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Dynamics of electron in a surface quantum well*

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This paper studies the quantum dynamics of electrons in a surface quantum well in the time domain with autocorrelation of wave packet. The evolution of the wave packet for different manifold eigenstates with finite and infinite lifetimes is investigated analytically. It is found that the quantum coherence and evolution of the surface electronic wave packet can be controlled by the laser central energy and electric field. The results show that the finite lifetime of excited states expedites the dephasing of the coherent electronic wave packet significantly. The correspondence between classical and quantum mechanics is shown explicitly in the system.

Keywords: quantum well, electronic wavepacket, autocorrelation function
PACC: 7320, 7320D

In surface physics, a detailed knowledge of the electron dynamics at surfaces is crucial for an understanding of a large variety of processes, ranging from electron scattering at surfaces to charge transport dynamics across interfaces, relevant to design electronic devices.[1−3] The electronic wave packet on a metal surface can be created by photoemission, and two-photon photoemission (2PPE) spectroscopy[4] permits us to study the dynamics of excited electrons in the time domain, the autocorrelation function of the wave packet can be measured directly.[5] The dephasing and lifetime of the electronic wave packet at metal surfaces are influenced by surface adsorptions and external static fields.[6,7] Moreover, with the increase of the laser incidence angle, the number of surface electrons increases obviously, due to the confinement of the quasi-static surface magnetic field and electric field.[8] The wave packet dynamics can be well described by the autocorrelation function, which is the overlapping between the wave function at time t and its initial state, $\langle\psi(t)|\psi(0)\rangle$, which can be measured by a pump-probe experiment.

Recently, the ultrafast electron dynamics of image-potential quantum states on metal surfaces have been investigated by time-resolved 2PPE (TR-2PPE) extensively. Time-resolved studies of the image-potential states have been done on Ag(100),[9] Cu(111),[10] and Cu(100).[9−12] The use of ultrashort laser pulses with large spectral width allows coherent excitation of several image-potential states, and make quantum beat spectroscopy of these states possible.[13−15] Especially Höfer *et al* have used TR-2PPE in combination with the coherent excitation of several quantum states to study the ultrafast electron dynamics of image states on metal surfaces, providing an accurate experimental determination of the lifetime of the first six image states on Cu(100).[4] And Chulkov and coworkers evaluated the lifetimes of image states on copper surfaces[16] and Borisov *et al* systematically calculated lifetimes of the image-state resonances on clean metal surfaces such as Cu(111), Ag(111), Au(111), and Be(0001),[17] which are in agreement with experimentally determined decay times.

In this paper, we investigate the dynamics of electron wave packets in a surface quantum well in the time domain. The electron is emitted from the metal surface with an L-gap by a short laser pulse. The system is similar to image state on metal surface but different in the following ways: the surface quantum well is formed by external electric field while the very weak imaginary potential is neglected. We obtain an analytical expression for the detached wave packet as the superposition of excited states. The behavior of these packets is affected by the laser center energy and the external field strength, which suggests that the wave packet might be controlled by the applied pulse energy and the electric field. Atomic units are used throughout the paper unless specially noted.

To investigate the electron wave packet in electric field near a surface, we consider the direction of the electric field as the z axis and use the cylindrical

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coordinates (ρ, z, ϕ), the Hamiltonian of the system is

$$H = \frac{1}{2}\left(P_\rho^2 + P_z^2\right) + V(z), \tag{1}$$

where $V(z)$ is defined by the potential energy

$$V(z) = \begin{cases} \infty & \text{for } z < 0, \\ Fz & \text{for } z > 0, \end{cases} \tag{2}$$

where F is the strength of electric field. The photo-emitted electron is bound in a z-direction linear potential well with an impenetrable flat surface at $z = 0$ and moves freely in the ρ direction. Equation (2) is a quite accurate model potential for metals with gap near the vacuum level.

