Effect of the conformational transitions on electron transfer in biological systems

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Abstract

The influence of the conformational changes in the system on the electron transfer (ET) is considered. In the present work it was assumed that the electron interacts with two baths. The influence of one bath is through the stochastic function $c(t)$ that characterizes the conformational changes of the system, and the other is a set of harmonic oscillators. The rate of ET was derived in the master equation approach. The solution of the generalized master equation for the gating processes was obtained. It was shown that the contribution to the temperature dependence of the rate constant that comes from electronic coupling could be dominant. The presented theory was used to provide an alternative elucidation of the cytochrome c oxidation in *Chromatium vinosum* photosynthetic bacteria.

1. Introduction

Electron transfer (ET) and atom or molecular transfer reactions play a central role in a variety of biological reactions. Understanding the mechanism of these reactions is of continuous interest [1–6]. It is by now well established that the proteins at room temperatures fluctuate around their average structure, and that these fluctuations have an important role in the protein function [7]. It has been suggested that protein fluctuations open pathways for molecular motion that are not available in the rigid proteins,

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by removing a steric hindrance or opening a gate [8]. It was shown in the works [9,10] that the biological ET reactions could be controlled by conformational transitions in ET complexes. The photosynthetic reaction centers are examples of systems, where ET may be influenced by the orientation of the reactants. In the bacterial reaction center the initial charge separation is not entirely vibrationally relaxed (rate of a picosecond or less), and the later states are not conformationally (pigments/proteins) relaxed prior to subsequent ET. A natural question that arises concerning the ET is the degree to which it can be influenced by the conformational changes of the protein. The temperature and detection-wavelength dependence of the rates of the primary ET reaction that was measured in Ref. [11] can reflect a distribution of reaction centers having differences in factors such as the distances or orientations between cofactors. The nonspherical structure of many biological redox components, as the molecules of bacteriochlorophyll and bacteriopheophytin in bacterial reaction centers, leads one to expect that the mutual orientation of the redox partners can significantly affect the rate of ET. It was shown in the works [12–14] that the electronic matrix elements that couple donor and acceptor states strongly depend on the mutual orientation between the cofactors. Thus, the transfer of electrons can be influenced by the transitions between the conformational states with different mutual donor–acceptor orientation [15].

A widely used approach describes the dissipative quantum system in terms of a stochastic Liouville equation [16–18]. The elimination of the bath degrees of freedom is performed by projection operator methods [19,20] or generalized cumulant expansions [21,22]. In this paper, we apply the projection operator methods and assume that the electron interacts with two baths. One acts through the stochastic function $c(t)$ that characterizes the conformational changes of the system, and the other is a set of harmonic oscillators. We assume that the vibrational modes have a sufficient time to relax to the equilibrium after each ET step. We consider the conformational changes independent on the electron localization. It means that we assume that the ET has a partially hot character.

2. Model

We start with a consideration of an ET system in which the electron has two accessible sites, embedded in a medium. We denote by $|j\rangle$ the state with electron localized at the jth site and $j = 1, 2$. The interaction of the solvent with the system depends on the electronic state $|j\rangle$ and we denote the medium Hamiltonian in the state $|j\rangle$ by H_j. The total model Hamiltonian for the system and medium is

$$H = H_0 + V \,, \tag{1}$$

where

$$H_0 = \sum_{j=1}^{2} |j\rangle [E_j + \varepsilon_j(c(t)) + H_j] \langle j| \,, \tag{2}$$

$$V = J(c(t))[|1\rangle\langle 2| + |1\rangle\langle 2|] \,, \tag{3}$$

where $E_1(E_2)$ is the site energy of the isolated donor (acceptor) molecule, and $\varepsilon_1(c(t))$ $\times (\varepsilon_2(c(t)))$ is a diagonal matrix element of the interaction Hamiltonian between the donor and acceptor molecules when the electron is localized on the donor (acceptor) and the system is in the conformational state $c(t)$. In the parameter $\varepsilon_1(c(t))(\varepsilon_2(c(t)))$, the electron interaction with the molecules of medium is also included when the electron is localized on donor (acceptor) molecule and the system is in the conformational state $c(t)$. $J(c(t))$ is the electronic coupling parameter and the Hamiltonian describing the reservoir consisting of harmonic oscillators is

$$H_j = \sum_{\alpha} \left\{ \frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 (x_\alpha - d_{j\alpha})^2 \right\} , \tag{4}$$

where, m_α and ω_α are the frequency and the mass of the αth oscillator, and $d_{j\alpha}$ is the equilibrium configuration of the αth oscillator when the system is in the electronic state $|j\rangle$.

