

Quantum coherence in surface-tip transfer of adatoms in AFM/STM

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An adiabatic theory has been developed to describe spontaneous transfer of adatoms from a surface to a tip in atomic force microscopy and scanning tunneling microscopy (AFM/STM). It is shown that, at sufficiently low temperatures, the influence of phonon and electron-hole excitations on the transfer process may become so small that coherent transitions of an adatom between the surface and the tip are possible. The adatom tunnels back and forth between the surface and the tip with a definite period that depends on the surface-tip separation. The effect is mainly due to a unique opportunity to vary the tunneling amplitude of the adsorbate by controlling the tip-surface separation distance. Two features contribute to the quantum coherence phenomenon being even more pronounced as compared to that of interstitial hopping in the bulk: (a) the electron density of states at the Fermi level, and (b) the lattice deformations associated with the presence of the adsorbate outside the surface are noticeably smaller than for an interstitial in the bulk. As a result, electron and phonon polaron effects, respectively, which reduce the mobility of the adatom with respect to surface-tip transition, are substantially suppressed at all temperatures. For typical AFM/STM tip velocities and separation distances, the coherent transition rate of chemisorbed hydrogen atoms at temperatures below 10 K for insulators and semiconductors, and below 0.1 K for metals, may not only be comparable with but also exceed the thermally activated (incoherent) transfer rates at room temperature. [S0163-1829(98)08108-9]

I. INTRODUCTION

Quantum coherence is an interesting phenomenon of time-correlated transitions between two or several levels in a quantum system. Examples of this are the inversion resonance of the NH_3 molecule,¹ strangeness oscillations of a neutral K-meson beam,² superconducting quantum interference devices,³ small current-driven Josephson's junctions,⁴ low-temperature tunneling of hydrogen or deuterium interstitials trapped by oxygen or nitrogen impurities in Nb,^{5,6} charge transfer in slow ion-atom collisions, and so on. As pointed out by Legget *et al.*,⁷ an experimental observation of a periodic transition between two macroscopically distinct states would shed some "light on the conflict at a macro level between the quantum-mechanical formalism and common sense ideas." Meanwhile, the development of surface imaging techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM) opens opportunities to study processes which, although of microscopic nature, affect such macroscopic quantities as the electron tunneling current (STM) and the force a cantilever experiences in AFM. In this work, we explore the possibility of coherent adatom transfer from the surface to a tip, and vice versa, for a typical AFM/STM experimental configuration.

It is worth noting that spontaneous adatom transfer between the surface and tip is closely related to diffusion of light interstitials in solids⁸⁻¹⁰ and adsorbates on solid surfaces.¹¹⁻¹³ Owing to strong coupling between the particle motion and phonon and electron-hole excitations, which play a role of dissipation, coherent transport is expected to manifest itself in atom diffusion mainly at low temperatures and for relatively light atoms (hydrogen, deuterium, helium). The competition between the coherent and incoherent mechanisms results in the diffusion coefficient decreasing at low

temperatures with increasing T , reaching a minimum value and starting to increase again, following the Arrhenius law at high temperatures $T \geq \Theta$ (here Θ is the Debye temperature).^{5,6} In particular, in the absence of dissipation forces, the diffusion process resembles band propagation rather than uncorrelated jumps from one site to another. Almost coherent transport was observed for muons in pure and doped aluminum^{11,12} and hydrogen in $\text{Nb}(\text{OH})_x$ [Refs. 13-15] in the temperature ranges from 0.03 to 1 and 0.2 to 70 K, respectively. Transition to temperature-independent tunneling diffusion of H and D on W(111) and W(211) surfaces below 125 and 144 K was demonstrated by Dharmadhikari and Gomer¹⁶ and Daniels, Lin, and Gomer.¹⁷ Quite recently, similar results were reported for hydrogen isotope diffusion on the Ni(111) surface.¹⁸

These experimental findings prompt the interesting possibility to observe a process of adatom coherent tunneling back and forth between the AFM/STM tip and the surface as the tip approaches the adsorption site. It should be stressed that spontaneous tunneling may occur without any external field, in contrast to the electric-field-assisted adatom transfer.¹⁹⁻²⁷ Recently, Louis and Sethna²⁸ discussed this issue, and pointed out the significant influence of dissipation due to coupling with the phonon environment. In view of the difficulty in evaluating the tunneling amplitude, these authors confined themselves to qualitative considerations, also neglecting the electron polaron and potential barrier fluctuation effects.

In this paper we consider the phenomenon of quantum coherence in adatom transfer in terms of adiabatic time-dependent theory, accounting consistently for electron and phonon polaron effects as well as potential barrier fluctuations. An explicit expression for the tunneling amplitude, the major quantity governing the process, is derived, and several

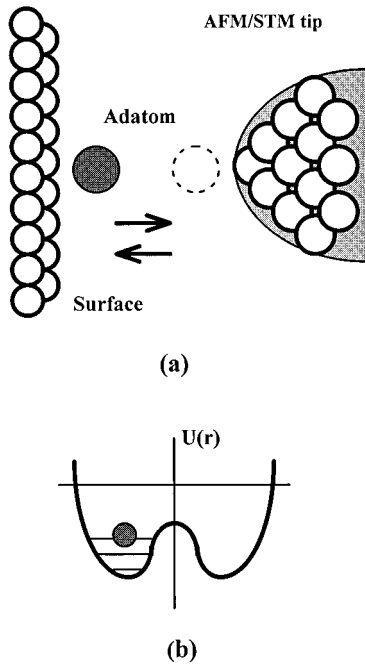


FIG. 1. Schematic representation of the adatom transfer between the surface and the AFM/STM tip (a), and the double-well potential corresponding to adsorption sites at the surface and the tip (b).

examples of time dependence of the transfer probability, calculated for realistic parameters and adsorbate-surface configurations, are presented. The major emphasis is put on analysis of the general picture of quantum coherence, while a more detailed mathematical formalism as well as a theory of incoherent transfer of adsorbates will be published elsewhere.²⁹

II. COHERENT TUNNELING WITHOUT DISSIPATION

Before going into details of the interaction of an adsorbate with the AFM/STM tip, we illustrate the basic process by considering a simplified problem of adatom tunneling between two potential wells without dissipation. We assume for a while that the tip velocity is zero, and that the tip is located at a certain distance from the surface, so that there are two potential wells corresponding to adsorption sites at the tip and surface (cf. Fig. 1). Even in the absence of dissipation, the system still possesses many degrees of freedom and, in order to simplify the problem further, we suppose that there are essentially two states corresponding to the adatom position either on the surface or at the tip. Those might be two ground levels in the potential wells. If the levels are aligned, resonant tunneling may take place, so that the adatom moves spontaneously from one well to another (an incoherent transition may occur between two levels with different energies, it is, however, much less likely). Since the basic features of the tunneling process do not change qualitatively when going from a nonsymmetrical to a symmetrical double well it is convenient to consider the wells to be symmetrical from the beginning. The Hamiltonian of the system is then described by a (2×2) matrix, with the diagonal terms being equal to the energy of the stationary state $H_{11} = H_{22} = -E_0$, and the nondiagonal terms $H_{12} = H_{21} = -\Delta_0/2$ as-

sumed to be responsible for the interaction between the wells, with Δ_0 being the tunneling amplitude or, alternatively, the ground level energy splitting. The appearance of the quantity Δ_0 is essentially due to a finite value of the potential barrier separating the wells, and to the nonzero probability for the adatom to penetrate into the under barrier region. Owing to the smallness of the penetration depth into the classically forbidden region, the tunneling amplitude is expected to be small compared to the ground level energy, $\Delta_0 \ll E_0$.

