DISTANT INTRAMOLECULAR ELECTRON TRANSFER

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ABSTRACT

We consider a very simple model to describe distant intramolecular electron transfer and discuss its application to the interpretation of experimental results in biological systems. The model assumes a one electron approximation, two electronic states coupled to one intrasite mode and one intersite mode. The weak vibronic coupling limit of the theory is used to the explanation of the weak temperature dependence of the electron transfer rates in pentaamine ruthenium (his-83) azurin.

1. INTRODUCTION

We were introduced to the problem of enzymatic catalysis 10 years ago by Professor Ricardo Ferreira. We proposed a perturbative approach to enzymatic catalysis, within the framework of the Frontier Orbital Theory, in which the enzyme mediates the electron from a bonding orbital of a substrate (HOMO) to an antibonding orbital of another substrate (LUMO)[1].

Electron transfer between two molecular species (intermolecular) or two localized sites in a molecule (intramolecular) is a subject of subtle interest in physical, chemical and biological sciences, with many technological applications (semiconductor devices, energy conversion, catalysis, etc.). In the functioning of living systems (enzymatic catalysis, photosynthesis, respiration, etc) electron transfer is believed to occur over large distance from a donor to an acceptor mediated by some molecular structure (bridge).

We are concerned with the intramolecular electron transfer. For bimolecular reactions in solution, or in the interface with electrodes, and for enzymatic catalysis, the diffusion of reactants is important but we may fix our attention to the intramolecular step which occurs in the activated complex. Electron transfer is believed to be the rate-determining step of many biological reactions.

A unified theoretical framework may be assumed for the description of electron transfer processes in condensed media[2]. The differences among classical, semiclassical, and quantum formulations mainly involve the way each one treats the nuclear coordinates[3]. Some assumptions on the formulation of biological electron transfer theory have been discussed and criticized in the recent literature: Born – Oppenheimer and Condón approximations[4], fast intramolecular relaxation and irreversibility[2,5], and nonadiabaticity and Fermi's golden rule[6].

In this theory the electron transfer rate is given by the expression

$$k = (2,\pi/\hbar)\ |T_{ab}|^2\ F \qquad (1)$$

where T_{ab} is the electronic exchange matrix element and F is the Franck-Condon factor.

There are two proposed mechanisms for the electronic exchange interaction: through space and through bond. At large distances the through bond mechanism may assume special importance. Bridging ligands may significantly enhance the effective interaction between the two localized wave functions. In proteins the polypeptide chain has been proposed to play the role of bridging goups. This kind of superexchange mechanism has been discussed in great detail in the recent literature[7]. The electronic matrix element T_{ab} describes the dependence of the electron transfer rate with the donor-acceptor separation distance.

The Franck-Condon factor (F) contains the dependence of the electron transfer rate with respect to the energy gap (driving force) and temperature. The form of the Franck-Condon factor is determined by the behavior of the nuclear coordinates coupled to the electron transfer process. Biological systems are quite complex, with a large number of degrees of freedom. However many processes are associated with changes in a small number of degrees of freedom, weakly coupled to the others[6,8], in an essentially irreversible process[5]. Vibronic coupling via high-frequency intramolecular modes ($\sim 400 cm^{-1}$) is believed to play a special role in biological electron transfer[9].

In this work we will discuss some aspects of the electronic and vibronic interactions. For the electronic interaction we will describe a super-exchange mechanism as a extension of the classical Mulliken's Charge Transfer Complex. An expression for T_{ab} will be obtained by using renormalization techniques to solve Dyson's equation on the Green's function formalism. The vibronic coupling will be described by assuming two classes of nuclear modes: intrasite modes, which play the role of accepting modes, and intersite modes, which play the role of promoting modes[10]. We will conclude by using a weak vibronic coupling approximation to reproduce the weak temperature dependent electron transfer rate observed in experiments[11].

2. MODEL HAMILTONIAN

We consider a Wannier-like one electron Hamiltonian at site representation:

$$H^e = \sum_i \epsilon_i a_i^+ a_i + \sum_{i,j>i} v_{ij}(a_i^+ a_j + a_j^+ a_i) \qquad (2)$$

The operator $a_i^+(a_i)$ creates (destroys) one electron at site i. The intersite exchange interaction is assumed to be different from zero only for nearest neighbors (i.e., $j = i \pm 1$). In this kind of phenomenological Hamiltonian the electron-electron interaction is missing. The one electron model has been shown to be adequated to describe the general features of the distant electron transfer process, which is dependent on the long-range tail of the wave function[12].

