Semiclassical Theory for Tunneling of Electrons Interacting with Media[†]

Alexander L. Burin,* Yuri A. Berlin,* and Mark A. Ratner*

Department of Chemistry, Center for Nanofabrication and Molecular Self-Assembly, and Materials Research Center, Northwestern University, 2145 North Sheridan Road, Evanston, Illinois 60208-3113

Received: October 13, 2000; In Final Form: December 12, 2000

The exact semiclassical wave function for a tunneling electron, coupled to the degrees of freedom of a host medium, is constructed. This permits a description of electron dynamics within the barrier. As a specific application, the result is used to calculate the tunneling amplitude for the electron interacting with the single vibrational mode of the medium. In agreement both with experiment and with previous numerical study two regimes of tunneling, i.e., polaron-type vibronic transport and superexchange, are found depending on the relationship of the Buttikker−Landauer tunneling time and the vibrational period. The evolution of the media interacting with the tunneling particle is described.

I. Introduction

Charge transfer between electron donor and acceptor,[1,2] or between two metals coupled by a molecular bridge,[3] occurs by quantum tunneling, when the barrier separating initial and final states is high enough. The tunneling electron moving onto the molecular bridge can change the bridge degrees of freedom. The induced change of the bridge state influences the tunneling particle and modifies its tunneling rate. Therefore, the interaction with the media can become very important for various charge-transfer phenomena.

Semiclassical approaches have been extremely important in application to chemical phenomena as diverse as barrier tunneling,[4] bimolecular collisions,[5] inelastic scattering,[6] and electron transfer.[7] In this work we develop a semiclassical picture for description of the tunneling of an electron through an energy barrier when the barrier contains internal degrees of freedom that can interact with the electron. This very significant issue in charge-transfer problems has been examined using many different and powerful theoretical approaches.[2] The semiclassical trajectory analysis offers several important advantages, including generality with respect to barrier shape and medium modes as well as facile and attractive physical interpretation.

Theoretical understanding of interaction effects is based on the Buttiker−Landauer concept of tunneling time τ_0, i.e., the time the electron spends under the barrier.[8] This time can be expressed as the duration of motion under the inverted barrier

$$\tau_0 = \frac{\sqrt{m}L}{\sqrt{2\Delta}} \tag{1.1}$$

where m is the electron mass, L is the barrier length, and Δ estimates the barrier height.[9]

Let the degrees of freedom of the medium be characterized by a characteristic frequency Ω_M. If the tunneling is relatively fast, i.e.

$$\Omega_M \tau_0 < 1 \tag{1.2}$$

the medium dynamics is unable to follow the tunneling particle. In this situation slow excitations reduce the tunneling rate when initial and final equilibrium states of the medium differ from each other[10,11] because of their nonorthogonality. In the opposite case where

$$\Omega_M \tau_0 > 1 \tag{1.3}$$

the medium follows the motion of tunneling particle; with strong coupling to vibrations, this can lead to formation of a polaron. In the intermediate regime, where $\Omega_M \tau_0 \sim 1$, inelastic processes during tunneling are most probable.[8]

Usually, electronic tunneling is considered to be faster than vibronic relaxation because of the difference in electronic and atom masses.[12a] Therefore, the dynamic interaction effects should be weak. However in molecular bridges or wires the parameters can be different. The tunneling time can be increased by the applied voltage or by lowering the molecular orbital energies via bridge substitution, both of which lower the barrier (see eq 1.1 and Figure 1). Then the current changes significantly due to inelastic processes.[13,14] The slow tunneling regime can also occur for a sufficiently long molecular bridge. Recent numerical analysis within the tight binding approach[15] shows that the energetics of tunneling change in that regime. The tunneling barrier is lowered by media modes since the dynamic interaction assists tunneling.

The significance of dynamic interaction effects on the tunneling is the main motivation for this work. The common analysis of particle tunneling accompanied by the dynamic interaction with the medium is generally a hard problem, and most theoretical work evaluating such effects is largely numerical (see, e.g., most recent papers[13−19]). The development of analytical theory becomes easier, when the semiclassical approach is applicable; i.e., the tunneling barrier height exceeds other energies, characterizing the medium.[12b] Then the basis along the tunneling coordinate can be limited to the component decreasing with respect to this coordinate. However, even within the semiclassical approach, the analytical theory of dynamic interaction effects on the tunneling is usually restricted to the case of electron−vibration interaction.[12a,b] Below we extend the semiclassical analysis to almost any type of electron−medium interactions with the exception of exchange. In section II we

---

Tunneling of Electrons Interacting with Media

J. Phys. Chem. A, Vol. 105, No. 12, 2001 **2653**

Molecular wire unoccupied level

$\Delta(\phi_B)$ tunneling barrier

$\phi_B/2$

Fermi Levels

$\phi_B/2$

Molecular wire

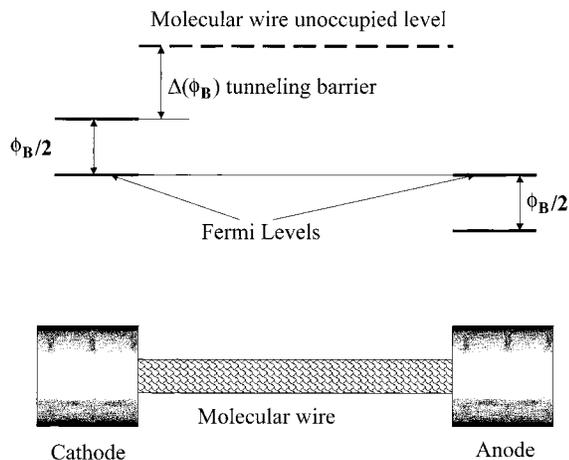Cathode   Anode

Figure 1. Positions of Fermi levels of leads with respect to the lowest unoccupied molecular level of wire under applied bias voltage ϕ_B. The voltage drops are assumed to occur at the interfaces between wire and metals. Therefore, the bias voltage shifts Fermi levels of left and right leads by $+(-)\phi_B/2$, respectively, and leaves molecular levels unchanged.

construct the semiclassical wave function for the tunneling particle plus medium, exact within the semiclassical approach. In section III this result is applied to calculate the interaction effect on the tunneling amplitude and the medium evolution during tunneling for the simple model of interaction with a single vibration mode. This model describes the interaction of the tunneling electron with the most significant optic mode of vibration. The limits of fast and slow tunneling described by eqs 1.1 and 1.2 are considered separately. The results derived in section III for a slow medium (see eq 1.2) are shown to reproduce earlier theoretical findings[12] obtained for the tunneling of electron interacting with vibrations within the semiclassical approach. Some conclusions following from our treatment are formulated and briefly discussed in section IV.