The wave function of the adsorbate may be presented as a simple superposition of two functions corresponding to the unperturbed states of the adsorbate at the surface (1) and the tip (2),

$$\psi = C_1 \psi_1 + C_2 \psi_2, \quad (1)$$

with the expansion coefficients C_1 and C_2 satisfying the system of coupled equations which follow directly from the Schrödinger equation¹ (atomic units, $\hbar = e = m = 1$, are used, unless otherwise specified)

$$i \partial C_{1(2)} / \partial t = -(\Delta_0/2) C_{2(1)}. \quad (2)$$

The condition $\Delta_0 \ll E_0$ implies that the coefficients C_1 and C_2 are slowly varying functions of time as compared to the functions ψ_j , $j=1$ and 2 . Assuming the adsorbate to be initially on the surface [$C_1(0) = 1$], the solution to the system of equations (2) is straightforward. In particular, the probability to find the adsorbate at the tip at time t is determined by the coefficient C_2 squared, and reads

$$P(t) = \sin^2(\Delta_0 t/2). \quad (3)$$

Thus the probability oscillates between zero and 1, implying that the adatom tunnels back and forth between the tip and the surface with period $2/\Delta_0$. For instance, at any moment $t = (2n+1)\pi/\Delta_0$ the adatom is located at the tip, and half-way between those times at the surface, with the probability $P = 1$.

Result (3) represents the essence of the quantum coherence phenomenon: oscillations with a period determined by a quantity of a strictly quantum origin, with no analog in classical physics. Unfortunately, the quantum beats of type (3) can hardly materialize in a pure form. In reality, the adatom transfer occurs in the bath of phonons and weakly bound electrons and is, therefore, accompanied by phonon and electron-hole excitations. In addition, even at the lowest temperatures, the tunneling process takes place against the background of zero vibrations of host atoms. Finally, the tip is expected to move toward or across the surface, and its motion introduces new constraints. First, the tunneling amplitude becomes time dependent, increasing from zero to a certain maximum value corresponding to the distance of closest approach between the potential wells. Second, the tip-adsorbate interaction time may be quite large, so that incoherent, thermally stimulated, jumps may occur before the coherent tunneling starts to dominate the adatom transfer. Quantum mechanically, this means that by this time the wave function of the adsorbate will be represented by an admixture of different states with uncorrelated phase differ-

ences. The influence of those effects on quantum coherence, and the proper modification of formula (3), are considered in the following sections.

III. INFLUENCE OF DISSIPATIVE PROCESSES AND TIP MOTION ON COHERENT TUNNELING

Although the motion of the tip with respect to the surface may be quite arbitrary, it is supposed for simplicity that the tip slides parallel to the surface at a fixed separation distance d . The adatom is assumed to be located at a certain adsorption site at the origin of the coordinates, and the tip passes over the adsorption site at time $t=0$. In addition, the adatom mass M is assumed to be small compared to the mass of the host atoms of the lattice M_h , $M \ll M_h$. It is also assumed that there are at least two identical potential wells at the tip and surface, and that the adatom may tunnel between two ground states of the wells. An assumption about the identity of the wells is not crucial for the theory developed below and may, in principle, be removed. Basically, the full physical picture of the problem is contained in the inequalities

$$\omega_e \gg \omega_0 \gg \omega_{ph} \gg v/a \quad (4)$$

where ω_e , ω_0 , and ω_{ph} are the frequencies for the electron subsystem, adatom vibration, and phonon excitations, respectively, while v is the tip velocity, and a is the average interatomic distance in a solid. Each inequality in expression (4) has its own particular meaning. Thus the typical tip-adsorbate interaction time $\tau_1 \sim a/v \sim 10^{-2} - 10^{-5}$ s is large compared to any other characteristic time, which is at most of the order of $\tau_{ph} \sim \omega_{ph}^{-1} \sim 10^{-11} - 10^{-12}$ s. Therefore, the electron and phonon subsystems adjust smoothly to the tip motion, and for any tip position there exists a fixed electron-phonon configuration which determines, in turn, the motion of the adsorbate in the potential wells located either on the surface or at the tip. The condition $\omega_0 \gg \omega_{ph}$ is due to the fact that $M \ll M_h$, and is imposed to insure quick motion of the adatom in an individual well with respect to the lattice vibrations. On the other hand, the obvious requirement $\omega_e \gg \omega_0$ means that the majority of electrons respond rapidly to the motion of the adatom, so that to a first approximation the wave function of the system may be described by quasistationary adiabatic states:^{30,31}

$$|nsv\mathbf{I}\rangle = \varphi_n(\mathbf{r}_e, \mathbf{r}, \mathbf{u}, \mathbf{R}) \psi_{s\mathbf{I}}(\mathbf{r}, \mathbf{u}, \mathbf{R}) \Phi_{sv\mathbf{I}}(\mathbf{u}, \mathbf{R}). \quad (5)$$

Here \mathbf{r}_e , \mathbf{r} , and \mathbf{u} are the electronic, adatom, and phonon variables, respectively, and the radius vector $\mathbf{R} = \mathbf{R}(t)$ determines the tip position with respect to the adsorption site \mathbf{I} at time t . The quantum number sets n and s refer to the electronic and adatom states, while v is the number of phonons. One should distinguish between the adiabaticity of wave function (5) with respect to the tip motion and the adiabatic response of the electron states to the adatom transfer. The electronic wave function on the right-hand side nonadiabatically readjusts as compared to that of the unperturbed state when the coupling between the adatom and electron motion is neglected. This readjustment stems from the fact that those electron-hole excitations with energies $\varepsilon \ll \omega_0$ cannot follow the adatom transitions adiabatically. The same is true, and even more so, regarding the phonon excitations, since ω_0

