Theor Chim Acta (1986) 69: 89–100

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Influence of intersite modes on the exchange interaction in electron transfer at large distances*

J. N. Onuchic and A. A. S. da Gama*****

Division of Chemistry and Chemical Engineering****, California Institute of Technology,
Pasadena, CA, 91125, USA

(Received April 25, revised August 23/Accepted October 30, 1985)

We consider the dependence of the exchange interaction in electron transfer processes on the intersite vibrational modes. We assume, in particular, that high-frequency intramolecular modes of proteins may play this role in biological processes. We compare our model with that for tunneling through a time dependent barrier and with other works which considered the dependence of the exchange interaction on the nuclear coordinates.

Key words; Electron transfer — Metalloproteins — Medium influence in the electronic matrix element

1. Introduction

In this work we are concerned with electron transfer over large distances in biological systems, particularly proteins. In some circumstances, for example, when mixed valence or excited species are present electron transfer can take place between two localized electronic states [1, 2].

Electron localization or delocalization has been a subject of subtle interest in physics [3], chemistry [4] and biology [5] for many years. Mixed valence compounds, for example, have been classified [4] and experimentally identified [6]

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* Work partially supported by the Brazilian Agency CNPq and by the NSF (Grant PCM-8406049)

** On leave of absence from Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560, São Carlos, SP, Brazil

*** On leave of absence from Departamento de Física, Universidade Federal de Pernambuco, 50000, Recife, Pe, Brazil

**** Contribution No. 7325

as completely localized (or delocalized) and partially localized, where localization or delocalization depends on the electronic interaction between the two "localized" wave functions and on the magnitude of the vibronic coupling on each trapping site. The interesting regime to be explored is the one where localization can be characterized within the time scale of some experimental measurement, and the transfer rate between the two trapping sites can be measured.

There are two proposed mechanisms for electron transfer. In one of them the transfer rate is a function of the small overlap of the two spatially localized wave functions (through space mechanism) [2]. In the other mechanism, bridging groups significantly enhance the effective overlap between the localized functions (through bond mechanism) [7]. At specially large distances, this second mechanism may assume special importance. Depending on the energy of the localized state relative to some "medium" extended states, and on the electronic hopping interaction between the bridging units, the "through bond" wave function decay with distance may be slower than the direct interaction. The role of this kind of essentially superexchange mechanism has been discussed in great detail in the recent literature [7-9]. The main aim of the present work is to discuss the possibility of the influence of the intersite "medium" modes on the electronic interaction, which can be "through space" or "through bond", since, for the latter, an effective interaction, which replaces the direct interaction, may be defined [9].

Electron migration at large distances has been observed in biological systems. Particular interest has been devoted to the photosynthetic system [1, 2]. Heme proteins, and some other systems with well established molecular structure, have been used in recent intramolecular electron transfer experiments [10-12].

In large biological systems, like proteins with mixed valence sites, the polypeptide chain has been proposed to play the role of bridging group in a "through bond" mechanism. Since the protein chain can be modeled as a 1-D periodic structure, it has been treated by solid state techniques to investigate general feature of the system [13].

To advance a theoretical model for electron migration in this kind of system we should start with a simplified model. There are, actually, three main theories for thermal electron transfer processes [1, 2]: the classical Marcus' theory [14], the semi-classical model developed by Hopfield [15] and the quantum one, first formulated by Levich, Dogonadze and collaborators [16] and later by Jortner and collaborators [17]. The differences among them are basically in the way each one treats the "nuclear" coordinates. By nuclear coordinates we mean nuclear vibrations and librations, solvent motion and any other "slow" effect which may be coupled to the transfer process. A good discussion of the differences between the electron transfer theories was presented in a recent review by Marcus [18].

All these theories have a strong relationship with the theories of radiationless processes [19] and transport of small polarons [20]. The small polaron theory follows from the molecular crystal model, which assumes negligible overlap between neighboring sites. In this model, the electron-lattice interaction plays the role of trapping the electron by lowering the site energy when the electron is present.