II. Semiclassical Wave Function for a Tunneling Particle Interacting with the Medium

The tunneling of a particle interacting with the medium can be described by the Hamiltonian (we set $\hbar = 1$ throughout)

$$\hat{H} = -\frac{1}{2m}\cdot\frac{d^2}{dx^2} + U(x) + \hat{V}_M(x) + \hat{H}_M \qquad (2.1)$$

Here coordinate x describes the motion of the electron of the mass m, $U(x)$ is the external static potential energy, $\hat{H}_M$ describes the medium degrees of freedom interacting with the moving electron, and $\hat{V}_M(x)$ describes the interaction between the medium and the electron. We will focus here on the molecular wire situation, where the potential $U \sim \Delta$ forms the barrier for tunneling from the left lead ($x = 0$) to the right lead ($x = L$), and the barrier height is given by the energy Δ. The interaction is selected to equal zero at the beginning of the tunneling trajectory $V_M(0) = 0$. This can be achieved by the appropriate definition of the medium Hamiltonian $\hat{H}_M$.

To simplify the problem, we assume that tunneling proceeds along a single, optimum trajectory, which involves a certain number of bridge orbitals. In more rigorous study, several other semiclassical trajectories can be taken into account. They may interfere with the optimum trajectory constructively or destructively. However, if a system has no special symmetry (e.g., spin degeneracy), the contribution of various semiclassical trajectories to the tunneling amplitude will differ significantly by the

absolute value. As a result, the contribution of the optimum trajectory will dominate.

Molecular current flow discussions are usually based on orbital (tight-binding) rather than barrier pictures. In that picture, one could discuss hole-type and electron-type superexchange mediated respectively by occupied or empty bridge orbitals. Such local consideration will, in the simplest situation, be functionally identical to the local barrier-tunneling picture used here.

We are interested in the solution of the stationary Schrödinger equation defined by the Hamiltonian (2.1) with eigenenergy E. To proceed, the tunneling path will be separated into a set of small segments. The interaction with each segment is taken x-independent and equal to some characteristic average value. Then the medium and electron problems can be decoupled within each segment and the expression for the exact function can be obtained as a superposition of products of electronic and medium states. Finally, the continuity requirement in the semiclassical form will be taken to bind the solutions at various segments in the limit of zero segment length and infinite number of segments. This enables us to construct the semiclassical wave function of the problem under the barrier.

One can separate the total tunneling path $(0, L)$ into N small segments $(0, x_1)$, (x_1, x_2), ..., (x_{n-1}, L). Assuming that the potential energy U and interaction with the medium V_M do not change within each small segment (x_{i-1}, x_i), one can replace them by mean values, i.e.

$$\tilde{U}(x) = U_i = U((x_i + x_{i+1})/2)$$

$$\hat{V}_M(x) = V_{M,i} = V_M((x_i + x_{i+1})/2)$$

$$x_i < x < x_{i+1} \qquad (2.2)$$

Then the eigenstates of the stationary Schrödinger equation with energy E, defined by the Hamiltonian (2.1) with interactions U and V_M replaced according to eq 2.2, can be constructed within each segment (x_{i-1}, x_i). They are the products of the eigenstates of the media $|\alpha_{i,m}\rangle$ and the semiclassical one-dimensional "plane waves" with the imaginary momentum, $\exp(\pm p_{i,m}x)$, because the domain under the barrier is classically forbidden. Hence

$$\Psi^i_{m,E} = |\alpha_{i,m}\rangle \exp(\pm p^i_{m,E}(x - x_i))$$

$$(\hat{V}_{M,i} + \hat{H}_M)|\alpha_{i,m}\rangle = E_{i,m}|\alpha_{i,m}\rangle$$

$$p^i_{m,E} = \sqrt{(2m)(-E + U_i + E_{i,m})} \sim \sqrt{(2m)(-E + \Delta)} \qquad (2.3)$$

The imaginary momentum $p_{i,m}$ is defined to ensure that the total energy $E = E_{i,m} - p^2_{m,E}/(2m)$ satisfies the stationary Schrödinger equation for the whole system.

The solution within the ith segment can be written as

$$|\Psi^i_E\rangle = \sum_m [c^{i-}_{E,m}|\alpha_{i,m}\rangle \exp(-p^i_{m,E}(x - x_i)) +$$

$$c^{i+}_{E,m}|\alpha_{i,m}\rangle \exp(+ p^i_{m,E}(x - x_i))] \quad (2.4)$$

For definiteness, we consider the eigenstate under the barrier as the continuation of the left lead state mostly occupying the space $x < 0$. Then the wave function should decrease exponentially under the barrier. Within the semiclassical approximation we will keep only the decreasing term in eq 2.4, which corresponds to the exponential tail of the semiclassical state

$$|\Psi^i_E\rangle = \sum_m c^i_{E,m}|\alpha_{i,m}\rangle \exp(-p^i_{m,E}(x - x_i)) \qquad (2.5)$$

This assumption corresponds to the standard "noninteracting" semiclassical approach.[20] One can show that it is justified for our problem, when the tunneling barrier Δ exceeds the characteristic electron−medium interaction energy. This approximation is physically reasonable since the tunneling barrier is usually given by the electronic energy scale $\sim 1−2$ eV, while the interaction with the medium is defined by the reorganization energy $\sim 0.1−0.5$ eV.

To construct the eigenstate under the barrier, we expand the solutions (2.5) within the whole set of N segments from the initial point $x = 0$ to the end point $x = L$. One then needs to make N binding steps between neighboring segments and then take the limit $N \to \infty$. The binding conditions are continuity requirements for eigenfunctions (2.5) between subsequent segments. The treatment should also demand the continuity of the derivative between each pair of subsequent segments, but this is irrelevant since we are using the reduced semiclassical basis set (2.5) instead of the total set (2.4).

Consider the elementary binding step between segments i and $i + 1$. The solution in the segment i is expressed by eq 2.5, while the solution in the segment $i + 1$ can be written as

$$|\Psi_E^{i+1}\rangle = \sum_m c_{E,m}^{i+1}|\alpha_{i+1,m}\rangle \exp(-p_{m,E}^{i+1}(x - x_{i+1})) \quad (2.6)$$

The continuity between solutions eqs 2.5 and 2.6 at $x = x_{i+1}$ requires

$$\sum_m c_{E,m}^i|\alpha_{i,m}\rangle \exp(-p_{m,E}^i(x_{i+1} - x_i)) = \sum_m c_{E,m}^{i+1}|\alpha_{i+1,m}\rangle \quad (2.7)$$

Projecting eq 2.7 onto the medium states in segment $i + 1$, one can express the set of coefficients c^{i+1} in terms of the set c^i as

$$c_{E,m}^{i+1} = \sum_a \langle\alpha_{i+1,m}|\alpha_{i,a}\rangle \exp(-p_{a,E}^i(x_{i+1} - x_i))c_{E,a}^i \quad (2.8)$$