Using the standard projection operator techniques [23–25], we can derive a generalized master equation for the populations

$$\partial_t P_1(t) = - \int_0^t W_{12}(t,\tau) P_1(\tau) \, d\tau + \int_0^t W_{21}(t,\tau) P_2(\tau) \, d\tau , \tag{5a}$$

$$\partial_t P_2(t) = - \int_0^t W_{21}(t,\tau) P_2(\tau) \, d\tau + \int_0^t W_{12}(t,\tau) P_1(\tau) \, d\tau , \tag{5b}$$

where

$$W_{12}(t,\tau) = \frac{2}{\hbar^2} Re \left\{ \langle Q(t,\tau) \rangle_{md} \exp \left[\frac{i(E_1 - E_2)}{\hbar}(t-\tau) \right] \right.$$

$$\left. \times \exp \left\{ \sum_{\alpha} \frac{E_{12}^\alpha}{\hbar \omega_\alpha} [(\bar{n}_\alpha + 1)e^{-i\omega_\alpha(t-\tau)} + \bar{n}_\alpha e^{i\omega_\alpha(t-\tau)} - (2\bar{n}_\alpha + 1)] \right\} \right\} , \tag{6a}$$

$$W_{21}(t,\tau) = \frac{2}{\hbar^2} Re \left\{ \langle Q(t,\tau) \rangle_{md} \exp \left[\frac{i(E_1 - E_2)}{\hbar}(t-\tau) \right] \right.$$

$$\left. \times \exp \left\{ \sum_{\alpha} \frac{E_{12}^\alpha}{\hbar \omega_\alpha} [(\bar{n}_\alpha + 1)e^{i\omega_\alpha(t-\tau)} + \bar{n}_\alpha e^{-i\omega_\alpha(t-\tau)} - (2\bar{n}_\alpha + 1)] \right\} \right\} , \tag{6b}$$

where, $\bar{n}_\alpha = [\exp(\hbar \omega_\alpha / k_B T) - 1]^{-1}$ is the thermal population of the αth mode,

$$E_{12}^\alpha = \tfrac{1}{2} m_\alpha \omega_\alpha^2 (d_{1\alpha} - d_{2\alpha})^2 \tag{7}$$

is the reorganization energy of the αth mode when the system transfers from state $|1\rangle$ to state $|2\rangle$, and

$$Q(t,\tau) = J(c(t)) \exp \left[\frac{i}{\hbar} \int_\tau^t \Delta(c(t_1)) \, dt_1 \right] J(c(\tau)) , \tag{8}$$

where $\Delta(c(t)) = \varepsilon_1(c(t)) - \varepsilon_2(c(t))$. In the derivation of Eq. (5) the projector operator D was used in the form

$$DB = \sum_{j=1}^{2} \langle Tr(|j\rangle\langle j|B)\rangle_{md}\rho_j|j\rangle\langle j| \,, \tag{9}$$

where ρ_j is the equilibrium medium density matrix in the state $|j\rangle$,

$$\rho_j = \exp(-H_j/k_BT)/Tr^Q\{\exp(-H_j/k_BT)\} \,.$$

The bracket $\langle\rangle_{md}$ is the ensemble average over all possible realizations of $c(t)$. By definition, $Tr \equiv Tr^e Tr^Q$ where Tr^e, Tr^Q are the partial traces over the ET system and the medium, respectively.

3. Conformational transitions

Now, we define the transitions between conformational states of the system. We assume that there exist two conformational states A and B with the free energies E_a and E_b. The transfer between these two states is characterized by the random function $c(t)$ that takes on any of two values which we denote by a, b. This process is defined by the differential equation for conditional probabilities,

$$\partial_t P(a,t|y,t_0) = -\lambda P(a,t|y,t_0) + \mu P(b,t|y,t_0) \,, \tag{10a}$$

$$\partial_t P(b,t|y,t_0) = \lambda P(a,t|y,t_0) - \mu P(b,t|y,t_0) \tag{10b}$$

and the initial conditions

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

Here, λ is the transition rate from the state A to the state B and μ is the transition rate from B to A. We suppose that these two parameters do not depend on the localization of the electron. Using the Kramers model of the description of protein conformational dynamics, we have [26,27]

$$\lambda = \frac{\Omega_a}{2\pi} \exp\left[-\frac{U}{k_bT}\right] \,, \tag{11a}$$

$$\mu = \frac{\Omega_b}{2\pi} \exp\left[-\frac{U + E_a - E_b}{k_bT}\right] \,, \tag{11b}$$

where $\Omega_a(\Omega_b)$ is the well frequency of the conformational state A(B), and U is an activation energy. The stationary solutions of Eq. (10) are

$$P(a) = \frac{\mu}{\lambda + \mu}, \quad P(b) = \frac{\lambda}{\lambda + \mu} \,. \tag{12}$$