The connections between the energy eigenvalue spectrum of a quantum system and the classical dynamics of particles can be explored through the time-dependence of wave packet solutions of the Schrödinger equation. The normalized eigenfunctions in the quantum well are given by[18]

$$\begin{aligned}\psi_n = & \frac{1}{\left(\frac{2}{F^2}\right)^{1/6}\left(z_n \mathrm{Ai}^2\left[-z_n\right] + \mathrm{Ai}'^2\left[-z_n\right]\right)^{1/2}} \\ & \times \mathrm{Ai}\left[(2F)^{1/3} z - z_n\right],\end{aligned} \tag{3}$$

where

$$\begin{aligned} z_n &= (2F)^{-2/3} q_n^2 \\ &= (2F)^{-2/3} 2\left(\frac{F^2}{2}\right)^{1/3}\left[\frac{3\pi}{2}\left(n - \frac{1}{4}\right)\right]^{2/3} \\ &= \left[\frac{3\pi}{2}\left(n - \frac{1}{4}\right)\right]^{2/3}. \end{aligned} \tag{4}$$

Where Ai is the Airy function. The corresponding energy eigenvalues are

$$E_{zn} = \left(\frac{F^2}{2}\right)^{1/3}\left[\frac{3\pi}{2}\left(n - \frac{1}{4}\right)\right]^{2/3}. \tag{5}$$

Any non-stationary wave packet formed as a superposition of energy eigenstates $\psi(z)$ can be represented as

$$\Psi(z,t) = \sum_n C_n(\mathrm{t})\,\psi_n(z)\,\mathrm{e}^{-\mathrm{i}E_n t/\hbar}, \tag{6}$$

where E_n is the corresponding eigenvalue. And we assume the weighting coefficients c_n as a Gaussian function with time-dependent coefficients $C_n(t) = c_n \mathrm{e}^{-t/2\tau_n}$. The decay of the excited states is taken into account by lifetimes τ_n of the population in each state. All lifetimes of excited states in our model system are assumed to be given by $\tau_n \propto n^3$ which is extensively used for image states in Ref.[19].

For further discussion it is instructive to investigate the autocorrelation function of this system. The autocorrelation function, which is extensively used in the study of the time-development of a quantum wave packet in bound state systems,[20] is defined in one-dimension as

$$\begin{aligned} A(t) &= \int_{-\infty}^{+\infty} \psi^*(x,t)\,\psi(x,0)\,\mathrm{d}x \\ &= \sum_{n=1}^{\infty} |C_n(t)|^2\,\mathrm{e}^{\mathrm{i}E_n t/\hbar}, \end{aligned} \tag{7}$$

which explicitly depends on the energy spectrum. The autocorrelation function is directly related to the observable ionization signal[21,22] in the pump-probe type experiments. Expanding the energy in a Taylor series about the centrally excited n_0, we obtain the derivative terms which define distinct time scales depending on n_0:

$$\begin{aligned} T_{\mathrm{cl}} &= \frac{2\pi\hbar}{|E'(n_0)|}, \\ T_{\mathrm{rev}} &= \frac{2\pi\hbar}{|E''(n_0)|/2}, \\ T_{\mathrm{super}} &= \frac{2\pi\hbar}{|E'''(n_0)|/6}. \end{aligned} \tag{8}$$

The three time scales T_{cl}, T_{rev}, and T_{super} are classical period, revival time, and superrevival time, respectively. For the current system, we can obtain the three time scales

$$\begin{aligned} T_{\mathrm{cl}} &= \frac{2\pi\hbar}{|E'(n_0)|} \\ &= 2\left(\frac{2}{F^2}\right)^{1/3}\left[\frac{3\pi}{2}\left(n_0 - \frac{1}{4}\right)\right]^{1/3}, \\ T_{\mathrm{rev}} &= \frac{2\pi\hbar}{|E''(n_0)|/2} \\ &= \frac{8}{\pi}\left(\frac{2}{F^2}\right)^{1/3}\left[\frac{3\pi}{2}\left(n_0 - \frac{1}{4}\right)\right]^{4/3}, \\ T_{\mathrm{super}} &= \frac{2\pi\hbar}{|E'''(n_0)|/6} \\ &= \frac{12}{\pi^2}\left(\frac{2}{F^2}\right)^{1/3}\left[\frac{3\pi}{2}\left(n_0 - \frac{1}{4}\right)\right]^{7/3}. \end{aligned} \tag{9}$$