Biological systems are quite complex. The states of such systems must be described by statistical operators or density matrices. Due to the large number of degrees of freedom, a dynamical description of these systems using the above theories seems to be impossible. However many processes are associated with changes in a small number of degrees of freedom, weakly coupled to the others, in an essentially irreversible process [15, 17, 21, 22]. De Vault has called attention to the special role of vibronic coupling via high-frequency modes ($\sim 400\ \mathrm{cm}^{-1}$) in biological electron transfer processes [2].

At large distances, the electron transfer process has been assumed in the conventional theories to be non-adiabatic and to respect the Franck-Condon principle. Because of the latter the electronic exchange interaction is assumed to be important for only a single nuclear configuration.

The applicability of the Born-Oppenheimer and Condon approximations to electron transfer at large distances has been questioned [23]. For very weak electronic exchange matrix elements ($\sim 10^{-4}$ eV) the influence of nuclear coordinates on this interaction energy may be of some importance. In this work we consider the influence of the intersite and intrasite modes on these matrix elements. These two types of modes are considered separately, but the influence of them together is an important problem to be studied as an extension of the present model.

2. Theoretical model

In order to obtain a reasonable model for electron migration in molecules of biological interest we shall start with a simple model and later improve it. As we already discussed, an intramolecular electron transfer between two well localized states(sites) is considered. Because we are working in the Born-Oppenheimer approximation, and considering a one electron problem, the Hamiltonian depends only parametrically on the nuclear coordinates, i.e.,

$$\mathbf{h}_{\mathrm{el}} = h_{el}(x;\ \vec{X}_1, \vec{X}_2, \vec{X}_b) \tag{1}$$

where x is the electronic coordinate and $\vec{X}_1$, $\vec{X}_2$ and $\vec{X}_b$ are the nuclear coordinates of the localized modes on site 1 and site 2, and the intersite modes, respectively.

Each site is characterized by a one electron energy level plus all the localized vibrational modes. The one electron model is used because it has been shown to be adequate to describe the general features of the distant electron transfer problem, which is dependent on the long-range tail of the wave function [24]. On site 1, for example

$$H_{site1} = \varepsilon_1(\vec{X}_1) a_1^{\dagger} a_1 + \sum_i \hbar\omega_i (b_i^{\dagger} b_i + 1/2) \tag{2}$$

where $a\dagger(a)$ and $b\dagger(b)$ are respectively fermion and boson creation (anihilation) operators. The one electron energy parameter is defined as

$$\varepsilon_1(\vec{X}_1) = \int \varphi_1^*(x; \vec{X}_1)\mathbf{h}_{\text{el}}\varphi_1(x; \vec{X}_1)\, dx \tag{3}$$

where the site energy ε_1 and the site localized wavefunctions are assumed dependent only on the localized site modes.

Using the linear approximation for the expansion of $\varepsilon_1(\vec{X}_1)$ in the nuclear coordinates we obtain the "small polaron" term, i.e.,

$$\varepsilon_1(\vec{X}_1) = \varepsilon_1 + \sum_i g_i\hbar\omega_i(b_i^\dagger + b_i) \tag{4}$$

and define the electron-vibration constant as usual [25]

$$g_i = (2/M_i\hbar\omega_i^3)^{1/2}[\partial\varepsilon_1(\vec{X}_1)/\partial X_i]|X_i^0 \tag{5}$$

where X_i^0 is the equilibrium displacement of normal mode i without coupling. The "polaron" term changes the equilibrium position and energy of the site localized modes depending on whether or not the electron is on the site.

To allow the transfer of the electron between the two centers we shall include an intersite exchange perturbation

$$H_{int} = V_{12}(\vec{X}_1, \vec{X}_2, \vec{X}_b)(a_1^\dagger a_2 + a_2^\dagger a_1) \tag{6}$$

where the two centers electronic integral is

$$V_{12}(\vec{X}_1, \vec{X}_2, \vec{X}_b) = \int \varphi_2^*(x; \vec{X}_2)\mathbf{h}_{\text{el}}\varphi_1(x; \vec{X}_1)\, dx. \tag{7}$$