The solution of Eq. (10) that characterizes the conformational transitions will be used below in the derivation of the rate constants.

4. One-mode approximation

For the sake of simplicity, we assume that the bath can be described by one-vibrational mode. In this approximation we have

$$
W_{12}(t,\tau) = \frac{2}{\hbar^2} Re \left\{ \langle Q(t,\tau) \rangle_{md} e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{q/2} I_q(2S\sqrt{\bar{n}(\bar{n}+1)}) \right.
$$

$$
\times \left. \exp\left[\frac{i}{\hbar}(\varepsilon_0 - q\omega)(t-\tau) \right] \right\} , \tag{13a}
$$

$$
W_{21}(t,\tau) = \frac{2}{\hbar^2} Re \left\{ \langle Q(t,\tau) \rangle_{md} e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n}+1}{\bar{n}} \right)^{q/2} I_q(2S\sqrt{\bar{n}(\bar{n}+1)}) \right.
$$

$$
\times \left. \exp\left[\frac{i}{\hbar}(\varepsilon_0 + q\omega)(t-\tau) \right] \right\} , \tag{13b}
$$

where $\varepsilon_0 = E_1 - E_2$, $S = m\omega(d_1 - d_2)^2/2\hbar$ and I_q is the modified Bessel function. Generally, the expression for $\langle Q(t,\tau) \rangle_{md}$ is cumbersome so that we present some limiting cases. We assume without loss of generality that $\Delta(a) \geqslant \Delta(b)$ and $\lambda \geqslant \mu$.

4.1. Slow-modulation limit

We first examine the slow-modulation limit. In this limit, we assume that the condition $\hbar(\lambda + \mu) \ll \Delta(a) - \Delta(b)$ is fulfilled. Using the solution of Eq. (10) we get [28]

$$
\langle Q(t,\tau) \rangle_{md} = P(a)J(a)^2 \exp\left[\frac{i}{\hbar} \Delta(a)(t-\tau) - \lambda(t-\tau) \right]
$$

$$
+ P(b)J(b)^2 \exp\left[\frac{i}{\hbar} \Delta(b)(t-\tau) - \mu(t-\tau) \right] . \tag{14}
$$

Assuming that the Markovian approximation can be used the integro-differential equations (5) can be changed to the master equations

$$
\partial_t P_1(t) = -\Gamma_{1\to2}P_1(t) + \Gamma_{2\to1}P_2(t) , \tag{15a}
$$

$$
\partial_t P_2(t) = -\Gamma_{2\to1}P_2(t) + \Gamma_{1\to2}P_1(t) \tag{15b}
$$

with the rate constants

$$
\Gamma_{i\to j} = \int_0^{\infty} W_{ij}(t)\, dt .
$$

Assuming that at the initial time the electron is localized at site 1, Eq. (15) can be easily solved to give

$$P_1(t) = \frac{\Gamma_{2\to 1}}{\Gamma_{1\to 2} + \Gamma_{2\to 1}} + \frac{\Gamma_{1\to 2}}{\Gamma_{1\to 2} + \Gamma_{2\to 1}} \exp\{-[\Gamma_{1\to 2} + \Gamma_{2\to 1}]t\} , \tag{16a}$$

$$P_2(t) = 1 - P_1(t) . \tag{16b}$$

In the slow-modulation limit we have

$$\Gamma_{\substack{1\to 2 \\ (2\to 1)}} = P(a)J(a)^2 e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{q/2} I_q(2S\sqrt{\bar{n}(\bar{n}+1)})$$

$$\times \frac{2\lambda/\hbar^2}{(\omega_a \mp q\omega)^2 + \lambda^2}$$

$$+ P(b)J(b)^2 e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty} \left(\frac{\bar{n}+1}{\bar{n}}\right)^{q/2} I_q(2S\sqrt{\bar{n}(\bar{n}+1)})$$