It is convenient to relate the intermediate momentum to the value p_0^i that would occur if the medium energy remains the same as at the beginning of tunneling. Assume that the initial state of the media is $|\alpha_0\rangle$ with energy E_{M0}. If the energy of the medium remains unchanged during the tunneling to the segment i from the segment 0, the momentum at the segment i will be $p_{i,0} = \sqrt{(2m)(-E+U_i+E_{M0})}$ (see eq 2.3). The exponent in eq 2.8 can be rewritten generally as

$$\exp(-p_{i,0}\Delta x - (p_{a,E}^i - p_{i,0})\Delta x)$$

$$\Delta x = x_{i+1} - x_i \quad (2.9)$$

The difference of momenta in eq 2.9 describes the dynamic interaction with the medium during tunneling. It should be small in comparison with the initial value of the momentum $p_{i,0}$ since we have assumed that the interaction energy with the medium is less than the tunneling barrier Δ. Accordingly, one can expand the momentum difference in eq 2.9 over the energy difference between initial and intermediate medium states making use of the momentum definition in eq 2.3

$$p_{a,E}^i - p_{i,0} \approx \frac{2}{v_i}(E_{i,a} - E_{M0})$$

$$v_i = \frac{p_{i,0}}{m} \quad (2.10)$$

Here v_i defines the imaginary speed of tunneling at the segment i. Since the ratio $\Delta\tau = \Delta x/v$ is the time of tunneling through

segment i in the inverted barrier, one can rewrite eq 2.8 in terms of energy changes and tunneling time as

$$c_{E,m}^{i+1} = \exp(-\Delta S_0) \sum_a \langle\alpha_{i+1,m}|\alpha_{i,a}\rangle \exp(-\Delta\tau_i(E_{i,a} - E_{M0}))c_{E,a}^i \quad (2.11a)$$

$$\Delta S_0 = p_{i,0}\Delta x$$

$$\Delta\tau_i = \frac{\Delta x}{v_i} \quad (2.11b)$$

One can express the transform (2.11) as the action of a tunneling time-dependent operator

$$\exp(-\Delta S_0 + \Delta\tau_i E_{M0}) \exp[-(\hat{V}_M(\tau_i) + \hat{H}_M)\Delta\tau_i] \quad (2.12)$$

where the tunneling time τ_i is related to the segment position x_i by the classical mechanics relation for the inverted barrier

$$\tau_i = \int_0^{x_i} \frac{\sqrt{2m}\,dx}{\sqrt{-E + U(x) + E_{M0}}} \quad (2.13)$$

The wave function at some tunneling time τ corresponding to the point $x(\tau)$ of the tunneling path can be expressed through the tunneling (imaginary) time-ordered product of operators (2.12) acting on the initial state of the medium. In the limit $\Delta\tau \to 0$ this can be expressed in the integral form as

$$\Psi_M(x(\tau)) = \exp(-S_0(\tau))T^{-1}\{\exp(-\int_0^\tau d\tau' \, (\hat{V}_M(\tau') + \hat{H}_M))\} \exp(\hat{H}_M\tau)\Psi_M(x{=}0) \quad (2.14)$$

where $S_0(\tau) = \int_0^{x(\tau)}dx \, \sqrt{(2m)(-E+U(x))}$ is the classical under barrier action calculated neglecting the interaction with the medium, and the symbol $T\{...\}$ stands for the (imaginary) time τ ordered tunneling exponent. Remember that, for convenience, the interaction $\hat{V}_M$ in eqs 2.1 and 2.14 is defined to have $\hat{V}_M(0) = 0$. The product of two exponential operators can be expressed in more compact form as follows

$$\Psi_M(x(\tau)) = \exp(-S_0(\tau))T^{-1} \times$$
$$\exp\{-\int_0^\tau d\tau'\hat{V}_M(\tau',-i(\tau'-\tau))\}\Psi_M(x{=}0)$$
$$V_M(\tau't) = \exp(itH_M) V_M(\tau') \exp(-itH_M) \quad (2.15)$$

To describe the whole tunneling process, one needs the eigenfunction (2.14) at the end of the tunneling barrier $x = L$, corresponding to the total tunneling time

$$\tau_0 = \int_0^L \frac{\sqrt{2m}\,dx}{\sqrt{-E + U(x) + E_{M0}}} \quad (2.16)$$

We denote the initial state of the medium as $|\alpha,0\rangle$ and final state as $|\beta,L\rangle$. The matrix element for the tunneling process accompanied by the transition from the state $|\alpha\rangle$ to the state $|\beta\rangle$ can be expressed as

$$t_{\alpha\beta} = B_0 \exp(-S_0(\tau_0))\langle\beta,L|\hat{A}|\alpha,0\rangle$$
$$\hat{A} = T^{-1} \exp\{-\int_0^{\tau_0} d\tau' \, \hat{V}_M(\tau',-i(\tau'-\tau_0))\} \quad (2.17)$$

Here B_0 is a characteristic preexponent for the semiclassical tunneling matrix element between right and left electronic states, if the bridge is considered as a perturbation (see, e.g., ref 11). Calculation of B_0 is outside of a scope of a semiclassical

Tunneling of Electrons Interacting with Media

J. Phys. Chem. A, Vol. 105, No. 12, 2001 **2655**

approach. The operator $\hat{A}$ describes the evolution of the medium during tunneling.

Evaluation of the matrix element (2.17) is easier, when the same basis set is used for initial and final states. The medium eigenstate $|\beta,L\rangle$ at the end of the tunneling path can be expressed in terms of the corresponding state $|\beta,0\rangle$ at the beginning of the tunneling path using the unitary operator of adiabatic transfer as

$$|\beta,L\rangle = \hat{\Pi}|\beta,0\rangle$$
$$\langle\beta,L| = \langle\beta,0|\hat{\Pi}^{-1} \tag{2.18}$$

For the system without degeneracy, this operator can be defined through the time ordered exponent of the perturbative interaction term:

$$\hat{\Pi} = T\exp\{i\int_{-\infty}^{0}dt\,\hat{V}(\tau_0,t)\} \tag{2.19a}$$

$$\hat{V}(\tau,t) = \exp(iH_M t)\hat{V}(\tau)\exp(-iH_M t) \tag{2.19b}$$

Then the tunneling matrix element eq 2.17 within the basis of final medium states $|\beta\rangle \equiv |\beta,L\rangle$ is given by

$$t_{\alpha\beta} = B_0\exp(-S_0(\tau))\langle\beta|\Pi^{-1}T\exp\{-\int_0^{\tau_0}d\tau\,'\hat{V}_M(\tau',-i(\tau'-\tau_0))\}|\alpha\rangle \tag{2.20}$$

