Tunneling Time for Electron Transfer Reactions

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The tunneling time for nonadiabatic electron transfer reactions described within the superexchange model is estimated using a Büttiker type internal clock: the electron is taken to possess two internal spin states that are weakly coupled on the bridge. By studying the transition probability between these channels during the tunneling process the traversal time through the bridge can be estimated. Like the Büttiker−Landauer result it is linear in the bridge length, but its dependence on the barrier energy U_B approaches the Büttiker−Landauer form only in the limit of strong interstate coupling (broad band). In the "normal" superexchange (weak coupling) limit it is inversely proportional to the barrier energy.

1. Introduction

Nonadiabatic electron transfer via quantum mechanical tunneling[1] is characteristic of processes ranging from photosynthesis[2] to conduction through molecular wires.[3] While the factors governing such electron transfer processes are well understood and their transfer rates can be estimated, little is known about the tunneling process itself. The issue of how long the tunneling particle actually spends in the classically forbidden region of the potential is of particular interest. In tunneling systems the concept of tunneling time is often invoked in order to get an intuitive feeling about the course of the observed rate process.

Büttiker, Landauer, and co-workers[4−7] have suggested an estimate for the tunneling time based on imposing an internal clock on the tunneling system, for example, a sinusoidal modulation of the barrier height. At modulation frequencies much smaller than the inverse tunneling time the tunneling particle sees a static barrier which is lower or higher than the unperturbed barrier depending on the phase of the modulation. At frequencies much higher than the inverse tunneling time the system sees an average perturbation and so no effective change in the barrier height, but inelastic tunneling can occur by absorption or emission of modulation quanta. The inverse of the crossover frequency separating these regimes is the estimated tunneling time τ. For tunneling through the 1-dimensional rectangular barrier

$$V(x) = \begin{cases} U_B; & x_1 \le x \le x_2 \\ 0 & \text{otherwise} \end{cases} \qquad (1)$$

and provided that $D = x_2 - x_1$ is not too small and that the tunneling energy E is sufficiently below U_B, this analysis gives

$$\tau = \sqrt{\frac{m}{2(U_B - E_0)}}D \qquad (2)$$

for a particle of mass m and energy $E_0 < U_B$. A similar result is obtained by using other equivalent clocks, for example, a barrier localized small coupling between two internal states of the tunneling particle.[5] Note that τ increases linearly with the barrier width D, and that its dependence on the tunneling energy E_0 can be expressed by $\tau = D/v_I$, where $v_I = [2(U_B - E_0)/m]^{1/2}$ is the absolute value of the (imaginary) velocity.

The interpretation of τ defined above as the characteristic time for the tunneling process is debatable, and other candidates for this title can be suggested. Still, disregarding semantics, this time is relevant for an important practical reason: it is the time that should be used to estimate the relative importance of interactions that affect the tunneling particle while in the barrier. One aspect of this issue is often encountered in studies of electron transfer in molecular systems. During electron transfer the electron can interact with internal vibrational motions of the barrier molecule and with external solvent modes. If the time during which the tunneling particle is actually in contact with the barrier is known, then simplifying approximations can be made for the calculation of rates and transmission probabilities. For example, interactions with vibrational modes possessing periods much larger than the contact time could be treated adiabatically, while interactions with motions whose periods are much smaller than the contact time could be replaced by time-averaged interactions. As defined, the "tunneling time" τ is a measure of this contact time. The purpose of this letter is to calculate the analogue of the result of eq 2 for the superexchange model of bridge-mediated electron-transfer processes.

