I. INTRODUCTION

The scanning tunneling microscope (STM) can potentially revolutionize the field of electrochemistry. The realistic possibility of observing the atomic structure of an electrode surface under working conditions has attracted much effort since the applicability of “underwater” tunneling microscopy was demonstrated less than a decade ago.1,2 While atomic resolution can be achieved and the change in electrode structure can be observed during an electrochemical process, a full understanding of the tunneling process and of the observed signal is still lacking. Some question, such as the role played by the dynamical response of the tip and the electrode in the tunneling process, the effect of the electronic structure of the adsorbate site on the tunneling current or the origin and nature of noise in the observed signal, are relevant chemical interface: (a) What is the effect of the molecular structure of the solvent near the solvent-electrode interface on the tunneling? (b) How does the dynamical response of the solvent affect the tunneling process? (c) How do unadsorbed solutes affect the STM operation? More specifically these issues boil down to the practical questions regarding the solvent effect on the barrier to tunneling, on the STM resolution and on the observed noise in the tunneling current.

It has been suggested3-7 that one manifestation of solvent effect on the STM operation is the unusually low (relative to expectations based on experience from the solid-vacuum interface) barrier to tunneling observed in underwater STM experiments.3 Such observations can be related to uncertainties in the vertical scaling of the tip displacement due to tip-surface interaction forces,8 however, some of the observations are done at tip-surface separations large enough for this effect not to be very significant. Schmickler and Henderson4 have considered the electronic polarizability of the solvent as the possible source of barrier lowering. The same effect is the source of reduction of the threshold for photoemission in liquids relative to the corresponding vacuum value.9 For tip and surface represented by jellium with $r_f=2$ and a solvent with $\epsilon_r=1.88$ (water), Schmickler and Henderson estimate a barrier lowering of $\sim1.2$ eV, of the same order as the solvent induced reduction of the work function. From the microscopic point of view this lowering is related to the location of the bottom of the solvent conduction band below the vacuum level. A different but physically equivalent approach is use extensions of the superexchange model of electron transfer, whereas an effective barrier lowering is caused by the presence of low lying electronic states in the barrier.10

Arguing that the result of Schmickler and Henderson considerably underestimate the magnitude of the observed effect, Sass, Gimzewski, and co-workers6,7 have suggested two additional sources for the apparent barrier lowering. The first is the contribution of the solvent nuclear dielectric response, which for water is known to be dominated by fast inertial motion on a time scale of a few tens of femtoseconds. The second originates from tunneling events controlled by rare fluctuations in the solvent configuration in the space between the tip and the surface. Such spontaneously occurring rare configurations characterised by very low barriers may dominate the tunneling current which itself depends exponentially on the barrier height. In particular these authors suggest that configurations that could support a solvated state of the electron enhance the tunneling by the existence of such resonance states in the barrier. Essential differences from regular resonance tunneling are the facts that the barrier structure may be affected by the presence of the tunneling electron and that the resonances in the present situation have very short lifetimes.

The possibility that transient structures that support resonance tunneling may lead to an overall enhancement of the tunneling process may be dismissed at least as far as dielectric structures concerned: Solvent reorganization en-
ergy $W_R$ for forming the polarization cavity that will support the solvated electron (of radius $a \sim 2$ Å) can be estimated from

$$W_R = \frac{e^2}{2a} \left( \frac{1}{\varepsilon_{op}} - 1 \right)$$

to be $\sim 1$ eV. The thermal probability $\exp(-W_R/k_BT)$ to form such a structure at room temperature is far smaller than the possible gain in tunneling probability. It is still possible that other rare structures (e.g., an ion located in the tunneling path) may have an essential effect on the tunneling current. In addition, resonance tunneling via intermediate electronic levels of molecules adsorbed on the tip or on the electrode may also take place. In the present work however we do not consider this possibility and focus on the effect of the barrier dielectric fluctuations.

Numerical simulations of solvation dynamics in several neat dielectric solvents indicate that for singly charged species the time evolution is well accounted for by linear response theory. This suggests that at least the effect of the dynamical response (as opposed to the rare quasistatic fluctuations) of the solvent may be accounted for by a linear theory. This is equally true for the nuclear and the electronic solvent response which, excluding chemical reactions involving the solvent, differ from each other essentially by their time scales. On this level of the theory the dielectric barrier may be represented by a set of harmonic oscillators coupled linearly to the tunneling electron. This is analogous to the Caldeira-Leggett model used extensively in the past decade to describe tunneling in dissipating systems, with the important difference that coupling to the "phonon bath" exists only in the barrier region. Therefore, in spite of the linear form of the electron-phonon coupling, the Hamiltonian is not linear, in contrast to the Caldeira-Leggett model.

In the present work we investigate tunneling through a dielectric barrier within such a model. The barrier is taken to be a dielectric film of thickness $d$ lying in the $xy$ plane, so that tunneling takes place in the $z$ direction. The corresponding Hamiltonian is taken to be

$$H = H_1 + H_B + H_{el-B}$$

(1)

$$H_1 = -\frac{\hbar^2}{2m} \nabla^2 + U(z),$$

(2)

$$H_B = H_B(\{Q\}),$$

(3)

$$H_{el-B} = U_B(z) V(\{Q\}),$$

(4)

where $U(z)$ is the static part of the barrier potential and $H_B$ is the Hamiltonian of the polarization fluctuations denoted by a set of coordinates $\{Q\}$. The electron-medium coupling will be taken to be of the same form used for the electron solvent coupling in electron transfer theory, except that it is multiplied by $U_B(z)$, a function which is different from zero only in the barrier region. In our particular application we take

$$U_B(z) = \begin{cases} U_1 & z < -d/2 \\ U & d/2 < z < -d/2 \\ U_2 & z > d/2 \end{cases}$$

(5)

where $U > U_1$, $U_2$ and

$$U_B(z) = \begin{cases} 1 & -d/2 < z < d/2 \\ 0 & -d/2 < z > d/2 \end{cases}$$

(6)

A similar model was recently investigated by Sebastian and Doyen within a path integral approach. While their method is in principle general, these authors have focused on the effect of the barrier dynamics on the elastic tunneling probability. When the barrier response is slow relative to the tunneling time their treatment results in the usual expression for tunneling through a potential barrier, averaged over a Gaussian distribution of barrier heights. Following Persson and Baratoff these authors have also investigated the possible effects of the dynamical image associated with the response of the metal electrode. This effect is disregarded in the present mode which focus on the barrier response and its effect on the elastic and inelastic tunneling probabilities and their numerical estimate in broad range of relevant physical parameters. We use two different approaches. The first is the Bardeen transfer Hamiltonian formalism extended to include inelastic tunneling. The second is based on a generalization of the WKB formalism to many degrees of freedom. The former approach is shown to be valid in the common case of slow barrier dynamics, and in this limit the two approaches give identical results for the tunneling current. The latter approach is useful also in the limit where the barrier dynamics is as fast as the tunneling process. In both cases we apply usual dielectric models for the barrier to estimate the effect of the barrier dynamics on the tunneling probability, the tunneling current and on the relative magnitudes of the elastic and inelastic components of these quantities.

II. DETAILS OF THE MODEL

We now consider the model we use for the description of the effect of solvent polarization fluctuations on the electron tunneling through a thin dielectric film between two metals. We first focus on the Hamiltonian (1)-(4) and the physical parameters appearing in it.

For the electrostatic interaction $H_{el-B}$ between the tunneling electron and the solvent polarization in the dielectric we take

$$H_{el-B} = -U_B(z) \int d^3 r' P(r') \cdot D(r', r).$$

(7)

Here, $P(r')$ is the polarization of the solvent and $D(r', r)$ is the electrostatic displacement due to the presence of an electron at a point $r = (z, r_0)$ in the film between two metals. Form (7) is similar to that taken in dielectric theories of electron solvation and electron transfer, except that the interaction is assumed to vanish when the electron is outside the film. Also, the source displacement field $D$ is taken in correspondence with the given geometry: $D$ is derived from the potential of a charged particle located at position $r$ between two grounded metal plates.


Downloaded 10 Mar 2004 to 132.66.16.12. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp
\[ \mathbf{D}(r',r) = - \nabla_{r'} \phi(r',r), \]  

\[ \phi(r',r) = \frac{4\pi^2}{S} \sum_{q_{||}} \exp[iq_{||}(r' - r)] \times \sinh[q_{||}(z' + d/2)] \sinh[q_{||}(d/2 - z')] \frac{q_{||}}{\sinh(q_{||}d)}, \]  

(8)

(9)

where \( S = L_{x}L_{y} \) is the surface area in the parallel direction, \( e \) is the electron charge, and \( z' \) and \( z'_{1} \) are the smaller and the larger of the values \( z \) and \( z' \). The sum is over \( q \) vectors in the \( xy \) plane.

