Atom oscillations in the scanning tunneling microscope

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The atom tunneling across the potential barrier separating the surface and the tip of the scanning tunneling microscope is investigated by semiclassical methods, and by integrating numerically the time-dependent Schrödinger equation. It is shown that the barrier crossing is explained by the resonance phenomenon of quantum coherence oscillations, rather than by exponential decay. The occurrence of these resonances at the variation of the bias voltage is studied for the first two isomeric states of a Xe atom in a surface-tip potential of double-well shape. The resonant bias voltages for these two states practically coincide, and at the first common resonance the effect of the environmental temperature is discussed. The results provide a useful frame for understanding the mechanism of atom transfer in scanning tunneling microscopy.
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I. INTRODUCTION

The reversible atom transfer in the tunnel junction of the scanning tunneling microscope (STM) becomes increasingly important for molecular-level manipulations, surface quantum-chemical reactions, or microelectronic devices. This process is observed at application of a voltage pulse[1] between the conducting surface and tip of the STM, and has a rate which increases as a power of the current. The present models assume that atoms are trapped in the STM junction by a surface-tip potential of double-well shape,[2] though the switching mechanism between the two wells is not yet known. In general, one assumes that transfer appears by heating-assisted electromigration,[1,3] or the combined effect of thermal activation at the ambient temperature and excitation by the inelastic scattering of the tunneling electrons.[2] However, these models give only partial explanation of the experimental results.

A model based on atom tunneling through the potential barrier was proposed in Ref. 4. Before tunneling the atom is supposed to be in a statistical mixture of isomeric states localized on the surface, and the transfer rate is defined by the thermal average of the corresponding WKB rates.

The isomeric states decay exponentially in open space, but in a double-well potential (DWP) they have an oscillatory behavior.[5] For an arbitrary DWP, a metastable state never tunnels completely, and in practice the irreversible transfer across the barrier can be explained only by the existence of some external decoherence mechanism. However, in special resonance conditions it is possible to observe quantum coherence oscillations (QCO's) when the wave packet is localized alternatively in each of the two wells.[5] If the decoherence factors could be reduced, then such oscillations might also be observed in the STM potential.[6]

The aim of this paper is to determine the characteristic time scale of atom tunneling in STM starting from the exact treatment of the quantum dynamics in DWP. Therefore, the tunneling of the first two isomeric states of a Xe atom localized initially on the surface is investigated by numerically solving the time-dependent Schrödinger equation (TDSE). Resonant bias voltages and QCO periods are obtained, and compared with semiclassical estimates. The effect of the thermal noise is included by calculating the tunneling probability for a statistical mixing between these two states.

In Sec. II we present time scales relevant to the occurrence of QCO or exponential decay. Section III contains numerical results obtained by semiclassical calculations and by solving the TDSE for a Xe atom in the pair plus dipole double-well potential of the STM junction. Conclusions are summarized in Sec. IV.

II. CHARACTERISTIC TIME SCALES OF THE TUNNELING PROCESS

The tunneling represents a special case of decay, when the quantum system undergoes a transition between two different classical regions, separated by a potential barrier. If the regions are isolated by an infinite barrier, then each is characterized by its own set of eigenstates. When the barrier is finite, these eigenstates become nonstationary wave packets. For a one-dimensional potential with a single metastable minimum the tunneling of an isomeric state ψ is irreversible, and its escape probability ρ increases in time according to an exponential law

$$\rho(t)=1-e^{-\lambda t} \tag{1}$$

where λ can be estimated using the Gamow formula

$$\lambda=\frac{\omega_i}{2\pi}e^{-2\int_{xi}^{xo}\sqrt{2M(V(x)-E_r)/\hbar^2}dx}. \tag{2}$$

Here $\omega_i/2\pi$ is the oscillation frequency in the isomeric well, and xi and xo are the turning points at the barrier.

