

Dynamic effects in long-distance biological electron transfer reactions

Emile S. Medvedev[†] and Alexei A. Stuchebrukhov
Department of Chemistry, University of California,
Davis, CA 95616

[†]Institute of Chemical Physics Problems, Russian Academy of Sciences
142432 Chernogolovka, Moscow, Russia

Abstract

A general expression for the rate of bridge mediated electron transfer reaction is derived which takes into account effects of nuclear dynamics of donor and acceptor complexes as well as those of the bridge. The theory includes treatment of a non-Born-Oppenheimer effect specific for a long distance electron transfer. The derived expression for the rate is designed for applications in numerical studies of long range electron transfer reactions in proteins.

1 Introduction

Recent experimental measurements of the rates of long-range electron transfer (ET) reactions in proteins by Dutton and Gray and co-workers [1]-[4] and their debate of the role of the protein medium in biological electron transfer have prompted an active development of general theory and computer simulations of such reactions [5]. In this paper we continue our analysis [6], [7] of the role of the dynamics of the protein medium and other nuclear dynamic effects in biological electron transfer reactions.

Usually, long-range electron transfer reactions are discussed within the framework of general non-adiabatic theory developed originally for "short-range" reactions [8], [9]. In this theory the reaction rate is described by the well known semi-classical expression:

$$k = \frac{2\pi}{\hbar} |T_{DA}|^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp \left[-\frac{(\lambda + \Delta G^0)^2}{4\lambda k_B T} \right]. \quad (1.1)$$

Here λ and ΔG^0 are the standard reorganization energy and driving force of the reaction, and T_{DA} is the coupling of the initial and final electronic states. When applied to long-range reactions this coupling is treated as an effective one, arising due to the presence of the atoms of the protein medium in between the redox centers. These atoms, or the bridge, provide intermediate virtual states for superexchange coupling which make a long-range electronic communication between redox centers possible [10], [11].

The above expression assumes that electron transfer occurs as a single thermally assisted tunneling jump, when the two electronic states on the donor (D) and acceptor (A) complexes become resonant in the course of thermal fluctuations. The factor $|T_{DA}|/\hbar$ in the above expression can be interpreted as the transfer rate at the transition state, and the rest of the expression gives simply the fraction of the molecules at the transition state. (The distribution of the energy difference between D and A states is Gaussian, and the transition state in this formulation is a state in which the two levels are within $\pm\pi|T_{DA}|$ from each other).

*Lecture presented at the 17th IUPAC Symposium on Photochemistry, Sitges, Barcelona, Spain, 19–24 July 1998. Other presentations are published in this issue, pp. 2147–2232.

In such a formulation the long-distance reactions conceptually do not seem to be much different from any other short-range non-adiabatic reactions. The only modification is that T_{DA} now depends on the D-A separation. One can question, however, the limits of the applicability of Eq. (1.1) to long-range reactions on the grounds that the dynamics of the bridge atoms (i.e., atoms of the protein medium) are not taken into account in it. Furthermore, the above formulation includes some tacit assumptions, which are valid for short-range reactions but are hard to justify for long-range ET. The assumptions of Eq. (1.1) are as follows.

a) The transfer matrix element T_{DA} in a short-range theory is assumed to be some constant independent of the configuration of the system (the Condon approximation). In reactions in proteins, however, electronic coupling T_{DA} is due to quantum mechanical tunneling and therefore T_{DA} strongly depends on the configuration of the protein medium between D and A, as well as on the tunneling energy. In the course of thermal fluctuations, the structure of the protein medium constantly changes, and the D and A levels cross at different energies. That is the transition state of the reaction is not uniquely defined. T_{DA} , therefore, should be expected to be some function of the tunneling energy, as well as configuration of the protein medium. These effects should be taken into account in a more detailed theory.