Since the electrostatic interaction between an external charge and a dielectric environment involves the induced longitudinal polarization, \( P(r) \) in Eq. (7) can be represented by

\[ P(r) = \sum_{q} \frac{q}{|q|} \exp(iq_{||}r) P(q), \]

\[ q = (q_{z},q_{||}); \quad P(-q) = -P^{*}(q). \]  

(10)

Following common practice, we will assume that the normal component of the polarization vanishes at the interfaces, namely, at \( z = \pm d/2 \). A convenient way to achieve this is to redefine \( P(q) \) in Eq. (10) so that

\[ P(r) = \sum_{q} \frac{q_{||}}{|q|} \exp(iq_{||}r) P(q), \]

(10a)

where \( q_{z} \) and \( q_{||} \) are the components of the wave vector in the directions perpendicular and parallel to the metal surfaces, and to require that \( P(q_{||},-q_{z}) = P(q_{||},q_{z}) \) [and consequently \( P(-q_{||},q_{z}) = -P^{*}(q_{||},q_{z}) \)]. This leads to

\[ P = P_{\|} + P_{\perp}, \]

\[ P_{\|}(r) = 2 \sum_{q_{||}} \sum_{q_{z}=0} \frac{P(q) \exp(iq_{||}r_{||})}{|q||q_{||}|} \times \left( 1 - \frac{1}{2} \delta_{q_{z},0} \right) \cos[q_{z}(z + d/2)], \]

\[ P_{\perp}(r) = 2i \sum_{q_{||}} \sum_{q_{z}=0} \frac{P(q) \exp(iq_{||}r_{||})}{|q||q_{||}|} \times \sin[q_{z}(z + d/2)], \]

(11)

where \( q_{z} \) takes only discrete values,

\[ q_{z} = \pi n / d, \quad n = 0, 1, 2, \ldots \]  

(11a)

Substituting Eqs. (8), (9), and (11) into Eq. (7) we obtain the following expression for the electron polarization interaction:

\[ H_{\text{el-\delta}}(r) = -8\pi e i U_{\delta}(z) \sum_{q_{||}} \sum_{q_{z}=0} \frac{1}{|q||q_{||}|} \times \left( 1 - \frac{1}{2} \delta_{q_{z},0} \right) f(q_{z},z) P(q) \exp(iq_{||}r_{||}) \]

\[ \times \sinh[q_{||}(d/2 - z)] + (-1)^{n} \sinh[q_{||}(d/2 + z)] \]

\[ \sinh(q_{||}d), \]  

(12)

Equation (12) shows that the interaction Hamiltonian \( H_{\text{el-\delta}} \) depends on the position, \( (r_{||},z) \), of the electron inside the barrier. The term \( \exp(iq_{||}r_{||}) \) in \( H_{\text{el-\delta}}(r) \) causes deflection of the electron from its initial direction in the \( xy \) plane, from the incident wave vector \( k_{||}^{0} \) to the final wave vector \( k_{||} \), with \( k_{||}^{0} = -k_{||} = q_{||} \).

The problem of electron tunneling in the presence of interaction (12) with underlying phonons is very complicated, and we resort to two simplifications which, though quite drastic, preserve the essential physics of the process. First we note that the most important contribution to the tunneling current comes from electrons with \( k_{||}^{0} = 0 \) which are not deflected from the normal direction during the tunneling process. Deflected electrons will encounter longer tunneling paths and therefore exponentially smaller tunneling probabilities. The tunneling probability for an electron with a given \( k_{||} \) is essentially \( \exp\left[-\frac{|(2m\hbar^{2})(U - E_{\text{el}} + \hbar^{2}k_{||}^{2}(2m)^{1/2})\times \exp(-k_{||}d/2\kappa)}{E_{\text{el}}\times \exp(-k_{||}d/2\kappa)}\right] \) where \( \kappa = [(2m\hbar^{2})(U - E_{\text{el}})^{1/2}] \) and \( E_{\text{el}} \) is the electron energy. This imposes a natural cutoff, \( \Lambda = (\kappa/d)^{1/2} = (\kappa/d)^{1/2} \) on the \( q_{||} \) summation in Eq. (12). For \( \kappa d \gg 1 \) this limits this summation to small magnitudes of \( q_{||} \), and since the largest contribution to the tunneling current for a given total electron energy comes from the \( q_{||} = 0 \) term, we will approximate the term multiplying \( P(q) \) in Eq. (12) by its \( q_{||} = 0 \) value, i.e.,

\[ f(q_{z},z) = \cos[q_{z}(z + d/2)] \]

\[ \frac{- \sinh[q_{||}(d/2 - z)] + (-1)^{n} \sinh[q_{||}(d/2 + z)]}{\sinh(q_{||}d)}. \]  

(13)

Substituting Eqs. (8), (9), and (11) into Eq. (7) we obtain the following expression for the electron polarization interaction:

\[ H_{\text{el-\delta}}(r) = -8\pi e i U_{\delta}(z) \sum_{q_{||}} \sum_{q_{z}=0} \frac{1}{|q||q_{||}|} \times \left( 1 - \frac{1}{2} \delta_{q_{z},0} \right) f(q_{z},z) P(q) \exp(iq_{||}r_{||}) \]

\[ \times \sinh[q_{||}(d/2 - z)] + (-1)^{n} \sinh[q_{||}(d/2 + z)] \]

\[ \sinh(q_{||}d). \]  

(12)

Equation (12) shows that the interaction Hamiltonian \( H_{\text{el-\delta}} \) depends on the position, \( (r_{||},z) \), of the electron inside the barrier. The term \( \exp(iq_{||}r_{||}) \) in \( H_{\text{el-\delta}}(r) \) causes deflection of the electron from its initial direction in the \( xy \) plane, from the incident wave vector \( k_{||}^{0} \) to the final wave vector \( k_{||} \), with \( k_{||}^{0} = -k_{||} = q_{||} \).

The problem of electron tunneling in the presence of interaction (12) with underlying phonons is very complicated, and we resort to two simplifications which, though quite drastic, preserve the essential physics of the process. First we note that the most important contribution to the tunneling current comes from electrons with \( k_{||}^{0} = 0 \) which are not deflected from the normal direction during the tunneling process. Deflected electrons will encounter longer tunneling paths and therefore exponentially smaller tunneling probabilities. The tunneling probability for an electron with a given \( k_{||} \) is essentially \( \exp\left[-\frac{|(2m\hbar^{2})(U - E_{\text{el}} + \hbar^{2}k_{||}^{2}(2m)^{1/2})\times \exp(-k_{||}d/2\kappa)}{E_{\text{el}}\times \exp(-k_{||}d/2\kappa)}\right] \) where \( \kappa = [(2m\hbar^{2})(U - E_{\text{el}})^{1/2}] \) and \( E_{\text{el}} \) is the electron energy. This imposes a natural cutoff, \( \Lambda = (\kappa/d)^{1/2} = (\kappa/d)^{1/2} \) on the \( q_{||} \) summation in Eq. (12). For \( \kappa d \gg 1 \) this limits this summation to small magnitudes of \( q_{||} \), and since the largest contribution to the tunneling current for a given total electron energy comes from the \( q_{||} = 0 \) term, we will approximate the term multiplying \( P(q) \) in Eq. (12) by its \( q_{||} = 0 \) value, i.e.,

\[ \frac{1}{|q||q_{||}|} \left( 1 - \frac{1}{2} \delta_{q_{z},0} \right) f(q_{z},z) P(q) \exp(iq_{||}r_{||}) \]

\[ \times \left( 1 - \frac{1}{2} \delta_{q_{z},0} \right) f(q_{z},z) P(q), \]  

(14)

where

\[ f(q_{z},z) = \cos[q_{z}(z + d/2)] \]

\[ \frac{- \sinh[q_{||}(d/2 - z)] + (-1)^{n} \sinh[q_{||}(d/2 + z)]}{\sinh(q_{||}d)}. \]  

(15)

For now we also make an additional simplification of \( H_{\text{el-\delta}}(r) \) by replacing \( f(q_{z},z) \) with a \( z \) independent constant. The simple procedure is to replace \( f(q_{z},z) \) by its average over the barrier,

\[ \bar{f}(q_{z},z) = \frac{1}{d} \int_{-d/2}^{d/2} dz \ f(q_{z},z). \]  

(16)

We later show that this is a reasonable approximation in the slow barrier limit, while for a fast barrier it can be used to obtain rough estimates of the tunneling probability.