Putting all of the above parts together, including the energy term of the intersite modes, we obtain

$$\begin{aligned} H = {} & \varepsilon_1 a_1^\dagger a_1 + \varepsilon_2 a_2^\dagger a_2 \\ & + \sum_{i(site1)} [\hbar\omega_i(b_i^\dagger b_i + 1/2) + g_i\hbar\omega_i(b_i^\dagger + b_i)a_1^\dagger a_1] \\ & + \sum_{j\,(site2)} [\hbar\omega_j(b_j^\dagger b_j + 1/2) + g_j\hbar\omega_j(b_j^\dagger + b_j)a_2^\dagger a_2] \\ & + \sum_{k(bridge)} \hbar\omega_k(b_k^\dagger b_k + 1/2) + \sum_{i,j,k} V_{12}(X_i, X_j, X_k)(a_1^\dagger a_2 + a_2^\dagger a_1). \end{aligned} \tag{8}$$

In this work we intend to discuss the dependence of V_{12} on the nuclear coordinates. It is important to mention that previous works, by Ratner [25] in particular, considered the dependence of V_{12} on the nuclear coordinates. We will compare our results with the previous ones. We are also going to discuss our model in light of a result obtained by Buttiker and Landauer [26] for tunneling through a time modulated barrier, i.e.

$$V(x, t) = V_0(x) + V_1(x)\cos\omega t. \tag{9}$$

In the next section we solve two simple cases of Eq. (8): V_{12} dependent only on one site localized mode, and V_{12} dependent on one intersite mode. We will discuss how the dependence of V_{12} on the nuclear coordinate can be considered as a modulation of the zero order intersite exchange interaction and the different results when fast or slow intersite modes are coupled to the electron transfer.

3. A simple application

As a first application we consider only one localized vibration, on one of the two sites, and we suppose this nuclear coordinate affects V_{12}. This dependence of V_{12} on the localized nuclear coordinates has already been considered by Ratner [25] as $V_{12} = V_{12}(X_1 - X_2)$, where X_1 and X_2 are the coordinates of the localized vibrations at the center 1 and 2, respectively.

The two site Hamiltonian with one localized mode on site 1 is

$$\begin{aligned} H = {} & \varepsilon_1 a_1^\dagger a_1 + \varepsilon_2 a_2^\dagger a_2 + g\hbar\omega(b_1^\dagger + b_1)a_1^\dagger a_1 \\ & + \hbar\omega(b_1^\dagger b_1 + 1/2) + V_{12}(X_1)(a_1^\dagger a_2 + a_2^\dagger a_1). \end{aligned} \tag{10}$$

A picture of the two localized sites is shown in Fig. 1.

Since we have only a linear correction from the "polaron" coupling we can define

$$\hbar\omega(b_1^\dagger b_1 + 1/2) + g\hbar\omega(b_1^\dagger + b_1) = \hbar\omega(b_*^\dagger b_* + 1/2) + \Delta\varepsilon \tag{11}$$

where $b_*^\dagger(b_*)$ are the boson operators for the shifted oscillator, when the electron is on the donor, and for reasons of convenience, we include $\Delta\varepsilon$ in ε_1. Then we can write the time dependent eigenfunctions for each center as

$$\begin{aligned} &\textit{site } 1{:}\,|n, 1\rangle = (n!)^{-1/2} \exp\{-i[\varepsilon_1 + (n+1/2)\hbar\omega]t/\hbar\} b_*^{\dagger n} a_1^\dagger|0\rangle \\ &\textit{site } 2{:}\,|m, 2\rangle = (m!)^{-1/2} \exp\{-i[\varepsilon_2 + (m+1/2)\hbar\omega]t/\hbar\} b_1^\dagger a_2^\dagger|0\rangle \end{aligned} \tag{12}$$

where n and m represent the number of vibrational quanta in the harmonic oscillator.

By using time dependent perturbation theory, and then Fermi's golden rule, we evaluate the transition rate from the initial thermally averaged states $|n, 1\rangle$ to a manifold of final states $\{|m, 2\rangle\}$.

$$k = (2\pi/\hbar) \sum \rho(n)|\langle m|v_{12}(X_1)|n\rangle|^2 \delta[(\varepsilon_1 + n\hbar\omega) - (\varepsilon_2 + m\hbar\omega)] \tag{13}$$

where $\rho(n)$ is the thermal density of initial states.