Elastic tunneling occurs without change of the medium state with the conservation of the index α. Assuming initial thermal equilibrium, the elastic tunneling amplitude taking the interaction with the medium into account becomes

$$t_{coh} = B_0\exp(-S_0(\tau))\langle\Pi^{-1}T\exp\{-\int_0^{\tau_0}d\tau'\hat{V}_M(\tau',\tau'-\tau)\}\rangle \tag{2.21}$$

where averaging is done over the Boltzmann distribution of medium states for temperature T. For both elastic and inelastic transfer, one can make use of the Fermi Golden rule and eq 2.20 to compute the charge-transfer tunneling rate $W(\epsilon)$ between initial and final particle states with energy difference ϵ, which is dissipated to the medium excitations (see, e.g., ref 11). As a result, we get

$$W(\epsilon) = \langle\sum_\beta t_{\alpha\beta}{}^2\delta(\tilde{E}_\beta - E_\alpha + \epsilon)\rangle$$

$$= \frac{B_0{}^2\exp(-2S_0(\tau_0))}{2\pi}\int_{-\infty}^{+\infty}dt\,e^{i\epsilon t}\langle\hat{A}^+\exp(i\hat{H}_f t)\hat{A}\times$$
$$\exp(-i\hat{H}_i t)\rangle \tag{2.22}$$

Here the Hamiltonians $\hat{H}_i$ and $\hat{H}_f$ describe the medium properties at the beginning and the end of trajectory, respectively,

$$\hat{H}_i = \hat{H}_M$$
$$\hat{H}_f = \hat{H}_M + \hat{V}_M(\tau_0) \tag{2.23}$$

The energies E_α and $\tilde{E}_\beta$ are the energies of initial and final Hamiltonian eigenstates α and β, and $\hat{A}$ was defined by the second line in eq 2.17.

The exact semiclassical expression for tunneling matrix elements, given by eqs 2.20 and 2.21 are the main results of this section. The rest of the paper is devoted to the application of the formalism to the problem of a tunneling electron in a molecular wire, interacting with a vibrational mode.

III. Interaction of a Tunneling Electron with a Vibration Mode

We will apply the results of the previous section to the model of electron tunneling through a long molecule, connecting two metal leads under applied bias voltage.[3] The interacting medium modes will be limited, in this example, to a single vibration. Usually the Fermi levels of metals are located within the HOMO/LUMO gap of the bridge[21] and the energy difference between the Fermi energy and the lowest unoccupied molecular level forms the tunneling barrier (see Figure 1).[22] The height of this barrier differs for different metals and molecules ranging from several eV[23] to almost vanishing in carbon nanotubes.[24,25] We consider the barrier Δ sufficiently large to apply a semiclassical formalism.

In a symmetric junction, the bias voltage ϕ_B shifts Fermi levels of right and left leads by $\phi_B/2$ up and down, respectively. The applied voltage is considered to be so small that the density of states at the Fermi levels does not change when the Fermi level is shifted by $\phi_B/2$. Assume, following the consideration of ref 21, that the drop of potential mostly occurs at the interface between the molecule and metals (see Figure 1). Then the tunneling barrier is controlled by the applied voltage and changes as

$$\Delta(\phi_B) = \Delta(0) - \frac{\phi_B}{2} \tag{3.1}$$

Accordingly, the tunneling time eq 1.1 increases with increasing ϕ_B and the tunneling regime can be changed from fast (1.2) to slow (1.3) at sufficiently large ϕ_B.

Usually, a tight binding Hückel-type model is used to consider the electron transport through molecular wires occurring by tunneling between separated atomic orbitals.[14−16,21,24] However, covalent networks of most bridges seem strong enough to provide quasi-continuous charge motion rather than a set of jumps between discrete points.[23,24]

Generally, the tight-binding model is appropriate when the overlap of the atomic orbitals is small. The effective mass of the moving charge scales as the inverse tunneling matrix element between neighboring orbitals (see, e.g., ref 9) and should be large in comparison with the electronic mass if the tight-binding model is appropriate. However the bare electronic mass can be used to treat the data of ref 23 for the $(CH_2)_n$ molecular wire. Accordingly, the continuous media model may be more appropriate than the tight-binding one for that problem (which is sensible, since polyalkanes have very large bandwidths).[26]

Note that even for a wide-gap semiconductor such as a DNA chain, the effective mass of the carrier (hole) seems to be close to the standard electronic mass, which suggests the possible relevance of a continuous model even there.[27] Thus, the continuous model can be adequate to treat the electron transport through the molecular wire.

To simplify the effect of electron−vibration interaction, we keep only one significant optic mode. The ability to describe the most significant aspect of the complex electron−vibration interaction using a single relevant optical mode has been suggested by Zerbi et al.[28] In particular, this assumption is sufficient to describe the emission spectrum (see discussion in ref 29 and references therein).

The opposite assumption of the significance of acoustic vibrations has been used in ref 12. There it has been motivated

by the smaller amplitude of vibrations for optic modes than for acoustic ones. However, charge should interact more strongly with the polarized optic mode than with the quasi-neutral acoustic vibration. Additionally, the dynamic interaction becomes stronger, when the tunneling time equation (1.1) is closer to the vibration period. Certainly, the tunneling time of a light electron is closer to the period of optical vibrations than of acoustic vibrations.

Accurate theory should of course treat all interactions. The purpose of this section is to demonstrate the main effect of vibrations on the tunneling, which is clear within the framework of the single mode model. The generalization to interaction with many modes is straightforward.[30]

The characteristic energy of the relevant mode can be estimated as $\hbar\Omega \sim 0.2$ eV (see, e.g., refs 27 and 28). This mode can be, for instance, the most strongly coupled C−H or C−C vibrations.[31] The vibrations can be described by the Hamiltonian

$$\hat{H}_M = \frac{\hat{p}^2}{2M} + M\Omega^2 \frac{\hat{u}^2}{2} \tag{3.2}$$

where $\hat{p}$ and $\hat{u}$ are the momentum and displacement operators and M is the effective mass of the vibration.

We take the electron−vibration interaction in the standard form, which linearly depends on the displacement $\hat{u}$, i.e.

$$\hat{V}_M(\tau) = -\gamma(\tau)\hat{u} \tag{3.3}$$

where $\gamma(\tau)$ is the interaction constant, different at different positions (or tunneling times) of the moving electron. This approach is standard for the electron−vibration interaction.[30,32] It corresponds to the expansion in the lowest order of the small vibration amplitude u. Expressions (2.21) and (2.22) can be evaluated analytically for the interaction (3.3), while the problem becomes more complicated for the bilinear interaction.