In Sec. IV the WKB approximation is used to obtain the tunneling current without invoking approximation (16). In what follows we focus on the slow barrier case and adopt approximation (16). Note that \( \bar{f} \) vanishes when \( q_{z} \) and therefore \( n \) are zero. Thus finally,
Next consider the solvent polarization fluctuations. Following common practice these will be described using the effective Hamiltonian method, whereupon the solvent is represented by a set of harmonic oscillators with the frequencies \(\omega_{q\nu}\). It is assumed that the Fourier components of polarization \(P(q)\) are linearly related to the dimensionless coordinates \(Q_{q\nu} = a_{q\nu}^+ + a_{q\nu}\) of the effective oscillators with coefficients \(A_{q\nu}\), i.e., \(P(q) = \sum_q A_{q\nu} Q_{q\nu}\). This assumption leads to the following explicit forms for the bath Hamiltonian [Eq. (3)] and for the electron–bath coupling [Eq. (4)],

\[
H_B = \sum_{q\nu} \hbar \omega_{q\nu} a_{q\nu}^+ a_{q\nu},
\]

\[
H_{cl-B}(r) = -8\pi e i U_g(z) \sum_q \sum_{q\nu \geq 0} \frac{1}{q\xi} \tilde{f}(q\xi) P(q); \quad \Lambda = (\kappa/d)^{1/2}.
\]

III. TUNNELING RATE: THE INELASTIC BARDEEN’S FORMALISM

In this section we extend the Bardeen transfer Hamiltonian formalism to describe the effect of polarization fluctuations on electron tunneling through dielectric barriers. For a static rectangular barrier Bardeen has obtained the following gold rule type expression for the transition rate:

\[
W_{IF} = \frac{2\pi}{\hbar} |J_{IF}|^2 |P(E_F)|,
\]

where \(I\) and \(F\) denote the initial (incident) and final (transmitted) electronic states and the transition matrix element \(J_{IF}\) involves the \(z\) component of the current density operator (\(z\) is the tunneling direction)

\[
J_{IF} = \langle I|J(z_*)|F\rangle = -\frac{\hbar^2}{2m} \int \left[ \Psi_F^* \frac{\partial \Psi_F}{\partial z} - \Psi_F \frac{\partial \Psi_F^*}{\partial z} \right] \times \delta(z-z_*) \, d^3r.
\]

Here, \(z_*\) is an arbitrary point in the barrier region, whose actual position in the barrier does not affect the matrix element. \(\Psi_I\) and \(\Psi_F\) are the eigenfunctions of auxiliary Hamiltonians with semi-infinite barriers. Thus for the problem under consideration, for an electron tunneling from left to right \(\Psi_I\) is an eigenfunction of the Hamiltonian with a potential given by Eqs. (5) and (6) only extended to \(+\infty\) [\(U'(z) = U_1\) at \(z < -d/2\) and \(U'(z) = U\) at \(z > -d/2\)]. Similarly \(\Psi_F\) corresponds to the Hamiltonian with the barrier extended \(-\infty\) [\(U'(z) = U_2\) for \(z > d/2\) and \(U'(z) = U\) at \(z < d/2\)]. Evaluation of the right-hand side of Eq. (24) for a square barrier \((U_1 = U_2)\) leads to

\[
|J_{IF}|^2 = \frac{\hbar^4}{m^2 I^2} \frac{16 k_l^2}{(k_l^2 + \kappa_f^2)} \exp(-2\kappa_f d),
\]

where \(\kappa_f = \frac{1}{\hbar} \sqrt{2m(E_{el} - U_1)}\) and \(k_l = \frac{1}{\hbar} \sqrt{2m(U - E_{el}')}\).

Here, \(E_{el}'\) is the initial energy of the tunneling electron. The transmission probability \(P_{IF}\) is related to the transition rate by

\[
W_{IF} = P_{IF} j_1 I_F = \frac{\hbar k_l}{mL},
\]

where \(j_1\) is the incident flux and \(L\) is the normalization length, in the \(z\) direction, of the electronic functions. Using the density of final electron states \(P(E_F) = mL(2\pi\hbar^2 k_F)^{-1}\) in Eq. (23), Eqs. (23), (25), and (27) lead to the conventional expression for the transmission probability.

Consider now the case of the fluctuating barrier defined by the effective reduction caused by this component, in the spirit discussed by Schmickler and Henderson.

\[
\text{effective reduction caused by this component, in the spirit discussed by Schmickler and Henderson.4}
\]
by Eqs. (3) and (4), We assume that the characteristic time scales of the polarization variables \( \{Q\} \), namely the inverse frequencies \( \{\omega_{qv}\} \) are much slower than that of the electron. The latter is determined by the tunneling time, which, for elastic tunneling, is given by

\[
\tau = \int_{-d/2}^{d/2} \frac{m}{2} \left( [U(z) - E_{el}(z)]^{1/2} \right)^{1/2} \frac{d z}{d z}.
\]

We will also assume that the phonon energies \( \hbar \omega_{qv} \) are much lower than the relative barrier height \( U - E_{el} \). In this case Eq. (28) provides a good estimate of the tunneling time also for inelastic tunneling events. These assumptions are valid when the barrier dynamics is dominated by nuclear (orientational) polarization fluctuations.

Under these assumptions the overall electron-phonon tunneling wave functions \( \Psi_I \) and \( \Psi_F \) may be written in the spirit of the Born–Oppenheimer approximation as

\[
\Psi_I = \psi(z) \chi^{(F)}(Q) \chi^{(I)}(Q_{qv}), \quad \Psi_F = \psi(z) \chi^{(F)}(Q) \chi^{(I)}(Q_{qv}).
\]  

Here, \( \psi^{(F)} \) are the eigenfunctions of the electronic Hamiltonians

\[
H_{el}^{(I)} = -\hbar^2 / 2m \nabla^2 + U^{(I)}(z) + U_{\text{el}}^{(I)}(z) \sum_{q,v} c_{qv} \omega_{qv} \]

(30)

and \( U^{(I)}(z) \) and \( U_{\text{el}}^{(I)}(z) \) constitute semi-infinite barriers as described above and where the term containing \( U_B \) is due to solvent polarization. The functions \( \psi^{(F)} \) and \( \psi^{(I)} \) can in turn be written as products of free waves in the direction parallel to the barrier and tunneling functions in the perpendicular direction. The latter will be denoted \( \psi'(z) \) and \( \psi''(z) \). They are given by

\[
\psi'(z) = \begin{cases} 
L^{-1/2} \exp(ik_1(z + d/2)) & \text{at } z < -d/2 \\
(1 - S_{II}) \exp(-\kappa(z + d/2)) & \text{at } z > -d/2
\end{cases}
\]

(31)

\[
\psi''(z) = \begin{cases} 
L^{-1/2} (1 - S_{FF}) \exp(\kappa F(z - d/2)) & \text{at } z < d/2 \\
exp(-ik_F(z - d/2)) + S_{FF} \exp(ik_F(z - d/2)) & \text{at } z > d/2
\end{cases}
\]

(32)

where

\[
S_{II} = \frac{i k_1 - \kappa_1}{ik_1 - \kappa_1}, \quad S_{FF} = \frac{i k_F - \kappa_F}{ik_F - \kappa_F},
\]

\[
k_{II} = \frac{1}{\hbar} \sqrt{2m(E_{el}^{(F)} - U_{el}(z))}, \quad \kappa_{II}(Q) = \frac{1}{\hbar} \sqrt{2m \left( U + U_B \sum_{q,v} c_{qv} \omega_{qv} - E_{el}^{(F)} \right)}.
\]

(33a)

(33b)

\[E_{el}^{(I)} \text{ and } E_{el}^{(F)} \text{ are the electron energies in initial and final states,}
\]

\[L \text{ is the normalization length and } Q = \{Q_{qv}\}.
\]

The Hamiltonian for the slow polarization subsystem which is characterized by the eigenfunctions \( \chi^{(F)} \) has the form

\[
H_{ph}^{(I)} = H_{ph} + E_{el}^{(I)} + \sum_{q,v} c_{qv} \omega_{qv} \langle \psi^{(I)}(z) | U_{el}(z) | \psi^{(F)}(z) \rangle.
\]

(34)

The matrix element \( \langle \psi^{(I)}(z) | U_{el}(z) | \psi^{(F)}(z) \rangle \) is proportional to \( L^{-1} \) and vanishes as \( L \to \infty \), where \( L \) is the normalization length in the z direction. As a result the polarization Hamiltonians have the same form in the initial and the final electronic states and differ only in their electronic energy origins. In this respect the present theory differs from usual models of electron transfer described by the same formalism. The net energy of the whole electron-phonon system

\[
E = E_{el}^{(I)} + E_{el}^{(F)} + E_{ph}^{(I)} + E_{ph}^{(F)},
\]

(35a)

\[E_{ph}^{(I)} = \sum_{q,v} E_{ph}^{(I)}(q,v),
\]

(35b)

is conserved in the tunneling process.