2. Model and Method

Figure 1 depicts a simple superexchange model for an electron transfer between a donor state 0 and a quasi-continuous acceptor manifold $\{r\}$ through a series of bridge levels 1, 2, ..., N. In molecular electron-transfer processes, 0 is one of a manifold of

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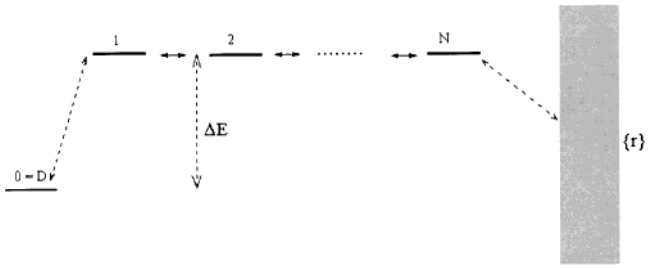

Figure 1. Simple superexchange model for an electron transfer between a donor state 0 and a quasi-continuous acceptor manifold $\{r\}$ through a series of bridge levels 1, 2, ..., *N*.

donor vibronic states (including solvent nuclear states) and the final expression for the transfer rate includes a thermal averaging over this manifold. Similarly, the manifold $\{r\}$ corresponds to the manifold of acceptor vibronic states. When the molecular bridge connects between two metal electrodes, these continuous manifolds correspond to the metal electronic states but the model structure is unaltered. To calculate the Büttiker−Landauer time we will use an internal clock similar to that used by Büttiker:[5] The electron is taken to possess two internal (spin) states, $\sigma = \alpha,\beta$ that are coupled to each other *only on the bridge*. In the basis of local molecular states $|n,\sigma\rangle$, $n = 0, 1, 2, ..., N, \{r\}$; $\sigma = \alpha,\beta$, the Hamiltonian takes the form

$$H = \sum_{\{n\}}\sum_{\sigma=\alpha}^{\beta} E_n|n\sigma\rangle\langle n\sigma| + \sum_{\sigma=\alpha}^{\beta}(V_{0,1}|0,\sigma\rangle\langle 1,\sigma| + V_{1,0}|1,\sigma\rangle\langle 0,\sigma|) + \sum_{n=1}^{N-1}\sum_{\sigma=\alpha}^{\beta}(V_{n,n+1}|n,\sigma\rangle\langle n+1,\sigma| + V_{n+1,n}|n+1,\sigma\rangle\langle n,\sigma|) + \sum_{r}\sum_{\sigma=\alpha}^{\beta}(V_{N,r}|N,\sigma\rangle\langle r,\sigma| + V_{r,N}|r,\sigma\rangle\langle N,\sigma|) + u\sum_{n=1}^{N}(|n,\alpha\rangle\langle n,\beta| + |n,\beta\rangle\langle n,\alpha|) \quad (3)$$

In the first (diagonal) term, the sum over $\{n\}$ corresponds to all states $n = 0, 1, ..., N, \{r\}$. In our application below we will take $E_n = E_B$, same for all bridge levels $n = 1, ..., N$ and denote the energy gap $E_B - E_0$ by ΔE. The second and fourth terms describe respectively the couplings between the donor level 0 and the first bridge level 1, and between the last bridge level N and the acceptor manifold $\{r\}$. The third term accounts for the nearest neighbor coupling on the bridge. Without the last term there is no coupling between the two internal states and tunneling occurs independently in the two channels.

The last term in eq 3 corresponds to an $\alpha-\beta$ coupling that occurs only when the electron occupies the bridge levels. This coupling supplies the required internal clock. The electron starts in state $|0,\alpha\rangle$ at $t = 0$, and the transition probabilities into the final manifolds $\{r\alpha\}$ and $\{r\beta\}$ are

$$P_\alpha = \sum_r |C_{r\alpha}(t\to\infty)|^2$$
$$P_\beta = \sum_r |C_{r\beta}(t\to\infty)|^2 \quad (4)$$

where $C_{r\sigma}(t)$, $\sigma = \alpha,\beta$ are the amplitudes of the corresponding states at time *t*. The ratio

$$R_\beta \equiv \frac{P_\beta}{P_\alpha + P_\beta} \xrightarrow{u\to 0} \frac{P_\beta}{P_\alpha} \quad (5)$$

can be identified as the transition probability from channel α to channel β during the tunneling event. Since this transition occurs only on the bridge, R_β can measure the corresponding traversal time. Note the significance of the limit taken in eq 5: An ideal clock would induce a transition between channel α and channel β without affecting the overall transmission probability, i.e., would satisfy $P_\alpha(u) + P_\beta(u) = P_\alpha(0)$. This does not happen for finite *u* because the induced splitting between the two "spin" levels affects the energies of the diagonalized bridge levels and therefore the effective barrier height and the overall transmission probability.