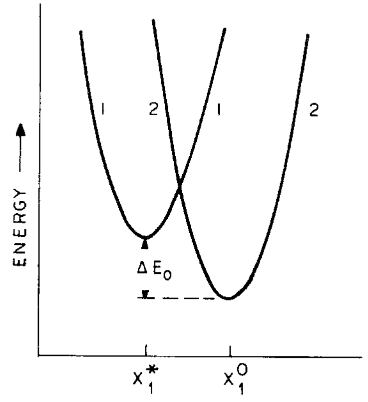

Fig. 1. A diagramatic representation of the two localized states

X_1^* – Is the minimum energy position when the eletron is insite 1

This result is equivalent to the one obtained by Ratner [25].

It is useful to assume at this point that the localized modes do not influence the exchange interaction, i.e., X_1 is treated in the Condon approximation. The dependence of V_{12} on one intersite nuclear coordinate (X_b) is now considered. Assuming we have one localized mode X_1 and one intersite mode X_b, V_{12} is expanded to first order in the intersite coordinate

$$V_{12}(X_b) = V_{12}^0 + V_{12}^{b-} - b_b^\dagger + V_{12}^{b+} b_b \tag{14}$$

where we make a Condon approximation for the X_1 coordinate. The difference between V_{12}^{b-} and V_{12}^{b+} is due to the dependence of the integral over the electronic coordinate (Eq. 7) on the nuclear configuration.

Then, we obtain the following Hamiltonian:

$$\begin{aligned} H = {} & \varepsilon_1 a_1^\dagger a_1 + \varepsilon_2 a_2^\dagger a_2 + g\hbar\omega(b_1^\dagger + b_1) a_1^\dagger a_1 + \hbar\omega(b_1^\dagger b_1 + 1/2) \\ & + \hbar\omega_b(b_b^\dagger b_b + 1/2) + [V_{12}^0 + V_{12}^{b-} b_b^\dagger + V_{12}^{b+} b_b](a_1^\dagger a_2 + a_2^\dagger a_1). \end{aligned} \tag{15}$$

The time dependent eigenfunctions for the two states are:

$$\begin{aligned} |n_b, n, 1\rangle = {} & (n_b! n!)^{-1/2} \exp\{-i[\varepsilon_1 + (n+1/2)\hbar\omega \\ & + (n_b + 1/2)\hbar\omega_b] t/\hbar\} b_b^{\dagger n_b} b_*^{\dagger n} a_1^\dagger |0\rangle \\ |m_b, m, 2\rangle = {} & (m_b! m!)^{-1/2} \exp\{-i[\varepsilon_2 + (m+1/2)\hbar\omega + (m_b + 1/2)\hbar\omega_b] t/\hbar\}. \\ & \cdot b_b^{\dagger m_b} b_1^{\dagger m} a_2^\dagger |0\rangle \end{aligned} \tag{16}$$

and the transition rate

$$\begin{aligned} k = 2\pi/\hbar & \sum_{n_b, m_b} \rho(n_b) \sum_{n,m} \rho(n) |V_{12}^0 \langle m|n\rangle|^2. \\ & \cdot \delta[(\varepsilon_1 + n\hbar\omega) - (\varepsilon_2 + m\hbar\omega)] + [|V_{12}^{b-}\langle m|n\rangle\langle m_b|b_b^\dagger|n_b\rangle|^2 \\ & + |V_{12}^{b+}\langle m|n\rangle\langle m_b|b_b|n_b\rangle|^2]. \\ & \cdot \delta[(\varepsilon_1 + n\hbar\omega) - (\varepsilon_2 + m\hbar\omega) + \hbar\omega_b(n_b - m_b)] \end{aligned} \tag{17}$$

where $\rho(n_b)$ is the initial thermal density of states of the bridging modes.