The generalization of the Bardeen’s procedure for the present case which includes electron–phonon coupling is described in Appendix A. It leads again to the tunneling rate of the form (23), where \( \rho(E_F) \) is the density of final states of the electron-phonon system and the matrix element \( J_{IF} \) now given by

\[
J_{IF} = \langle \chi_I | J_{IF}(Q) | \chi_F \rangle,
\]

(36)

where the matrix element involves integration over all phonon coordinates, and where \( J_{IF}(Q) \) is given by

\[
J_{IF}(Q) = \frac{\hbar^2}{2mL} \frac{4k_F k_F(Q) + \kappa_F(Q)}{(ik_F - \kappa_F(Q))(ik_F - \kappa_F(Q))}\exp(-1/2)(\kappa(Q) + \kappa(Q))\right]
\]

(37)
In writing Eq. (37) we have neglected correction terms of order \((E_{el}^I - E_{el}^F)/U\) (see Appendix A).

Equation (37) is an expression for the electronic tunneling matrix element, which is an operator in the polarization (phonon) space. Assuming that polarization fluctuations are initially in thermal equilibrium the transition rate takes the form

\[
W_{IF} = \frac{1}{\hbar} \int dE_{el}^I \sum_i \exp(-\beta E_{ph}^i) \times \sum_F |\langle \chi_i | J_F(Q) | \chi_F \rangle|^2 \times \delta(E_{el}^I + E_{ph}^i - E_{el}^F - E_{ph}^F) \rho(E_{el}^F),
\]

where \(Z\) is the canonical partition function

\[
Z = \sum_I \exp(-\beta E_{ph}^I)
\]

and where the sums over \(I\) and \(F\) in Eqs. (38) and (39) are sums over phonon states only. Following conventional procedure, Eq. (38) can be rewritten in the form

\[
W_{IF} = \frac{1}{\hbar} \int dE_{el}^I \int dt \exp(i(E_{el}^I - E_{el}^F)t/\hbar) \times \langle J_{IF}(0) J_{IF}(t) \rangle_T \rho(E_{el}^F),
\]

where \(J_{IF}(t) = J_{FI}(t)\) is given by Eq. (29b) with \(I\) and \(F\) interchanged and

\[
J_{FI}(t) = \exp(iH_{ph}t) J_{FI} \exp(-iH_{ph}t) = J_{FI}(Q(t))
\]

and where the symbol \(\langle \rangle_T\) denotes the thermodynamic averaging over initial phonon states.

Next, the current-current correlation function in Eq. (40) has to be evaluated. A simple tractable approximation to this function is obtained by expanding \(\kappa_I(Q)\) and \(\kappa_F(Q)\) in Eq. (37) as power series in \(Q\), keeping the zero order terms \(\kappa_I(Q=0)\) and \(\kappa_F(Q=0)\) in the pre-exponential terms and up to first order terms in the exponent, i.e.,

\[
\exp[-(d/2)(\kappa_I(Q) + \kappa_F(Q))]
\]

\[
= \exp\left(-\frac{d}{2}(\kappa_I + \kappa_F)\right) - \sum_{q\nu} b_{q\nu} Q_{q\nu},
\]

\[
= \frac{2m}{\hbar^2 \kappa} \frac{1}{(U-E_{el}^I)^{1/2}} \frac{1}{(U-E_{el}^F)^{1/2}} c_{q\nu}.
\]

This leads to

\[
W_{IF} = \frac{1}{\hbar^2} \int dE_{el}^I |D|^2 \exp \left( \frac{\sum_{q\nu} |b_{q\nu}|^2 (2n_{q\nu} + 1)}{2n_{q\nu} + 1} \right) \times \int_0^\infty dt \exp(i(E_{el}^I - E_{el}^F)t/\hbar) \times \exp\left(\sum_{q\nu} |b_{q\nu}|^2 [n_{q\nu} + 1] \exp(i\omega_{q\nu}t) + n_{q\nu}\right) \times \exp(-i\omega_{q\nu}t) \rho(E_{el}^F).
\]

where

\[
n_{q\nu} = \left\{ \exp(\beta \hbar \omega_{q\nu}) - 1 \right\}^{-1},
\]

\[
D = \frac{2\kappa_I\kappa_F(\kappa_I + \kappa_F)\exp[-(d/2)(\kappa_I + \kappa_F)]}{(ik_I - \kappa_I)(-ik_F - \kappa_F)} \frac{\hbar^2}{mL}
\]

and where the density of final electron states will be approximated by the free electron expression

\[
\rho(E_{el}^F) = mL/(2\pi \hbar^2 k_F).
\]

In what follows we limit our model to a single phonon branch and suppress the summation over \(\nu\). Also the summation over \(q=(q_I,q_J)\) can be simplified by recalling that the summand can be approximated by its value for \(q_I=0\), so that

\[
\sum_{q\nu} S(q) \approx \frac{L_x L_y}{(2\pi)^2} \pi \Lambda^2 \sum_{q>0} S(q).\]

This leads to

\[
W_{IF} = \frac{1}{\hbar^2} \int dE_{el}^I |D|^2 \exp \left( \frac{\sum_{q>0} |b_{q}\nu|^2 (2n_{q\nu} + 1)}{2n_{q\nu} + 1} \right) \times \int_0^\infty dt \exp(i(E_{el}^I - E_{el}^F)t/\hbar) \times \exp\left(\sum_{q>0} |b_{q}\nu|^2 [n_{q\nu} + 1] \exp(i\omega_{q\nu}t) + n_{q\nu}\right) \times \exp(-i\omega_{q\nu}t) \rho(E_{el}^F).
\]

with [using Eqs. (20), (22), and (42b)]

\[
|b_{q\nu}|^2 \approx \frac{2m}{\hbar^2 \kappa} \frac{\omega_q |f(q)|^2}{q^4} \left(\frac{1}{\epsilon_{as}(q)} - \frac{1}{\epsilon_{op}(q)}\right),
\]

\[
\kappa = \left((2m/\hbar^2)(U-E_{el})\right)^{1/2}.
\]

Note that for simplification of the notation we write \(q\) instead of \(q_I\).

Next we consider several particular cases

(1) The rigid barrier limit. In this limit (no phonons, \(b_{q\nu} = 0\))—the rate, Eqs. (43) and (47) becomes \(W_{IF} = (2\pi/\hbar)|D|^2 \rho(E_{el}^F)\). For the symmetric case, \(U_1 = U_2\) using Eq. (27) leads to the following expression for the transmission probability:

\[
P_{IF} = \frac{16k_I^2 k_F^2 \exp(-2\kappa d)}{(k_I^2 + k_F^2)^2} \equiv P_{IF}^0
\]
which is the elastic tunneling result [cf. Eqs. (23), (25), and (27)].

(2) Total tunneling probability. An approximate analytical evaluation of the tunneling rate, Eq. (43) is possible if we assume that the main contribution to \( W_{\text{tot}} \) comes from final electron energies \( E_{\text{f}}^j \) not too different from the initial value \( E_{\text{i}}^j \). This assumption holds for small electron-phonon coupling \( |\beta_{ij}|^2 < 1 \). In this case we can disregard the dependence of the parameters \( D \), \( |\beta_{ij}|^2 \), and \( \rho \) on \( E_{\text{f}}^j \), then, assuming that the energy of the tunneling electron is high enough above the Fermi energy of the accepting electrode, extend the integration over \( E_{\text{f}}^j \) to the whole \((-\infty, \infty)\) axis to get

\[
P_{\text{IF}} = P_{\text{IF}}^0 \exp \left( \frac{8m^2e^2}{\hbar^2\kappa} C_h \right), \tag{50a}
\]

\[
C_h = \sum_q \omega_q \left( \frac{1}{\epsilon_{\text{el}}(q)} - \frac{1}{\epsilon_{\text{op}}(q)} \right) \frac{|f(q)|^2}{q^2} (1/2 + n_q). \tag{50b}
\]

Here we have approximated \( h_q \) by taking \( E_{\text{cl}}^F = E_{\text{cl}}^I \) in Eq. (42b). The term in the exponent is positive, so Eq. (50) implies that independent of the values of system parameters (the strength of electron-polarization interaction, the temperature, the frequencies of polarization oscillations, etc.) the coupling of the tunneling electron to polarization fluctuations in the barrier always causes an increase in the total tunneling probability compared with its rigid barrier value. This result is intuitively expected, because the exponential dependence of the tunneling probability on barrier height implies that averaging over height fluctuations about the static height value yields a larger result. Note that this holds also for the zero points fluctuations at \( T=0 \). Also note that this is characteristic of a model where the fluctuations appear only in the barrier region. When coupling to phonons exist also outside the barrier region (for instance, in the case electron transfer reactions between two molecules) it can lead to either an increase or a decrease of the tunneling probability.\(^{24}\)