$$\times \frac{2\mu/\hbar^2}{(\omega_b \mp q\omega)^2 + \mu^2} , \tag{17}$$

where $\hbar\omega_a = \varepsilon_0 + \Delta(a)$ and $\hbar\omega_b = \varepsilon_0 + \Delta(b)$. In the high-frequency mode approximation where we assume that the condition $\omega \gg \lambda, \mu$ is fulfilled, we get

$$\Gamma_{\substack{1\to 2 \\ (2\to 1)}} = \frac{2\pi}{\hbar^2\omega} e^{-S(2\bar{n}+1)} \left[P(a)J(a)^2 \left(\frac{\bar{n}+1}{\bar{n}}\right)^{\pm q_a/2} I_{q_a}(2S\sqrt{\bar{n}(\bar{n}+1)}) \right.$$

$$\left. + P(b)J(b)^2 \left(\frac{\bar{n}+1}{\bar{n}}\right)^{\pm q_b/2} I_{q_b}(2S\sqrt{\bar{n}(\bar{n}+1)}) \right] , \tag{18}$$

where $q_a = \omega_a/\omega$ and $q_b = \omega_b/\omega$. In the derivation of (18) from (17) it was used that

$$\frac{2\alpha/\hbar^2}{(\omega_b \mp q\omega)^2 + \alpha^2} = \frac{2}{\hbar^2\omega} \frac{\alpha/\omega}{(\omega_b/\omega \mp q)^2 + (\alpha/\omega)^2} \to \frac{2\pi}{\hbar^2\omega} \delta\left(\frac{\omega_b}{\omega} \mp q\right) \tag{19}$$

for $\alpha/\omega \ll 1$. When we also assume that $\hbar\omega \gg k_B T$ we have

$$\Gamma_{1\to 2} = P(a) \frac{2\pi J(a)^2}{\hbar^2\omega} e^{-S} S^{q_a} \frac{1}{q_a!} + P(b) \frac{2\pi J(b)^2}{\hbar^2\omega} e^{-S} S^{q_b} \frac{1}{q_b!} , \tag{20a}$$

$$\Gamma_{2\to 1} = P(a) \exp\left[-\frac{\hbar\omega_a}{k_B T}\right] \frac{2\pi J(a)^2}{\hbar^2\omega} e^{-S} S^{q_a} \frac{1}{q_a!}$$

$$+ P(b) \exp\left[-\frac{\hbar\omega_b}{k_B T}\right] \frac{2\pi J(b)^2}{\hbar^2\omega} e^{-S} S^{q_b} \frac{1}{q_b!} . \tag{20b}$$

In this approximation the temperature dependence of the rate constant is fully determined by the conformational transitions.

4.2. High-modulation limit

Now, we examine the high-modulation limit where we assume that the condition $\hbar(\lambda + \mu) \gg \Delta(a) - \Delta(b)$ is fulfilled. We have [28]

$$\langle Q(t,\tau)\rangle_{md} = [P(a)J(a) + P(b)J(b)]^2 \exp[i\varpi(t-\tau) - \Theta(t-\tau)]$$

$$+ P(a)P(b)[J(a) - J(b)]^2 \exp[i\varpi(t-\tau) - (\lambda+\mu)(t-\tau)], \quad (21)$$

where $\varpi = (\Delta(a) + \Delta(b))/2\hbar$ and

$$\Theta = \frac{[\Delta(a) - \Delta(b)]^2}{4\hbar^2(\lambda+\mu)}\left[1 - \left(\frac{\lambda-\mu}{\lambda+\mu}\right)^2\right]. \quad (22)$$

In the Markovian approximation we get the rate constants in the form

$$\Gamma_{\substack{1\to 2\\(2\to 1)}} = [P(a)J(a) + P(b)J(b)]^2 e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty}\left(\frac{\bar{n}+1}{\bar{n}}\right)^{q/2}$$

$$\times I_q(2S\sqrt{\bar{n}(\bar{n}+1)})\frac{2\Theta/\hbar^2}{(\Omega \mp q\omega)^2 + \Theta^2}$$

$$+ P(a)P(b)[J(a) - J(b)]^2 e^{-S(2\bar{n}+1)} \sum_{q=-\infty}^{\infty}\left(\frac{\bar{n}+1}{\bar{n}}\right)^{q/2}$$

$$\times I_q(2S\sqrt{\bar{n}(\bar{n}+1)})\frac{2(\lambda+\mu)/\hbar^2}{(\Omega \mp q\omega)^2 + (\lambda+\mu)^2}, \quad (23)$$