$\gg \omega_{ph}$. The slow electron and phonon excitations give rise to the so-called electron and phonon polaron effects, which eventually slow down the tunneling process and lead to a modification (renormalization) of the unperturbed tunneling amplitude $\Delta_0 = \langle s\mathbf{I} | H_{\text{int}} | s\mathbf{I} + g \rangle$, H_{int} being the part of the Hamiltonian responsible for the tunneling process between two wells at the adsorption sites \mathbf{I} and $\mathbf{I} + g$.^{8-10,30-32}

Apart from the polaron effect, vibrational fluctuations of the tip and surface lattices deform the potential barrier shape (fluctuational barrier preparation), increasing the tunneling probability.³⁰ Therefore, the coherent transfer is always accompanied by competition between the electron and phonon polaron effects, on the one hand, and the fluctuational barrier preparation, on the other hand, and is generally described by the matrix element $\Delta = \langle nsv\mathbf{I} | H_{\text{int}} | nsv\mathbf{I} + g \rangle$ (for the transition between the tip and the surface, $g = \mathbf{R}$). Note that, by virtue of the tip position being time dependent, the matrix element is a function of time, $\Delta = \Delta(t)$. The coherent tunneling is realized for the energy of the system E_{nsv} at any electron, phonon, and tip-surface configuration, and ‘‘not only at the moments when the identity of two wells is restored by fluctuations.’’⁸ Evaluation of Δ implies calculation of elements diagonal in nv , or integration over the electronic and phonon variables, and eventually reduces to a thermal-equilibrium averaging procedure.

A finite value of temperature leads to appearance of two relaxation times t_e and t_{ph} which characterize the coupling between the adatom tunneling process and electron-hole (t_e) and phonon (t_{ph}) excitations. Coherence is fully destroyed (the coherent bandwidth shrinks to zero, $\Delta = 0$) by interaction with electrons and phonons when the relaxation times t_e and t_{ph} are small compared with the dwell time of the adatom at the adsorption site t_d , $t_e, t_{ph} \ll t_d$. This phenomenon is well known in the theory of tunneling with dissipation.^{7,10,33,34} In the opposite limiting case $t_e, t_{ph} \gg t_d$, the destructive influence of the electron and phonon excitations on the wave function phase can be neglected, and the probability to find the adatom at the tip oscillates according to the law

$$P(t) = \sin^2 \left[(1/2) \int_{-\infty}^t \Delta(t')/dt' \right], \quad (6)$$

where the amplitude Δ represents the energy-level splitting of the ground state. The dwell time of the adsorbate at one of the wells is about Δ^{-1} , and the electron and phonon relaxation times are of the order of $t_e \sim (2\pi bT)^{-1}$ and $t_{ph} \sim 10^{-6} \Theta^{-1} (\Theta/T)^9$,^{10,35} respectively, where the parameter b is proportional to the squared product of the electron density at the Fermi level and the electron-adatom scattering amplitude. At temperatures below several tens of K, the phonon relaxation time becomes a macroscopic quantity. Hence, at low enough temperatures $T \ll \Theta$, the dominant mechanism of coherent band destruction is interaction with electron-hole excitations. From this it follows that in order for expression (6) to hold true, the tunneling amplitude Δ has to satisfy the condition

$$\Delta \gg \max\{2\pi bT, 10^6 \Theta (T/\Theta)^9\}. \quad (7)$$

The first term in the curly brackets on the right-hand side of Eq. (4) exceeds greatly the second one in the case of metals

at temperatures below 10 K. This term, however, becomes negligible for insulators and semiconductors, characterized by a low density of conduction-band electrons. For typical metal surfaces the quantity $b \sim 5 \times 10^{-3}$, which is an order of magnitude less than in the bulk,^{36,37} and the energy-level splitting $\Delta \gg 3 \times 10^{-2}$ T. Thus, for instance, in the temperature range from 0.01 to 10 K, the quantity Δ is supposed to be large compared to $3 \times 10^{-8} - 3 \times 10^{-5}$ eV, respectively.

IV. TUNNELING AMPLITUDE

To show that criterion (7) is fulfilled for typical AFM/STM tip-surface separation distances, it is necessary to have an explicit expression for Δ . Introducing the zero-temperature exponents $b \ln(\omega_0/\Delta)$ and $\Phi(0)$ for the electron and phonon polaron effects, respectively, and the argument of the fluctuational-barrier-preparation exponential $\chi(0)$ (for details, see Refs. 9, 10, 31, and 38) we arrive at the self-consistent equation for the tunneling amplitude:

$$\Delta = \Delta_0 \exp[-b \ln(\omega_0/\Delta) - \Phi(0) + \chi(0)]. \quad (8)$$

In the latter expression, we omitted the time dependence of the tunneling amplitude induced by the tip motion, for convenience, in order to concentrate on the temperature dependence of the factors on the right-hand side of Eq. (8).

It is easy to convince ourselves that in the case of tip-surface transfer of adatoms the first term in the square brackets on the right-hand side of Eq. (8) is small compared to unity, and may be neglected. Indeed, the adatom frequency is about $\omega_0 \sim 0.1$ eV, while the energy-level splitting is expected to be of the order of $\Delta \sim 10^{-4} - 10^{-6}$ eV for the separation distance between the two wells of the order of the average interatomic distance in a solid. [Note that in a typical AFM/STM configuration the distance between the tip and the surface is about $d \sim (3-5)$ Å, measured between the outmost atomic planes]. Bearing in mind that the adsorbate-surface spacing is $h \sim 1$ Å,³⁹ and that the transfer probability reaches a maximum value for the minimal separation distance between the centers of the potential wells, we find the separation distances of interest to be of the order of $R = d - 2h \sim a \sim (1-3)$ Å. Therefore, the first exponent $b \ln(\omega_0/\Delta) \sim 0.05 \ll 1$.