The complete Hamiltonian also contains a sum of vibrational energies:

$$H^v = \sum_k \hbar\omega_k (b_k^+ b_k + \tfrac{1}{2}) \qquad (3)$$

and the vibronic coupling (H^{ev}), which can be accounted by the dependence of ϵ_i and v_{ij} on the nuclear coordinates[10]

$$\epsilon_i = \epsilon_i^\circ + \sum_{k_i} g_{k_i} \hbar\omega_{k_i} (b_{k_i}^+ + b_{k_i}) \qquad (4)$$

$$V_{ij} = V_{ij}^\circ + \sum_{k_{ij}} (V_{k_{ij}}^- b_{k_{ij}}^+ + V_{k_{ij}}^+ b_{k_{ij}}^-) \qquad (5)$$

where k_i and k_{ij} represent, respectively, intrasite and intersite nuclear modes.

3. ELECTRONIC INTERACTION

We consider one orbital φ_A localized on site A, one orbital φ_B localized on site B and a set of bridging orbitals $[\varphi_X]$. The wave functions for the states with an extra electron on site A or site B are

$$\psi_a = |\varphi_A \bar{\varphi}_A \cdots \varphi_X \bar{\varphi}_X \cdots \varphi_B \qquad (6)$$

$$\psi_b = |\varphi_A \cdots \varphi_X \bar{\varphi}_X \cdots \varphi_B \bar{\varphi}_B|$$

This two level problem has a secular equation

$$\begin{vmatrix} \epsilon_a - E & V_{ab} \\ V_{ba} & \epsilon_b - E \end{vmatrix} = 0 \qquad (7)$$

For distant electron transfer we may assume tha V_{ab} is virtually zero. However, the participation of intermediate states, associated to virtual excitation of electrons (holes) to empty (occupied) orbitals of the bridging ligands, may contribute to an effective interaction between the localized distant orbitals. This superexchange model can easily be associated to a new secular equation[13]

$$\begin{vmatrix} \epsilon_a - E & V_{ab} \cdots & V_{ai} & \cdots \\ V_{ba} & \epsilon_b - E \cdots & V_{bi} & \cdots \\ \vdots & \vdots & & \\ V_{ia} & V_{ib} & \cdots & \epsilon_i - E \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix} = 0 \qquad (8)$$

where i stands for excited states with one electron (hole) in unoccupied (occupied) bridging orbitals. This (n + 2) x (n + 2) secular equation, where n is the number of virtual excitations, can be converted to a new 2 x 2 secular equation

$$\begin{vmatrix} \epsilon_a - E - \Delta_a & V_{ab} - \Delta_{ab} \\ V_{ab} - \Delta_{ba} & \epsilon_b - E - \Delta_b \end{vmatrix} = 0 \qquad (9)$$

where $\Delta_{a(b)}$ is called the self energy of site a(b)

$$\Delta_{a(b)} = \underset{\sim}{H}_{a(b)} \underset{\sim}{(H-E)^{-1}} \underset{\sim}{H}^+_{a(b)} \qquad (10)$$

and Δ_{ab} is the super-exchange interaction

$$\Delta_{ab} = \underset{\sim}{H}_a \underset{\sim}{(H-E)^{-1}} \underset{\sim}{H}^+_b \qquad (11)$$

$\underset{\sim}{H}_{a(b)}$ is a (1xn) matrix containing the interactions between the orbital localized on site a(b) and the bridging orbitals. $\underset{\sim}{(H-E)}^{-1}$ is a (n x n) diagonal matrix called resolvent, or Green's function, with respect to the subspace $[\Psi_i]$.

For a linear chain conecting site a to site b

$$\Delta_{ab} = V_{a1}\, G_{1n}(E) V_{nb} \qquad (12)$$

where $G_{1n}(E)$ is the matrix element of the Green's function which relates the two extreme sites of the bridging chain. The introduction of the Green's function has the advantage of allowing the use of techniques developed to treat the problem of localized states in solids[14]. All matrix elements of the Green's function in the site representation can be obtained from the Dyson's equation EG = 1 + HG. For the model system in figure 1 we associate a set of equations

$$(E - \epsilon_0)\, G_{00} = 1 + V_{01}\, G_{10}$$

$$\begin{aligned}
(E - \epsilon_1)\, G_{10} &= V_{10}\, G_{00} + V_{12}\, G_{20} \qquad (13)\\
&\vdots \quad\quad \vdots \quad\quad \vdots\\
(E - \epsilon_{n-1})\, G_{n-1,0} &= V_{n-1,n-2} G_{n-2,0} + V_{n-1,n}\, G_{n,0}\\
(E - \epsilon_n)\, G_{n,0} &= V_{n,n-1}\, G_{n-1,0} + V_{n,n+1}\, G_{n+1,0}
\end{aligned}$$