Looking carefully at the result of the above equation we can think about this problem forgetting the bridging modes and considering a time dependent exchange interaction, i.e.

$$V_{12} = V_{12}^0 + V_{12}^- \exp(i\omega_b t) + V_{12}^+ \exp(-i\omega_b t) \tag{18}$$

where +/− is associated with absorption/emission of a vibrational quantum during the transition. We define

$$V_{12}^+ = V_{12}^{b+} \sqrt{\overline{n_b}} \quad \text{and} \quad V_{12}^- = V_{12}^{b-} \sqrt{\overline{n_b} + 1} \tag{19}$$

where $\overline{n_b} = [\exp(\hbar\omega_b/kBT) - 1]^{-1}$ is the average number of phonons in the harmonic oscillator.

The difference between V_{12}^{+} and V_{12}^{-} is due to the dependence of the integral over the electronic coordinate on the nuclear configuration. In the classical limit $\bar{n}_b \gg 1$ $(k_b T \gg \hbar\omega_b)$, and without integrating over the electronic coordinate, the potentials in Eqs. (9) and (19) are equivalent. The relationship between the matrix elements of $V_{12}^{\pm}$ and V_{12}^{0} can be used to get some insight about the interaction of the "traveling" electron and the intersite medium mode.

The simplest model for electron transfer considers tunneling through a static barrier between two symmetric square wells separated by a distance R (symmetric because the energy for both sites is the same in the crossing point), as it is shown in Fig. 2. In our case instead of considering only a static barrier we include an oscillatory term $(V_1/2)(b_b^{\dagger}+b_b)$ for the coupling between the electronic and nuclear coordinate, i.e. a similar situation to the one considered by Buttiker and Landauer in [26]. Following Redi and Hopfield [27] we use the following wave functions for the barrier region between the two wells

$$\psi_1 = (2k_0^2/a\chi_1^2)^{1/2} \exp\left[-\chi_1(x+R/2)\right]$$

$$\psi_2 = (2k_0^2/a\chi_2^2)^{1/2} \exp\left[+\chi_2(x-R/2)\right] \tag{20}$$

where k_0^2 (E_0 in Fig. 2) is the energy of the infinite square well in units of $\hbar^2/2m$, R is the separation between the wells, a is the size of the wells, and χ_1^2, χ_2^2 are the binding energies of sites 1 and 2 respectively. Assuming the deep well condition $a\chi \gg 1$ (there is almost all particle density inside the well), for the static barrier (symmetric wells) the tunneling matrix element can be evaluated using Bardeen's transmission current [27];

$$V_{12}^{0} = (2\hbar^2 k_0^2/m\chi a) \exp(-\chi R) \tag{21}$$

The tunneling matrix elements for the time dependent barrier can be obtained by changing the energy of one well by $\pm\hbar\omega_b$ (for example, in the Hamiltonian of Eq. (15), it is the donor energy), and using perturbation theory. The results

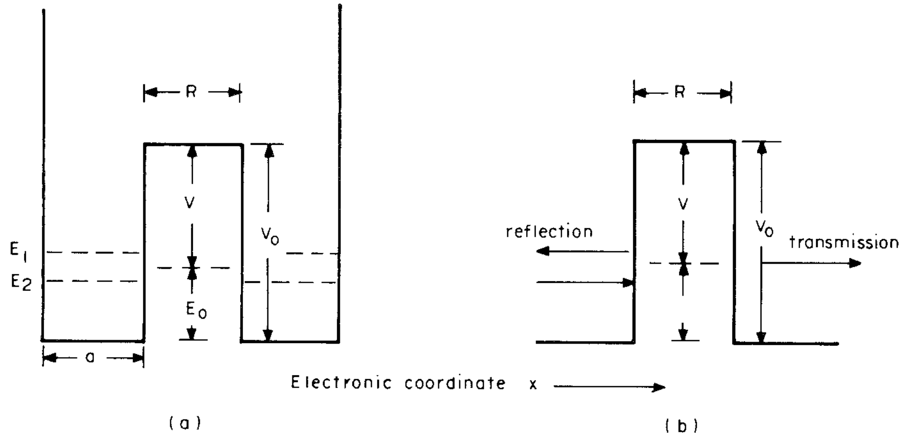

Fig. 2. **a** Two square wells model for electron transfer. **b** Tunneling through a square barrier