As follows from Appendix A, the phonon polaron factor $\Phi(0) \sim (\delta a/u_0)^2$, where δa is the typical shift of the surface-atom equilibrium position due to the presence of the adatom, and \mathbf{u}_0 is the zero-temperature vibration displacement of the host atoms. Particularly, for a H interstitial in the Nb lattice $\delta a \sim 0.18$ (Ref. 32) and $u_0 \sim 0.1$, and we find $\Phi(0) \sim 3.2$. This qualitative estimate is in perfect agreement with the result [$\Phi(0) = 3.3$] from the variational procedure calculations by Teichler.³² Surface layer relaxation in the vicinity of the occupied adsorption site is expected to be much less than that in the bulk of a bcc lattice, primarily because of larger distances between an adatom and host atoms. Indeed, according to Ref. 39 the change of the outermost lattice spacing in a surface layer for the case of H adsorbates on metals is less than 1% (~ 0.06 a.u.). As a result, the phonon polaron effect for adsorbate tunneling is quite small, $\Phi(0) \leq 0.3$. Turning now to the influence of the barrier fluctuations, we obtain $\chi(0) \sim (u_0/\lambda)^2$ (cf. Appendix A for details), where $\lambda \sim (2MD)^{-1/2}$, and D is the potential

well depth. The quantity λ , by its physical meaning, represents the absolute value of the imaginary de Broglie wave length of the adatom for the under barrier motion (or the effective penetration depth into the classically forbidden region) and decreases with the adatom mass. The exponent $\chi(0)$ allows a simple interpretation. The lattice vibrations create holes in the potential barrier of the order of the atomic displacement u_0 , through which an adsorbate may escape into a neighboring well. The smaller is the imaginary part of the de Broglie wavelength λ the easier it is for the adatom to slip out of the well. The estimate of the parameter $\chi(0)$ is again made for a separation distance of the order of $\sim a$, so that the assessment is valid for interstitial diffusion in the bulk as well. From these estimates it follows that the phonon polaron effect dominates at small host atom displacements when $u_0 < \sqrt{\delta a \lambda}$, whereas, in the opposite case of $u_0 > \sqrt{\delta a \lambda}$, the barrier fluctuations substantially increase the tunneling amplitude. Analysis shows that for adatoms at metal surfaces the inequality $\chi(0) > \Phi(0)$ usually holds true due to the small scale of the lattice deformation δa . Therefore, the coupling between the adatom motion and phonon excitations does not decrease the tunneling amplitude. This conclusion agrees well with the experimental observation of the anomalous diffusion of deuterium adatoms on the W(111) surface¹⁶ when the effect of the larger mass of deuterium as compared to hydrogen is almost completely compensated for by the increase of Δ owing to the barrier fluctuations. Since the parameter $\chi(0)$ increases proportionally to the host atom displacement squared, the effect of barrier fluctuations may be even more pronounced at high temperatures.⁴⁰ Concluding, we note that the time dependence of the potential barrier fluctuations may be ignored in virtue of host atoms' moving much more slowly than the adsorbate tunneling across the barrier. Indeed, the potential barrier fluctuations are significant in time τ_f determined by the inverse phonon frequencies, $\tau_f \sim 1/\omega_{\text{ph}}$, which is much larger than the typical time the adatom spends under the barrier, $\tau_b \sim 1/\omega_0$, so that $\tau_b \ll \tau_f$.

For the purpose of the present analysis it is sufficient to demonstrate that the condition $\Delta_0 \gg 2\pi bT$ may be easily fulfilled, so that the tunneling amplitude is large enough without taking into account the barrier fluctuation renormalization. Assuming that the adatom moves in a three-dimensional spherically symmetric potential well, one can find the energy-level splitting corresponding to the unperturbed potential directly from the Schrödinger equation by a method analogous to that of Ref. 41,

$$\Delta_0 = (\pi/M)R\phi^2(R/2)f^2(R/2), \quad (9)$$

where $\phi(r)$ is the unperturbed ground-level wave function, and the function f describes the effect of the potential barrier decrease along the line connecting the two wells. In the case of the Pöschl-Teller potential $U(r) = -D/\cosh^2(ar)$,⁴² which reproduces well the basic features of the three-dimensional oscillator, expression (9) reduces to

$$\Delta_0 = (4D/1\sqrt{\pi\beta})\cos^{-2\beta}(l/2)\sinh^2(l/2)\exp[\beta l(l)], \quad (10)$$

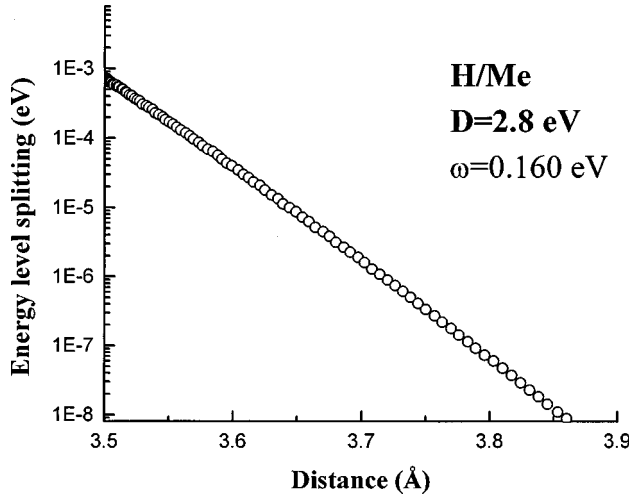


FIG. 2. The dependence of the tunneling amplitude on the tip-surface separation distance. Calculations are made for the Poschl-Teller potential for a hydrogen adatom. The potential well depth is $D=2.8$ eV, and the adsorbate frequency $\omega=0.160$ eV.

α and β being the parameters characterizing the potential-well width and depth, respectively,

$$\alpha = \omega_0 \sqrt{M/2D}, \quad \beta = -1/2 + [1/4 + (2D/\omega_0)^2]^{1/2}, \quad (11)$$

and $l = \alpha R$ being the dimensionless separation distance. In formula (10), $I(l)$ denotes the integral

$$I(l) = \int_0^{l/2} [\cosh^{-2}(l-r) - \cosh^{-2}l] \coth(r) dr. \quad (12)$$

As an illustration, in Fig. 2 the dependence of the energy-level splitting Δ_0 on the separation distance R , calculated by formula (10), is shown for input parameters $D=2.8$ eV and $\omega_0=0.160$ eV, which are typical for hydrogen adsorption at metal surfaces.^{43,44} It is seen that the tunneling amplitude varies from 0.72×10^{-3} to 0.21×10^{-8} eV for the distance between the tip and the surface adsorption site ranging from 3.5 to 3.9 Å. In particular, in the distance range from 3.5 to 3.6 Å the tunneling amplitude is larger than 0.4×10^{-4} eV, and condition (7) is well satisfied for temperatures $T < 2$ K.