To relate the ratio R_β to the time spent on the barrier we consider a system described by the time-dependent Hamiltonian

$$H_t = |\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta| + U(t)(|\alpha\rangle\langle\beta| + |\beta\rangle\langle\alpha|)$$
$$U(t) = u \text{ for } 0 \le t \le \tau;\ U(t) = 0 \text{ otherwise} \quad (6)$$

the implication being that *u* is nonzero only when the electron is on the bridge, therefore τ measures the time during the tunneling event. If this system is in state α at $t \le 0$, then, provided that $u\tau \ll 1$, the probability that it crossed into state β at $t \ge \tau$ is $(U\tau/\hbar)^2$. Comparing this to eq 5 yields

$$\tau = \frac{\hbar R_\beta^{1/2}}{|u|} \quad (7)$$

Equation 7 provides a convenient starting point to compute the "tunneling time" τ for our electron-transfer model. The result should not depend on *u*, which can therefore be chosen small enough for our purpose.

3. Steady State Calculation

The time-dependent wave function for the system described by the Hamiltonian eq 1 is

$$\Psi(t) = \sum_{\sigma=\alpha}^{\beta} C_{0\sigma}(t)|0\sigma\rangle + \sum_{n=1}^{N}\sum_{\sigma=\alpha}^{\beta} C_{n\sigma}(t)|n\sigma\rangle + \sum_r\sum_{\sigma=\alpha}^{\beta} C_{r\sigma}(t)|r\sigma\rangle \quad (8)$$

and the equations of motion for the coefficients *C* are ($\hbar = 1$ is used throughout the derivation)

$$\dot{C}_{0\sigma} = -iE_0C_{0\sigma} - iV_{01}C_{1\sigma} \quad ;\sigma = \alpha,\beta \quad (9)$$

$$\dot{C}_{n\alpha} = -iE_nC_{n\alpha} - iV_{n,n-1}C_{(n-1)\alpha} - iV_{n,n+1}C_{(n+1)\alpha} - iuC_{n\beta} \quad ;n = 1, ..., N \quad (10)$$

$$\dot{C}_{n\beta} = -iE_nC_{n\beta} - iV_{n,n-1}C_{(n-1)\beta} - iV_{n,n+1}C_{(n+1)\beta} - iuC_{n\alpha} \quad ;n = 1, ..., N \quad (11)$$

$$\dot{C}_{N\alpha} = -iE_NC_{N\alpha} - iV_{N,N-1}C_{(N-1)\alpha} - i\sum_r V_{Nr}C_{r\alpha} - iuC_{N\beta} \quad (12)$$

$$\dot{C}_{N\beta} = -iE_NC_{N\beta} - iV_{N,N-1}C_{(N-1)\beta} - i\sum_r V_{Nr}C_{r\beta} - iuC_{N\alpha} \quad (13)$$

$$\dot{C}_{r\sigma} = -iE_rC_{r\sigma} - iV_{rN}C_{N\sigma} \quad ;\sigma = \alpha,\beta \quad (14)$$

For our purpose it is sufficient to follow a standard procedure, integrating eq 14 and substituting the result in eqs 12 and 13, to replace the terms containing sums over *r* in the latter equations by corresponding level shifts and widths, i.e.,

$$i\sum_r V_{Nr}C_{r\sigma} \rightarrow (iD_N + \Gamma_N)C_{N\sigma} \quad \sigma = \alpha,\beta \tag{15}$$

The level shift D_N and the width Γ_N are given by

$$D_N - \frac{1}{2}i\Gamma_N = \lim_{\eta\to 0}\sum_r \frac{|V_{rN}|^2}{E_0 - E_r + i\eta} \tag{16}$$