If the stable well is bounded, then in general ψ remains confined to the isomeric well, without tunneling. An exception is the case of the QCO resonance, appearing when ψ is a linear combination of two quasidegenerate eigenstates having energies separated by a gap $\Delta E_{\rm res}$, very small in comparison with the average level spacing in the stable well, $\hbar\omega_f$. In this case

$$\rho(t)=(1-\cos(\pi t/T_{\max}))/2, \tag{3}$$

oscillating between 0 and 1 with the half-period

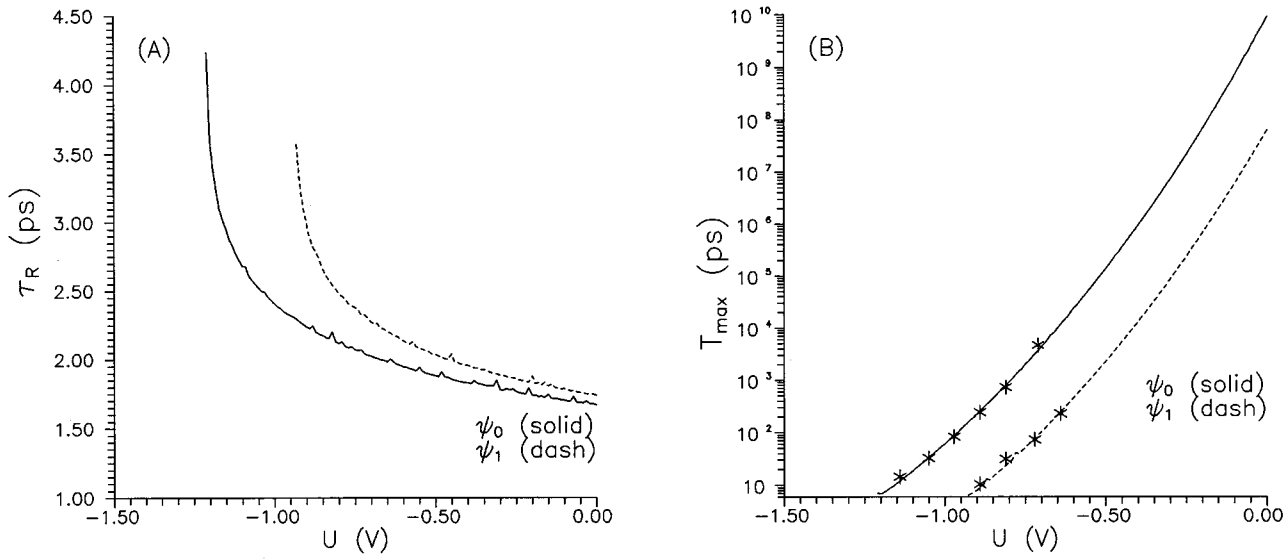

FIG. 1. Time scales for atom tunneling. Semiclassical estimates of τ_R (A) and $T_{\max}$ (B), as functions of the bias voltage.

$$T_{\max}=\frac{\hbar\pi}{\Delta E_{\rm res}}. \tag{4}$$

In the WKB approximation, $\Delta E_{\rm res}\approx 2V_{fi}$, with

$$V_{fi}=\frac{\hbar}{2\pi}\sqrt{\omega_i\omega_f}e^{-\int_{xi}^{xo}\sqrt{2M(V(x)-E_r)/\hbar^2}dx} \tag{5}$$

denoting the tunneling matrix element.[7]

The average level spacing is related to the recurrence time

$$\tau_R(E)=\frac{2\pi}{\omega_f(E)}, \tag{6}$$

which is the period of the closed orbit with the energy E in the stable well. In other words, this is the total time required for a particle to travel from the barrier to the outer wall of the stable well, to be reflected, and to come back to the barrier. As was shown in Ref. 8, during this time interval the decay follows the exponential law of Eq. (1).

The time scale of the tunneling phenomena discussed here is given by $T_{\max}$, τ_R, and λ^{-1}. These time intervals are not independent, but related by the equation

$$\lambda=\left(\frac{\pi}{2}\right)^2\frac{\tau_R}{T_{\max}^2}. \tag{7}$$

The pure QCO described by Eq. (3) appears when the density of states in the stable well is very low, and $\tau_R\to 0$. In this limit, the time evolution at resonance is periodic, but slow, with a period $(2T_{\max})$, much greater than the ''classical'' expected value τ_R. The exponential decay of the isomeric state occurs when $\tau_R>\lambda^{-1}$ (the irreversibility condition), because in this case τ_R is long enough to allow a complete tunneling.