To check the accuracy of formula (10), we calculated the tunneling amplitude of hydrogen interstitials trapped by oxygen in a Nb bcc lattice for $D=0.427$ eV, $\omega_0=0.158$ eV, and the separation distance between the two wells, $R=1.17$ Å.⁴⁵ The theoretically evaluated tunneling amplitude $\Delta_0=0.17$ meV is in good agreement with the experimental value $\Delta_0=0.17-0.21$ meV obtained from neutron scattering.^{12,14}

V. QUANTUM OSCILLATIONS OF TRANSFER PROBABILITY

Expression (6) was derived under the assumption that the transfer process is coherent, and that the adatom is initially located at the surface adsorption site. The coherent process is possible, however, only when condition (7) is fulfilled. It is clear that at large separation distances the tunneling amplitude may be small compared to the inverse electron-hole

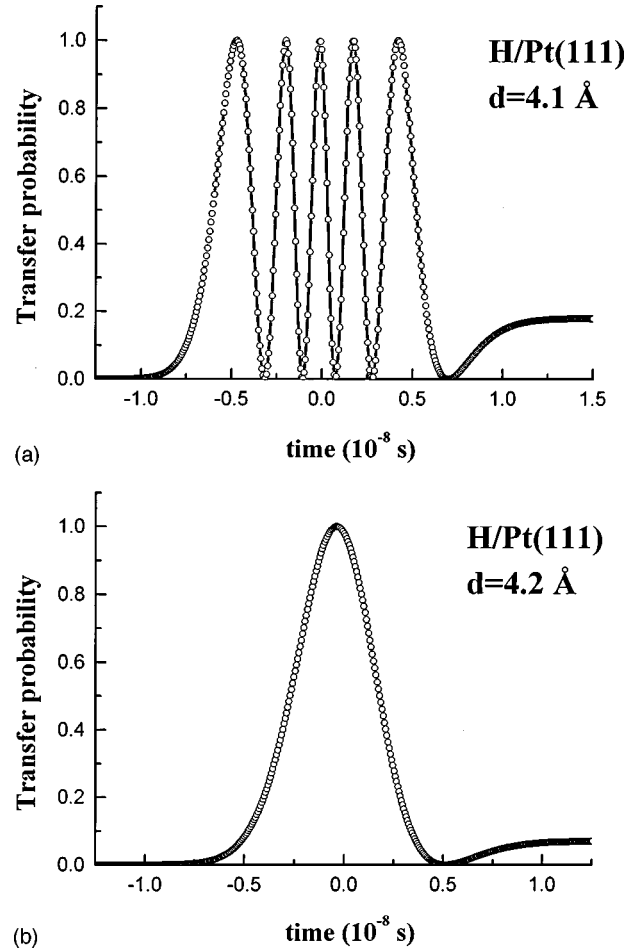


FIG. 3. (a) The oscillations of the transfer probability as a function of interaction time. Calculations are made for a hydrogen atom adsorbed at a Pt(111) surface. The potential well depth and the frequency are equal to 2.58 and 0.152 eV, respectively. The tip-surface separation distance is $d=4.1$ Å. (b) The same as in Fig. 2(a) except for the tip-surface distance $d=4.2$ Å.

relaxation time, and therefore incoherent transitions may take place before the adatom transfer becomes coherent. Hence, in order for formula (6) to be applicable, it is necessary that the probability to find the adatom at the tip by the time the tunneling amplitude reaches a value comparable with $2\pi bT$ be small compared to unity. In the case of the tip sliding parallel to the surface, this requirement imposes the following condition on the tip velocity:

$$v \gg 2\pi bT \sqrt{\lambda d / \ln(\Delta_0 / 2\pi bT)}. \quad (13)$$

Inequality (13) simply implies that the typical time during which the tunneling amplitude changes noticeably is small compared to the electron-hole relaxation time.

Figures 3(a) and 3(b) display the transfer probability of a hydrogen atom adsorbed initially on a Pt(111) surface to the Pt tip as a function of time, i.e., the probability of finding the adatom at the tip at time t . Calculations are made by formula (6) for the tip-surface separation distances $d=4.10$ (a) and 4.2 Å (b). The potential well depth and the vibrational frequency are set equal to 2.58 and 0.152 eV, respectively.⁴³ The adsorbate-surface spacing 1.19 Å is calculated from the H-Pt bond length 2.0 Å,⁴³ assuming the adatom to be located

in a threefold-coordinated center site (fcc or hcp). The tip velocity is set equal to $v = 1$ cm/s to satisfy inequality (13) for temperatures below 0.01 K. The maximum value of the tunneling amplitude is about 2×10^{-6} eV, and condition (7) is well fulfilled. Note that a coherent transition from one fcc (hcp) site to another equivalent site at the surface is highly improbable due to the large distance between the respective adsorption sites (2.77 \AA). The transition from fcc to hcp sites is characterized by the smaller jump distance (1.59 \AA) and larger tunneling amplitude. However, fcc and hcp adsorption sites are not equivalent with respect to the ground energy levels. The corresponding levels are expected to be separated by a gap of about 0.01 eV,³⁷ which drastically reduces the incoherent fcc-hcp transition probability at low temperatures (cf. Appendix B for details).

As is seen from Fig. 3(a), the probability to find the adatom at the tip increases rapidly with time, and then exhibits several oscillations between 0 and 1 before reaching the value 0.18 as the tip departs from the adsorption site. The period of oscillations is about 2.5 ns.

The dependence of the transfer probability on time changes substantially as the distance between the tip and the surface increases [cf. Fig. 3(b)]. For instance, it follows from Fig. 3(b) that, at $d = 4.2 \text{ \AA}$, the adatom first tunnels to the tip and then comes back to the surface. After that, with a probability of about 7%, the adatom tunnels to the tip again. Generally, as the quantity d augments, the tunneling amplitude decreases, and the number of oscillations drops quickly. Further increase in the distance of closest approach leads to an exponential decrease of the probability to find the adatom at the tip.

When satisfying criterion (9) we assumed the density of electrons at the Fermi level to be equal to the average density of conduction electrons. In a number of cases the density-of-states value at the Fermi level may be substantially lower than that for other energies in a conduction band, and this may also suppress the contribution of the electron-hole excitations to destruction of coherence.

It should be stressed that, in the case of semiconductors and insulators, the temperature range where the quantum coherence in tip-surface adatom transfer may be observed is much wider due to a low density of conduction electrons and consequently larger electron-hole relaxation times. For example, the number of low-energy electron-hole excitations in normal uniform semiconductors is of the order of the density of free carriers in the conduction band, i.e., about $n \sim n_0 \exp(-\Delta\varepsilon/T)$, $\Delta\varepsilon$ being the energy gap between the conduction and valence bands. The quantity n_0 is three orders of magnitude smaller than the bulk density of quasifree electrons in metals, even at room temperature. In addition, the energy gap $\Delta\varepsilon$ is about 1 eV for typical semiconductors such as Si or Ge and, therefore, the density of electron-hole excitations n is at least four or five orders of magnitude smaller than that in a metal. Since the parameter b is proportional to n^2 , it is clear that conditions (7) and (13) are fulfilled practically at all temperatures below 10 K for relevant tip velocities and tunneling amplitudes. As an example, in Figs. 4(a) and 4(b) the dependence of the transfer probability on time is shown for H adsorbed on a diamond (001) surface. The potential well depth ($D = 4.05$ eV) is calculated from the experimental value of the vibrational frequency (ω_0

