

Wave packet dynamics of the photodetachment of H^- near dielectric surface

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The wave packet dynamics of the photodetachment of H^- near dielectric surface are studied by using the wave packet evolution and the autocorrelation function. The results show that the evolutions of the autocorrelation function and the wave packet in the time domain correspond well with each other. Besides, we consider the influence of the electronic state lifetime on the wave packet evolution and the autocorrelation function. Numerical simulation shows that the evolution of the photodetached electronic wave packet near the dielectric surface exhibits some properties similar to the time-resolved two-photon photoemission intensity of surface electron.

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Understanding the wave packet dynamics of electronic excitations at surfaces is of both fundamental interest and technological importance. In surface physics, a detailed knowledge of electron dynamics on surfaces is crucial for the understanding of a large variety of processes, ranging from electron scattering on surfaces to charge transport dynamics across surface, relevant to design new electronic devices^[1–3]. Ultrashort laser pulses have made it possible to produce and detect coherent superposition of electronic Rydberg states. Such superposition forms electronic wave packets, whose evolution and dynamics are related with the fundamental problems of quantum mechanics and have attracted much attention in the past decade. In certain quantum systems with nonlinear energy spectra, a suitably prepared wave packet will regain its initial form periodically during the course of its evolution. This is known as the revival and the fractional revivals of the wave packet. It is shown that the phenomena of revival and fractional revival occur in the wave packet dynamics of various atomic, molecular, and optical systems such as Rydberg atoms, harmonic oscillator, various potential wells, and molecular vibrational states^[4–6]. A quantity that reflects the underlying wave packet dynamics is the autocorrelation function, which is the overlapping between the wave function at time t and its initial state $\langle \psi(t) | \psi(0) \rangle$. It can be measured by the pump-probe experiment. Recently, the electron wave packet dynamics on metal surfaces have been studied^[7–9]. However, the study on the electron wave packet dynamics near a dielectric surface is very little. In this letter, we study the wave packet dynamics of the photodetached electron on dielectric surface. In this system, the surface electron is photodetached from a negative hydrogen ion (H^-). The photodetachment properties of H^- in external fields have been investigated quite intensively in the past two decades, such as in electric field, in parallel electric and magnetic fields, in crossed electric and magnetic fields, etc.^[10–12] Besides, the surfaces have significant influence on the physical and chemical properties of ions adsorbed on or near them. Recently, the photodetachments of H^- near an elastic interface in different

external fields and H^- near a metal surface have been studied^[13–17]. As to the photodetachment of negative ion near a dielectric interface, to our knowledge, none has given the study. By using the wave packet evolution and the autocorrelation function, we study the wave packet dynamics of the photodetachment of H^- near the dielectric surface. Numerical simulation shows that the evolution of the photodetached electronic wave packet near the dielectric surface exhibits some properties similar to the time-resolved two-photon photoemission intensity of the surface electron.

The physical picture of the photodetached electron wave packet of H^- near a dielectric surface is as follows. The H^- ion sits above a dielectric surface which is perpendicular to the z -axis. A z -polarized laser is used for the photodetachment. When the laser is applied to the negative ion near a surface, it may absorb a photon, then the active electron is detached and moves away from the hydrogen atom. According to the electrostatic image method^[16], the potential acting on the active electron in the ion-surface system can be described as

$$V = V_b + V_c + V_i, \quad (1)$$

where V_b is the interaction potential between the active electron and the hydrogen atom, which is a short-range potential^[12]; V_c is the interaction potential of the electron with the image nucleus, which is also a short-range potential; V_i is the interaction potential between the detached electron and the image electron $e' = \alpha e$, which is a Coulomb-like attractive image potential:

$$V_i = \begin{cases} -\frac{\alpha e^2}{z} & z > 0 \\ \infty & z \leq 0 \end{cases}, \quad (2)$$

where $\alpha = \frac{1}{4}(\frac{\epsilon-1}{\epsilon+1}) > 0$, ϵ is the dielectric constant. Therefore, the Hamiltonian of the detached electron near a dielectric surface (in atomic units) is

$$H = \frac{P^2}{2} + V_b(r) + V_c(r) - \frac{\alpha}{z}. \quad (3)$$

The effects of the short-range potentials of the nucleus and the image nucleus V_b and V_c can be ignored after