The dependence of the interaction constant on the tunneling time τ describes its coordinate dependence (see eq 2.13, showing the relation between coordinate and tunneling time). It is convenient to express the interaction constant through the corresponding reorganization energy E_R (oscillator equilibrium energy change due to the perturbation; see, e.g., refs 1, 2, 7, and 33)

$$E_R(\tau) = \frac{1}{2}\frac{\gamma^2}{M\Omega^2}$$

$$M\Omega^2\frac{u^2}{2} - \gamma(\tau)u = -E_R(\tau) + M\Omega^2\frac{(u - u_{eq}(\tau))^2}{2}$$

$$u_{eq}(\tau) = \frac{\gamma(\tau)}{M\Omega^2} \tag{3.4}$$

For estimates we will use the reorganization energy typical for organic molecules, $E_R \sim 0.4$ eV.[1,7,33]

When an electron enters or leaves the bridge, its interaction with the molecular bridge modes almost vanishes and we can put

$$\gamma(0) = \gamma(\tau_0) = 0 \tag{3.5}$$

where τ_0 is the total tunneling time defined in eq 2.16. Since the initial and final basis of medium states are the same, the adiabatic operator equation (2.19) is unity and can be omitted in the definition of the average elastic tunneling amplitude equation (2.21). For the case of electron transfer in donor−

bridge−acceptor systems, the interaction constant is generally different at the beginning and the end of the tunneling ($\gamma(\tau_0) \neq 0$). Then one can construct the adiabatic operator, taking into account that the change of eigenstates of the medium Hamiltonian equation (3.4) during tunneling can be described as a shift of the equilibrium position to $u_{eq}(\tau)$. Accordingly, the change of vibrational states during tunneling from the donor to the acceptor can be represented by the coordinate shift operator as

$$\hat{\Pi}(\tau) = \exp\left(\frac{\gamma(\tau)}{M\Omega^2}\partial_u\right) \tag{3.5a}$$

To compute the elastic tunneling amplitude equation (2.20), one needs to evaluate the tunneling time dependent interaction operator equation (2.15). Making use of the second quantization representation of the oscillator displacement,[34] we get

$$\hat{V}_M(\tau') = -\gamma(\tau')u = -\gamma(\tau')\sqrt{\frac{1}{2M\Omega}}(b^+ + b)$$

$$\hat{V}_M(\tau', -i(\tau' - \tau_0)) = -\gamma(\tau')\,u(-i(\tau' - \tau_0)) =$$
$$-\gamma(\tau')\sqrt{\frac{1}{2M\Omega}}(b^+ e^{\Omega(\tau' - \tau_0)} + b e^{-\Omega(\tau' - \tau_0)})$$

$$\hat{\Pi}^{-1}(\tau_0) = \exp\left(-\frac{\gamma(\tau_0)}{M\Omega^2}\partial_u\right) = \exp\left(-\frac{\gamma(\tau_0)}{M\Omega^2}\sqrt{\frac{M\Omega}{2}}(b - b^+)\right)$$
$$\tag{3.6}$$

where operators b^+ and b describe the creation or annihilation of a vibrational excitation. Since for the case of interest (molecular wire) eq 3.5 holds, one can ignore the effect of the adiabatic transfer operator. Then the elastic tunneling amplitude can be evaluated by making use of the Wick theorem for Bose operators[20] as

$$t_{coh} = B_0 \exp(-S_0(\tau)) \exp\left[\frac{1}{2M\Omega}\int_0^{\tau_0}d\tau'\,\gamma(\tau')\int_{\tau'}^{\tau_0}d\tau'' \times\right.$$
$$\left.\gamma(\tau'')\,(e^{\Omega(\tau' - \tau'')}(1 + \nu_\Omega) + \nu_\Omega e^{-\Omega(\tau' - \tau'')})\right]$$

$$\nu_\Omega = \frac{1}{\exp\left(\frac{\hbar\Omega}{k_B T}\right) - 1} \tag{3.7}$$

In the static limit for the vibrations ($\Omega = 0$), this result is equivalent to the semiclassical approach of ref 12a.

Note that the proposed formalism also allows the exact treatment of a harmonic donor−bridge−acceptor system, where the operator $\hat{\Pi}$ is of major importance because of reorganization. The difference with eq 3.7 is the presence of the additional exponential factors. It can be shown that at low frequency this contribution dominates.[7,34] At low temperature this donor/acceptor coupling difference reduces the tunneling amplitude by the Franck−Condon factor $\exp(-\gamma^2/(4M\Omega^3))$ in exact agreement with many previous studies (see, e.g., refs 1, 2, 10, 11, and 35). This factor represents the overlap integral between the initial and final ground states of the vibrational medium and solvent, which differ by the shift of the oscillator center by $u_{eq}(\tau_0)$ (eq 3.4). Therefore, the nonorthogonality of medium states at the beginning and the end of tunneling can reduce the elastic tunneling amplitude and charge transfer rate (donor−bridge−acceptor systems). In sharp distinction for the molecular wires, initial and final medium vibrational states are the same, since charge is initially outside of the molecule and finally leaves it.

Tunneling of Electrons Interacting with Media

J. Phys. Chem. A, Vol. 105, No. 12, 2001 **2657**

Returning to the wire situation, for the optical mode $\hbar\Omega \sim 0.2$ eV, so one can neglect the effect of the temperature and set the population factor $\nu_\Omega = 0$ at room temperature. Making use of the boundary conditions eq 3.5, one can expand the interaction constant in a Fourier series. This gives

$$\gamma(\tau) = \sum_{n=1}^{\infty} \gamma_n \sin\left(\frac{\pi\tau n}{\tau_0}\right)$$

$$\gamma_n = \frac{2}{\tau_0} \int_0^{\tau_0} d\tau \, \gamma(\tau) \sin\left(\frac{n\pi\tau}{\tau_0}\right) \qquad (3.8)$$

If $\gamma(\tau)$ is positive (or negative) during the whole tunneling path, then the components γ_n with $n > 1$ will be smaller in comparison to γ_1 due to the oscillations of the integral in eq 3.8. This can hold for ionic vibrations perpendicular to the molecular axes, since negatively charged electrons attract positive ions and repel negative ions. Therefore, we consider the tunneling exponent in eq 3.7 by keeping only one term in eq 3.8, namely

$$\gamma(\tau) = \gamma_1 \sin\left(\frac{\pi\tau}{\tau_0}\right) \qquad (3.9)$$

The effect of higher harmonics can also be evaluated analytically; this does not change the qualitative behavior but makes the analysis much more complicated.

To describe the effect of interaction, we calculate the tunneling amplitude eq 2.20 and the average energy of the tunneling particle along the tunneling path.

Making use of the definition eq 3.9, one can calculate the tunneling amplitude eq 3.7. As a consequence, we get

$$t_{0,\text{med}} \propto B_0 \exp(-S_0(\tau_0)) \times$$
$$\exp\left[\frac{E_R}{\hbar\Omega}\left(\frac{\Omega\tau_0}{2\left(1+\frac{\pi^2}{(\Omega\tau_0)^2}\right)} + \left(\frac{\pi}{\Omega\tau_0}\right)^2 \frac{1+\exp(-\Omega\tau_0)}{\left(1+\frac{\pi^2}{(\Omega\tau_0)^2}\right)^2}\right)\right] \qquad (3.10)$$

where E_R is the maximum reorganization energy (see eq 3.4) in the middle of the tunneling path.