In our previous work [6], [7], we have shown that dynamics of the atoms in the protein medium result in modification of the conventional theory, in which the possibility of inelastic tunneling, i.e., the energy exchange between the tunneling electron and the protein matrix, is taken into account.

b) The Frank-Condon factors of the quantum vibrational modes of D and A complexes should be included in the rate expression when applied to reactions in proteins. These are so-called quantum nuclear effects (see, e.g., [9]) in ET. In principle, it is not difficult to make appropriate adjustments in Eq. (1.1) since the standard short-range quantum non-adiabatic theory does include these factors. In long-range transfer, however, the quantum nuclear effects, as we will show, are coupled to variations of electron tunneling energy and therefore a modified treatment is needed.

c) Finally, a usual way of evaluating the transfer matrix element T_{DA} in the above expression involves the Born-Oppenheimer (BO) approximation. Again, although this is a valid assumption for small molecular systems, for a long-range ET system this may not be so. The transfer matrix element in this case is defined by a weak overlap of the exponentially small tunneling tails of electronic D and A wave functions, in the region far from both D and A molecular complexes. It has been shown earlier [12]-[15] that in the asymptotic region of the electronic wave functions, the BO approximation breaks down. Although it is difficult to give an exact estimate, for a specific protein, of the largest distance within which the BO approximation holds, it is clear that since there is a finite speed of propagation of the local perturbation of the electronic wave function¹ the electrons will follow the motion of the nuclei of D/A complexes adiabatically only within a certain finite distance from the complexes. Beyond this distance the BO approximation is not applicable.

Another argument which leads to the same conclusion, is that within the BO approximation one neglects the non-adiabatic perturbation which results in a small (if electronic terms are well separated) mixing of different electronic states. At the redox sites, i.e., in the core region where the wave function is large (i.e., of the order of unity in atomic units) these corrections are much smaller than the wave function itself and can be safely neglected. However, in the asymptotic region, where the wave function is extremely small, the non-adiabatic corrections can be comparable or even larger than the BO wave function itself.

¹ A rough estimate would be one interatomic distance, i.e., one to two angstroms, per $\tau = \hbar/V$ where V , of the order of an eV, is the typical interaction energy. This estimate gives 3Å/fs.

It is clear from the above remarks, that long-distance reactions are, in fact, conceptually quite different and much more complex than the short-range ones. Unfortunately it is not known how strongly, in general, experimental rates actually deviate from the prediction of Eq. (1.1), since *independent* measurements of the electronic coupling, reorganization energy, and the driving force are not available. On the other hand, it is well known that in proteins it is very difficult to observe the inverted region predicted by Eq. (1.1) [16].

In this paper, we further develop our analysis of the dynamic effects published earlier [6], [7], and present a formulation of the theory of ET rate that addresses the questions mentioned above. We derive an expression for the rate which takes into account both the dependence of the electronic matrix element T_{DA} on the nuclear coordinates of the D and A complexes, and those of the bridge, as well as its dependence on the tunneling energy. We show that the problem of a possible breakdown of the BO approximation can be avoided if a special vibronic basis set is used. In this basis the tunneling energy is not a definite quantity, but rather has a distribution of possible values which are defined by the Frank-Condon factors of D and A complexes.

Although the factors described above have been discussed to some extent in the literature before, no suitable expression for the rate of the reaction that could be used in a numerical analysis has been published. Our goal here is to derive an expression that would be specifically useful for numerical applications. Our general formula is based on the assumption that the electronic coupling matrix element T_{DA} can be evaluated as a function of nuclear coordinates of the system around its equilibrium configuration, and for different tunneling energies. Other ingredients of the new expression are various Frank-Condon factors, standard free energy, classical reorganization energy, and the spectrum of vibrational modes of the protein matrix.

2 The Rate of Long-Range Electron Transfer

2.1 Hamiltonian and the transfer amplitude

We begin with a description of the Hamiltonian of the system and the zeroth-order states used in the calculation.

The full microscopic Hamiltonian including nuclei is

$$H(r, q_d, q_b, q_a) = K_e(r) + V_d(r, q_d) + V_b(r, q_b) + V_a(r, q_a) + H_{nucl}(q_d, q_b, q_a), \quad (2.1)$$

where the terms are: the kinetic energy of the electron, the potential at the donor, bridge, and acceptor sites (these potentials depend on the electronic coordinate r and nuclear coordinates of the respective complexes), and H_{nucl} is the Hamiltonian of free donor, bridge, and acceptor vibrations.