the electron is detached^[12]. By solving the Schrödinger equation, we find that the detached electron's motions in the x - and y -directions are free, therefore, this system can be reduced to a problem with free motion in the (x, y) plane and bound in the z -direction. The eigenfunction of the photodetached electron in the z -direction is similar to that of the one-dimensional (1D) hydrogen atom with the orbital quantum number $l=0$, which is given by

$$\psi_n(z) = \begin{cases} Aze^{-\alpha z/n} F(1-n, 2, 2\alpha z/n) & z > 0 \\ 0 & z \leq 0 \end{cases}, \quad (4)$$

where A is the normalized constant and $F(1-n, 2, 2\alpha z/n)$ is the confluent hypergeometric function. The eigenenergy of the system is

$$E_n = -\frac{\alpha^2}{2n^2} \quad (n = 1, 2, \dots). \quad (5)$$

We assume the initial wave packet in the z -direction is

$$\psi(z, 0) = \left(\frac{2}{\pi\sigma^2}\right)^{1/4} e^{-(z-z_0)^2/\sigma^2} e^{ip_0(z-z_0)}, \quad (6)$$

where z_0 and p_0 are the initial position and momentum in the z -direction, σ is the width of the wave packet. Here, we take $z_0 = 0$, $\sigma = 1.5$.

When a short laser pulse is applied to the H^- system, a wave packet is created to excite the photodetached electron coherently to several eigenstates. Any nonstationary wave packet formed as a superposition of energy eigenstate $\psi_n(z)$ can be described as

$$\psi(z, t) = \sum_n C_n(t) \psi_n(z) e^{-iE_n t/\hbar}. \quad (7)$$

The time-dependent factor $C_n(t) = c_n e^{-t/2\tau_n}$ with $c_n = \langle \psi_n(z) | \psi(z, 0) \rangle$ is the weighting coefficient, and τ_n is the lifetime of each eigenstate.

Another quantity to describe the underlying wave packet dynamics is the autocorrelation function, which is the overlapping between the wave function at time t and its initial state:

$$A(t) = \langle \psi(z, t) | \psi(z, 0) \rangle = \sum_{n=1}^{\infty} |C_n(t)|^2 e^{-iE_n t/\hbar}. \quad (8)$$

In many experiments, a localized wave packet is excited with an energy spectrum which is tightly spread around a large central value of the quantum number n_0 , so that $n_0 > \Delta n > 1$. Therefore, we can make a Taylor expansion of E_n around the central value E_{n_0} , giving

$$E_n \approx E_{n_0} + E'_{n_0}(n - n_0) + \frac{E''_{n_0}}{2}(n - n_0)^2 + \frac{E'''_{n_0}}{6}(n - n_0)^3 + \dots, \quad (9)$$

where $E'_{n_0} = (dE_n/dn)_{n=n_0}$ and so forth. Accordingly, we define three characteristic time scales as

$$T_{cl} = 2\pi/|E'_{n_0}|, T_{rev} = 4\pi/|E''_{n_0}|, T_{sr} = 12\pi/|E'''_{n_0}|, \quad (10)$$

where T_{cl} is the classical period, T_{rev} is the revival period, and T_{sr} is the super revival period. In our system,

$T_{cl} < T_{rev} < T_{sr}$, hence we can keep the first four terms in the expansion (Eq. (9)). The autocorrelation function can be described as

$$A(t) = \sum_{n=1}^{\infty} |C_n(t)|^2 e^{-it[E_{n_0} + \frac{2\pi}{T_{cl}}(n-n_0) + \frac{2\pi}{T_{rev}}(n-n_0)^2 + \frac{2\pi}{T_{sr}}(n-n_0)^3]/\hbar}. \quad (11)$$