In the slow tunneling regime eq 1.3 the correction to the tunneling exponent is proportional to the tunneling time. The tunneling amplitude (3.10) can be approximated by

$$t_{0,\text{med}} \propto B_0 \exp(-S_0(\tau_0) + E_R\tau_0/2) \qquad (3.11)$$

The result (3.11) can be interpreted by assuming that the vibrational mode remains in the ground state during the whole tunneling path, thus reducing the tunneling barrier by the reorganization energy equation (3.4). Accordingly, the total tunneling action should be redefined as

$$S = S_0 - \int_0^{\tau_0} d\tau \, E_R(\tau) \qquad (3.12)$$

leading exactly to the result eq 3.11. Note that in the limit of the very fast mode $\Omega \to \infty$, the correction to the tunneling exponent in eq 3.12 vanishes as Ω^{-2}. It is understandable that stiff oscillations will not have any effect.

In the fast tunneling regime eq (1.2) the correction to the tunneling action vanishes as $\gamma_0^2 \tau_0^2/(\pi^2 M\Omega)$, when $\tau_0 \to 0$. In accordance with ref 11 the medium is too slow to follow the tunneling electron and remains in the same quantum state during the whole process. The reduction of the tunneling amplitude due to the difference of the vibrational states before and after
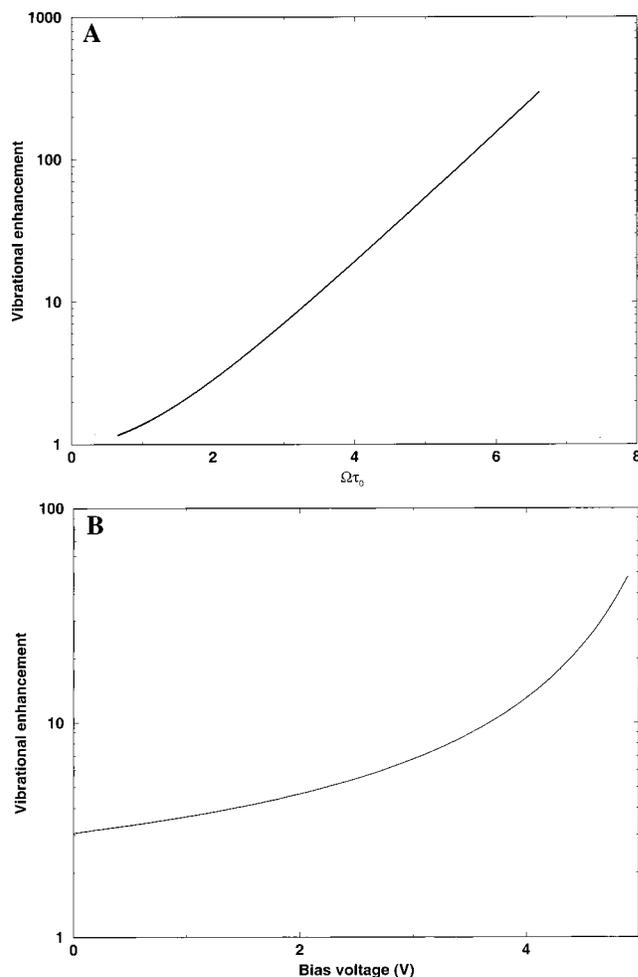

Figure 2. Dependence of the vibrational enhancement $t_{0,\text{med}}/[B_0 \exp(-S_0(\tau_0)]$ of the tunneling amplitude on (A) tunneling time and (B) applied voltage. The parameters are rectangular barrier of the height $\Delta = 3$ eV, length $L = 5$ nm, medium mode energy $\hbar\Omega = 0.2$ eV, reorganization energy $E_R = 0.4$ eV.

tunneling[10,11] does not occur for the molecular wire model because these medium states are the same.

It follows from eq 3.7 and eq 3.10 that the vibrational interaction always enhances the tunneling amplitude. The same conclusion follows from a theoretical study of Sumetskii[12b] if the vibrational interaction exists only within the region under the barrier. This enhancement is stronger for slow tunneling eq (1.3). The dependence of the tunneling enhancement factor on the tunneling time and applied voltage is shown in Figure 2 for bridge parameters reasonable for organic molecular wires. As can be seen from this figure, the enhancement can reach several orders of magnitude. Note that the transition rate (2.22) scales as the squared tunneling amplitude, so the observable effect can really be strong.[21] If, however, vibrations are assumed to affect only the inelastic processes, the electron–vibration interaction can decrease the transition rate, as has been found by Persson and Baratoff.[36] Nevertheless, our results show that the enhancement of tunneling rate due to the electron–vibration interaction dominates (cf. eq 3.10), at least in the case where the semiclassical approach is valid. The latter condition is not satisfied in the situation of resonant tunneling studied by Person and Baratoff.[36]

Generally, the current through a molecular wire can be described in terms of the charge-transfer rate;[24] cf. eq 2.22. The elastic tunneling amplitude provides a reasonable qualitative understanding of the transport phenomenon.[11] In particular, at

2658 *J. Phys. Chem. A, Vol. 105, No. 12, 2001*

Burin et al.

low temperature and at low applied voltage the tunneling transition occurs directly between Fermi levels of right and left leads and the elastic tunneling amplitude defines the relevant matrix element for the tunneling process.[24] Detailed studies of the transfer rate given by (2.22) will be published elsewhere.

The general expression eq 2.15 describes the semiclassical medium wave function depending on the position $x < L$ (tunneling time $\tau < \tau_0$ passed from the beginning of the process). This wave function contains detailed information about the medium state and therefore how the medium assists tunneling. Below we calculate this function for the single mode problem under consideration and study mean energies for the medium and tunneling particles, to describe the energy redistribution during tunneling. Initially, the medium is in the ground state. Then, according to eq 2.15, the medium wave function corresponding to the tunneling time τ can be expressed as

$$|M,\tau\rangle =$$

$$\frac{T \exp\{-\int_0^\tau d\tau\, '\hat{V}_M(\tau',\tau'-\tau)\}|0\rangle}{\sqrt{\langle 0|(T\exp\{-\int_0^\tau d\tau\, '\hat{V}_M(\tau',\tau'-\tau)\})^+ T\exp\{-\int_0^\tau d\tau\, '\hat{V}_M(\tau',\tau'-\tau)\}|0\rangle}}$$

$$(3.13)$$

Here $|0\rangle$ is the ground state of the vibrational mode and the operator $\hat{V}_M$ is defined by eq 3.6. Since operators A and B with a constant commutator satisfy the equality, $e^A e^B = e^B e^A e^{[A,B]}$, while the ground state has the property $b|0\rangle = 0$, the expression for the wave function (3.13) can be rewritten as

$$|M,\tau\rangle = \exp\left(-\frac{\eta^2(\tau)}{2} + \eta(\tau)b^+\right)|0\rangle$$

$$\eta(\tau) = -\sqrt{\frac{1}{2M\Omega}} \int_0^\tau d\tau'\, \gamma(\tau')\, e^{\Omega(\tau'-\tau)}$$

$$= -\sqrt{\frac{E_R}{\Omega}} \frac{1}{1+\left(\frac{\pi}{\Omega\tau_0}\right)^2}\left[\frac{\pi}{\Omega\tau_0}\left(\cos\left(\frac{\pi\tau}{\tau_0}\right) - e^{-\Omega\tau}\right) - \right.$$

$$\left. \sin\left(\frac{\pi\tau}{\tau_0}\right)\right] \quad (3.14)$$

The above result enables us to express the mean energy change of the vibrational mode during tunneling as

$$\Delta E_v(\tau) = \langle M,\tau|\frac{\hat{p}^2}{2M} + M\Omega^2\frac{\hat{u}^2}{2} - \gamma(\tau)\hat{u} - \hbar\Omega/2|M,\tau\rangle \quad (3.15)$$