III. RESONANT ATOM TRANSFER IN THE STM POTENTIAL

The present numerical estimates concern the tunneling of a Xe atom in the biased STM double-well potential of Ref. 2. For a fixed surface-tip geometry and zero bias, this potential may be approximated by the fourth-order polynomial

$$V_p(x)=C_0+C_1x+C_2x^2+C_3x^3+C_4x^4. \tag{8}$$

The coefficients have been obtained by interpolation, such that $C_0=0.45$ meV, $C_1=0.77$ meV/Å, $C_2=-55.64$ meV/Å^2, $C_3=-11.59$ meV/Å^3, and $C_4=44.51$ meV/Å^4. For a bias voltage U applied on the surface, the potential becomes $V(x)=V_p(x)+V_d(x)$, with

$$V_d(x)=-U\frac{\mu_0}{2w}\left\{\frac{1}{0.3+0.7(w+x)^4/L^4}-\frac{1}{0.3+0.7(w-x)^4/L^4}\right\} \tag{9}$$

denoting the dipole term. Here $\mu_0=0.3D$ ($1D=3.335\times 10^{-30}$ C m), $w=2.2$ Å, and $L=1.56$ Å.

The characteristic times $T_{\max}$ and τ_R calculated using Eqs. (4) and (6) are represented as a function of U in Fig. 1. The values obtained for τ_R [Fig. 1(A)] indicate that, independently of bias, the stage of exponential decay, if it appears, cannot exceed a few picoseconds. This is too small to ensure a significant transfer probability, though during this time it is possible to define the average transfer rate proposed in Ref. 4,

$$\lambda=\frac{\sum_i e^{-E_i/k_BT}\lambda_i}{\sum_i e^{-E_i/k_BT}}, \tag{10}$$

where T is the temperature, E_i are the energies of the isomeric levels, and λ_i the corresponding escape rates given by Eq. (2).

The semiclassical estimates obtained for $T_{\max}$ using Eq. (4) have values depending continuously on U in a wide interval, ranging over ten orders of magnitude, from milliseconds to picoseconds, as it is shown in Fig. 1(B). However,