obtained, shown in the next equation, can be related to the time independent matrix element by assuming $\hbar\omega_b \ll V, E_0$ (typical values for biological problems are of $\hbar\omega_b \simeq 400\ \mathrm{cm}^{-1} = 0.05$ eV and $V \sim 2$ eV [27]):

$$\begin{aligned} V_{12}^{b\pm} &= \langle\psi_2(\chi_2)|V_1/2|\psi_1(\chi_1)\rangle \\ &= \langle\psi_2(\hbar^2\chi_2^2/2m)|V_1/2|\psi_1(\hbar^2\chi_2^2/2m \pm \hbar\omega_b)\rangle \\ &\sim \pm(V_1/2\hbar\omega_b)[1-\exp(\mp mR\omega_b/\hbar\chi)]V_{12}^0 \end{aligned} \tag{22}$$

where $mR/\hbar\chi = \tau$ is the traversal time defined by Buttiker and Landauer [26] and χ_2 is equal to χ in Eq. (21).

The relation between ω_b and τ^{-1} determines the influence of the barrier modulation. At low frequencies ($\omega_b \ll \tau^{-1}$) the tunneling electron sees a static barrier. At high frequencies ($\omega_b \gg \tau^{-1}$) the tunneling occurs through an averaged barrier of mean height V_0. It is important to recall that this is valid only for this specific electronic interaction and more generally we must recognize that V_{12}^0 and $V_{12}^{\pm}$ are dependent on the model assumed for this interaction. Furthermore, the source for the barrier oscillation in our model is the electron-phonon interaction, then $V_{12}^{\pm}$ is proportional to the amplitude of vibration of the bridge coordinate, and the transmission coefficient for absorption or emission is temperature dependent.

To obtain the final rate equation we have to use a distribution function for the intrasite mode and work out the sum over the Franck-Condon overlap integrals. From Eq. (17–19) we can write each contribution as

$$k = (2\pi/\hbar)|V_{12}^{0,\pm}|^2 \sum_{n,m} |\langle m|n\rangle|^2 \rho(n) \cdot \delta[\Delta E_{0,\pm} + (n-m)\hbar\omega] \tag{23}$$

where $\Delta E_0 = \varepsilon_1 - \varepsilon_2$ and $\Delta E_{\pm} = \Delta E_0 \pm \hbar\omega_b$.

Following the conventional procedure we use the generating function method [19] and write Eq. (23) in the form

$$k = (|V_{12}^{0,\pm}|^2/\hbar^2)\exp(-G_0)\int_{-\infty}^{+\infty} dt \exp\left[-i(\Delta E_{0,\pm}t/\hbar) + G_+(t) + G_-(t)\right] \tag{24}$$

where

$$\begin{aligned} G_+(t) &= (\Delta^2/2)(\bar{n}+1)\exp(i\omega t) \\ G_-(t) &= (\Delta^2/2)\bar{n}\exp(-i\omega t) \\ G_0 &= G_+(0) + G_-(0) = (\Delta^2/2)(2\bar{n}+1) \end{aligned}$$

and Δ is the reduced displacement of the two site curves $(X_1^0 - X_1^*)$ at Fig. 1. The reorganization energy of the intrasite nuclear coordinates can be expressed in terms of Δ as $E_r = \hbar\omega(\Delta^2/2)$. G_0 is often used as a parameter to quantify the magnitude of the vibronic coupling. Analytical expressions for k are in general obtained at the weak coupling limit ($G_0 \leq 1$) or at the strong coupling limit ($G_0 \gg 1$). From Jortner [17] we can obtain for the weak coupling limit (small reorganization energy, $E_r \leq \hbar\omega$ and/or low-temperature $k_BT \ll \hbar\omega$):

$$k = (2\pi|V_{12}^{0,\pm}|^2/\hbar^2\omega)(\bar{n}+1)^p \exp(-G_0)[(\Delta^2/2)^p/p!] \tag{25}$$