(3) The elastic component of the tunneling probability. This component can be obtained by limiting the integration over \( E_{\text{f}}^j \) in Eq. (43) to the interval \((E_{\text{cl}}^I - \eta, E_{\text{cl}}^I + \eta)\) and taking the limit \( \eta \to 0 \) at the end of the calculation. This procedure yields (see Appendix B)

\[
P_{\text{IF}}^\text{el} = p_{\text{IF}}^0 \exp \left( \frac{4m^2e^2}{\hbar^2\kappa} \sum_q \omega_q \left( \frac{1}{\epsilon_{\text{el}}(q)} - \frac{1}{\epsilon_{\text{op}}(q)} \right) \right.
\]

\[
\times \frac{|f(q)|^2}{q^2} (1/2 + n_q) \prod_q \left( \frac{1}{\epsilon_{\text{el}}(q)} - \frac{1}{\epsilon_{\text{op}}(q)} \right) \frac{|f(q)|^2}{q^2} \sqrt{(n_q + 1)n_q}. \tag{51}
\]

Here, \( I_0(z) \) is the modified Bessel function of order zero. The inelastic part of the transition probability, \( P_{\text{IF}}^\text{inel} = P_{\text{IF}} - P_{\text{IF}}^\text{el} \) can be obtained from Eqs. (50) and (51).

(4) The high temperature limit. When \( T \gg \hbar \omega_0/k_B \) the parameter \( C \) of Eq. (50b) becomes \( C = (k_B T/\hbar) C_h \) where

\[
C_h = \frac{1}{\pi} \sum_q \omega_q \left( \frac{1}{\epsilon_{\text{el}}(q)} - \frac{1}{\epsilon_{\text{op}}(q)} \right) \frac{|f(q)|^2}{q^2} = \sum_q C_q, \tag{52}
\]

Accordingly, in this limit

\[
P_{\text{IF}} = p_{\text{IF}}^0 \exp \left( \frac{8m^2e^2k_B T}{\hbar^2\kappa} C_h \right) \tag{53}
\]

while the elastic component, \( P_{\text{IF}}^\text{el} \), takes the form

\[
P_{\text{IF}}^\text{el} = p_{\text{IF}}^0 \exp \left( \frac{4m^2e^2}{\hbar^2\kappa} k_B T \sum_q C_q \right) \times \prod_q I_0 \left( \frac{4m^2e^2}{\hbar^2\kappa} k_B T C_q \right). \tag{54}
\]

Polarization fluctuations are seen to enhance both the total tunneling probability and its elastic component relative to the corresponding rigid barrier value. This enhancement may be considerable at high enough temperature. It is interesting to note that the asymptotic properties of the Bessel function imply that \( P_{\text{IF}} \) and \( P_{\text{IF}}^\text{el} \) coincide in the limit

\[
\frac{mk_B T}{\hbar^2} \frac{d^2}{U-E_{\text{cl}}} C_h \gg 1
\]

with exponential accuracy. (For \( T=300 \text{ K} \), \( d=10 \text{ A} \), and \( U-E_{\text{cl}} = 1 \text{ eV} \) this implies \( 5 \cdot 10^{-5} C_h \gg 1 \), so this inequality is not satisfied in realistic situations.) It should be emphasized that Eq. (43) and consequently Eqs. (53) and (54) are valid only provided that thermally activated overbarrier transitions do not contribute appreciably to the overall current. Thus the divergence of these results for \( T \to \infty \) is obviously unphysical.

(5) The low temperature limit. When \( T \ll \hbar \omega_0/k_B \) the total and elastic tunneling probabilities become

\[
P_{\text{IF}} = p_{\text{IF}}^0 \exp \left( \frac{8m^2e^2}{\hbar^2\kappa} C_h \right), \tag{55}
\]

\[
P_{\text{IF}}^\text{el} = p_{\text{IF}}^0 \exp \left( \frac{4m^2e^2}{\hbar^2\kappa} C_1 \right), \tag{56}
\]

where

\[
C_1 = \frac{1}{2} \sum_q \omega_q C_q. \tag{57}
\]

In this limit the total tunneling current can be considerably larger than its elastic component, thus inelastic transitions (in which the electron loses energy) play an important role. Note that the functions \( C_h \) and \( C_1 \) which determine the magnitude of the coupling of the tunneling system to polarization fluctuations in the high and the low temperature limits respectively are different.

The above results can be generalized to account for many phonon branches. In this case we find that the parameters \( C \) [Eq. (50b)], \( C_h \) [Eq. (52)], and \( C_1 \) Eq. (57) take the forms

\[
C = \frac{1}{\pi} \sum_q \omega_q \rho_q \left[ f(q) \right]^2 \int_{-\infty}^{\infty} d\omega \frac{\text{Im} \epsilon(q,\omega)}{|\epsilon(q,\omega)|^2} (n(\omega) + 1/2), \tag{58}
\]

s = \frac{d^2}{24}. \tag{68}

The calculation of the elastic component of the tunneling probability within this approximation leads to the following expressions for Eqs. (C4) and (C18):

\[ \gamma_2 = \frac{2e^2\kappa}{\hbar d^2} \left( 1 + \frac{1}{\epsilon_{st}} \right) \tau + \frac{1}{\omega} (e^{-\omega\tau} - 1), \tag{68} \]

While the other equations above remain the same.

IV. TUNNELING RATE: THE QUASICLASSICAL METHOD

An alternative approach to the effect of barrier dynamics on quantum tunneling is based on a generalization of the WKB approximation for systems with many degrees of freedom.\(^{18}\) It is valid provided that the usual conditions for validity of the one-dimensional WKB approximation are satisfied, and in addition when the quasiclassical trajectory in the multidimensional space \((z,\{Q_i\})\) does not deviate too much from the \(z\) axis and when the phonon energies are small relative to \((U - E_d)\). When applied to systems which interact with the thermal environment throughout all space, the results of this approach compare well with those of the more familiar imaginary free energy method. Here the thermal interactions are restricted to the barrier region. In this section we briefly review this approach in the framework of our model, and compare the resulting tunneling probability to that obtained using the Bardeen’s formalism. We show that in the relevant dynamical range, i.e., barrier dynamics slow relative to the tunneling rate, \((\omega_q < 1)\), the two approaches, though based on different sets of model assumptions, yield essentially identical results. The WKB approach can describe the tunneling process also in the fast barrier limit, \((\omega_q > 1)\). This limit may be relevant for the consideration of the effect of electronic polarization in the barrier on the tunneling process.

Application of WKB approach\(^{18(b)}\) to the system described by the Hamiltonian (1)–(4) yields the following expression for the tunneling probability (see Appendix C):

\[ P_{TF} = P_{TF}^0 \exp \left( \sum_q \left( 2\alpha_q + \beta_q n_q \right) \right). \tag{61} \]

General expressions for \(\alpha_q\) and \(\beta_q\) are given in Ref. 18(b). Expressions for the rectangular barrier case are given by Eqs. (C1)–(C5). These results indicate that approximation (16) replacing the electron–phonon coupling by a position independent constant has to be exercised with caution. In the slow barrier limit replacing \(f(k,z)\) by Eq. (16) is in fact a good approximation (see Appendix C). Using this approximation for rectangular barrier with arbitrary dynamics leads to

\[ \alpha_q = \frac{2e^2\kappa}{\hbar d^2} C_q \left[ \tau - \frac{1}{2\omega_q} \left( 1 - \exp(-2\omega_q\tau) \right) \right], \tag{62a} \]

\[ \beta_q = \frac{2e^2\kappa}{\hbar d^2 \omega_q} C_q (\exp(\omega_q\tau) - \exp(-\omega_q\tau))^2, \tag{62b} \]

where \(\tau\) is the tunneling time determined by Eq. (28). For the case of slow polarization dynamics \((\omega_q \tau \ll 1)\) the quasiclassical equation for tunneling probability reduces to Eq. (50) obtained above in the framework of Bardeen transfer Hamiltonian formalism. [Note that the parameter \(md^2/(U - E_d)\) which appears in Eq. (50a) is equal to \(2r^2\), cf. Eq. (28).] In the opposite limit \((\omega_q \tau \gg 1)\) Eq. (61) becomes

\[ P_{TF} = P_{TF}^0 \exp \left[ \frac{2e^2\kappa}{\hbar d^2} \sum_q C_q \left( \frac{1}{\omega_q} \exp(2\omega_q\tau)n_q \right) \right]. \tag{63} \]

When the barrier is not slow relative to the tunneling electron, e.g., when the dynamics of the electronic polarization in the barrier is important. Eqs. (62) and (63) can be used as rough estimates only. Alternatively, using the general relations (C1)–(C5) we can compute the tunneling probability without resorting to the averaging approximation (16). In particular, in the fast barrier limit \((\omega_q \tau \gg 1)\) this leads to expressions (C13) and (C14) for \(\alpha_q\) and \(\beta_q\), respectively.