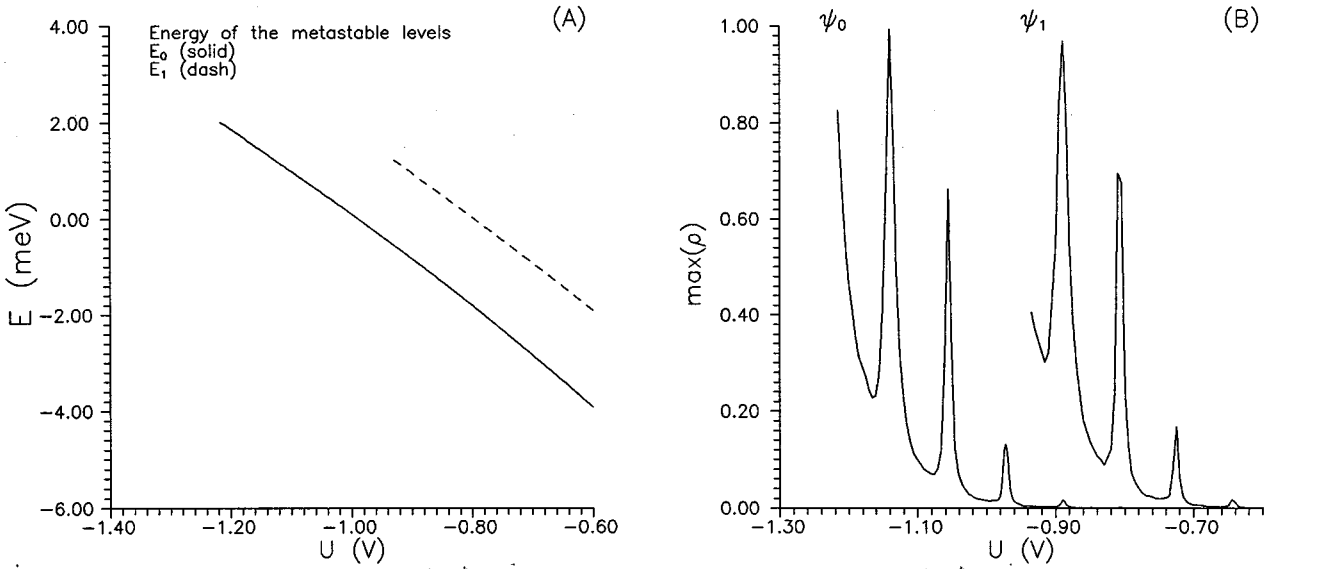

FIG. 2. Resonances in atom tunneling. The energies (A) and the maximum attained by ρ within 20 ps (B) for the first two isomeric states as a function of the bias voltage.

these estimates do not give the position of the resonances, and more precise calculations are necessary.

The isomeric levels are related to the eigenstates of the Xe atom in the modified potential

$$V_{\mathrm{mod}}(x)=\begin{cases} V(x) & \text{if } x\leqslant x_b \\ V(x_b)+\alpha(x-x_b)^2/2 & \text{if } x>x_b\,, \end{cases}$$

which is obtained by replacing the stable well of $V(x)$ by a quadratic term rising up from the top of the barrier located at x_b. The eigenstates ψ_i of this potential have been calculated by the Runge-Kutta integration of the stationary Schrödinger equation

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2}+V_{\mathrm{mod}}(x)\right]\psi_i(x)=E_i\psi_i(x). \tag{11}$$

Here M is the Xe mass, and V_{mod} was defined by choosing $\alpha=100$. The variation of the first two eigenvalues E_0 and E_1 when U decreases from 0 until the barrier disappearance (≈ -1.2 V), is presented in Fig. 2(A). This shows that the energy slopes $\sigma_k=|dE_k/dU|$, $k=0$ and 1, are $\sim$12 meV/V for both states, and the energy gap $\Delta E=E_1-E_0$ is $\sim$1.8 meV, independently of U. Therefore, if the atom is thermally equilibrated with the environment when $U=0$, then it will remain in this state during the voltage pulse of -0.8 V applied for switching. At the STM operation temperature of 4 K, the equilibrium occupation numbers of the first two states have the ratio $n_1/n_0=\exp(-\Delta E/k_BT)\sim 0.005$, and thus the contribution of ψ_1 to the atom transfer is small. However, n_1/n_0 may increase above this value due to the excitation produced by the inelastic scattering of the tunneling electrons, and a junction current of 200 nA can produce a ratio $n_1/n_0\sim 0.015$.[2]

The values of U corresponding to QCO's have been determined by investigating the time evolution of the metastable wave packets ψ_0 and ψ_1 obtained from Eq. (11). The time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi(x,t)}{\partial t}=\left[-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x^2}+V_p(x)+V_d(x)\right]\psi(x,t) \tag{12}$$

was solved with the initial condition $\psi(x,0)=\psi_i(x)$, $i=0$ and 1, by the iterated leap-frog method[9] using the time step $dt=6.58\times 10^{-5}$ ps and the spatial grid $[x_{\min},x_{\max}]=[-1.2\ \text{Å},2\ \text{Å}]$ divided by 320 points. At each time step we calculated the probability ρ of finding the atom localized in the stable well, close to the tip

$$\rho(t)=\int_{x_b}^{x_{\max}}dx\ \psi^*(x,t)\psi(x,t). \tag{13}$$

The maximum ρ_m attained by $\rho(t)$ within the time interval $[0,t_m]$, for $t_m=20$ ps, is represented as a function of the bias voltage in Fig. 2(B). The peaks indicate the resonances, and for ψ_0 the first appears at $U=-1.141$ V, the same as it was obtained before[6] using initial wave packets of Gaussian shape. This resonance has $T_{\max}=14.37$ ps, and the peak value is 1. For the other resonances the peak values ρ_m are lower, indicating that $T_{\max}$ is larger than t_m. $T_{\max}$ can be estimated in this case using Eq. (3), and is given by

$$T_{\max}=t_m\frac{\pi}{2\arcsin(\sqrt{\rho_m})}. \tag{14}$$

These values are represented in Fig. 1(B) by star symbols, and a comparison with the semiclassical estimates shows a very good agreement.