We introduce two sets of exact electronic-vibrational states. The energies and wavefunctions of the states *localized* at donor, bridge, and acceptor, respectively, satisfy the following equations:

$$(K_e + V_d + H_{nucl} - E_i^{(0)}) |i^{(0)}\rangle = 0, \quad (2.2)$$

$$(K_e + V_b + H_{nucl} - E_p^{(0)}) |p^{(0)}\rangle = 0, \quad (2.3)$$

$$(K_e + V_a + H_{nucl} - E_f^{(0)}) |f^{(0)}\rangle = 0. \quad (2.4)$$

The superscript (0) means that these are the zeroth-order states for the perturbation treatment. The second set represents *delocalized* states. For these states we have

$$(K_e + V_d + V_b + H_{nucl} - E_i) |i\rangle = 0, \quad (2.5)$$

$$(K_e + V_b + V_a + H_{nucl} - E_f) |f\rangle = 0, \quad (2.6)$$

where $|i\rangle$ is close to $|i^{(0)}\rangle$ at the D site but, unlike $|i^{(0)}\rangle$, has a long tail over the bridge. Using Eqs. (2.1), (2.5), and (2.6) we obtain the following exact relation:

$$\begin{aligned} \langle i | H | f \rangle &= \langle i | K_e + V_d + V_b + V_a + H_{nucl} | f \rangle \\ &= E_f \langle i | f \rangle + \langle i | V_d | f \rangle \equiv E_i \langle i | f \rangle + \langle i | V_a | f \rangle. \end{aligned} \quad (2.7)$$

For transitions between resonant delocalized states, $E_i = E_f$, we obtain

$$\langle i | V_d | f \rangle = \langle i | V_a | f \rangle \equiv T_{if}(E_i), \quad (2.8)$$

where $T_{if}(E_i)$ is the full electronic-vibrational (vibronic) transition amplitude.

We will solve Eqs. (2.5) and (2.6) perturbatively. Up to the first order the energies and wavefunctions are

$$E_i = E_i^{(0)}, \quad |i\rangle = |i^{(0)}\rangle + \sum_p \frac{\langle p^{(0)} | V_b | i^{(0)} \rangle}{E_i^{(0)} - E_p^{(0)}} |p^{(0)}\rangle, \quad (2.9)$$

and similarly for $|f\rangle$. The transition amplitude (2.8) becomes

$$T_{if}(E_i) = \sum_p \left\{ \frac{\langle i^{(0)} | V_b | p^{(0)} \rangle \langle p^{(0)} | V_d | f^{(0)} \rangle}{E_i^{(0)} - E_p^{(0)}} + \frac{\langle i^{(0)} | V_d | p^{(0)} \rangle \langle p^{(0)} | V_b | f^{(0)} \rangle}{E_f^{(0)} - E_p^{(0)}} \right\}. \quad (2.10)$$

Here, the first term with $\langle p^{(0)} | V_d | f^{(0)} \rangle$ is negligible since V_d is localized on D where $|f^{(0)}\rangle$ vanishes. In Eq. (2.10) one can substitute V_a for V_d according to Eq. (2.8), in which case the second term will be small by a similar reason. Taking into account that $E_i^{(0)} = E_i = E_f = E_f^{(0)}$, we obtain the transition amplitude in two equivalent forms

$$T_{if}(E_i^{(0)}) = \sum_p \frac{\langle i^{(0)} | V_d | p^{(0)} \rangle \langle p^{(0)} | V_b | f^{(0)} \rangle}{E_i^{(0)} - E_p^{(0)}} = \sum_p \frac{\langle i^{(0)} | V_b | p^{(0)} \rangle \langle p^{(0)} | V_a | f^{(0)} \rangle}{E_i^{(0)} - E_p^{(0)}}. \quad (2.11)$$

Now, we introduce explicit expressions for the zeroth-order functions. The localized D function is written in the form

$$\begin{aligned} |i^{(0)}\rangle &= |d\rangle |dm'_i\rangle |bk_i\rangle |an_i\rangle \equiv |d; dm'_i, bk_i, an_i\rangle \\ &\equiv \varphi_d(r, q_d) \chi_{dm'_i}(q_d - \delta_d) \chi_{bk_i}(q_b) \chi_{an_i}(q_a). \end{aligned} \quad (2.12)$$

Here, the electron is localized on D, its coupling with the D vibrations is strong, and therefore the D wavefunction is written in the BO representation as a product of a purely electronic part φ and a vibrational function χ_d with a shifted equilibrium position of the nuclear coordinates by δ_d . The coupling with the bridge and acceptor vibrations in this zeroth-order state is small. Therefore, the electronic wave function does not depend on their coordinates, and the respective vibrational functions, χ_b and χ_a , are not shifted from the equilibrium positions $q_b = q_a = 0$. In Eq. (2.12) and on, the prime labels quantum numbers of vibrations with shifted equilibrium positions due to the electron-phonon coupling. In a similar manner we obtain the zeroth-order functions localized on bridge and acceptor, respectively,

