J/\hbar$ and a ET rate

$k = J^2 P(a)P(b) / \hbar^2(\lambda + \mu)$. The frequency of oscillations depends on the probability to find

system in the state A from which the electron transfer is possible. This probability is defined by

the free energies of the conformational states A and B and does not depend on the transition

rates λ, μ .

In the adiabatic approximation we assume that $J/\hbar \gg \lambda + \mu$. We get

$$W(t) = \frac{1}{2} \left\{ 1 + P(a) \cos\left(\frac{J}{\hbar}t\right) e^{-\lambda t} + P(b) \cos\left(\frac{\lambda\mu\hbar}{J}t\right) e^{-\mu t} \right\} \quad (22)$$

This describes damped coherent oscillations with a fast frequency $\omega_1 = J/\hbar$ and electron transfer rate $k_1 = \lambda$ and slow frequency of oscillations $\omega_2 = \hbar\lambda\mu/J$ with electron transfer rate $k_2 = \mu$. We have a adiabatic regime of electron transfer where the electron transfer rates are independent on the electronic coupling, but is controlled by the conformational variations of the system. In this limit the slow frequency depends on $\lambda\mu$ and through these parameters on both the viscosity of the medium and the potential barrier between the conformational states.

IV. Slow-modulation limit

Now we examine the slow-modulation limit. In this limit we assume that $\lambda + \mu \ll [\varepsilon(a) - \varepsilon(b)]/\hbar$. In this case we have[26]

$$K_{\varepsilon_j}(a, t_{2j} / a, t_{2j-1}) = e^{i\varepsilon_j\omega_a(t_{2j}-t_{2j-1})} e^{-\lambda(t_{2j}-t_{2j-1})} \quad (23)$$

where $\omega_a = (\varepsilon_0 + \varepsilon(a))/\hbar$ and $f(p)$ have the form

$$f(p) = \frac{p + \lambda}{(p + \lambda)^2 + \omega_a^2} \quad (24)$$

Substituting the quantity $f(p)$ defined in Eq.(24) into Eq.(15) we get $\tilde{W}(p)$ in the form

$$\tilde{W}(p) = \frac{1}{p} - \frac{P(a)}{2p} \frac{\frac{J^2}{\hbar^2} (p + \lambda) / \{(p + \lambda)^2 + \omega_a^2\}}{p + \frac{J^2}{\hbar^2} \frac{p + \lambda}{(p + \lambda)^2 + \omega_a^2} \frac{p + \mu}{p + \lambda + \mu}} \quad (25)$$

In this case we derive only the long time behavior of $W(t)$. We have

$$W(t) = \frac{1}{2} + \frac{1}{2} e^{-\frac{J^2\mu\lambda/\hbar^2}{(\lambda+\mu)(J^2/\hbar^2 + \lambda^2 + \omega_a^2)}t} \quad (26)$$

which results in the following expression for ET rate constant

$$k = \frac{J^2\mu\lambda/\hbar^2}{2(\lambda + \mu)(J^2/\hbar^2 + \lambda^2 + \omega_a^2)} \quad (27)$$

In the limit $J^2/\hbar^2 \gg \lambda^2 + \omega_a^2$ we have adiabatic electron transfer where ET rate constant yields the following form

$$k = \frac{1}{2} \frac{\mu\lambda}{\lambda + \mu} \quad (28)$$

In the nonadiabatic limit $J^2/\hbar^2 \ll \lambda^2 + \omega_a^2$ the ET rate constant have the form

$$k = 2P(a) \left(\frac{J}{2\hbar}\right)^2 \frac{\lambda}{\lambda^2 + \omega_a^2} \quad (29)$$

This result is similar to that which was obtained in our previous work[26] for the short correlation time τ_c of the solvent. In the absence of the molecular dynamics where $\lambda = 0$, $\mu = 0$, $P(a) = 1$ quantity $W(t)$ shows oscillatory behavior

$$W(t) = 1 - \frac{J^2/\hbar^2}{\omega_a^2 + J^2/\hbar^2} \sin^2\left\{t \frac{1}{2} \sqrt{\omega_a^2 + J^2/\hbar^2}\right\} \quad (30)$$

V. Discussion

We have studied the electron transfer in systems with two conformational states where electron can be transferred only from the state which we denote as A. It was found an exact analytical non-perturbative solution for unbiased case in the high-modulation limit. This allows to get the exact way by which the electron reaches its steady state in contrary to the works where only the rate constant was derived. The rate constant describes only the velocity by which the electron reaches its steady state and does not tell anything about its oscillatory motion.

We can see that conformational changes of the system destroy the oscillatory behavior of $W(t)$ and causes a shift in the frequency of oscillations. The frequencies are influenced by the parameters λ , μ which characterizes the dynamics of conformational changes. The damped coherent oscillations of population of donor state are obtained in the high modulation limit. In

the long-time limit $t \rightarrow \infty$ there exist an equal probability of finding the electron on the donor or acceptor. This is due to the parameters λ, μ which are not dependent on the localization of electron (what is assumption of our model) and so neither of two electronic states is favored from the side of the bath. The temperature changes, viscosity of the medium, potential barrier between the conformational states have an influence on the frequency of oscillations through the parameters λ, μ . In the unbiased case of high-modulation limit when the condition $J/\hbar \gg \lambda + \mu$ is fulfilled or when $J^2/\hbar^2 \gg \lambda^2 + \omega_a^2$ is in the slow modulation limit the electron transitions are limited by the dynamics of conformational transitions and do not depend on the electronic coupling J . Such dependence is a classification of the adiabatic limit.

In this paper we also attempt to discuss the question: What is the influence of conformational variations of the system on the quantum tunneling of electrons in the biological systems. In the special case of conformational variations used in present paper the ET rate increases with increasing of λ, μ in the adiabatic limit but the ET rate decreases in the nonadiabatic regime. From this follows that there must exist optimal dynamics of conformational variations with maximum value of the ET rate. This optimal dynamics can be easily found in the case when $\lambda = \mu$. In the high modulation limit the ET rate gets the maximum when $2\lambda = J/\hbar$. The probability to find electron on the donor can be expressed in the form

$$W(t) = \frac{1}{2} + \frac{1}{2} e^{-\frac{J}{2\hbar}t} \cos\left(\frac{J}{2\hbar}t\right) \left(1 + \frac{J}{2\hbar}t\right) \quad (31)$$

In this regime the ET rate has the same value as the frequency of the quantum oscillation. The maximum value of the ET rate is $J/2\hbar$. In the long-range electron transfer which is of primary importance in biological systems characteristic value $J/2\hbar \sim 10^9 \text{ s}^{-1}$ and typical value of λ is of the same order. The optimal dynamics of conformational variations for electron transfer can be achieved in the biological objects at some temperature which is the most proper for reaction rate.

For the sake of clarity we do not incorporate the interaction of tunneling electron with the bath of harmonic oscillator into our model. Such model can be realized in the systems where conformational transitions are present and the coupling of tunneling electron to vibrational modes of the environment is weak.

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