In particular,

$$\Gamma_N = 2\pi\sum_r |V_{rN}|^2\,\delta(E_0 - E_r) = 2\pi(|V_{rN}|^2\rho_R)_{E_r=E_0} \tag{17}$$

where ρ_R is the density of states in the $\{r\}$ continuum. Equations 9−13 can then be solved for the initial conditions $C_{0\alpha}(t=0) = 1$ and $C_{j\sigma}(0) = 0$ for all other j and σ. A simpler route is provided by a steady state formalism similar to that used in ref 8. A steady state is imposed on eqs 9−13 by replacing eq 9 with the condition $C_{0\alpha}(t) = C_{0\alpha}\exp(-iE_0t)$ (where $C_{0\alpha}$ is some constant amplitude) and by taking the time dependence of all other amplitudes to be given by $C_{j\sigma}(t) = C_{j\sigma}^{ss}e^{-iE_0t}$. This leads to the following equations for the steady states amplitudes $C_{j\sigma}^{ss}$:

$$\Delta EC_{1\alpha}^{ss} + V_{10}C_{0\alpha}^{ss} + V_{12}C_{2\alpha}^{ss} + uC_{1\beta}^{ss} = 0 \tag{18}$$

$$\Delta EC_{1\beta}^{ss} + V_{12}C_{2\beta}^{ss} + uC_{1\alpha}^{ss} = 0 \tag{19}$$

$$\Delta EC_{n\alpha}^{ss} + V_{n,n-1}C_{(n-1)\alpha}^{ss} + V_{n,n+1}C_{(n+1)\alpha}^{ss} + uC_{n\beta}^{ss} = 0 \quad n = 2, ..., N-1 \tag{20}$$

$$\Delta EC_{n\beta}^{ss} + V_{n,n-1}C_{(n-1)\beta}^{ss} + V_{n,n+1}C_{(n+1)\beta}^{ss} + uC_{n\alpha}^{ss} = 0 \quad n = 2, ..., N-1 \tag{21}$$

$$(\Delta\tilde{E} - i\Gamma_N/2)C_{N\alpha}^{ss} + V_{N,N-1}C_{(N-1)\alpha}^{ss} + uC_{N\beta}^{ss} = 0 \tag{22}$$

$$(\Delta\tilde{E} - i\Gamma_N/2)C_{N\beta}^{ss} + V_{N,N-1}C_{(N-1)\beta}^{ss} + uC_{N\alpha}^{ss} = 0 \tag{23}$$

where $\Delta E = E_n - E_0$; $n = 1, ..., N$, and where $\Delta\tilde{E} = \Delta E + D_N$.

Consider first the case where $u = 0$, i.e., there is no coupling on the bridge between the "spin" states. In this case the equations for $C_{n\alpha}^{ss}$ do not couple to those for $C_{n\beta}^{ss}$(for any n) and take the form

$$(\Delta\tilde{E} - i\Gamma_N/2)C_{N\alpha}^{ss} + V_{N,N-1}C_{(N-1)\alpha}^{ss} = 0 \tag{24}$$

$$\Delta EC_{n\alpha}^{ss} + V_{n,n-1}C_{(n-1)\alpha}^{ss} + V_{n,n+1}C_{(n+1)\alpha}^{ss} = 0 \quad n = 2, ..., N-1 \tag{25}$$

$$\Delta EC_{1\alpha}^{ss} + V_{10}C_{0\alpha}^{ss} + V_{12}C_{2\alpha}^{ss} = 0 \tag{26}$$

To the lowest order in $V/\Delta E$ this yields

$$C_{N\alpha}^{ss} = (-1)^N\frac{V_{N,N-1}}{\Delta E - i\Gamma_N/2}\prod_{n=1}^{N-1}\frac{V_{n,n-1}}{\Delta E}C_{0\alpha}^{ss} \tag{27}$$

The *steady state* electron-transfer flux can be written either as $k|C_{0\alpha}^{ss}|^2$ where k is the electron-transfer rate, or as $\Gamma_N|C_{N\alpha}^{ss}|^2$. Disregarding $\Gamma_N^2/4$ relative to ΔE^2, this leads to

$$k = \Gamma_N\prod_{n=1}^{N}\left|\frac{V_{n,n-1}}{\Delta E}\right|^2 \tag{28}$$

which is the usual superexchange result for this model. Note that in this weak bridge-coupling limit, $\Delta E = E_B - E_0$ is a good approximation for the barrier energy $\Delta U = U_B - E_0$, where U_B is determined by the lowest energy eigenvalue of the bridge Hamiltonian.