Using Eq. (7), we calculate the time evolution of the probability density $|\psi(z, t)|^2$ for the photodetached electron of H^- near a GaAs dielectric surface. For the GaAs dielectric, the dielectric constant $\epsilon = 13.18$, then α is 0.86. Figure 1(a) shows that the time evolution of the probability density $|\psi(z, t)|^2$ is composed of two quantum states of $n = 3$ and 4 with initial pulse momentum $p_0 = 0.06$ a.u. as a function of distance from the z surface. Figure 1(a) is the wave packet evolution without considering the lifetime of the surface state. The result shows that the wave packet exhibits good revival structure with classical period $T = h/(E_3 - E_4) = 135.21$ fs. The maximum probability peak for finding the photodetached electron oscillates back and forth from the surface with a period $T = 135.21$ fs. Figure 1(b) is the wave packet evolution with considering the lifetime of the surface electronic state. For the electronic states of $n=3$ and 4, the lifetimes are 348.84 and 826.87 fs. It is shown that due to the influence of the lifetime of the electronic state, the amplitudes of probability density decrease gradually with the time evolution.

Figure 2 shows the time evolution of the quantum probability density with the initial pulse momentum $p_0 = 0.1$ a.u., and the wave packet contains five eigenstates ($n = 5-9$) in the vicinity of $n_0 = 7$. The wave packet displays much more dramatic spatial dynamics and its revival structure is not exact. The maximum probability density concentrates at a distance of approximately 180 a.u. from the surface. Figure 2(a) is the result without considering the lifetime of the electronic state; Fig. 2(b) is the result with considering the influence of the lifetime of the electronic states.

In order to demonstrate the photodetached electron wave packet revival structure clearly, we plot the autocorrelation function of photodetached electron of H^- near a GaAs dielectric surface, as shown in Figs. 3 and 4. Figure 3 shows the autocorrelation function of the wave packet composed of two eigenstates of $n=3$ and 4. Figure 3(a) is the evolution of the autocorrelation function

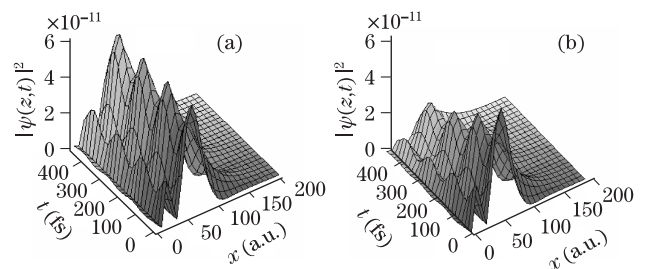


Fig. 1. Time evolution of the probability density $|\psi(z, t)|^2$ for the photodetached electron of H^- near a GaAs dielectric surface. (a) without and (b) with considering the lifetime of the electronic state. The probability density is composed of two states of $n = 3$ and 4 with initial pulse momentum $p_0 = 0.06$ a.u.

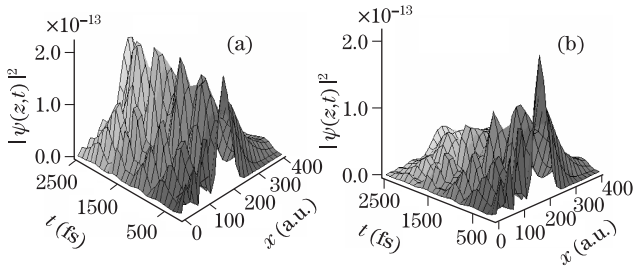


Fig. 2. Time evolution of the probability density $|\psi(z,t)|^2$ composed of five eigenstates ($n = 5-9$) in the vicinity of $n_0 = 7$, the initial pulse momentum $p_0 = 0.1$ a.u. (a) without and (b) with considering the lifetime of the electronic state.

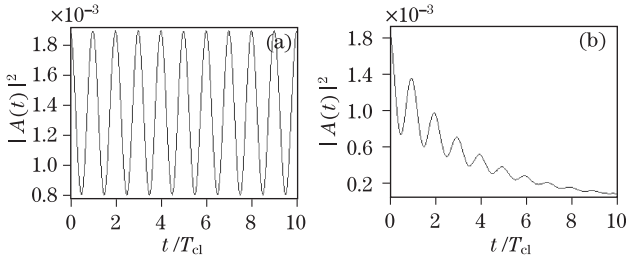


Fig. 3. Evolution of the autocorrelation function composed of two eigenstates $n = 3$ and 4 over ten classical periods (a) without and (b) with considering the lifetime of the electronic state.