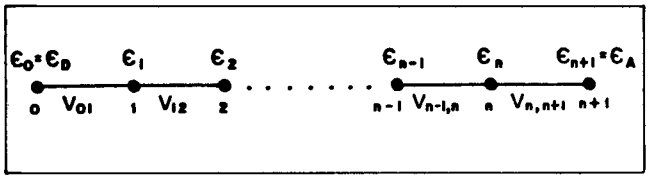

Fig. 1 – Model for a I-D chain with a donor (D) at site 0 and an acceptor (A) at site n + 1.

We assume a donor in site 0 and an acceptor in site n + 1 and solve this set of equations by eliminating all intermediate sites (renormalization)[15]. The resulting equation is

$$(E - \epsilon_0 - \Delta_0)\, G_{00} = 1 + \frac{V_{01} \ldots V_{n,n+1}}{(E-\epsilon_n) \ldots (E-\epsilon_1-\Delta_1)}\, G_{n+1,0} \qquad (14)$$

where Δ_i, the self energy of site i, is defined by

$$\Delta_i = \frac{V_{i,i+1}^2}{E - \epsilon_{i+1} - \Delta_{i+1}} \qquad (15)$$

and the renormalized through bond interaction is

$$\Delta_{ab} = \frac{V_{01}\, V_{n,n+1}}{E - \epsilon_1 - \Delta_1} \prod_{i=1}^{n-1} \left(\frac{V_{i,i+1}}{E - \epsilon_{i+1} - \Delta_{i+1}} \right) \qquad (16)$$

The sites out of the pathway from n to 1 give no contribution to Δ_i, i.e.: $\Delta_n = 0$ ($\epsilon_k = \infty$ for all k before i on a particular pathway)[14].

If we make a periodic approximation for the bridging chain

$$\Delta_{ab} = \frac{2\, V_{01}\, V_{n,n+1}}{[E + (E^2 - 4V^2)^{1/2}]} \exp(-\alpha R_{ab}) \qquad (17)$$

with $\alpha = a^{-1}\ n\,\{2V/[E-(E^2-4V^2)^{1/2}]\}$

Here a is the unit cell dimension, V is the intersite interaction through the periodic chain and E the energy of the Localized state related to a band of bandwidth 4V. Equation 17. or equivalent ones. has been used to estimate the distance dependence of the electronic interaction, T_{ab}, in biological systems.

4. VIBRONIC INTERACTION

We consider only two vibrational modes: one intrasite mode at the acceptor and one intersite mode. The intrasite mode is assumed to be the one directly coupled to the initial and final states and plays the role of an accepting mode. The intersite mode plays the role of a promoting mode and may be interpreted as a source of time dependence of the exchange interaction[10], i.e.:

$$T_{ab} = T_{ab}^{\circ} + T_{ab}^{-} \exp(i\omega_{ab} t) + T_{ab}^{+} \exp(-i\omega_{ab} t) \qquad (18)$$

where +/– is associated to absorption / emission of a vibrational quantum during the electron transfer.

This model assumes that the Franck-Condon factor is governed by the vibronic coupling via the intrasite mode. From the multiphonon formalism a general expression for the Franck-Condon factor is[2]

$$F = (\hbar\omega_a)^{-1} \exp[-g_a(2\bar{n}_a + 1)]\, I_p\, \{2g_a [\bar{n}_a (\bar{n}_a + 1)]^{1/2}\}\, [(\bar{n}_a+1)/\bar{n}_a]^{p/2} \qquad (19)$$

where $\bar{n}_a = [\exp(h\omega_a/k_BT) -]^{-1}$ is the average occupation number of the harmonic oscillator that represents the relevant intrasite mode of frequency ω_a, $\rho \equiv \Delta E/h\omega_a$ is the reduced energy gap and g_a is the vibronic coupling parameter. The intersite mode effect the energy gap reducing (or increasing) by $\hbar\omega_{ab}$.