It is interesting to note that the resonances of ψ_0 and ψ_1 appear at almost the same bias voltages, separated by equal intervals of $\sim$80 mV. The first common resonance appears at $U\sim -0.89$ V, and in this case the initial wave packets and the potential function are shown in Figs. 3(A) and 4(A). The corresponding dynamics of the localization probability on the tip at the resonance and near resonance is represented in Figs. 3(B) and 4(B), respectively.

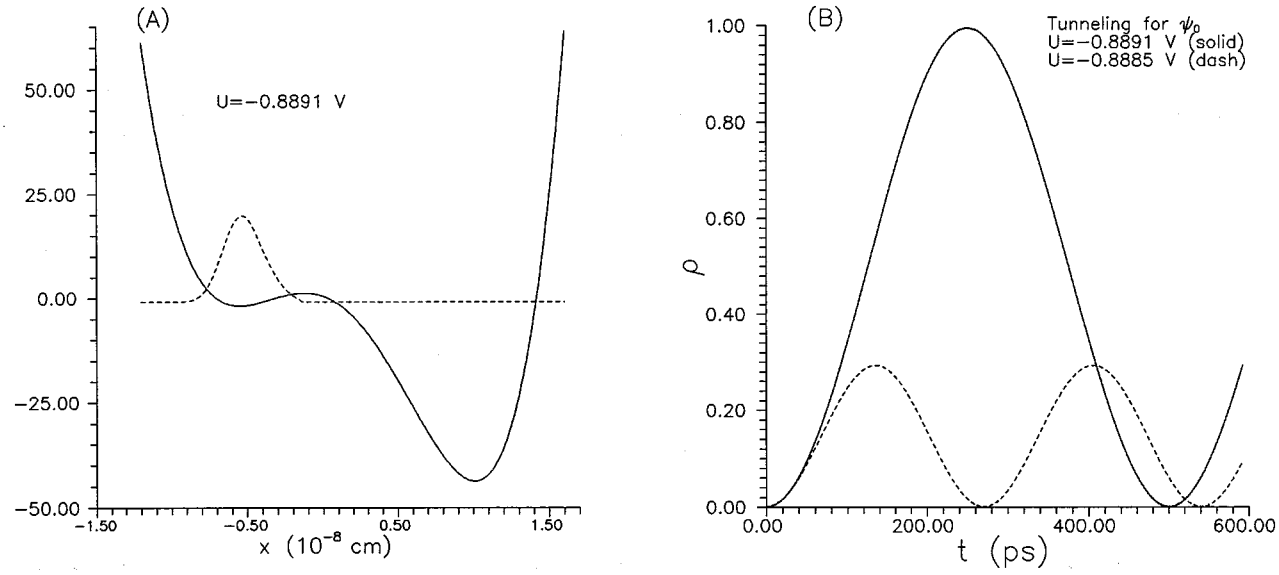

FIG. 3. The resonance of ψ_0 at $U=-0.8891$ V. The potential $V(x)$ in meV (solid) and the initial wave function multiplied by 10 (dash) (A), and ρ as a function of time at resonance (solid) and near resonance (dash) (B).

If the atom adsorbed on the surface is thermally equilibrated, and only the first two isomeric levels are considered, then the localization probability on the tip can be expressed by the average

$$\rho_{\mathrm{mix}}(t)=\frac{\sum_{i=0,1} e^{-E_i/k_BT}\rho_i(t)}{\sum_{i=0,1} e^{-E_i/k_BT}}, \tag{15}$$

where $\rho_i(t)$ is given by Eq. (13) with $\psi\equiv\psi_i$, $i=0$ and 1. The calculations at $T=4$ K indicate that at the first common resonance ρ_{mix} closely follows the behavior of ρ_0, excepting the small times, when ρ_{mix} is slightly above ρ_0 (Fig. 5).