Inserting related expressions into Eqs.(6) and (7), we calculate numerically the time evolution of wave packets and the autocorrelation function for the detached electron in electric fields near an elastic surface, and the results are shown in Figs.1 to 4.

Figure 1 shows the temporal and spatial evolution of the detached electron wave packet probability $z^2 |\psi(z,t)|^2$ resulting from calculated coefficients as a Gaussian function. For the current system, the lifetimes of eigenstates are not available experimentally, but we can borrow the results of the image state both in experimental[4] and theoretical results.[16,17] The lifetime of the $n = 2$ image state on Cu(100) is $\tau_2 = 120$ fs, which is assumed to be the lifetime of the second excited state of the current system and other lifetime of eigenstates obtained by extrapolating from τ_2 with the n^3 power law. Figure 1(a) shows the probability density $z^2 |\psi(z,t)|^2$ of a pure $n = 3$ state (i.e. without a coherent mixture of adjacent states) as a function of distance from the surface ($z = 0$) for various time delays after the excitation. The amplitude decays with time evolution due to the finite lifetime of this state. For the limiting case, the photo-emitted wave packet dynamics is simple, which contrasts with that quantum beat phenomena depicted in Figs.1(b) and 1(c). The bandwidth of the Gaussian pulse is large enough to excite several levels within one n manifold. In Fig.1(b), $z^2 |\psi(z,t)|^2$ exhibits strong temporal modulations close to the surface. This modulation is compensated by the small oscillations of $z^2 |\psi(z,t)|^2$ at a distance of ∼8 nm where the probability density is mainly concentrated.