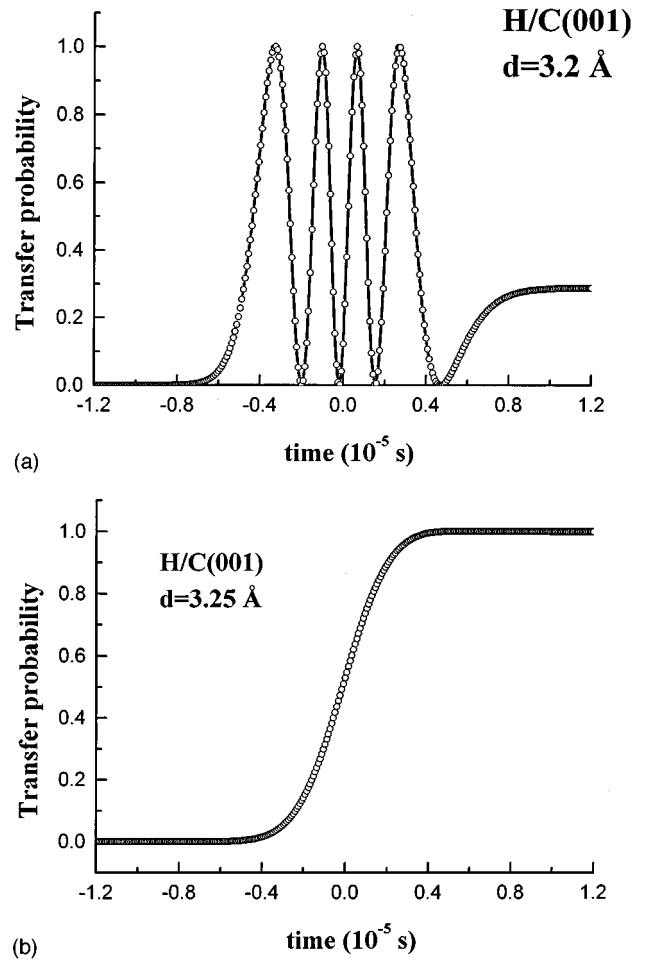


FIG. 4. (a) The oscillations of the transfer probability as a function of interaction time. Calculations are made for a hydrogen atom adsorbed on a C(001) (diamond) surface. The potential well depth and the frequency are equal to 4.05 and 0.363 eV, respectively. The tip-surface separation distance is $d = 3.2 \text{ \AA}$. (b) The same as in Fig. 3(a), except for the tip-surface distance $d = 3.25 \text{ \AA}$.

$= 0.363$ eV) (Ref. 46) and the binding energy of hydrogen chemisorbed on the C surface (3.87 eV).⁴⁷ The H-C bond length is 1.09 \AA and the adatom surface spacing $h = 1.02 \text{ \AA}$.⁴⁶ The tip velocity is set equal to $v = 10^{-3}$ cm/s. Except for the time scale determined by the choice of the tip velocity, the character of the dependence $P(t)$ is the same as in Figs. 2(a) and 2(b). The transfer probability oscillates at smaller separation distances and varies more smoothly as the quantity d increases.

The tip velocity and the its height above the surface may, in principle, be adjusted in such a way (for given parameters characterizing the double well) that the probability for the adatom to be transferred to the tip reaches unity by the time the tunneling amplitude starts to decrease rapidly. In the latter case the argument of the sine in Eq. (3) no longer changes noticeably, and the quantity $P(t)$ remains almost constant in the course of time. In other words, the tip may pick up the adatom with the probability 100%, and carry it away from the initial adsorption site. This situation is illustrated in Fig. 4(b). Such an experiment would require prior knowledge of parameters involved or proper calibration of the transfer probability.

The transition rate (the number of atoms transferred per unit time) may be defined as the absolute value of the time derivative of the transfer probability. The transition rate is very sensitive to the distance of closest approach d . Thus, for the H/C(001) system, it varies from 10^3 to 10^9 atom/s as the distance d decreases from 3.5 to 3.2 Å. Those values are comparable, and sometimes larger than those for thermally activated diffusion of hydrogen in metals.⁴⁸

Finally, we would like to discuss the important issue of the alignment of the energy levels in the wells. In the general case of a moving tip and nonsymmetrical wells, the levels are shifted with respect to each other by the time-dependent quantity $\xi = \xi(t)$ due to distance-dependent interaction. As the tip approaches the adsorption site the levels may intersect, so that at a certain time $\xi = \xi(t_0) = 0$, and Landau-Zener type transitions⁴⁹ become possible. In order for multiple coherent tunneling events to take place, the gap between the two levels during the dwell time of the particle in a well should be small compared to the tunneling amplitude, so that $\delta\xi = (\partial\xi(t_0)/\partial t)t_d \ll \Delta$. The latter condition can be rewritten in a more convenient form as

$$\Delta^2 \gg v \partial\xi/\partial a. \quad (14)$$

The gradient $\partial\xi/\partial a$ does not exceed 0.1 eV/Å. Substituting the tip velocity value $10^4 - 10^6$ Å/s into inequality (14), we find $\Delta > 10^{-7} - 10^{-5}$ eV, which falls into the typical range of tunneling amplitudes.

The alignment of two arbitrary levels in the wells may also be achieved by sweeping the bias voltage between the tip and the surface. It can be readily shown that the electric field E , if weak enough not to disturb the potential-well shape and distribution of conduction electrons, may be, nevertheless, quite sufficient to bring ξ to zero without destroying coherence. The important aspect here is an additional energy gain of the adatom in the external field. This energy gain should be small compared to the splitting of the ground level to ensure resonant tunneling. To estimate the value of the voltage bias, we note that the energy gain of the adsorbate in one of the wells due to the presence of the electric field E is about $pE - \mu E^2$, p and μ being the induced dipole moment and polarizability of the adatom, respectively. This quantity has to be small compared to the coherent bandwidth, so that $\Delta \gg \mu E^2$. For a hydrogen atom, $\mu \sim 1$, and the electric field is supposed to be in the range of $E \sim 10^{-3} - 10^{-4}$ a.u. for the tunneling amplitude of about $\Delta \sim 10^{-5} - 10^{-7}$ ($3 \times 10^{-6} - 3 \times 10^{-4}$ eV), which corresponds to a bias voltage of about 0.03–0.3 eV or to the so-called low voltage limiting case in STM.

VI. CONCLUSIONS

By theory and calculation we predict the following phenomenon, which should be observable at low enough temperatures.

(1) The coherent transfer of adatoms between a surface and an AFM/STM tip can be observed below 10 K for semiconductors and insulators, and below 0.1 K, in the case of metals. The tip velocity, however, should be high enough to prevent incoherent tunneling of the adsorbate to the tip before coherent oscillations occur.