$$\begin{aligned} |p^{(0)}\rangle &= |b\alpha\rangle |dm\rangle |b\alpha k'\rangle |an\rangle \equiv |b\alpha; dm, b\alpha k', an\rangle \\ &\equiv \varphi_{b\alpha}(r, q_b) \chi_{dm}(q_d) \chi_{b\alpha k'}(q_b - \delta_{b\alpha}) \chi_{an}(q_a), \end{aligned} \quad (2.13)$$

$$\begin{aligned} |f^{(0)}\rangle &= |a\rangle |dm_f\rangle |bk_f\rangle |an'_f\rangle \equiv |a; dm_f, bk_f, an'_f\rangle \\ &\equiv \varphi_a(r, q_a) \chi_{dm_f}(q_d) \chi_{bk_f}(q_b) \chi_{an'_f}(q_a - \delta_a). \end{aligned} \quad (2.14)$$

In Eqs. (2.12)-(2.14) subscript i refers to the initial quantum numbers (electron is on the D) and f to the numbers of the final states (electron is on A) whereas numbers with no subscript refer to the virtual states (electron is on the bridge); α labels the electronic states of the bridge. The energies of these states are

$$E_i^{(0)} = J_d + \varepsilon_{dm'_i} + \varepsilon_{bk_i} + \varepsilon_{an_i}, \quad (2.15)$$

$$E_p^{(0)} = J_{b\alpha} + \varepsilon_{dm} + \varepsilon_{b\alpha k'} + \varepsilon_{an}, \quad (2.16)$$

$$E_f^{(0)} = J_a + \varepsilon_{dm_f} + \varepsilon_{bk_f} + \varepsilon_{an'_f}, \quad (2.17)$$

where J 's and ε 's stand for electronic and vibrational energies, respectively. The electronic energies $J_{d,b\alpha,a}$ are the minima of the corresponding adiabatic potentials.

Next, the wavefunctions (2.12)-(2.14) are to be inserted into Eq. (2.11) and integrated over the electronic coordinates. Let us introduce the following notations for electronic matrix elements as functions of vibrational coordinates:

$$V_{d,b\alpha}^d(q_d, q_b) \equiv \langle d | V_d | b\alpha \rangle = \int \varphi_d(r, q_d) V_d(r, q_d) \varphi_{b\alpha}(r, q_b) dr, \quad (2.18)$$

and similarly for $V_{d,b\alpha}^b(q_d, q_b)$ by replacing V_d with V_b ; and

$$V_{b\alpha,a}^b(q_b, q_a) \equiv \langle b\alpha | V_b | a \rangle = \int \varphi_{b\alpha}(r, q_b) V_b(r, q_b) \varphi_a(r, q_a) dr, \quad (2.19)$$

and similarly for $V_{b\alpha,a}^a(q_b, q_a)$ by replacing V_b with V_a . These matrix elements are functions of nuclear coordinates. (Yet, sometimes we will omit their arguments to shorten the notations). With the use of the above definitions, the matrix elements in Eq. (2.11) become

$$\begin{aligned} \langle i^{(0)} | V_d | p^{(0)} \rangle &= \langle dm'_i, bk_i, an_i | V_{d,b\alpha}^d(q_d, q_b) | dm, b\alpha k', an \rangle \\ &= \langle dm'_i, bk_i | V_{d,b\alpha}^d(q_d, q_b) | dm, b\alpha k' \rangle \delta_{n_i n}, \end{aligned} \quad (2.20)$$

$$\begin{aligned} \langle p^{(0)} | V_b | f^{(0)} \rangle &= \langle dm, b\alpha k', an | V_{b\alpha,a}^b(q_b, q_a) | dm_f, bk_f, an'_f \rangle \\ &= \langle b\alpha k', an | V_{b\alpha,a}^b(q_b, q_a) | bk_f, an'_f \rangle \delta_{mm_f}, \end{aligned} \quad (2.21)$$

and similar expressions are obtained for other matrix elements entering Eq. (2.11).