During a voltage pulse of -0.8 V the isomeric ground state of the Xe atom encounters about 10 resonances. Each resonance extends over an energy interval $\sim\Delta E_{\mathrm{res}}=\hbar\pi/T_{\mathrm{max}}$, which corresponds to an interval of the bias voltage of $\Delta U_{\mathrm{res}}=\Delta E_{\mathrm{res}}/\sigma_0$. Thus for a linear pulse with a constant slope $\mu\equiv|dU/dt|$ the isomeric state ψ_0 remains in the resonance region during a time

$$T_c=\frac{\Delta U_{\mathrm{res}}}{\mu}=\frac{\hbar\pi}{\mu\sigma_0 T_{\mathrm{max}}}. \tag{16}$$

For a linear pulse decreasing from 0 to -0.8 V in 64 ms, the crossing time T_c becomes comparable to $T_{\mathrm{max}}/2$ when $U\sim-0.49$ V. The resonances crossed while $U>-0.49$ V have $T_c\ll T_{\mathrm{max}}$ and therefore the tunneling probability re-

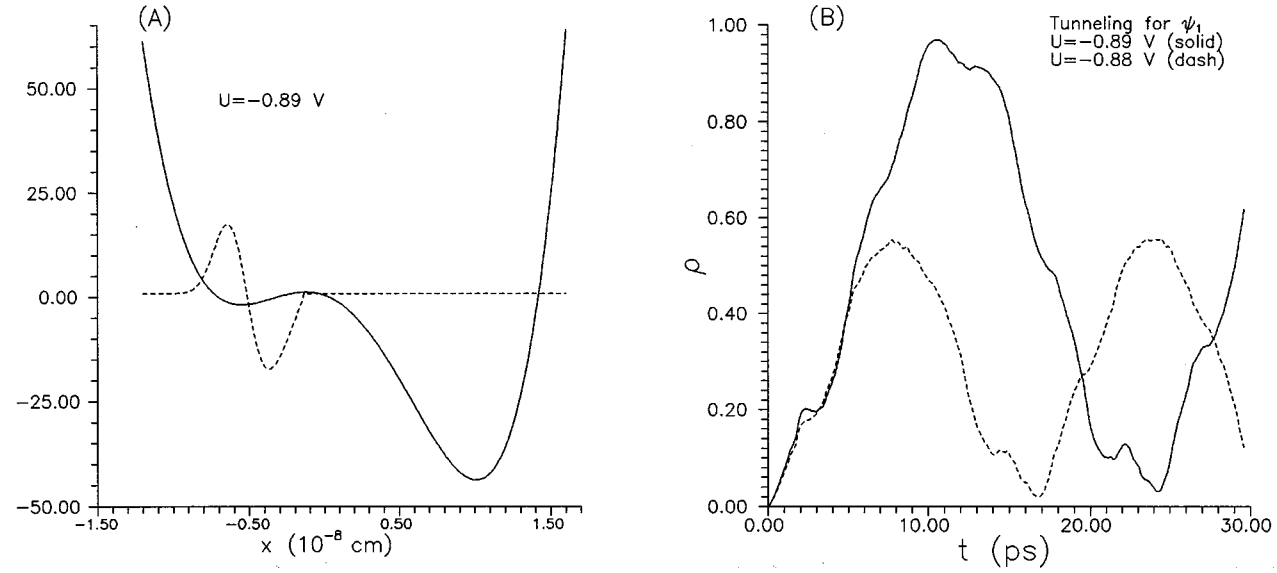

FIG. 4. The resonance of ψ_1 at $U=-0.89$ V. The potential $V(x)$ in meV (solid) and the initial wave function multiplied by 10 (dash) (A), and ρ as a function of time at resonance (solid) and near resonance (dash) (B).