where $p = \Delta E_{0,\pm}/\hbar\omega$ is the reduced effective energy gap (assumed to be an integer). For $p \geq 2$ the use of the Stirling approximation for $p!$ is quite good and k can be expressed as

$$k = (2\pi |V_{12}^{0,\pm}|^2/\hbar^2\omega) \exp(-G_0) \exp(-\gamma p)/(2\pi p)^{1/2} \tag{26}$$

where $\gamma = \ln[p/(\Delta^2/2)(\bar{n}+1)] - 1$, for $\gamma > 0$ Eq. (26) expresses the energy gap law for radiationless processes.

The strong coupling limit (large reorganization energy and high temperature) reproduces the well-known activated rate equation:

$$k = (2\pi |V_{12}^{0,\pm}|^2/\hbar)(4\pi E_r k_B T^*)^{-1/2} \exp(-E_A^{0,\pm}/k_B T^*) \tag{27}$$

where the effective temperature is defined by $k_B T^* = (\hbar\omega/2) \coth(\hbar\omega/2k_B T)$ and the activation energy is $E_A^{0,\pm} = (\Delta E_{0,\pm} - E_r)^2/4E_r$. This result can also be obtained by semiclassical approximation [15] and the classical expression [14] is reproduced at sufficiently high temperatures ($k_B T \gg \hbar\omega$) when $k_B T^* = k_B T$.

4. Discussion

In this model we consider the possible influence of intersite "medium" modes on the exchange interaction (transfer matrix) of electron transfer processes. High-frequency intramolecular modes of the protein may play a special role in this "phonon assisted" transfer matrix in biological systems, i.e., the electron may be interacting with the nuclear bridging modes "while travelling" between the two trapping sites.

The coupling of the two sites to a common boson field is considered as a way to describe inelastic tunneling [28]. However, the time dependent transfer matrix leads to a different physical interpretation. The intrasite and the intersite modes play different roles in the process. In some ways this separation is similar to the one of promoting and accepting modes in the theory of radiationless processes [29]. Indeed the intrasite modes are identified as the accepting modes. The main effect of the vibronic coupling is included on the unperturbed Hamiltonian to describe the initial and final states and the intrasite modes are the ones directly coupled to the donor and acceptor centers. The intersite modes may be less sensitive to the change of charge on the two localized sites. However, in particular for electron transfer at large distances, the "electron traveling time" may be sufficiently long to make the electron-bridging modes interaction effective. To avoid higher orders of perturbation, the "promoting factor" is considered a one-phonon mechanism. The first consequence is that the conventional multiphonon factor changes only by one order ($p \pm 1-$phonon process), and it is assigned to the intrasite modes. The second consequence is that "V_{12}" is no longer a pure electronic factor, i.e. $V_{12}^{\pm}$ are related to the vibronic coupling between the "traveling electron" and the bridging modes. The magnitude of the effect depends on V_1, which is related to the intersite mode vibronic coupling, and on the relation between ω_b and τ^{-1} in Eq. (22). For typical values of barrier height, for example, 1.5 eV, at a distance of 13 Å, and with $\hbar\omega_b = 400\ \mathrm{cm}^{-1}$, if

$V_1/2\hbar\omega_b = 10$, this effect is significantly large. However, much more experimental and theoretical work is necessary for a clearer interpretation of the mechanism of intersite mode vibronic coupling and, therefore, to obtain reasonable estimates for these parameters.

The separation of nuclear vibrations in low- and high-frequency modes has often been used in the electron transfer theory ([17], for example). However, in this work only high-frequency modes are considered because for slow-modes the validity of the non-adiabatic limit is questionable, and this is not a point we intend to discuss here.