In Eq. (2.11) the summation is over $p = \alpha m k' n$. With the use of Eqs. (2.20) and (2.21), the first equality in Eq. (2.11) for the transition amplitude is recast as

$$T_{if}(E_i^{(0)}) = \sum_{\alpha k'} \frac{\langle dm'_i, bk_i | V_{d,b\alpha}^d | dm_f, b\alpha k' \rangle \langle b\alpha k', an_i | V_{b\alpha,a}^b | bk_f, an'_f \rangle}{J_d + \varepsilon_{dm'_i} + \varepsilon_{bk_i} - J_{b\alpha} - \varepsilon_{dm_f} - \varepsilon_{b\alpha k'}}. \quad (2.22)$$

Further, we assume that the change of vibrational energy of the bridge is small compared to the electronic energy difference, $|J_d - J_{b\alpha}| \gg |\varepsilon_{b\alpha k'} - \varepsilon_{bk_i}|$, and we replace $\varepsilon_{b\alpha k'} - \varepsilon_{bk_i}$ with an average vibrational energy change of the bridge, $\overline{\Delta\varepsilon_b}$. This assumption implies that, for a long bridge, the electron is delocalized to a significant extent, hence the bridge oscillators only slightly shift their equilibrium positions and their Franck-Condon factors are not favorable for large changes in quantum numbers. Then, the summation over k' can be performed using the closure relation, which turns the product of two double integrals in the numerator into a single triple integral.

We introduce the following notations for electronic and vibrational energy changes: $\Delta G^0 =$

$J_a - J_d < 0$, $\Delta\varepsilon_d = \varepsilon_{dm_f} - \varepsilon_{dm'_i}$, $\Delta\varepsilon_b = \varepsilon_{bk_f} - \varepsilon_{bk_i}$, and $\Delta\varepsilon_a = \varepsilon_{an'_f} - \varepsilon_{an_i}$. We also define the energy of the tunneling electron, E , as the total initial energy, $E_i^{(0)}$, minus the vibrational energy left on D, ε_{dm_f} , minus the vibrational energy of the bridge, $\varepsilon_{b\alpha k'}$, and minus the initial vibrational energy of A, ε_{an_i} (the latter does not change when the electron leaves D). Inserting (2.15), we obtain

$$E = J_d - \Delta\varepsilon_d - \overline{\Delta\varepsilon_b}. \quad (2.23)$$

Now, the total transition amplitude can be expressed in terms of a purely electronic transition amplitude at a fixed nuclear configuration and a given E ,

$$T_{DA}(E; q_d, q_b, q_a) \equiv \sum_{\alpha} \frac{V_{d,b\alpha}^d(q_d, q_b) V_{b\alpha,a}^b(q_b, q_a)}{E - J_{b\alpha}} \equiv \sum_{\alpha} \frac{V_{d,b\alpha}^b(q_d, q_b) V_{b\alpha,a}^a(q_b, q_a)}{E - J_{b\alpha}}. \quad (2.24)$$

[The second, equivalent relation is obtained from the right-hand side equality in Eq. (2.11)]. Then the full vibronic transition amplitude (2.22) takes the form

$$T_{if}(E_i^{(0)}) = \langle dm'_i, bk_i, an_i | T_{DA}(E; q_d, q_b, q_a) | dm_f, bk_f, an'_f \rangle. \quad (2.25)$$

According to Eqs. (2.18), (2.19), and (2.24) the electronic amplitude $T_{DA}(E; q_d, q_b, q_a)$ is a function of nuclear coordinates. This is similar to the usual BO approximation except that the meaning of energy E is now different. Namely, in the BO case E is a function of the nuclear configuration whereas in Eqs. (2.23)-(2.25) it is a function of the vibrational energy changes on donor and bridge. Thus, we have expressed the full transition amplitude via the purely electronic amplitude $T_{DA}(E; q_d, q_b, q_a)$.

Next we invoke the Condon approximation for D and A vibrations by fixing the nuclear coordinates at their equilibrium values, $q_d = q_d^0$ and $q_a = q_a^0$. For bridge vibrations this does not apply since, because of a weak electron-phonon coupling, their equilibria are not shifted between the initial and final states, and therefore their Franck-Condon overlaps vanish identically. Hence, the dependence of $T_{DA}(E; q_d^0, q_b, q_a^0)$ upon q_b has to be retained.