(2) The transfer probability oscillates in time when the

dwell time of the adatom in one of the wells is small compared not only to electron-hole and phonon relaxation times, but also to the typical tip-adsorbate interaction time.

(3) The tunneling amplitude can be controlled by varying the tip-surface separation distance, and may be made large compared to inverse electron-hole and phonon relaxation times.

(4) The influence of the electron and phonon polaron effects is substantially compensated for by potential barrier fluctuations, and may have little significance for coherent tunneling at low temperatures.

(5) The phenomenon of quantum coherence offers, in principle, an opportunity to manipulate atoms on a surface without external electric field. However, experimental implementation of such a manipulation may prove to be difficult owing to the tunneling amplitude being extremely sensitive to variation of physical parameters. On the other hand, the strong dependence of the oscillation period on the separation distance may be used for precise determination of the tip height above the adsorption site.

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APPENDIX A: ESTIMATES OF THE PHONON POLARON AND POTENTIAL BARRIER FLUCTUATION FACTORS

The estimate of the phonon polaron factor can be obtained from the general formula for the quantity $\Phi(T)$ as a function of temperature. Making use of the explicit expression for the phonon polaron factor, known from the small polaron theory,^{50,51} we have

$$\Phi(T) = \sum_{\mathbf{k}, \alpha} |W_{\mathbf{k}\alpha}|^2 [1 - \cos(\mathbf{k} \cdot \mathbf{g})] (1 + 2n_{\mathbf{k}\alpha}), \quad (A1)$$

where

$$W_{\mathbf{k}\alpha} = (2M_h \omega_{\mathbf{k}\alpha}^3 N)^{-1/2} \sum_j \left(\frac{\partial U(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_j} \right)_{\mathbf{R}^0} \mathbf{e}_{\mathbf{k}\alpha} \times [\exp(i\mathbf{k} \cdot \mathbf{R}_j) - 1], \quad (A2)$$

and $n_{\mathbf{k}\alpha}$ is the average number of phonons with the wave vector \mathbf{k} and polarization α . In Eq. (A2), N is the number of normal modes; $\mathbf{e}_{\mathbf{k}\alpha}$ is the polarization vector, and $U(\mathbf{r}, \mathbf{R})$ is the potential field in which the adsorbate moves, so that \mathbf{R} denotes the equilibrium positions of host atoms in the presence of the adsorbate. The radius vector \mathbf{R}^0 represents the equilibrium positions of lattice atoms without the adsorbate. It is implied that the quantities $\Phi(T)$ and $W_{\mathbf{k}\alpha}$ depend on the adatom quantum number s , and the first derivative of the potential energy is averaged over the s state. The respective subscripts are omitted for convenience.

Expanding the potential energy of interaction in Eq. (A2) into a Taylor series on the displacement of the equilibrium positions $\mathbf{R}_j - \mathbf{R}_j^0$, and confining ourselves to the first three terms, we transform Eq. (A1) to the expression

$$\Phi(T) = (M_h/4N) \sum_{\mathbf{k}, \alpha} (\delta a_{\mathbf{k}\alpha})^2 \omega_{\mathbf{k}\bar{\omega}} \coth(\omega_{\mathbf{k}\alpha}/2T). \quad (\text{A3})$$

Here the parameters $\delta a_{\mathbf{k}\alpha}$ are proportional to the equilibrium position displacements and describe the lattice deformation in the presence of the adsorbate. When deriving formula (A3), we used the explicit expression for the phonon distribution $n_{\mathbf{k}\alpha}$. Noticing further that the typical displacement of a host atom is about $u_0 \sim (M_h \omega_{\mathbf{k}\alpha})^{-1/2}$, from expression (A3) we obtain the estimate of the zero-temperature phonon polaron factor $\Phi(0) \sim (\delta a/u_0)^2$, δa being the typical deformation of the lattice.

Turning now to the potential barrier fluctuation factor, we note that in the zeroth approximation of host atom vibrations the bare tunneling amplitude is given by the expression $\Delta_0 = \Omega \exp(-B)$, where $\Omega \sim \omega_0$, and the quantity $B \sim R/\lambda \gg 1$ represents the exponent depending on the potential shape [cf. Eqs. (10) and (11)]. The potential field in which the adsorbate moves, however, is determined by the instantaneous positions of host atoms. Therefore, generally, the exponent B may be expanded into a power series of atomic displacements. The terms of this series diminish rapidly with their number, as this expansion in fact reduces to a series over the ratio of the average thermal atomic displacement u to the interatomic distance a , $u/a \ll 1$. Owing to the large value of the distance $R \gg \lambda$ the quantity $(Ru/\lambda a)$ may be comparable to and even larger than unity. As a result, the first nonvanishing term proportional to u/a in the aforesaid expansion may noticeably influence the tunneling amplitude. This correction is a hard core of the potential barrier fluctuation effect. As shown below, accounting for the potential barrier fluctuations always increases the tunneling probability.

Following Ref. 31, we introduce the real normal modes $q_{\mathbf{k}\alpha} = q_{\mathbf{k}\alpha}^0 + u_{\mathbf{k}\alpha}$ with the displacement coordinates $u_{\mathbf{k}\alpha}$ measured from the proper polaron displacement

$$q_{\mathbf{k}\alpha}^0 = \frac{1}{2} (q_{\mathbf{k}\alpha}^{(l)} + q_{\mathbf{k}\alpha}^{(l+g)}). \quad (\text{A4})$$

The quantity $q_{\mathbf{k}\alpha}^{(l)}$ represents the displacement of the normal modes due to the adatom position at the l th adsorption site. The exponent B can be written as function of the atomic displacement up to the first order term with respect to $u_{\mathbf{k}\alpha}$,

$$B(u) = B(0) + \sum_{\mathbf{k}\alpha} b_{\mathbf{k}\alpha} u_{\mathbf{k}\alpha}. \quad (\text{A5})$$

To find the potential barrier fluctuation factor, one has to average the function $\exp[-B(u) + B(0)]$ thermodynamically, with the exponent $B(u)$ defined by Eq. (A5), and take the logarithm of the resulting expression. Assuming a Gaussian distribution over atomic displacement, we obtain

$$\chi(T) = \ln \prod_{\mathbf{k}\alpha} (\xi_{\mathbf{k}\alpha}/2\pi)^{1/2} \int du_{\mathbf{k}\alpha} \exp \left[-\frac{1}{2} \sum_{\mathbf{k}\alpha} (\xi_{\mathbf{k}\alpha} u_{\mathbf{k}\alpha}^2 + 2b_{\mathbf{k}\alpha} u_{\mathbf{k}\alpha}) \right], \quad (\text{A6})$$

where $\xi_{\mathbf{k}\alpha} = 2M_h \omega_{\mathbf{k}\alpha} \tanh(\omega_{\mathbf{k}\alpha}/2T)$. Calculation of the right-hand side of Eq. (A6) is straightforward, and we arrive at the formula

$$\chi(T) = \frac{1}{2} \sum_{\mathbf{k}\alpha} (b_{\mathbf{k}\alpha}^2 / \xi_{\mathbf{k}\alpha}), \quad (\text{A7})$$

which can be also obtained from the general procedure of evaluation of the tunneling amplitude Δ .³¹ Since the coefficient $\xi_{\mathbf{k}\alpha}$ is proportional to the inverse average atomic displacement squared, while the quantity $b_{\mathbf{k}\alpha} \sim 1/\lambda$, we find that in the limiting case of small temperatures $\chi(0) \sim (u_0/\lambda)^2$.