where $\Omega = \varepsilon_0/\hbar + \varpi$. Assuming that $\omega \gg \lambda + \mu$ we get

$$\Gamma_{\substack{1\to 2\\(2\to 1)}} = \frac{2\pi}{\hbar^2\omega}[P(a)J(a)^2 + P(b)J(b)^2]e^{-S(2\bar{n}+1)}\left(\frac{\bar{n}+1}{\bar{n}}\right)^{\pm p/2}$$

$$\times I_p(2S\sqrt{\bar{n}(\bar{n}+1)}), \quad (24)$$

where $p = \Omega/\omega$. If $J(a) = J(b) = J$ we get

$$\Gamma_{\substack{1\to 2\\(2\to 1)}} = \frac{2\pi J^2}{\hbar^2\omega}e^{-S(2\bar{n}+1)}\left(\frac{\bar{n}+1}{\bar{n}}\right)^{\pm p/2} I_p(2S\sqrt{\bar{n}(\bar{n}+1)}). \quad (25)$$

This form of the rate constant was used to elucidate the cytochrome c oxidation in *Chromatium vinosum* photosynthetic bacteria in earlier works [29,30] and can be directly derived using Eqs. (13) and (21) in the case when $J(a)=J(b)$ and $\Delta(a)=\Delta(b)$. In this case, the electron does not feel the transitions between conformational states.

5. Application to reaction centers

Several mechanisms have been advanced to elucidate the ET from cytochrome c to the special pair of bacteriochlorophylls in the reaction center of the *Chromatium vinosum* photosynthetic bacteria [31]. The dominant interpretation has been given in

terms of vibronic coupling [29]. In the works [30] it has been proposed that the temperature dependence of the cytochrome c oxidation is due to two parallel ET processes from two distinct hemes of the cytochrome c. In this paper we consider, similarly as in the work [10], an alternative mechanism based on the conformational control of the ET. To elucidate the ET from cytochrome c to special pair we used the formula (20a) that can be expressed in the form

$$k(T) = \frac{\exp[-F/k_B T]}{1 + \exp[-F/k_B T]} k_A + \frac{1}{1 + \exp[-F/k_B T]} k_B , \tag{26}$$

where $F = E_a - E_b$ is the free energy difference between the conformational states A and B. It was assumed that $\Omega_a = \Omega_b$ and

$$k_A = \frac{2\pi J(a)^2}{\hbar^2 \omega} \exp[-S] S^{q_a} \frac{1}{q_a!} , \tag{27a}$$

$$k_A = \frac{2\pi J(b)^2}{\hbar^2 \omega} \exp[-S] S^{q_b} \frac{1}{q_b!} . \tag{27b}$$

Using the parameters $F = 1210$ cm^{-1} (0.15 eV), $\hbar\omega = 1000$ cm^{-1}, $E_r = S\hbar\omega = 2500$ cm^{-1}, $J(a) = 0.9$ cm^{-1}, $J(b) = 1.1 \times 10^{-3}$ cm^{-1}, $\hbar\omega_a = 2000$ cm^{-1}, and $\hbar\omega_b = 1000$ cm^{-1}, we get $k_A = 2.46 \times 10^8$ s^{-1} and $k_B = 2.94 \times 10^2$ s^{-1}. It was shown in the work [10] that $k(T)$ with such k_A, k_B and F fits very well the observed dependence of the ET rate constant on the temperature in the reaction center of *Chromatium vinosum* bacteria.

Because of the nonspherical structure of hemes and chlorophylls the mutual orientation of redox partners can significantly affect the rate of the ET. In the works [12,13] it was shown that relatively small changes in the mutual orientation of the planar molecules have a strong effect on the electronic coupling parameters and can practically stop the ET. It was assumed in the present article that the ET from cytochrome c to the special pair belongs to the so-called gated reactions. Because of fluctuations in the conformational states we assume that there is a small probability of ET in the case when the gate is closed. Thus, in the computations small values of $J(b)$ in comparison to $J(a)$ have been used.