When $u \neq 0$ (eqs 18−23) can be rearranged in the form

$$\mathbf{MC}_N = -\tilde{\mathbf{V}}_{N,N-1}\mathbf{C}_{N-1} \tag{29}$$

$$\mathbf{MC}_n = -\tilde{\mathbf{V}}_{n,n-1}\mathbf{C}_{n-1} - \tilde{\mathbf{V}}_{n,n+1}\mathbf{C}_{n+1} \quad n = N-1, N-2, ..., 1 \tag{30}$$

where

$$\mathbf{M} = \begin{pmatrix} 1 & \tilde{u} \\ \tilde{u} & 1 \end{pmatrix} \quad \tilde{u} = \frac{u}{\Delta E} \tag{31}$$

$$\tilde{\mathbf{V}}_{n,n-1} = \frac{V_{n,n-1}}{\Delta E}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad n = N, N-1, ..., 1 \tag{32}$$

$$\mathbf{C}_n = \begin{pmatrix} C_{n\alpha}^{ss} \\ C_{n\beta}^{ss} \end{pmatrix} \quad n = N, N-1, ..., 1 \tag{33}$$

$$\mathbf{C}_0 = \begin{pmatrix} C_{0\alpha}^{ss} \\ 0 \end{pmatrix} \tag{34}$$

and where we have again disregarded $(1/2)\Gamma_N$ relative to ΔE. To the lowest order in $V/\Delta E$ these equations lead to

$$\begin{pmatrix} C_{N\alpha}^{ss} \\ C_{N\beta}^{ss} \end{pmatrix} = (-1)^N\frac{V_{N,N-1}}{\Delta E - i\Gamma_N/2}\left(\prod_{n=1}^{N-1V}\frac{V_{n,n-1}}{\Delta E}\right)(M^{-1})^N\begin{pmatrix} C_{0\alpha}^{ss} \\ 0 \end{pmatrix} \tag{35}$$

and to the lowest order in u, assuming also $Nu \ll 1$

$$\mathbf{M}^{-1} = \begin{pmatrix} 1 & -\tilde{u} \\ -\tilde{u} & 1 \end{pmatrix} \rightarrow (\mathbf{M}^{-1})^N = \begin{pmatrix} 1 & -N\tilde{u} \\ -N\tilde{u} & 1 \end{pmatrix} \tag{36}$$

Using eq 36 in eq 35 yields

$$|C_{N\alpha}|^2 = \left|\prod_{n=1}^{N}\frac{V_{n,n-1}}{\Delta E}\right|^2|C_{0\alpha}|^2 \tag{37}$$

and

$$|C_{N\beta}|^2 = \left|\prod_{n=1}^{N}\frac{V_{n,n-1}}{\Delta E}\right|^2\left(\frac{Nu}{\Delta E}\right)^2|C_{0\alpha}|^2 \tag{38}$$

As before, the fluxes into the corresponding acceptor channels $\{r,\alpha\}$ and $\{r,\beta\}$ are $\Gamma_N|C_{N\alpha}^{ss}|^2$ and $\Gamma_N|C_{N\beta}^{ss}|^2$, respectively, and the ratio R_β (cf. eq 5) is

$$R_\beta = \left(\frac{Nu}{\Delta E}\right)^2 \tag{39}$$

and the traversal time on the bridge is (cf. eq 7)

$$\tau = \frac{\hbar N}{\Delta E} \tag{40}$$

We emphasize again that in the weak coupling limit considered above, the zero-order energy gap, ΔE, provides a good estimate for the actual barrier energy.