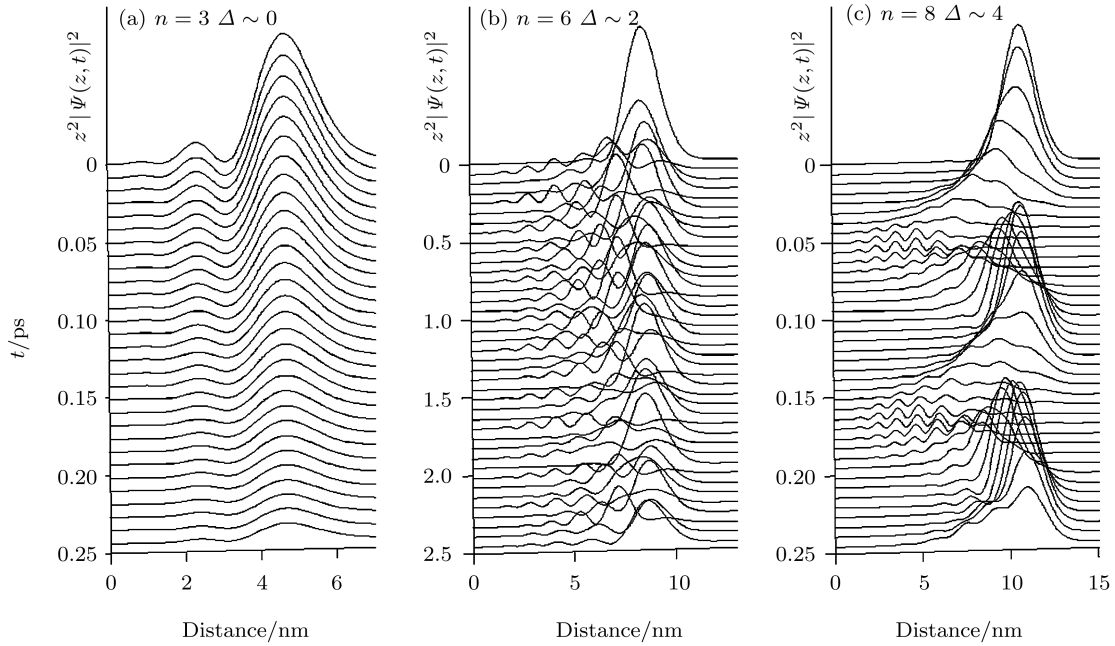


Fig.1. Calculated temporal evolution of the probability $z^2 |\psi(z,t)|^2$ for detached electrons from surface in quantum well for three cases: (a) one eigenstaete $n = 3$, (b) superposition of three levels in the vicinity of $n = 6$, (c) superposition of five excited states centered around $n = 8$. The electric field is fixed at $F = 400$ kV/cm directed along the z axis.

As the level spacing of the surface states decreases with increasing quantum number n, many states are excited with the same pump pulses except for large energy. Depending on the exact pulse parameters and the external field we can get rather complex beat patterns. For instance, as in the one shown in Fig.1(c), the wave packet contains five eigenstates $(6, 7, 8, 9, 10)$ in the vicinity of $n = 8$. The wave packet now displays much more dramatic spatial dynamics. It resembles the classical motion of an electron oscillating back and forth from the surface. Obviously a wave packet may involve many states, which leads to more complicated quantum beat phenomena. We also analyze the influences of the lifetime of excited states on the electronic wavepacket dynamics. In Fig.2, the wave packet evolves in the same way as that in Fig.1 except for the lifetime of the $n = 2$ state assumed to be 40 fs. We can see that the wave packet diminishes more quickly than that in Fig.1 due to the smaller lifetimes.

In Fig.3, we show how the electric field influences the wave packet. When the wave packet involves five levels in the vicinity of $n = 8$ in the same way as that in Fig.1(c), and the electric field increases from 100 to 400 kV/cm, we can see that the spatial distribution closes to the surface and the temporal evolution periodicity

decreases from Fig.3(a) to Fig.2(b). Using Eq.(9), we obtain classical periods of the two cases which are 0.2774 ps and 0.0997 ps, respectively. The time evolution of wave packets is periodic with the classical period excellently. The phenomena can be interpreted as follows: in strong electric field the electron is pushed close to the surface and has a high probability of being located to the surface and stronger interaction with the surface.