The contribution of the term corresponding to phonon emission (with V_{12}^- and ΔE_- in Eq. (23), in particular the effect of spontaneous emission ($\overline{n_b} = 0$ in Eq. (19)), can be important when we consider some electron transfer processes on the region of validity of the "energy gap law". These processes are predicted to occur when the electron transfer is associated with a small reorganization of the nuclear coordinates [30]. In this "weak coupling limit" the electron transfer rate can display weak temperature dependence, in particular for small energy gaps. Temperature dependence of radiationless transitions in this limit has been observed experimentally to be associated with the factor $(\bar{n}+1)^p$ [31]. In biological electron transfer, weak coupling limits may be observed when the metal sites are buried inside the protein pocket, protected from interaction with a polar medium [30]. The reorganization of the first coordination shell, here associated with the intrasite mode, has been observed to be small for $Ru^{II/III}(bpy)_3$ and $Ru^{II/III}(NH_3)_6$ [32]. $Ru(NH_3)_5$-histidine modified azurin, for example, was observed to have a weak temperature dependent intramolecular electron transfer rate from −10°C to 60°C [11].

In Fig. 3, we show the dependence of the electron transfer rate on the energy gap for the terms in ΔE_0 and ΔE_- within the weak coupling limit. The two contributions have to be summed up and the absolute magnitudes will depend

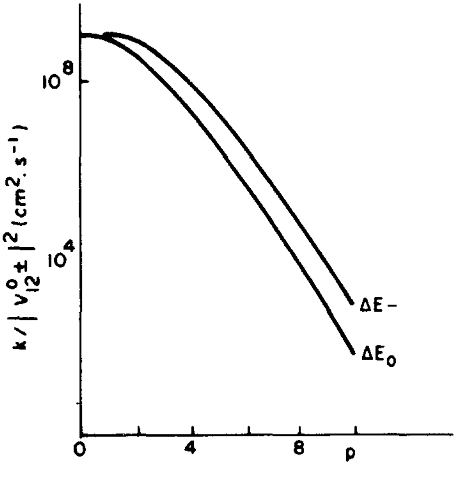

Fig. 3. Dependence of k with the energy gap on the weak coupling limit. $T = 300$°K.

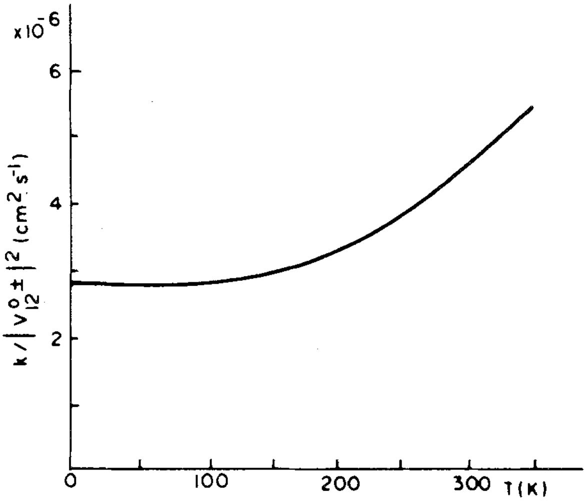

Fig. 4 Dependence of k with the temperature on the weak coupling limit. Plot for ΔE_0 and $p = 5$

on the parameter $A = (2\pi|V_{12}^{0,-}|^2/\hbar)$ which is different for each one. To illustrate the temperature dependence in this limit we also plot $k(\hbar\omega/A)$ versus T in Fig. 4. In this calculations we use the same value of 400 cm^{-1} for the intrasite modes, which is in agreement with the mean frequency of metal-ligand bonds in some metalloproteins. The reorganization energy is assumed to be $(E_r/\hbar\omega) \simeq 0.75$.

On the strong coupling limit, the reorganization energy being much larger than $\hbar\omega$, the difference in activation energy associated with ΔE_0 and ΔE_- may be very small. The interesting situation $\Delta E_0 = E_r$, which has also been used as an explanation for temperature independent electron transfer rates [17], has an activation energy associated with ΔE_- which is $E_a^{\pm} = \hbar\omega/2\Delta^2$. If, for example, we assume $E_r = 3000$ cm^{-1}, we have $E_A^{\pm} \simeq 13.3$ cm^{-1} which is too small to be characterized experimentally.

Acknowlegment. The authors are grateful to Dr. H. B. Gray, Dr. J. J. Hopfield, and Dr. D. N. Beratan for very helpful suggestions with regard to this manuscript.

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