There are two limiting form of equation 19, depending on the magnitude of the vibronic coupling and temperature. For large g_a, i.e.: $g_a > 1$, and high temperature $k_BT >> \hbar\omega_a$ the Franck-Condon factor is Arrhenius-like:

$$F = (4\pi\, E_r\, k_B T)^{-1/2} \exp(-E_a/k_B T) \qquad (20)$$

where $E_r = g_a h\omega$ is the reorganization energy and $E_a = (\Delta E_0 - E_r)^2/4E_r$ is the activation energy. For small g_a and /or low temperature the Franck-Condon factor has an energy gap law behavior. This limit is obtained from equation 19 by expanding the modified Bessel function $I_p\,\{2g_a[\bar{n}_a(\bar{n}_a+1)]^{1/2}\}$ for small arguments[16]

$$F = (h\omega_a)^{-1} \exp[-g_a(2\bar{n}_a+1)]\, \frac{[g_a(\bar{n}_a+1)]^p}{p!} \left[1 + \frac{g_a^2 \bar{n}_a(\bar{n}_a+1)}{p+1} + \ldots\right] \qquad (21)$$

If we retain only the first order term and introduce the Stirling approximation for p! ($p \gtrsim 2$)

$$F = (\hbar\omega_a)^{-1} \exp[-g_a(2\bar{n}_a + 1)]\, \exp(-\gamma p)\, /(2\pi p)^{1/2} \qquad (22)$$

where $\gamma = \ln[p/g_a(n_a + 1)] - 1$. For $\gamma > 0$ equation 22 is an expression of the energy gap law.

5. DISCUSSION

The theoretical description of the electron transfer phenomena in the condensed media predicts some general features which can be useful to interprete experimental results. We will fix our attention to the through bond mechanism for the electronic interaction and the weak coupling limit for the vibronic interaction. The experimental results with mixed valence compounds[7e,f] and rigid organic polymers[17] have stressed our confidence on the through bond mechanism. However, it is hardly believed that the through bond interaction in Ru modified azurin[11a], cytochrome c[11b] and myoglobin[18] follow the polypeptide chain. The through bond pathway in protein is still a open question. Calculations assuming periodic approximation for the polypeptide chain have compared primary to secondary chain pathways by setting the former with a 10 times larger conducting bandwidth[19].

We consider a special situation of the vibronic interaction. First we assume that both intrasite and intersite modes are high-frequency modes ($\sim 400 cm^{-1}$). The vibronic coupling parameter is taken to be small ($g_a < 1$). Weak vibronic coupling may be assumed for $Ru(NH_3)_5$· His, modified azurin and cytochrome c. In both of these metalloproteins the native metal sites are burried inside a hydrophobic protein pocket that is isolated from interactions with the solvent medium. Ressonant Raman Scattering of cytochrome c indicates small vibronic coupling ($g_a \simeq 1$)[21a]. Weak vibronic coupling may also be assumed for azurin[21b]. Further, Taube's work[20a] on $[Ru(NH_3)_5]^{2+/3+}$ bound to a nitrogen of bridging groups of mixed valence compounds and the electron exchange reactions of $[Ru(NH_3)_6]^{2+/3+}$ in solution studied by Sutin[20b] indicate a small reorganization for the Ru-N bonds. The situation for hemoglobin, however, could be quite different. Solvent can access the heme pocket and iron has one position available to interact with water, ions and other molecules in solution (unless a ligand bonds to iron in both oxidation states).

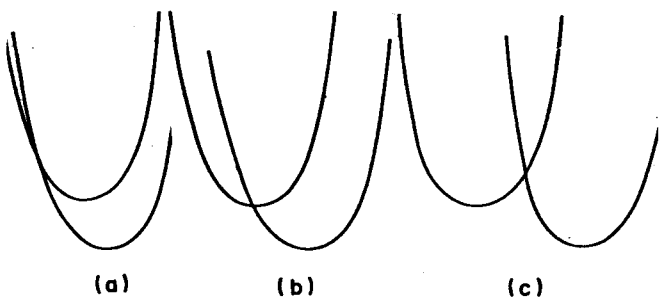

Fig. 2 – Potential energy surfaces for the reactants and products in the weak coupling limit (a), activationless condition (b), and the strong coupling limit (c).