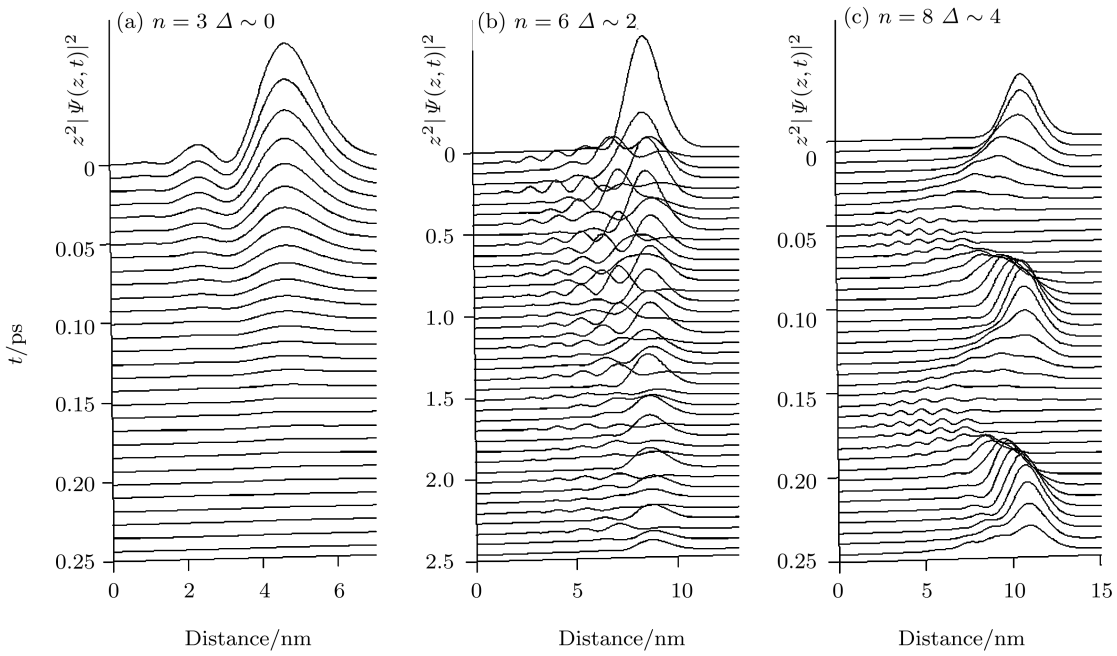


Fig.2. Wave packet evolution same as Fig.1 except for the lifetime of the $n = 2$ state assumed to be 40 fs.

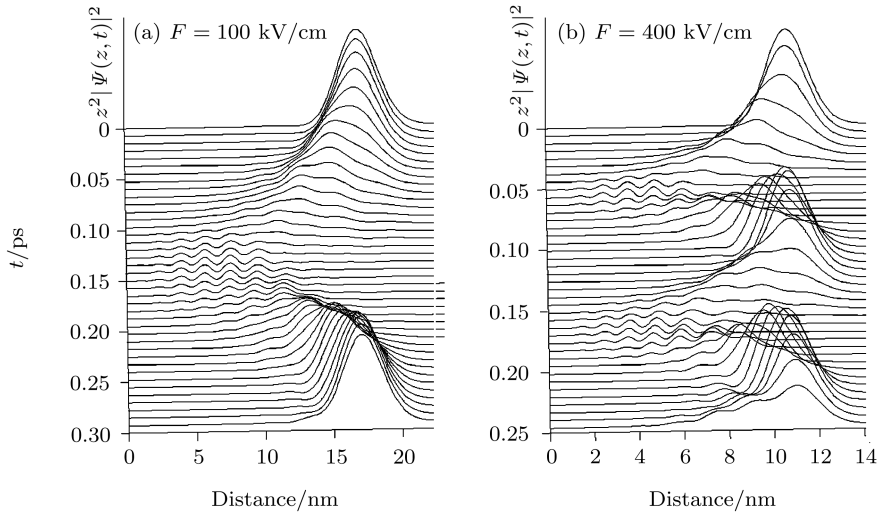


Fig.3. The dependence of the detached electron wave packet on the electric field. The wave packet was created by a superposition of five levels in the vicinity of $n = 8$ same as Fig.1(c) and the electric field is (a) $F = 100$ kV/cm, (b) $F = 400$ kV/cm.

The effect of excited state lifetime on quantum recurrence is shown in Fig.4. By taking the lifetime of excited state τ from finite to infinite, we calculate the square of the autocorrelation function for times up to and just beyond $t_{\rm rev}$ in Figs.4(a)–4(c). Consider a wave packet composed of only one eigenstate, for example $n = 3$ in Fig.4(a). As a consequence of their pure eigenstate in energy spectrum, they can be expected to decay with time evolution for the finite lifetime. On the other hand, consider a wave packet composed of a superposition of several eigenstates, such as one shown in Figs.4(b) and 4(c), there are several peaks in this spectrum. There is a familiar phenomenon called quantum revival depicted in the dot line which reflects that the excited states have

infinite lifetime. Using Eq.(9), we obtain revival and superrevival times of the two cases which are 3.438 ps, 44.480 ps, 5.119 ps and 89.256 ps respectively, and these analytical values agree well with autocorrelation in Figs.4(b) and 4(c). From these figures we can see that quantum revival is difficult to realize for a finite lifetime system, not mentioning super-quantum revival.