The result can be derived also by noting that when $u \neq 0$ states $|\alpha\rangle$ and $|\alpha\rangle$ could be transformed to a representation in which u is diagonal,

$$|+\rangle = \frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle) \quad |-\rangle = \frac{1}{\sqrt{2}}(|\alpha\rangle - |\beta\rangle) \tag{41}$$

with a corresponding splitting in barrier energies $\Delta U \mp u$. For the incident particle in the state

$$|\alpha\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle) \tag{42}$$

the transmitted wave function is (with $T(E)$ denoting the transmission amplitude)

$$\psi_t = \frac{1}{\sqrt{2}}[T(\Delta U - u)|+\rangle + T(\Delta U + u)|-\rangle] \tag{43}$$

The relative probability to be transmitted in state $|\beta\rangle = (1/\sqrt{2})(|+\rangle + |-\rangle)$ is

$$R_\beta = \frac{|\langle\beta|\psi_t\rangle|^2}{|\langle\psi_t|\psi_t\rangle|^2} = \frac{|\frac{1}{2}T(\Delta U - u) - \frac{1}{2}T(\Delta U + u)|^2}{\frac{1}{2}(|T(\Delta U - u)|^2 + |T(\Delta U + u)|^2)} \xrightarrow{u\to 0} |u|^2 \left|\frac{\partial \ln T(\Delta U)}{\partial \Delta U}\right|^2 \tag{44}$$

From eq 7 we therefore obtain the general result[7]

$$\tau = \hbar \frac{1}{|T(\Delta U)|}\left|\frac{\partial T(\Delta U)}{\partial \Delta U}\right| \tag{45}$$

and using (cf. eq 27 with $\Delta E \cong \Delta U$) $T \approx \Delta E^{-N}$ leads again to the result. More generally, we expect the transmission amplitude to satisfy an expression of the form

$$T(\Delta U) = \eta[\kappa(\Delta U)]\mathrm{e}^{-\kappa}(\Delta U)^N \tag{46}$$

so that

$$\tau = \tau_0 + \hbar N \frac{\mathrm{d}\kappa(\Delta U)}{\mathrm{d}(\Delta U)} \tag{47}$$

4. Relation to the Landauer−Buttiker Result

The "tunneling time" τ, eq 40, has been derived here for the standard superexchange model of electron transfer using the same reasoning that led to the result of eq 2 obtained by Buttiker and Landauer for tunneling through a rectangular barrier.[4−6] The result associates the tunneling time with the uncertainty time $\hbar/\Delta E$ and with the bridge length N in a way that is intuitively clear and could be anticipated. It is less obvious why this result for τ is independent of the bridge coupling parameters $V_{n,n+1}$. Moreover, the dependencies on the tunneling barrier seen in eqs 2 and 40 are qualitatively different. In this section we consider the correspondence between these results.

First, to facilitate this comparison between eqs 2 and 40, suppose that the bridge length is $D = Na$ and that the bridge functions $|n\rangle$ that define the representation of the Hamiltonian (eq 3) are localized about sites at positions $x_n = (n - 1/2)a$, $n = 1, ..., N$, along the bridge axis x. We focus on the bridge Hamiltonian, disregarding the internal (spin) states

$$H_B = E_B\sum_n |n\rangle\langle n| + V\sum_n (|n\rangle\langle n+1| + |n+1\rangle\langle n|) \tag{48}$$

For an infinite chain, the eigenfunctions of this 1-dimensional tight binding Hamiltonian are Bloch waves, $\psi k = \sum_n \mathrm{e}^{ikna}|n\rangle$ with the corresponding energies $E(k) = E_B + 2V\cos(ka)$. Consider now a tunneling process in which a free particle of energy $E_0 = \hbar^2 k_0^2/2m$ is incident from the left on this bridge. For $x < 0$, the wave function is $\exp(ik_0x) + R\exp(-ik_0x)$. For $x > D$ it is $T\exp(ik_0x)$. For $E_0 < E_B - 2V$ the wave function *in the interior* of the bridge region takes the form

$$\psi(x) = \sum_n (A\mathrm{e}^{-\kappa na} + B\mathrm{e}^{\kappa na})|n\rangle \tag{49}$$