Equation 3.15, in turn, defines the change of the tunneling barrier due to the dynamic medium response. Straightforward calculation with the wave function defined by eq 3.14 yields

$$\Delta E_v(\tau) = \hbar\Omega|\eta(\tau)|^2 - 2\gamma(\tau)\sqrt{\frac{1}{2M\Omega}}\eta(\tau) \quad (3.16)$$

The tunneling barrier change with time is shown in Figure 3 for slow and fast tunneling regimes. The results are in good agreement with the numerical study of refs 16 and 18. For the fast tunneling regime where $\Omega\tau_0 = 0.1$, changes in energy are very weak since the vibration does not have enough time to respond to the tunneling charge (the electron is never localized on the bridge). In the slow tunneling regime and for $\Omega\tau_0 = 10$, the energy barrier clearly follows the reorganization energy. Some deviation can be understood as the effect of a nonadiabatic switch on the interaction at $\tau = 0$, because eq 3.9 suggests the
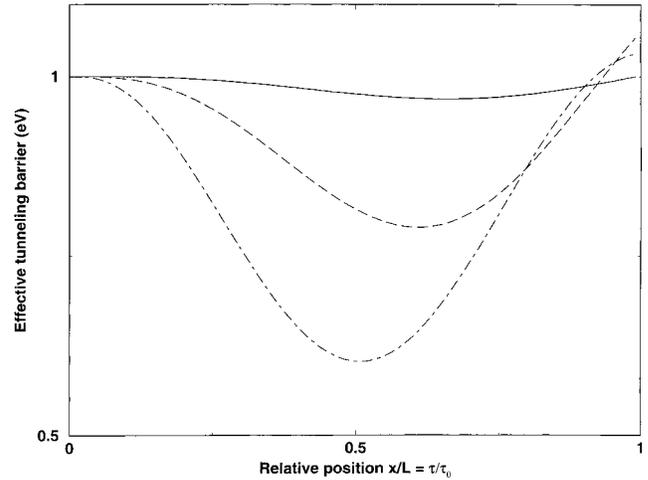

Figure 3. Dependence of the tunneling barrier reduction on the position of the electron under the rectangular barrier for fast (solid line), intermediate (dashed line) and slow (dash–dotted line) tunneling regimes. The tunneling barrier and the applied voltage are taken to be $\Delta = 2$ eV and 2 V, respectively. Values of other parameters are given in the text.

sharp turn-on of the tunneling barrier. For smoother behavior of the coupling constant the shift in tunneling barrier will follow the reorganization energy much more closely.

IV. Conclusions and Discussion

We have constructed the semiclassical wave function for a tunneling electron interacting with the medium. This wave function permits us to describe the evolution of the medium degrees of freedom caused by the tunneling electron.

Semiclassical expressions for matrix elements coupling initial and final states equation (2.17) and for the medium evolution during tunneling look similar to the standard real time expression for the evolution of the medium eigenstate. However, this similarity is not complete: Direct change from real time to imaginary does not lead to our results. Perhaps it is possible to suggest an easier alternative derivation (and improvement) of our result based on the imaginary time approach to the tunneling problem. To our knowledge this has not been done yet. Using the semiclassical matrix elements for medium transitions, we obtained the charge-transfer rate, for the processes, accompanied by the energy exchange with the media (dissipation).

The case of tunneling through a molecular wire has been considered in detail. The model of dynamic interaction of the tunneling electron with a single vibrational mode has been used. We have calculated the medium effect on the elastic tunneling amplitude. As opposed to the donor/acceptor charge transfer[3,33] or spin-boson problem[35] where vibronic descriptions of initial and final states differ, here the interaction with bridge vibrations enhances charge tunneling.[36] Our analysis shows that the most significant vibrational effect occurs in the slow tunneling regime, when the tunneling time exceeds the vibrational period (eq 1.2). In this regime the tunneling barrier can be substantially reduced, and the tunneling rate can increase by several orders of magnitude. The reduction of the tunneling barrier has been identified as the bridge reorganization energy. This is the adiabatic change of medium energy, when it follows the tunneling electron. Our results qualitatively reproduced the numerical studies of refs 16 and 18.

The medium wave function has been derived. The slow tunneling regime is shown to represent the polaron cloud that adiabatically follows the tunneling electron. This case can then

be addressed as the *polaron* tunneling regime in accordance with the suggestion of ref 18. In the opposite case of fast tunneling, the medium excitations cannot follow the tunneling electron. This case corresponds to the *superexchange* regime of independent particle tunneling.[37]

Our results can be applied to more general problems than the modeling study of section III. Straightforward generalization of the analytical expressions for the tunneling amplitude and the charge-transfer rate can also be made for the linear interaction with an arbitrary number of vibrations. Generalization can be made for the bilinear electron−vibration interaction. The expression for tunneling rate permits the direct analysis of the energy dissipation occurring during tunneling.[38] In addition to vibrations, the interaction of tunneling electrons with conduction electrons and the corresponding electronic friction effect for molecular wires can be addressed within a reasonable bosonization procedure for electron/hole pairs.[10] This work is currently in progress.

References and Notes

(1) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148. Billing, G. D.; Mikkelsen, K. V. *Advanced Molecular Dynamics and Chemical Kinetics*; Wiley: New York, 1997. Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology*; Wiley: Chichester, U.K., 1999.

(2) Bixon, M.; Jortner, J. *Adv. Chem. Phys.* **1999**, *106*, 35.

(3) Ratner, M. A.; Jortner, J. *Molecular Electronics*; Blackwell: Oxford, U.K., 1997. Aviram, A.; Ratner, M. A. *Molecular Electronics: Science and Technology*; New York Academy of Sciences: New York, 1998. Bumm L. A.; Arnold J. J.; Dunbar T. D.; Allara D. L.; Weiss P. S. *J. Phys. Chem B* **1999**, *103*, 8122.

(4) Makri, N.; Miller, W. H. *J. Chem. Phys.* **1989**, *91*, 4026. Miller, W. H.; Manz, J.; Jost, R.; Troe, J.; Gaspard, P.; Marcus, R. A. *Adv. Chem. Phys.* **1997**, *101*, 853.