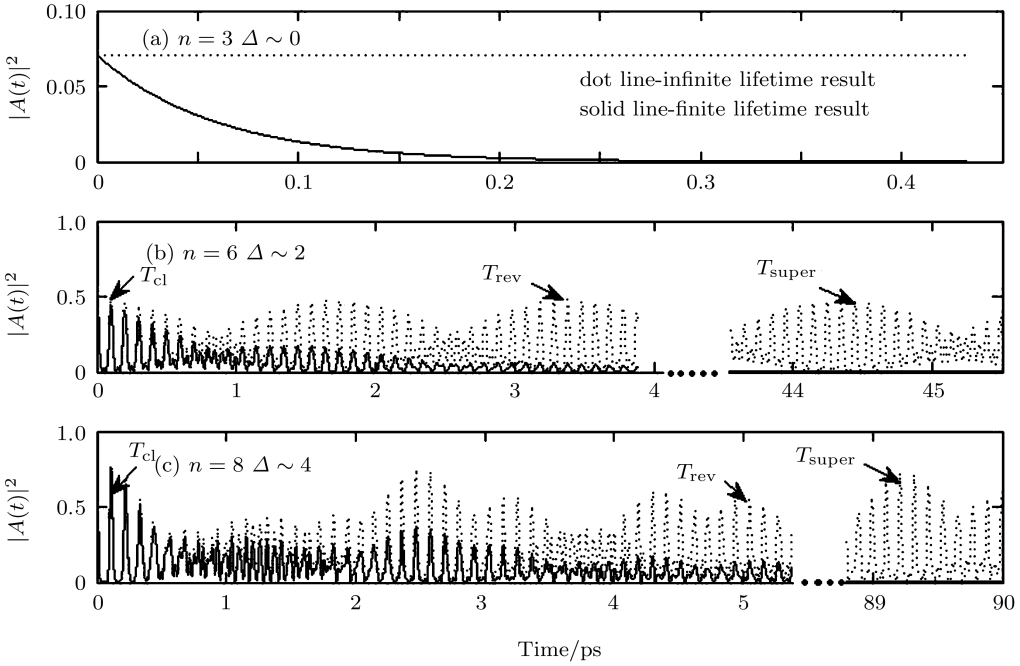


Fig.4. The absolute square of the autocorrelation function $|A\,(t)|^2$ for energy spectrum in Eq.(7) and the Gaussian distribution of energy eigenstates in Eq.(4) as a function of time in picoseconds, for three cases same as Fig.1: (a) $n = 3$, $\Delta \sim 0$, (b) $n = 6$, $\Delta \sim 2$, and (c) $n = 8$, $\Delta \sim 4$.

In summary, we have studied the dynamics of a detached electron wave packet in a surface quantum well in the time domain. This study provides a general framework for the understanding of the dynamics of detached electron wave packet from surface in the presence of external field and surface. We calculate the wave packet time evolution for different manifold eigenstates and discuss the influence of the electric field. Numerical calculation shows that the electron wave packet involves many surface states which display more dramatic spatial dynamics. We demonstrate that the stronger electric field makes the electron have a high probability close to the surface. And the autocorrelation function contains peaks which agree well with the analytical values of classical periodicity in our system. We also found that the lifetime of excited states influences the autocorrelation obviously.

For simplicity, we consider the surface as an elastic wall, which is a simple model for metal surfaces with L-gap. And finite lifetimes of discrete eigenstates are included to describe the interaction between the wave packet and surface. Our results may have some potential applications to time-resolved surface spectroscopy for adsorbed ions and/or atoms.

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