APPENDIX B: INCOHERENT TUNNELING RATE

The coherent transfer of adatoms from the surface to the tip may take place against the background of concurrent processes of incoherent diffusion between adjacent adsorption sites at the surface (tip). The major reason is that the distance separating two nearest nonequivalent adsorption sites is usually smaller than the tip-surface separation. However, those adsorption sites differ [sometimes only slightly, as in the case of fcc and hcp sites on a fcc(111) surface] in the potential shape, and this results in an energy gap ε between two levels of possible adsorbate positions in the respective potential wells. In order to analyze the influence of incoherent jumps on adsorbate mobility, we start with the expression for the transition rate w_{in} derived in perturbation theory¹⁰

$$w_{in} = 2\pi \gamma_0^2 \sum_{N,L} \rho_L | \langle N | \hat{\Lambda} | L \rangle |^2 \delta(E_L - E_N + \varepsilon), \quad (\text{B1})$$

where γ_0 is the overlap integral between the adatom wave functions pertaining to the two nonequivalent adsorption sites, ρ_L is the density matrix, and the operator $\hat{\Lambda}$ accounts for the polaron as well as potential fluctuation effects. The expression in the right-hand side of Eq. (B1) is obtained by the common procedure of averaging with respect to the initial states of the system L and performing a summation over the final states N .

The probability w_{in} can be presented in the following form:

$$w_{in} = \gamma_0^2 \exp[+2\chi(T)] \int_{-\infty}^{+\infty} dt \exp(i\varepsilon t) \times Sp \{ \hat{\rho}_0 \hat{\Lambda}_e^+(t) \hat{\Lambda}_{ph}^+(t) \hat{\Lambda}_e(0) \hat{\Lambda}_{ph}(0) \}, \quad (\text{B2})$$

where $\chi(T)$ is the usual barrier fluctuation exponent,³¹ $\hat{\rho}_0$ is the equilibrium density matrix, and $\hat{\Lambda}_e$ and $\hat{\Lambda}_{ph}$ are the electron and phonon polaron operators, respectively. For further analysis, it is advisable to introduce the renormalized tunneling energy width

$$\gamma = \gamma_0 \exp\{-b \ln(\omega_0/\eta T) - \Phi(T) + \chi(T)\}. \quad (\text{B3})$$

In formula (B3) the coefficient $\eta \sim 1$, the function $\Phi(T)$ describes the phonon polaron effect, and the parameter b reads³⁸

$$b = \rho^2(\varepsilon_F) \langle V_{qq'} \rangle^2 \quad (\text{B4})$$

$\rho(\varepsilon_F)$ and $\langle V_{qq'} \rangle$ being the electron density of states at the Fermi level and the Fourier transform of the Hamiltonian

responsible for interaction of the adatom with electron-hole excitations, averaged over the Fermi surface, respectively. To calculate integral (B2), we apply a procedure similar to that developed in Refs. 10 and 38, and transform expression (B2) to

$$w_{\text{in}} = 2\pi^{1/2}\gamma^2 \times \frac{\Xi \exp(\varepsilon/2T)}{\Xi^2 + \varepsilon^2} \cdot \frac{|\Gamma(1 + (\Xi + i\varepsilon)/2\pi T)|^2}{\Gamma(1 + \Xi/2\pi T)\Gamma(1/2 + \Xi/2\pi T)}, \quad (\text{B5})$$

where Ξ represents the total inverse relaxation time due to coupling with phonons and electron-hole excitations, and is given by the sum of inverse electron-hole (Ξ_e) and phonon (Ξ_{ph}) relaxation times,

$$\Xi = \Xi_e + \Xi_{\text{ph}}, \quad (\text{B6})$$

with the latter quantities defined by

$$\Xi_e = 2\pi b T, \quad (\text{B7})$$

$$\Xi_{\text{ph}} = \pi T \sum_{\mathbf{k}\alpha, \mathbf{k}'\beta} |C_{\mathbf{k}\alpha, \mathbf{k}'\beta}|^2 \frac{n_{\mathbf{k}\alpha} - n_{\mathbf{k}'\beta}}{\omega_{\mathbf{k}\alpha} - \omega_{\mathbf{k}'\beta}} \delta(\omega_{\mathbf{k}\alpha} - \omega_{\mathbf{k}'\beta}). \quad (\text{B8})$$

In formula (B8), $C_{\mathbf{k}\alpha, \mathbf{k}'\beta}$ is the expansion coefficient in the two-phonon term of the Hamiltonian,³⁸ and $n_{\mathbf{k}\alpha}$ is the aver-

age number of phonons with the frequency $\omega_{\mathbf{k}\alpha}$.

Confining ourselves to the limiting case of low temperatures ($T \ll \Theta$), we find from expression (B5) that under the conditions $\varepsilon \gg 2\pi T \gg \Xi$ the incoherent transition rate reduces to (cf. Ref. 52)

$$w_{\text{in}} = 2\gamma^2 \Xi / \varepsilon T, \quad (\text{B9})$$

In the case of metals the inverse relaxation time is determined by electron-hole excitations, $\Xi \sim \Xi_e$, and formula (B9) can be simplified,

$$w_{\text{in}} = 4\pi b \gamma^2 / \varepsilon. \quad (\text{B10})$$

Assuming that the ratio of the tunneling width to the level shift is small, $\gamma/\varepsilon \ll 1$, and taking into account that the product $4\pi b < 1$, we come to the conclusion that the transition rate is always much smaller than the tunneling width, $w_{\text{in}} \ll \gamma$. Since the coherent transition rate is about $w_{\text{coh}} = |\partial P / \partial t| \sim \Delta$, we find that under the comparable tunneling widths ($\Delta \sim \gamma$) coherent transitions dominate the tunneling process, $w_{\text{coh}} \gg w_{\text{in}}$. This estimate holds true for insulators and semiconductors as, at low temperatures, the inverse relaxation time Ξ_{ph} associated with phonon excitations diminishes much more rapidly with temperature than the quantity Ξ_e .³⁸

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