2.2 The reaction rate

The reaction rate is given by the Golden rule expression,

$$k = \frac{2\pi}{\hbar} \text{Av}_i \sum_f |T_{if}(E_i)|^2 \delta(E_f - E_i), \quad (2.26)$$

where Av_i stands for Boltzmann averaging over the initial states. The δ -function will be written in the form

$$\delta(E_f^{(0)} - E_i^{(0)}) = \int \delta(\Delta G^0 + \varepsilon_d + \Delta\varepsilon_b + \varepsilon_a) \delta(\varepsilon_d - \Delta\varepsilon_d) \delta(\varepsilon_a - \Delta\varepsilon_a) d\varepsilon_d d\varepsilon_a.$$

Now, defining the thermally averaged probabilities of D and A vibrational excitation/ deexcitation caused by Franck-Condon transitions as

$$f_d(\varepsilon) \equiv \text{Av}_{m'_i} \sum_{m_f} \langle dm'_i | dm_f \rangle^2 \delta(\varepsilon - \Delta\varepsilon_d), \quad (2.27)$$

$$f_a(\varepsilon) \equiv \text{Av}_{n_i} \sum_{n'_f} \langle an_i | an'_f \rangle^2 \delta(\varepsilon - \Delta\varepsilon_a), \quad (2.28)$$

we obtain our formula for the rate:

$$k = \frac{2\pi}{\hbar} \text{Av}_{k_i} \sum_{k_f} \int \left| \langle bk_i | T_{DA} (J_d - \varepsilon - \overline{\Delta\varepsilon_b}; q_d^0, q_b, q_a^0) | bk_f \rangle \right|^2 \times f_d(\varepsilon) f_a(-\Delta G^0 - \varepsilon - \Delta\varepsilon_b) d\varepsilon. \quad (2.29)$$

With this expression, we have achieved the main goal formulated in the Introduction - the ET rate is now expressed via electronic matrix element $T_{DA}(E; q_d, q_b, q_a)$ which is a function of tunneling energy E and nuclear coordinates of the system. For proteins the matrix element T_{DA} in this form can be calculated using methods developed recently and described elsewhere (see, e.g., Refs. [17]-[20]). In the next section we will discuss Eqs. (2.23)-(2.29) and their possible application for calculations of the ET rates in concrete molecules.

It is easy to show how Eq. (2.29) reduces to the Marcus formula, Eq. (1.1). Replacing the electronic matrix element with a constant T_{DA}^0 , we rewrite Eq. (2.29) as

$$k_0(\Delta G^0) = \frac{2\pi}{\hbar} |T_{DA}^0|^2 \int f_d^{(0)}(\varepsilon) f_a^{(0)}(-\Delta G^0 - \varepsilon) d\varepsilon, \quad (2.30)$$

where superscript (0) means that only low-frequency vibrations are taken into account. For harmonic oscillators with shifted equilibrium positions and the same frequencies in both electronic states, the spectral functions in Eqs. (2.27) and (2.28) are calculated by standard methods, and the Marcus formula is easily recovered in the high-temperature statistical limit (see, e.g., Ref. [21]).

Assume now that there are high- and low-frequency vibrations. Then the spectral functions can be written in the form

$$f_d(\varepsilon) \equiv \text{Av}_{m_i} \sum_{m_f} \langle dm_i' | dm_f \rangle^2 f_d^{(0)}(\varepsilon - \Delta\varepsilon_d), \quad (2.31)$$

and similarly $f_a(\varepsilon)$, where summations over quantum numbers refer to high-frequency vibrations and $f_d^{(0)}(\varepsilon)$ is a spectral function for low-frequency vibrations. After inserting these spectral functions into Eq. (2.29) we can calculate the integral over ε under assumption that the matrix element does not change significantly within a small interval around a point ε^* where the spectral functions overlap. The energy ε^* is a function of the quantum numbers of high-frequency vibrations. The remaining integral is $k_0(\Delta G^0 + \Delta\varepsilon_d + \Delta\varepsilon_a) / |T_{DA}^0|^2$. The rate takes the form

$$k = \text{Av}_{m_i' n_i} \sum_{m_f n_f'} \langle dm_i' | dm_f \rangle^2 \langle an_i | an_f' \rangle^2 C(\Delta\varepsilon_d, \Delta\varepsilon_a) k_0(\Delta G^0 + \Delta\varepsilon_d + \Delta\varepsilon_a), \quad (2.32)$$

where summation is over quantum numbers of high-frequency modes. The Franck-Condon factors give the probability for the system to reach a state which is close enough to resonance. The remaining energy difference is covered by the classical low-frequency vibrations. This results in the partial rate $k_0(\Delta G^0 + \Delta\varepsilon_d + \Delta\varepsilon_a)$, which is the Marcus rate with a driving force modified by the energy changes of the high-frequency vibrations on D and A. The factor $C(\Delta\varepsilon_d, \Delta\varepsilon_a) = |T_{DA}(J_d - \varepsilon^*) / T_{DA}^0|^2$ accounts for the fact that the electronic matrix element depends on the vibrational state of the high-frequency modes involved in this particular transition, being equal to unity when such a dependence is negligible as occurs in a short-distance ET. In the above expression $\Delta\varepsilon_d$ and $\Delta\varepsilon_a$ are not independent variables since they approximately satisfy the energy conservation law $\Delta G^0 + \Delta\varepsilon_d + \Delta\varepsilon_a \sim 0$. Therefore, C is a function of only one of these energy changes.