To conclude this section we note that the quasiclassical approximation, as well as the Bardeen approach, is valid only when the oscillator energies \(h\omega_q\) are much lower than the barrier height \(U - E_d\). As a result Eq. (63), (C13), and (C14) can be considered only as intermediate results, valid in the frequency interval \(1/\tau < \omega_q < (U - E_d)/\hbar\). See, however, the discussion at the end of Sec. V.

In the next section we provide some examples of model calculations for the behavior of the tunneling probability as a function of specific system parameters.

V. NUMERICAL RESULTS AND DISCUSSION

In what follows we provide the results of model calculations in order to demonstrate the behavior of our tunneling model for a range of physical parameters. For simplicity we consider an “Einstein model” for the polarization modes, taking all the frequencies equal, \(\omega_q = \omega\). We also disregard the \(q\) dependence of \(\epsilon_{st}\) and \(\epsilon_{op}\). Focussing on Eqs. (61)–(62) this implies

\[ \sum_q \alpha_q = \frac{2e^2\kappa}{\hbar d^2} \left( \frac{1}{\epsilon_{st}} - \frac{1}{\epsilon_{op}} \right) \left[ \tau - \frac{1}{2\omega} \left( 1 - e^{-2\omega\tau} \right) \right], \tag{64} \]

\[ \sum_q \beta_q n_q = \frac{2e^2\kappa}{\hbar d^2} \left( \frac{1}{\epsilon_{st}} - \frac{1}{\epsilon_{op}} \right) n \frac{1}{\omega} (e^{\omega\tau} - e^{-\omega\tau})^2 s; \tag{65} \]

where

\[ s = \sum_q \frac{|\tilde{f}(q)|^2}{q^2}; \quad q = l\pi/d; \quad l = 1,2,\ldots \tag{66} \]

Using Eq. (16) for \(\tilde{f}(q)\), \(s\) is evaluated to yield

\[ s = d^2/24. \tag{67} \]

The calculation of the elastic component of the tunneling probability within this approximation leads to the following expressions for Eqs. (C4) and (C18):

\[ \gamma_2 = \frac{2e^2\kappa}{\hbar d^2} \left( \frac{1}{\epsilon_{st}} - \frac{1}{\epsilon_{op}} \right) \left[ \tau + \frac{1}{\omega} (e^{-\omega\tau} - 1) \right]. \tag{68} \]
FIG. 1. Ratio between the tunneling probability $P$ and the corresponding static barrier result $P_0$ as a function of the barrier thickness $d$, for a system with the standard parameters: $\omega=100$ K, $T=300$ K, $U-E=1$ eV, $e_\text{st}=30$, and $e_\text{op}=2$. Full line—the total probability, dotted line—the elastic tunneling probability, and dashed line—the inelastic tunneling probability. These results were obtained using approximation (16). The dashed-dotted line shows the results for the total tunneling probability obtained from Eqs. (70) and (71) without invoking approximation (16).

For the calculations that do not invoke approximation (16) we start from Eqs. (C1)-(C5) and use $\omega_q=\omega$ and $n_q=n$ to get

$$\sum_q \alpha_q = \omega e^{-2\omega \sigma} \frac{1}{\omega} \left[ \sum_q G_2^+(q) \right]^2$$

and

$$\sum_q \beta_q n_q = 2n \omega \sum_q \left[ e^{\omega q G_2^+(q)} - e^{-\omega q G_2^-(q)} \right]$$

FIG. 2. Same as Fig. 1, now for $U-E=5$ eV and $\omega=5000$ K (other parameters stay the same). These results were obtained from Eqs. (70) and (71) without invoking approximation (16).

FIG. 3. $P/P_0$ as a function of temperature for a system with the “standard” parameters. Line notation is the same as in Fig. 1. [Approximation (16) was again used for the results represented by the lower three lines, but not for the dashed-dotted line.]

The sums over $q=(l\pi/d)$; $l=1,2,\ldots$ of the expressions involving $G_2^+(q)$ and $G_2^-(q)$, Eqs. (C3) and (C4) are evaluated numerically. The corresponding elastic tunneling probabilities were calculated analogously using Eq. (C17). In particular, in the fast barrier limit, $\omega_q \gg 1$, substitution of Eq. (15) in Eqs. (C13) and (C14) leads to the following expressions for Eqs. (70) and (71):

$$\sum_q \alpha_q = \frac{e^2 \omega \sigma}{6 \hbar} \left( \frac{1}{\omega \sigma} \right)$$

and

$$\sum_q \beta_q n_q = \frac{e^2 \omega \sigma}{6 \hbar} \left( \frac{1}{\omega \sigma} \right) n.$$

The results obtained in this way are displayed in Figs. 1–5. We have considered a symmetric barrier, $U_1=U_2$. Unless otherwise stated the following choice of parameters (henceforth referred to as “standard” was used: $d=10$ Å,
tron tunneling is seen as a relative enhancement of the tun-
phonon frequency \( \omega = 100 \text{ K} \) was used in this calculation.

The use of a position independent electron–barrier polariza-
tion interaction, obtained from averaging the actual in-
teraction over the barrier, is a reasonable approximation
when the barrier dynamics is slow. In the case of fast barrier
dynamics it underestimates the enhancement factor. This ob-
ervation is significant as earlier theoretical considerations of
this problem\(^5\) have assumed constant coupling.

Enhancement of the tunneling probability appears in
the elastic component of the tunneling current, in addition to
the opening of the inelastic channel.

Finally, consider the \( \omega \to \infty \) limit. Figure 5 displays the
results for the tunneling probabilities obtained from the qua-
sicalcassical approach for the "standard" parameters in the fre-
cquency range \( \omega = 0 - 10^6 \text{ K} \). As discussed above the Bardeen's
approach as formulated in Sec. III cannot be used in this
limit. For a simple linear model of electron–phonon coupling
it has been shown\(^8\) that the quasiclassical approach leads in
this limit to tunneling with renormalized static barrier and
electron mass. The results summarised in Appendix C and
displayed in Fig. 5 correspond to the same picture: As \( \omega \to \infty \)
the inelastic tunneling vanishes and the elastic tunneling
approaches a new static barrier value. It should be noted, how-
ever, that even though these results show the expected qual-
itative behavior, they should not be regarded as quantitatively
significant for two reasons: (a) When we focus on the effect of
relatively slow polarization modes on the tunneling pro-
cess we have assumed that the barrier function \( U(r) \) includes
the normalization effect due to the fast (electronic) compo-
nent of the barrier polarization. When \( \omega \to \infty \) the bare barrier
should be used. (b) The renormalization of the barrier is
associated with the solvation energy associated with the in-
teraction between the electron and the fast polarization
mode. For a point charge interacting with a continuum di-
etric this energy diverges. The resolution of this difficulty
is to take into account the discrete structure of the solvent,
 i.e., the associated cutoff in the \( q \)-space description of the
polarization. The results of Fig. 5 also correspond to a finite
deviation energy, however, this is due to the finite cutoff
imposed in Sec. II on the possible value of \( q \) from consid-
eration associated with the magnitude of the tunneling prob-
ability. Therefore the magnitude of the barrier height renor-
malization as reflected by the \( \omega \to \infty \) limit of the tunneling
probability shown in Fig. 5 does not necessarily reflect the
correct physical value.

VI. CONCLUSIONS

Tunneling through dielectric barriers has been studied.
The tunneling probability (both elastic and inelastic) is af-
fected by the barrier dielectric response, resulting in an enhanced tunneling probability on top of the effective barrier lowering associated with the instantaneous part of the barrier dielectric response. The enhancement depends on the barrier geometry, on the temperature and on the rate of the barrier dynamical response. Our results indicate that high frequency intramolecular modes are considerably more effective in enhancing the tunneling probability, however, the enhancement factors are too small to account for reported observations.