In the weak coupling limit (figure 2a) with coupling via high-frequency modes, the temperature dependence of the electron transfer rate may be very small. Weakly temperature dependent electron transfer rates have been observed early at the photosynthetic reation center of bacteria[2]. However, the strongly temperature dependent (Arrhenius-like) electron transfer rate from cytochrome c to bacteriochlorophyll at these photosynthetic systems have attracted much attention. Both Jortner's multiphonon expression and Hopfield's semiclassical one were used, assuming large reorganization of the nuclear coordinates, to reproduce the observed temperature dependence of the cytochrome c oxidation in **Chromatium**. The same strong coupling limit (figure 2c) allowed Hoffman to reproduce the temperature dependence observed in the electron transfer experiments with hybrid hemoglobins[22]. Jortner has assigned to the activationless condition (figure 2b) the weakness of temperature dependence observed for some electron transfer processes on the photosynthetic reaction center[2]. Marcus has called attention to the weak temperature dependence of electron transfer rates on the limit of small reorganization of the nuclear coordinates[20c]. We consider the weak coupling limit, via high frequency modes, to interprete the temperature independent rate observed in $Ru(NH_3)$ – His modified azurin[11a]. Assuming $p = 5$, $g = 1.5$ and $h_a = 400 cm^{-1}$ (i.e.: $\bar{n}_a = 0.22$ at 300K) the contribution of the second order term on the Bessel function expansion in equation 21 is within the experimental error (~20%). To reproduce the experimental rate we need to take $T_{ab} = 2.3 \times 10^{-8}$ ev. The tiny T_{ab} is not surprising, because a "through bond" mechanism via primary polypeptide chain is improbable (the shortest distance is 136Å). Moreover, we need no larger T_{ab} because, in opposition to the situation found in the cytochrome c oxidation in Chromatium, here the Franck-Condon factor is much larger and the observed electron transfer rate is much lower. From equation 16 we may estimate a $T_{ab} = 2.3 \times 10^{-8}$ at ~68Å through some π-bonding pathway, which is hardly the case for protein systems. At 136Å we would have to assume a unexpected $\alpha = 0.13$ in equation 17 to reproduce the value

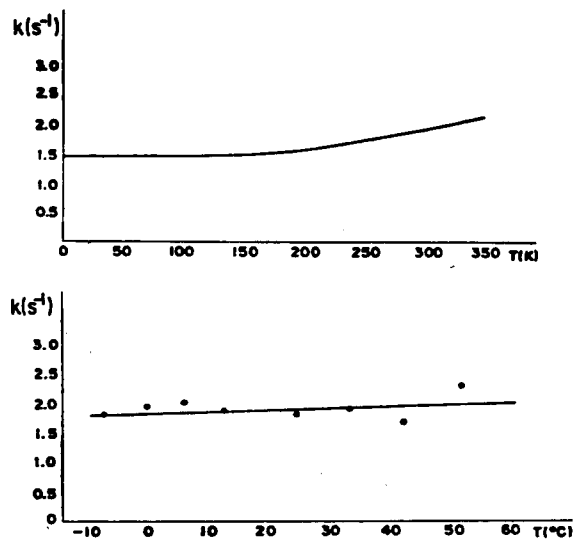

Fig. 3 – Temperature dependence of the electron transfer rate from 0 to 300K in the weak coupling limit for $h\omega_a = 400 cm^{-1}$, $g = 1,5$ and $p = 5$ (a), and comparison with the experimental resultes of reference 11a (b).

of T_{ab}. From the other side, a simple tunneting model[19] can question whether through bond mechanism can be used to the interpretation of electron transfer in biological system is still unsolved. However it is important to mention that all information of distances in proteins used here came from X-ray solid state measurements. In the functioning of biological systems, conformation changes can strongly modify our interpretation of the through bond interaction. In the enzymatic catalysis, for instance, the enzyme may be an efficient electron system only when bounded to the substrats, i.e., at the activated complex.

In figure 3 we show the electron transfer rates predicted for $Ru(NH_3)_5$ – His modified azurin from 0 to 350 K and to compare with experiments we set off the room temperature interval (−10 to 60°C). Weak temperature dependent rate has also been assigned to the intramolecular electron transfer in $Ru(NH_3)_5$ – His modified cytocrome c[11b]. If the parameters for that system are nearly the same, expect in the case there is a smaller driving force ($p \simeq 3$), then the increase in the electron transfer rate by an order of magnitude from azurin to cytochrome c system may be attributed to the "energy gap law" characteristic of radiationless processes in the weak coupling limit. Much experimental work have to be done, keeping the vibronic small and changing the driving force, to test the predictions of the model we have discussed here.

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