6. Discussion

We have chosen a simple model to interpret the cytochrome c oxidation. The presented theory gives several possibilities how to explain this experiment. For instance, the incorporation of conformational changes to the theories previously used to elucidate this problem. To do this it must be first solved the problem related to the Markovian approximation. Up to now, it was assumed that the Markovian approximation can be used and the generalized master equations defined by Eq. (5) can be changed to the ordinary rate equation (15) where the dynamics of the system is determined by the rate constants. To justify this change it has to be shown that the memory

kernels $W_{ij}(t, \tau)$ in Eq. (5) fulfill certain conditions. Specifically, it has to be shown that the memory kernels damp very quickly in comparison with the relaxation of the system to the steady state [32,33]. It means for example that in the slow modulation limit roughly saying the conditions $\lambda, \mu \gg \sqrt{P(a)J(a)}/\hbar$ and $\sqrt{P(b)J(b)}/\hbar$ must be fulfilled. Here λ and μ characterize the loss of memory and $\sqrt{P(a)J(a)}/\hbar$ and $\sqrt{P(b)J(b)}/\hbar$ characterize the "coherent propagation". It can be true in the high-temperature regime but generally at low temperature it is not fulfilled. In the case of *Chromatium vinosum* bacteria where we assume a strong decrease of coherent propagation with the decrease of the temperature, the Markovian approximation can be used also at relatively low temperatures (λ, μ can decrease 3 orders of magnitude with decreasing the temperature and Markovian approximation still can be used). We now come to the other problem: whether the Markovian approximation can be used in the case when the one mode approximation is used to describe the bath. In the case when it is impossible, Eq. (5) cannot be changed to the ordinary rate equation (15) and generally the relaxation of the system to the steady state has a nonexponential character. It is not easy to find the analytical solution of Eq. (5). In the relatively simple case when we assume that the ET has a gating character with $J(a) = J$, $J(b) = 0$, $E_{12}^{\alpha} = 0$, and when the conditions $\omega_a^2 \gg J^2/\hbar^2, \lambda^2$ are fulfilled, the solution of the generalized master equation (5) at the slow modulation limit has the form

$$P_1(t) = \frac{1}{2} + \frac{\hbar^2 \omega_a^2}{2(\hbar^2 \omega_a^2 + 4P(a)J^2)} \exp\left[-4P(a)\frac{J^2 \lambda}{\hbar^2 \omega_a^2} t\right]$$

$$+ \frac{4P(a)J^2}{2(\hbar^2 \omega_a^2 + 4P(a)J^2)} \exp[-\lambda t] \cos[\omega_a t] \tag{28}$$

and $P_2(t) = 1 - P_1(t)$. This equation describes the occupation probability which dominant part is damped with the slow rate $k_1 = 4P(a)J^2\lambda/\hbar^2\omega_a^2$. The minor part is damping with the rate $k_2 = \lambda$ and oscillates with the frequency ω_a. The result is similar to that obtained in the earlier study [34].

7. Conclusions

We have studied the ET in the system with two conformational states. The contribution to the temperature dependence of the rate constant from the electronic factor due to conformational transitions was first analytically computed in the works [35,36]. Usually this contribution is not taken into account explicitly when the temperature dependence of the ET rate is elucidated in the biological systems. The main purpose of the application of the present theory to the cytochrome c oxidation is to show that the conformational dynamics can play important role and the contribution to the temperature dependence of the rate constant that comes from the electronic couplings could be dominant at some specific condition.

It was assumed in the present work that the electron interacts with two baths. The first bath is a set of harmonic oscillators. The influence of another bath is through the stochastic function $c(t)$. In regard to this bath the ET has the hot character. The set of harmonic oscillator causes that the Gibbs–Boltzmann equilibrium is obtained

at long times and $P_1(\infty)/P_2(\infty) = \Gamma_{2\to1}/\Gamma_{1\to2} = \exp[-\Delta E/k_B T]$, where ΔE is the reaction heat. The second bath determines $P_1(\infty)/P_2(\infty) = 1$. Except these two limiting cases the behavior of $P_i(t)$ depends on parameters that determine the intensity of the interaction of the electron with these two baths. The equilibrium distribution between reactants and products is also a result of the coupling of the electron with both baths and generally is shifted from the Gibbs–Boltzmann equilibrium in the presence of conformational changes of the system.

It was shown that the presented theory could provide an alternative elucidation of the ET between cytochrome *c* and the special pair of bacteriochlorophylls in the reaction center of *Chromatium vinosum* bacteria. To get the more realistic description of charge transfer processes at low temperature in the system with conformational transitions, we need to find the solution of the generalized master equation (5) at the more general case, as is described by the expression (28). In this case, similarly to (28), the ET cannot be described by the single rate constant.

Acknowledgements

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