**APPENDIX A: THE INELASTIC BARDEEN’S FORMALISM**

Here, we follow Bardeen’s evaluation of the tunneling rate through a rectangular barrier. The solutions to the corresponding semi-infinite barriers problems are \( \Psi_f(r, Q) \) and \( \Psi_F(r, Q) \) with \( r = (z, r_l) \) denoting the electron, and \( Q = (Q_{qz}, \ldots) \) the phonon coordinates, respectively. The tunneling occurs in the \( z \) direction along which the barrier and the semi-infinite barriers are defined. The locations of the barrier edges are denoted \( z_a \) and \( z_b \) (corresponding to \(-d/2\) and \(d/2\) in the text). The general solution to the Schrödinger equation

\[
\frac{\partial \Psi(r, Q, t)}{\partial t} = -iH\Psi(r, Q, t) \tag{A1}
\]

is written in the form

\[
\Psi(r, Q, t) = C_f(t)\Psi_f(r, Q)e^{-iE_f t} + C_F(t)\Psi_F(r, Q)e^{-iE_F t}. \tag{A2}
\]

The Hamiltonian itself can be formally written as sums

\[
H = H_{0f} + H_{1f} + H_{0F} + H_{1F}, \tag{A3}
\]

where \( H_{0f} \) and \( H_{0F} \) correspond to the semi-infinite problems associated with \( \Psi_f \) and \( \Psi_F \), so that \( H_{0f}\Psi_f = E_f\Psi_f \) and \( H_{0F}\Psi_F = E_F\Psi_F \). Note that \( H_{0f} \) for \( z < z_b \) and \( H_{0F} = H \) for \( z < z_a \).

Inserting Eq. (A2) into Eq. (A1) and using, in the spirit of perturbation theory \( C_f \sim 1, C_F \sim 0, dC_f/dt \sim 0 \), leads to

\[
\frac{dC_F}{dt} \left[ \Psi_F^*e^{-iE_F t} - e^{-iE_F t}\Pi_{11}\Psi_f \right]. \tag{A4}
\]

Multiplying by \( \Psi_F^* \) and integrating yields

\[
M_{1F} = i \int dx \ dQ \ \Psi_F^*(r, Q)(H - H_{0f})\Psi_f(r, Q). \tag{A5}
\]

Since \((H - H_{0f})\Psi_f = (H - E_f)\Psi_f = 0\) for \( z < z_b \), and \((H - E_F)\Psi_F = 0\) for \( z > z_b \), we can write Eq. (A5) in the form

\[
M_{1F} = \int_{z_b}^{z_a} dz \ dQ \left[ \Psi_F^*(H - E_f)\Psi_f(H - E_F)\Psi_f \right]. \tag{A6}
\]

The integration in Eq. (A6) is taken over all \( r_l \) and \( Q \), and over the specified range in \( z \). Note that, since in the range \( z_a < z < z_b \) the integral in Eq. (A6) vanishes, the lower bound on the \( z \) integration can be any value, \( z_1 \), in this range. For \( E_f = E_F \) (expected by overall energy conservation) Eq. (A6) becomes

\[
M_{1F} = \int_{z_1}^{z_a} dz \ dQ \left[ \Psi_F^*H\Psi_f - \Psi_fH\Psi_F^* \right] \tag{A7}
\]

\[
= \int_{z_1}^{z_a} dz \ dQ \left[ \Psi_F^*T\Psi_f - \Psi_fT\Psi_F^* \right], \tag{A8}
\]

where \( T \) is the kinetic energy operator (electron and phonon) part of \( H \). In mass weighted coordinates \( \sqrt{mr-r,} \sqrt{M Q-Q,} \), this is essentially the Laplacian \( \nabla^2 \) in the multi-dimensional \((r, Q)\) space so that

\[
M_{1F} = \int_{z_1}^{z_a} dz \ dQ \left[ \Psi_F^*\nabla^2\Psi_f - \Psi_f\nabla^2\Psi_F^* \right]. \tag{A9}
\]

Using the divergence theorem, assuming that \( \Psi_f \) and/or \( \Psi_F \) and their derivatives vanish at \( Q \to \pm \infty, r_l \to \pm \infty \) and \( z \to \infty \) (the vanishing of \( \Psi_f \) at \( z \to \infty \) is related to the semi-infinite nature of the barrier) leads to

\[
M_{1F} = \int \ dQ \left[ \Psi_F^*\frac{\partial}{\partial z}\Psi_f - \Psi_f\frac{\partial}{\partial z}\Psi_F^* \right]_{z=z_1}. \tag{A10}
\]

Returning to the regular (not mass-weighted) coordinates yields

\[
M_{1F} = \int dz \ dQ \left[ \Psi_F^*\frac{\partial}{\partial z}\Psi_f - \Psi_f\frac{\partial}{\partial z}\Psi_F^* \right]_{z=z_1}. \tag{A11a}
\]

Now, if the wave function \( \Psi(z, r_l, Q) \) is separable, \( \Psi = \phi(z)\chi(Q) \) then \( M_{1F} \) can be rewritten as

\[
M_{1F} = \int dQ \ \chi_f^*(Q) M_{1F}(Q)\chi_f(Q), \tag{A11a}
\]

\[
M_{1F}(x) = -\frac{\hbar^2}{2m} \int dQ \left[ \phi_F^* \frac{\partial}{\partial z}\phi_f - \phi_f \frac{\partial}{\partial z}\phi_F^* \right]_{z=z_1}. \tag{A11b}
\]

In particular, if processes in which the electron is deflected from the perpendicular direction are disregarded, the \( r_l \) integration is trivial and Eq. (A11b) becomes

\[
M_{1F}(Q) = -\frac{\hbar^2}{2m} \left( \phi_F^*(z) \frac{\partial}{\partial z}\phi_f(z) - \phi_f(z) \frac{\partial}{\partial z}\phi_F^*(z) \right)_{z=z_1}. \tag{A11c}
\]

where \( \phi_f(z) \) and \( \phi_F(z) \) are given by Eq. (25). Using Eq. (25) in Eq. (A11c) leads to

\[
M_{1F}(Q) = -\frac{\hbar^2}{2m} \left( \frac{4k_F k_f}{2mL} (ik_f + k_F) - i(k_F - k_f) \right) x e^{-[d/2](k_f + k_F)z_1} e^{-z_1(k_f - k_F)}. \tag{A12}
\]
A rigorous derivation should have yielded a result independent of the arbitrary point $z_t$. The appearance of a (relatively weak) dependence on $z_i$ in Eq. (A12) is probably a result of the factorization $\Psi = \phi_X$, which is exact only if there is no electron–phonon coupling, i.e., when $\kappa_t = \kappa$. In the present paper we note that under the model assumption $U - U_{1(2)} \gg |E_{\text{el}} - E_{\text{el}}|$ we have

$$\frac{|\kappa_t - \kappa|}{|\kappa_t + \kappa|} \sim \frac{|E_{\text{el}} - E_{\text{el}}|}{|U - U_{1(2)}|} \ll 1$$

(A13)

and therefore disregard the factor containing $z_t$ in Eq. (A12). This leads to Eq. (37).

**APPENDIX B: THE ELASTIC COMPONENT OF THE TUNNELING PROBABILITY**

This component can be evaluated under the same assumptions that lead to Eq. (50), i.e., $|b_q|^2 \ll 1$ for all $q$. Limiting the integration over $E_{\text{el}}$ to the interval $(E_{\text{el}} - \eta, E_{\text{el}} + \eta)$, $(\eta > 0)$, Eq. (47) takes the form

$$W_{\text{el}} = B \int_{E_{\text{el}} - \eta}^{E_{\text{el}} + \eta} \int_{-\infty}^{\infty} dt \exp(i(E_{\text{el}} - E_{\text{el}})t/\hbar) C_{\text{el}}$$

with

$$B = \frac{1}{\hbar} \left[ |D|^2 \rho \exp \left( \sum_q |b_q|^2(2n_q + 1) \right) \right]_{E_{\text{el}} = E_{\text{el}}}$$

and

$$C_{\text{el}} = \exp \left( \sum_q |b_q|^2[(n_q + 1)\exp(i\omega_q t) + n_q] \right) \times \exp(-i\omega_q t)].$$

(B1)

Expanding the exponent in a power series and using the binomial theorem lead to

$$C_{\text{el}} = \prod_q \sum_{j=0}^{\infty} \left| b_q \right|^2 (n_q + 1)^j |n_q + 1\rangle |n_q + 1\rangle |e^{i}\rangle \left( 2i-j \right) |w_q\rangle.$$ (B2)

Inserting Eq. (B4) into Eq. (B1) and using the identity (for any $s \neq 0$)

$$\lim_{\eta \to 0} \int_{E_{\text{el}} - \eta}^{E_{\text{el}} + \eta} dt \exp(i(E_{\text{el}} - E_{\text{el}})t/\hbar) = 2\pi \hbar \delta_{E_{\text{el}}}$$

(B5)

and the definition of the modified Bessel function of order zero and argument $z$

$$I_0(z) = \sum_{j=0}^{\infty} \frac{(z/2)^{2j}}{(j!)^2}$$

(B6)

finally leads to

$$W_{\text{el}} = \frac{2\pi}{\hbar} |D|^2 \rho \exp \left( \sum_q |b_q|^2(2n_q + 1) \right) \times \left( \prod_q I_0(2|b_q|^2\sqrt{(n_q + 1)n_q}) \right.$$ (B7)

which is to be evaluated for $E_{\text{el}} = E_{\text{el}}$. The elastic transmission probability $P_{\text{el}}(E_{\text{el}})$ can be obtained substituting Eqs. (45), (46) and (B6) in Eq. (27).