3 Discussion

In this paper we have developed a theory which is designed for calculating the ET rate for a concrete macromolecule with use of a well-developed method of quantum-chemical calculations of the purely electronic tunneling amplitude at a fixed nuclear configuration. Our Eq. (2.25) shows that the full transfer amplitude T_{if} in the rate expression (2.26) can be represented as a vibrational matrix element of the electronic amplitude, $T_{DA}(E; q_d, q_b, q_a)$, where it is explicitly indicated that the amplitude is a function of donor, bridge, and acceptor nuclear coordinates, as well as the energy of the tunneling electron. This electronic amplitude can be calculated numerically for a particular molecule using, e.g., the methods developed in our group [17]-[18] (see also other work reviewed in Ref. [5]). The energy E , which is an ill-defined parameter in quantum-chemical calculations, now acquires a clear physical meaning given by Eq. (2.23). The remaining parameters of the model are shifts of the equilibrium positions of D and A vibrations which can be evaluated relatively easily using standard quantum chemistry codes.

In Eq. (2.25) we made the Condon approximation with respect to the local nuclear vibrations on D and A by replacing q_d and q_a with their equilibrium values q_d^0 and q_a^0 . This is a good approximation for strongly coupled nuclear coordinates the motion of which the electron follows adiabatically. Then, the probability of ET is essentially defined by the Franck-Condon factors of these vibrations. As for bridge vibrations, the coupling to them is weak for electron localized on D or A, so that their Franck-Condon factors vanish. Therefore, the full amplitude, $T_{DA}(E; q_d^0, q_b, q_a^0)$, still remains a function of bridge coordinates. In this approximation, with a neglect of non-BO contributions due to higher D/A electronic states, the ET rate is represented by Eq. (2.29). The functions $f_{a,d}(\varepsilon)$ defined in Eqs. (2.27) and (2.28) represent the spectra of electron's detachment (attachment) from D (to A). Since vibrations on D and A form two independent groups, the rate in Eq. (2.29) at given initial and final vibrational states of the bridge is proportional to the overlap of the two spectra, as discussed in our previous article [7]. The overlap part of Eq. (2.29) is an analog of the Förster formula for energy transfer.

A notable feature of Eq. (2.29) is the ε -dependence of the electronic ME. If there is some vibrational excitation left on D after the ET occurs ($\varepsilon > 0$), the electron tunnels at a more negative energy, i.e., deeper under barrier since $J_d < 0$. This result was obtained by Ivanov and Kozhushner [12] for an arbitrary model of the medium, and by Onuchic et al. [13] for a specific (Davydov's) model of the medium, a linear periodic chain with nearest-neighbor coupling.

If we assume an exponential dependence of the electronic ME upon the D-A distance,

$$T_{DA}^2(E) = (T_{DA}^0)^2 \exp[-\beta(E)r], \quad (3.1)$$

and calculate the integral in Eq. (2.29) by the method of steepest descent, then the saddle point ε_* will be r -dependent [12]. The crossover to the case of strong nonadiabaticity occurs at such r that $\varepsilon_*(r)$ shifts appreciably from its value at small r . In numerical calculations of the ET rate between local centers in solids, Ivanov and Kozhushner [12] and Onuchic et al. [13] have shown that it essentially affects the distance dependence of the ET rate, increasing the rate at long distances with respect to the value obtained with an ε -independent ME. Therefore, we expect that in proteins the effect will be significant, too.