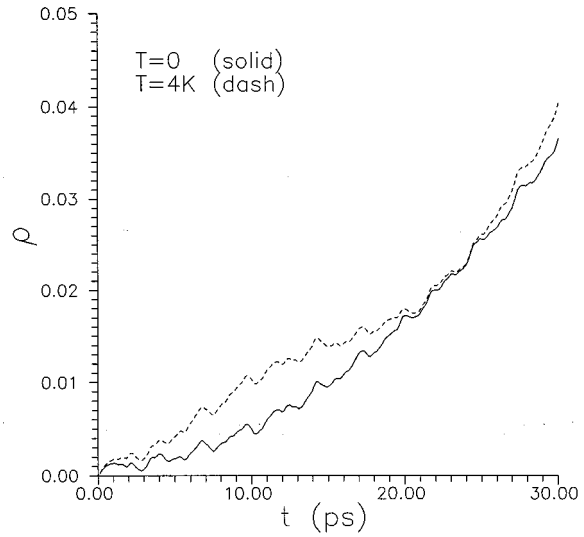

FIG. 5. Small-time behavior for tunneling at $U=-0.89$ V. ρ_0 (solid) and ρ_{mix} at $T=4$ K (dash) are given as functions of time.

mains small. The opposite situation appears for the resonances encountered when $U<-0.49$ V, because $T_c \gg T_{\max}$, and in principle the atom may oscillate many times between surface and tip during the resonance crossing.

IV. SUMMARY AND CONCLUSIONS

In this work we have investigated the oscillatory behavior of the atom transfer in STM, using both semiclassical methods, and solving exactly the quantum tunneling problem by numerically integrating the TDSE. Two initial wave packets have been used, the isomeric ground and first excited state obtained by solving the stationary Schrödinger equation in the metastable well.

In a static potential, the transition across the barrier can follow an exponential law only during times comparable to the period of classical oscillations in the stable well, τ_R. However, this time interval is too short [Fig. 1(A)], and cannot explain a complete tunneling. For certain resonant values of the bias voltage [Fig. 2(B)], the probability of localizations in the stable well may increase to 1 by quantum coherence oscillations. The semiclassical estimates show that the QCO period depends almost exponentially on the bias voltage, ranging from tens of picoseconds to tens of milliseconds. For the first resonances the agreement with the TDSE calculations is very good [Fig. 1(B)], indicating that these estimates are reliable. Therefore, they can be used for predictions near zero bias, where the numerical integration of the TDSE would require a large amount of computer time.

The energy of the two isomeric states depends linearly on the bias voltage with the same slope [Fig. 2(A)], and the two sets of resonant bias voltages almost coincide [Fig. 2(B)]. The first common resonance appears at $U\sim-0.89$ V, and the others at bias voltages increasing in equal steps of 0.08 V. The ψ_0 resonance which could have the main contribution to the atom transfer was selected introducing the notion of crossing time (T_c), discussed for the case of a linear voltage pulse.

The equality of the energy slopes ($\sigma_0=\sigma_1$) ensures that the voltage pulses do not change the thermal equilibrium population of the initial state. The effect of the thermal mixing in the metastable well was investigated at an environmental temperature of 4 K. This temperature effect proves to be small, and the main contribution to the tunneling comes from the isomeric ground state (Fig. 5). However, the heating produced by the tunneling electrons,[2] not considered here, may lead to higher effective temperatures, which could increase the contribution of the excited isomeric states.

In the atomic switch transfer experiments the Xe atom is always directed toward the positively biased electrode. This fact can be explained by the $6s$ resonance of Xe,[10] which can stabilize some extra negative charge. The QCO of a negative ion can influence the electron tunneling current, according to its effective lifetime and the oscillation period between surface and tip. Thus such atom oscillations could be observed by accurate measurements of the junction current.

When the decoherence produced by the electron current or the environmental temperature suppress the oscillations, the atom can be trapped on the tip. Therefore, further work for understanding the QCO decoherence in STM could shed some light on the atom transfer mechanism too.

The calculations presented in this work on the atom dynamics in the STM junction emphasize the oscillatory, rather than exponential, behavior of the localization probability. It can also be seen as providing a basis for understanding the mechanism of atom transfer, or giving practical recipes in constructing new quantum microelectronic devices.

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