**APPENDIX C: THE QUASICLASSICAL METHOD**

We follow Sumetskii (18th) and refer to equations from Ref. 18(b) as (n,S) where $n$ is the equation number in that paper. The tunneling probability for the electron interacting with the set of oscillators, which are initially at thermal equilibrium is given by Eq. (57.3) or our Eq. (61). The quantities $\alpha_q$ and $\beta_q$ appearing in Eq. (61) correspond to the influence of the zero point motions of the oscillators and of their thermal excitations, respectively, on the tunneling probability. These quantities are calculated from Eqs. (22.S), (23.S) and (43.S). It should be noted that the quantities $\alpha_q$ can be either positive or negative but the quantities $\beta_q$ are always positive. Consequently, the interaction with zero point oscillations can either increase or decrease the tunneling probability while the temperature dependent terms increase the tunneling probability. In the present model, where the electron–polarization interaction is localized in the barrier region, the coefficients $A_{\pm}^q$ in Eqs. (43.S) vanish and $\alpha_q > 0$. This implies an increase of the tunneling probability relative to the rigid barrier case at any temperature. For a rectangular barrier and the electron–polarization interaction (12) and (13), $\alpha_q$ and $\beta_q$ [Eqs. (43.S)] take the forms

$$\alpha_q = \omega_q |G_2^q|^2 \exp(-2\omega_q \kappa) + \gamma_2,$$ (C1)

$$\beta_q = 2\omega_q |G_2^q|^2 \exp(\omega_q \kappa) - G_2^- \exp(-\omega_q \kappa)^2$$ (C2)

with the parameters $G_2^\pm$ and $\gamma_2$ given by

$$G_2^\pm = \frac{\pm D_q}{2\omega q \kappa} \frac{m}{h} \int_{-d/2}^{d/2} dz \int_{-d/2}^{d/2} dz' \times f(q,z)dz,$$ (C3)

$$\gamma_2 = \frac{D_2^q}{2\omega q \kappa} \frac{m^2}{h^2} \int_{-d/2}^{d/2} dz \int_{-d/2}^{d/2} dz' \times \exp \left( \frac{m}{\hbar} \omega_q (z'-z)/\kappa \right) f(q,z)f(q,z'),$$ (C4)

$$\kappa = \frac{1}{\hbar} \sqrt{2m(U - E_{\text{el}})},$$

$$D_2^q = \frac{4\epsilon^2 \kappa}{h d^2} \left( \frac{1}{\epsilon_{\text{el}}(q)} - \frac{1}{\epsilon_{\text{op}}(q)} \right) \frac{\omega_q^2}{q^2}.$$ (C5)

If the electron–polarization interaction is independent of the position of the electron inside the barrier, i.e., the case considered in Sec. III, Eqs. (C1) and (C2) reduce to Eqs. (62a) and (62b) in the text. For the position dependent interaction of Eqs. (12) and (13) $\alpha_q$ and $\beta_q$ can also be evaluated ana-
lytically. The results of these calculations are discussed in the Sec. V. Simpler expressions are obtained in the slow and fast barrier limits. In the slow barrier case, Eqs. (C3) and (C4) become

$$G^+_{2, m} = \frac{D_q}{2 \omega_q \kappa} \frac{m}{h} \int_{-d/2}^{d/2} f(q, z) dz (1 + O(\omega_q \tau)), \quad (C6)$$

$$\gamma_2^+ = \frac{D_q^2}{2 \omega_q \kappa^2} \frac{m^2}{h^2} \left[ \int_{-d/2}^{d/2} dz f(q, z) \right] (1 + O(\omega_q \tau)), \quad (C7)$$

and

$$\alpha_q = \frac{2 \omega_q \kappa}{h d^2} \left( \frac{1}{\epsilon_{el}(q)} - \frac{1}{\epsilon_{qp}(q)} \right) \left| \frac{\tilde{f}(q)}{q^2} \right|^2 \omega_q \tau^2 (1 + O(\omega_q \tau)), \quad (C8)$$

$$\beta_q = \frac{8 \omega_q \kappa}{h d^2} \left( \frac{1}{\epsilon_{el}(q)} - \frac{1}{\epsilon_{qp}(q)} \right) \left| \frac{\tilde{f}(q)}{q^2} \right|^2 \omega_q \tau^2 (1 + O(\omega_q \tau)). \quad (C9)$$

We see that in this limit the tunneling probability is indeed determined by the average value of the electron–polarization interaction assumed in Sec. III. In this case the quasiclassical equation for tunneling probability reduces to Eq. (50) obtained from the Bardeen’s transfer Hamiltonian formalism.

In the opposite fast barrier limit, $$\omega_q \tau \gg 1$$, Eqs. (C3) and (C4) take the forms

$$G^+_{2, m} = \frac{D_q}{2 \omega_q \kappa} \frac{m}{h} \int_{-d/2}^{d/2} f(q, z) dz (1 + O(1/\omega_q \tau)), \quad (C10)$$

$$G^-_{2, m} = \frac{D_q}{2 \omega_q \kappa} \frac{m}{h} \exp(\omega_q \tau) \left( \frac{df(q, z)}{dz} \right) \int_{-d/2}^{d/2} dz (1 + O(1/\omega_q \tau)), \quad (C11)$$

leading to

$$\alpha_q = \frac{D_q^2}{2 \omega_q \kappa^2} \frac{m^2}{h^2} \int_{-d/2}^{d/2} dz f(q, z) (1 + O(1/\omega_q \tau)), \quad (C13)$$

$$\beta_q = \frac{D_q^2}{2 \omega_q \kappa^2} \frac{m^2}{h^2} \exp(2 \omega_q \tau) \left( \frac{df(q, z)}{dz} \right) \int_{-d/2}^{d/2} dz (1 + O(1/\omega_q \tau)). \quad (C14)$$

In this limit the averaging approximation (16) is not justified quantitatively.

In order to calculate the elastic component of the tunneling probability, Eq. (58.S) is to be evaluated for $$k_j = n_j$$ for all $$j$$. The probability for elastic tunneling is given by

$$P_{IF}^e = P_{IF}^0 \prod_q \exp(2 \gamma_q) \left[ 1 - \exp(-\hbar \omega_q / k_B T) \right] \times \sum_{n=0}^{\infty} \exp(-\hbar n_q \omega_q / k_B T) [L^2_n(2 \omega_q G^+_2 G^-_2)], \quad (C15)$$

where $$L^2_n(x)$$ is a Laguerre polynomial. The sum over them may be expressed in terms of a modified Bessel function of order zero and argument $$y, I_0(y)$$, using the following relation:

$$\sum_{n=0}^{\infty} \left( L^2_n(x) \right)^2 = \frac{1}{1-x} \exp\left( -\frac{2yx}{1-x} \right) I_0\left( \frac{2|y|^2}{1-x} \right). \quad (C16)$$

Thus Eq. (C15) becomes

$$P_{IF}^e = P_{IF}^0 \exp\left( \sum_q (2 \gamma_q - \phi_q \omega_q) \right) \sum_q I_0(\sqrt{(n_q+1)\omega_q} \phi_q), \quad (C17)$$

where

$$\phi_q = 4 \omega_q G^+_2 G^-_2. \quad (C18)$$

The slow barrier limit, $$\omega_q \tau \ll 1$$, is obtained substituting Eqs. (C6) and (C7) in Eq. (C17). In this case Eq. (51) obtained from the Bardeen’s transfer Hamiltonian formalism is recovered. The opposite fast barrier limit, $$\omega_q \tau \gg 1$$, may be obtained putting Eqs. (C10), (C11), and (C12) in Eq. (C17). Note that, since $$n_q \rightarrow 0$$ when $$\omega_q \tau \rightarrow \infty$$, the fast barrier limits of total tunneling probability, Eqs. (61), (C13), and (C14), and of its elastic component, Eqs. (17), (12), become identical in this limit.

**ACKNOWLEDGMENT**

This research was supported in part by the U.S.A.–Israel Binational Science Foundation.


25 The free electron mass was used throughout.