where κ corresponds to the imaginary momentum and satisfies

$$2V[\cosh(\kappa a) - 1] = E_B - 2V - E_0 \equiv \Delta U \tag{50}$$

Note that the energy gap ΔU is now related to the distance between the incident energy and the bottom of the conduction band. The coefficients R, T, A, and B can be determined from the four continuity relations for the wave function and its derivative at positions $x = 0,D$. To write the explicit forms of these relations we need an explicit form for $\psi(x)$ in the bridge near $x = 0,D$. For our purpose, however, its is sufficient to use the fact that these relations are linear:

$$\begin{aligned} 1 + R &= l_1A + l_2B \\ ik_0(1 - R) &= l_3A + l_4B \\ T &= r_1A\mathrm{e}^{-\kappa Na} + r_2B\mathrm{e}^{\kappa Na} \\ ik_0T &= r_3A\mathrm{e}^{-\kappa Na} + r_4B\mathrm{e}^{\kappa Na} \end{aligned} \tag{51}$$

where the l and the r coefficients are constants. Solving the last two equations for A and B in terms of T yields $A = c_1\mathrm{e}^{\kappa Na}T$ and $B = c_2\mathrm{e}^{-\kappa Na}T$ with other constants c_1 and c_2. Eliminating R from the first two equations yields a linear relationship between A and B of the form $L_1A + L_2B = 1$, with yet other constants L_1 and L_2. Together these relations therefore give

$$T = \frac{C_1\mathrm{e}^{-\kappa Na}}{1 + C_2\mathrm{e}^{-2\kappa Na}} \cong C_1\mathrm{e}^{-\kappa Na} \tag{52}$$

Using eqs 47, 50, and 52 and disregarding the possible energy dependence of C_1 (this will yield an N independent term in eq 53 below) now yields the traversal time for tunneling in the form

$$\tau = \frac{\hbar N}{2V\sqrt{\frac{\Delta U}{V} + \left(\frac{\Delta U}{2V}\right)^2}} \tag{53}$$

In the weak coupling limit, $\Delta U \gg V$, this gives $\tau = \hbar N/\Delta U$ and noting that in this limit $\Delta U \cong \Delta E$ we recover the result (eq 40). In the opposite limit, eq 53 becomes

$$\tau = \frac{\hbar N}{2\sqrt{V\Delta U}} \tag{54}$$

which is equivalent to the Buttiker−Landauer result (eq 2). In fact, eq 54 leads to eq 2 if we express V in terms of the effective mass for the band motion, $m = \hbar^2/2Va^2$.

4. Conclusion

The "tunneling time" τ has been derived here has having the same significance as originally discussed by Landauer and Buttiker: It measures the relative importance of processes that may occur on the barrier, or the bridge, during the tunneling event. For these processes to be efficient their characteristic time

has to be of the same order as this measure of duration for the tunneling event.

The result (eq 40) associates the tunneling time with the uncertainty time $\hbar/\Delta E$ and with the bridge length N. It is interesting to note that a result of exactly the same form is obtained for the time associated with resonance transmission through allowed band states, where in that case ΔE is half the bandwidth.[7] We have found that this form, with ΔE representing the energy barrier, measures the time scale associated with electron transmission in superexchange processes, where the intersite coupling on the bridge is assumed to be small relative to this energy gap. Within the framework of the same model, the Buttiker−Landauer result corresponds to the opposite strong coupling limit.

An important issue in bridge mediated electron transfer is the possible involvement of bridge nuclear motions in the transfer process. From the above discussion it is evident that this issue is directly associated with the bridge traversal time. For $\Delta E \sim 1$ eV and $N = 3-5$, eq 40 puts τ in the same range as intramolecular vibrations, indicating that they may play a significant role.

Note however that the result of eq 40 is an estimate for the time spent on the entire barrier, measured with respect to competing barrier processes. It should be kept in mind that other measures of time, defined and calculated in a way similar to that presented here, can be significant. For example, if a competing process occurs on one particular bridge site rather than on the entire bridge, it may be more significant to consider the time spent on a single bridge site during the tunneling process. This will be an analogue of the local tunneling times considered in generalizations of the Buttiker−Landauer problems.[9]

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