(5) Miller, W. H. *Faraday Discuss.* **1995**, *102*, 53.

(6) Skinner, D. E.; Miller, W. H. *Chem. Phys. Lett.* **1999**, *300*, 20.

(7) Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599.

(8) Buttiker, M.; Landauer, R. *Phys. Rev. Lett.* **1982**, *49*, 1739. Imry, Y.; Landauer, R. *Rev. Mod. Phys.* **1999**, *71*, S306. Gasparian, V. *Superlattice Microst.* **1998**, *23*, 809. Steinberg, A. M. *ibid.* **1998**, *23*, 823.

(9) For a generalization to the tight-binding model, see: Nitzan, A.; Jortner, J.; Wilkie, J.; Burin, A. L.; Ratner, M. A. *J. Phys. Chem. B* **2000**, *104*, 5661.

(10) Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W. *Rev. Mod. Phys.* **1987**, *59*, 1.

(11) Kagan, Yu.; Prokofev, N. V. *Quantum Tunneling in Condensed Media,* Kagan, Yu., Leggett, A. J., Eds.; Elsevier: Amsterdam, 1992.

(12) (a) Pazy, E.; Laikhtman, B. *Phys. Rev. B* **1999**, *59*, 15854. (b) Sumetskii, M. Yu. *Sov. Phys. JETP* **1985**, *62*, 355; Sumetskii, M. Yu. *Phys. Rev. B* **1992**, *46*, 4702.

(13) Pollard, W. T.; Friesner, R. A. *J. Chem. Phys.* **1994**, *100*, 5054. Skourtis, S. S.; Mukamel, S. *Chem. Phys.* **1995**, *197*, 367. Davis, W. B.; Wasielewski, M. R.; Ratner, M. A.; Mujica, V.; Nitzan, A. *J. Phys. Chem. A* **1997**, *101*, 6158. Bixon M.; Jortner J. *J. Chem. Phys.* **1997**, *107*, 5154. Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60.

(14) Ness, H.; Fisher, A. J. *Phys. Rev. Lett.* **1999**, *83*, 452.

(15) Emberly, E. G.; Kirczenow, G. *Phys. Rev. B* **2000**, *61*, 5740.

(16) Bonca, J.; Trugman, S. A. *Phys. Rev. Lett.* **1997**, *79*, 4874.

(17) Thompson, K.; Makri, N. *Phys. Rev. E* **1999**, *49*, R4729.

(18) Yu, Z. G.; Smith, D. L.; Saxena, A.; Bishop, A. R. *Phys. Rev. B* **1999**, *59*, 16001.

(19) Segal, D.; Nitzan, A.; Davis, W. B.; Wasielewski, M. R.; Ratner, M. A. *J. Phys. Chem. B* **2000**, *104*, 3817.

(20) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics: nonrelativistic theory;* Pergamon Press: Oxford, U.K., 1977.

(21) Mujica, V.; Roitberg, A. E.; Ratner, M. A. *J. Chem Phys.* **2000**, *112*, 6834. Xue, Y. Q.; Datta, S. *Phys. Rev. Lett.* **1999**, *83*, 4844.

(22) We have assumed that the transport occurs by electron tunneling. In the (more common) case of hole tunneling, see: Newton, M. D. *Chem. Rev.* **1991**, *91*, 767, the barrier height is still the same in a symmetric junction.

(23) Haag, R.; Rampi, M. A.; Holmin, R. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 7895. Holmin, R. E.; Haag, R.; Ismagilov, R. F.; Rampi, M. A.; Whitesides, G. M. To be published.

(24) Dresselhaus, M. S.; Eklund, P. C. *Adv. Phys.* **2000**, *49*, 705. Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6849 and 6856. Petrov, E. G.; Tolokh, I. S.; Demidenko, A. A.; Gorbach, V. V. *Chem. Phys.* **1995**, *193*, 237. Magoga M.; Joachim, C. *Phys. Rev B* **1997**, *56*, 4722. Datta, S.; Tian, W. *Phys. Rev. B* **1997**, *55*, R1914.

(25) The relationship between tight-binding and tunneling-barrier Hamiltonians is discussed by: Galperin, M.; Segal, D.; Nitzan, A. *J. Chem. Phys.* **1999**, *111*, 1569.

(26) For polyalkane bandwidth see, e.g.: Miao, M. S.; Van Camp, P. E.; Ladik, J. J.; Mintmire, J. W. *Phys. Rev. B* **1996**, *54*, 10430. Ladik, J. J. *Quantum Theory of Polymers as Solids*; Plenum: New York, 1987 and references therein.

(27) Berlin, Yu. A.; Burin, A. L.; Ratner, M. A. To be published.

(28) Castiglioni, C.; Lopez-Navarette, J. T.; Zerbi, G.; Gussoni, M. *Solid State Commun.* **1988**, *65*, 625. Tian, B.; Zerbi, G.; Müllen, K. *J. Chem. Phys.* **1991**, *95*, 3198.

(29) Burin, A. L.; Ratner, M. A. *J. Chem. Phys.* **1998**, *109*, 6102.

(30) The general coupling to vibrations appears in the polaron problem, one of the standard issue in narrow band conduction. The classic works are: Holstein, T. *Ann. Phys.* **1959**, *8*, 325 and 343.

(31) The coupling strengths can be observed using resonant Raman spectroscopy, see, e.g.: Meyers, A. B. *Chem. Rev.* **1996**, *96*, 911. Williams, R. D.; Hupp, J. T.; Ramm, M. T.; Nelsen, S. F. *J. Phys Chem. A* **1999**, *103*, 11172.

(32) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(33) Bolton, J. R.; Archer, M. D. *Electron Transfer in Inorganic, Organic and Biological Systems*; Advances in Chemistry Series 228; Bolton, J. R., Mataga, N., McLendon, G., Eds.; American Chemical Society: Washington, 1991; p 91.

(34) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1993.

(35) Phillips, P.; Silbey, R. J. *Phys. Rev. A* **1986**, *34*, 707.

(36) Persson, B. N. J.; Baratoff, A. *Phys. Rev. Lett.* **1987**, *59*, 339.

(37) Similar behavior involving vibronic coupling along the bridge modifying mechanism and increasing rate has been noted in donor/bridge/acceptor electron transfer; cf. e.g.: Ogawa, M. Y.; Wishart, J. F.; Young, Z. Y.; Miller, J. R.; Isied, S. S. *J. Phys. Chem.* **1993**, *97*, 11456 and refs 13 and 19 therein.

(38) Path integral studies of the electron-transfer problem enable one to obtain the exact answer for linearly-coupled harmonic models, see: Makri, N.; Sim, E. *J. Phys. Chem. B* **1997**, *101*, 5446. Evans, D. G.; Nitzan, A.; Ratner, M. A. *J. Chem. Phys.* **1998**, *108*, 6387.