In our previous papers [6] and [7] we used the approximation

$$T_{DA}(E; q_d^0, q_b, q_a^0) = T_{DA}^0(E) S_b(q_b), \quad (3.2)$$

where $T_{DA}^0(E) = T_{DA}(E; q_d^0, 0, q_a^0)$ and $S_b(q_b)$ is independent of E . (In Refs. [6] and [7] $S_b(q_b)$ was used in a linear or exponential form.) Then, the rate (2.29) is recast as

$$k = \frac{2\pi}{\hbar} A v_{k_i} \sum_{k_f} \langle b k_i | S_b | b k_f \rangle^2 \times \int \left| T_{DA}^0 \left(J_d - \varepsilon - \overline{\Delta \varepsilon_b} \right) \right|^2 f_d(\varepsilon) f_a \left(-\Delta G^0 - \varepsilon - \Delta \varepsilon_b \right) d\varepsilon. \quad (3.3)$$

This expression contains contributions from the $k_i \neq k_f$ transitions which we referred to as inelastic processes [6], [7]. Thus, the present formulation allows one to investigate both elastic ($k_i = k_f$) and inelastic ET reactions in biological molecules.

4 Acknowledgments

This work has been supported by the research grants from the National Institutes of Health (GM54052-02), and NIH Fogarty International Center (1 R03 TW00954-01). AAS acknowledges the fellowships from the Sloan and Beckman Foundations and ESM acknowledges the support of the Russian Foundation for Basic Research (98-03-33155a).

References

- [1] C. C. Moser, J. M. Keske, K. Warncke, R. S. Farid, and P. L. Dutton, *Nature* **355**, 796 (1992); R. S. Farid, C. C. Moser, and P. L. Dutton, *Curr. Opin. Struct. Biol.* **3**, 225 (1993).
- [2] M. J. Bjerrum, D. R. Casimiro, I-J. Chang, A. J. Di Bilio, H. B. Gray, M. G. Hill, R. Langen, G. A. Mines, L. K. Skov, J. R. Winkler, and D. S. Wuttke, *J. Bioenerg. Biomembr.* **27**, 295 (1995).
- [3] R. Langen, I. Chang, J. P. Germanas, J. H. Richards, J. R. Winkler, and H. B. Gray, *Science* **268**, 1733 (1995).
- [4] D. R. Casimiro, J. H. Richards, J. R. Winkler, and H. B. Gray, *J. Phys. Chem.* **97**, 13073 (1993).
- [5] S. S. Skourtis and D. N. Beratan, Theories of structure-function relationships for bridge-mediated electron transfer reactions. *Rev. Chem. Phys.* (1998) to be published.
- [6] I. Daizadeh, E. S. Medvedev, and A. A. Stuchebrukhov, *Proc. Natl. Acad. Sci. USA* **94**, 3703 (1997).
- [7] E. S. Medvedev and A. A. Stuchebrukhov, *J. Chem. Phys.* **107**, 3821 (1997).
- [8] R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **811**, 265 (1985).
- [9] A. M. Kuznetsov, *Charge Transfer in Physics, Chemistry, and Biology* (Gordon and Breach, Amsterdam, 1995).
- [10] H. M. McConnell, *J. Chem. Phys.* **35**, 508 (1961).
- [11] J. J. Hopfield, *Proc. Natl. Acad. Sci. USA* **71**, 3640 (1974).

- [12] G. K. Ivanov and M. A. Kozhushner, *Fizika Tverdogo Tela*, **20**, 9 (1978) [English transl.: *Sov. Phys. Solid State*, **20**, 4 (1978)]; *Chem. Phys.* **170**, 303 (1993).
- [13] J. N. Onuchic, D. N. Beratan, and J. J. Hopfield, *J. Phys. Chem.* **90** 3707 (1986).
- [14] D. Beratan, J. N. Onuchic, and J. J. Hopfield, *J. Chem. Phys.* **86**, 4488 (1987).
- [15] K. F. Freed, *J. Chem. Phys.* **84**, 2108 (1986).
- [16] G. A. Mines, M. J. Bjerrum, M. G. Hill, D. R. Casimiro, I-J. Chang, J. R. Winkler, and H. B. Gray, *J. Am. Chem. Soc.* **118**, 1961 (1996).
- [17] I. Daizadeh, J. N. Gehlen, and A. A. Stuchebrukhov, *J. Chem. Phys.* **106**, 5658 (1997).
- [18] A. A. Stuchebrukhov, *J. Chem. Phys.* **107**, 6495 (1997).
- [19] E. Heifets, I. Daizadeh, J. Guo, and A. A. Stuchebrukhov, *J. Phys. Chem.* **102**, 2847 (1998).
- [20] A. A. Stuchebrukhov, *J. Chem. Phys.* **108**, 8499 (1998).
- [21] E. S. Medvedev and V. I. Osherov, *Radiationless Transitions in Polyatomic Molecules* (Springer, Berlin, 1995), Chap.6.