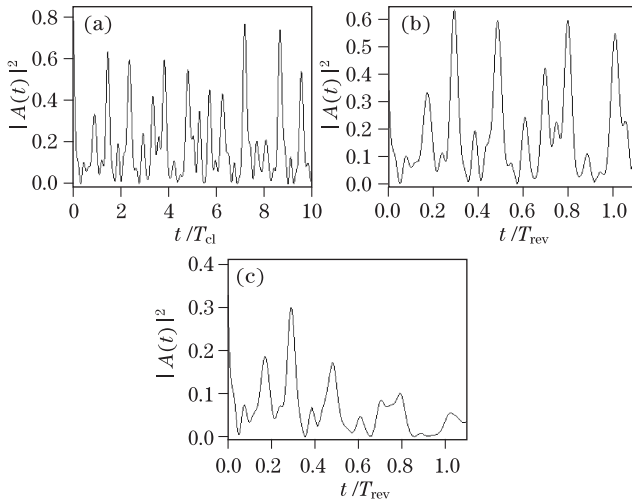


Fig. 4. Evolution of the autocorrelation function composed of five eigenstates ($n = 5-9$) in the vicinity of $n_0 = 7$. (a) Time evolution over ten classical periods, (b) time evolution over one revival period, and (c) evolution of the autocorrelation function considering the lifetime of the electronic state.

without considering the lifetime of the surface state. The wave packet exhibits good revival structure, which is recovered after one classical period $T = 135.21$ fs. Figure 3(b) is the case with considering the lifetime of the surface state, the amplitudes of the autocorrelation function decrease gradually with time evolution. Figure 4 is the autocorrelation function of the wave packet composed of five eigenstates $n = 5-9$ in the vicinity of $n_0 = 7$. Its classical period T_{cl} is 1118.94 fs, the revival period T_{rev} is 5221.74 fs, and the super revival period T_{sr} is 27414.12 fs. Figure 4(a) is the evolution of the autocorrelation function without considering the lifetime of the surface state over ten classical period, and the revivals of the wave

packet are not exact. Figure 4(b) is the evolution of the autocorrelation function over one revival period. The result shows that the wave packet collapses after a short period of time, but after a revival period, it regains its initial structure partially. Besides, the structures corresponding to fractional revivals at time $t = \frac{p}{q}T_{rev}$ (p and q are prime integers and $p < q$) are also apparent in each case. For example, the fractional revivals corresponding to $1/6T_{rev}$, $1/3T_{rev}$, $1/2T_{rev}$, \dots are prominent in Fig. 4(b). Figure 4(c) is the case with considering the lifetime of the surface state, the revival of the wave packet nearly disappears with the evolution of time.

Quantum beat spectrum of closely adjacent state is an additional approach for wave packet dynamics. Using a large bandwidth of pump pulse, we are able to coherently excite more than one eigenstate of this system. For the simple case of coherent excitation of two levels n and $n+1$, the oscillations in the quantum beat spectrum reflect the beating between the corresponding wave functions $\psi_n(t) = |n\rangle e^{-iE_n t/\hbar}$ and $\psi_{n+1}(t) = |n+1\rangle e^{-iE_{n+1} t/\hbar}$. In wave packet dynamics, the quantum beat spectrum is usually inspected by the time-resolved two-photon photoemission (2PPE) intensity. If there is no loss of coherence, the 2PPE intensity $I(t)$ after the pulse will be given by

$$I(t) \propto |C_n(t)\psi_n(t) + C_{n+1}(t)\psi_{n+1}(t)|^2. \quad (12)$$

Figure 5 shows the photodetached electron quantum beat spectra of closely adjacent states. In Fig. 5(a), the pump pulse predominantly excites electrons into $n = 3$ and 4 states. The beating period is equal to the classical period $T = \hbar/(E_3 - E_4) = 135.21$ fs between the $n=3$ and 4 quantum states. The time evolution of the autocorrelation function (Fig. 3(b)) and the 2PPE intensity shows good qualitative agreement. When the laser pulse excites more electronic state, more interference among them occurs and results in more complicated quantum beat phenomena. Figure 5(b) is the 2PPE intensity composed of five quantum states ($n = 5-9$) around $n_0 = 7$. The beating period observed for short delays is $T = \hbar/(E_5 - E_6) = 538.28$ fs. The oscillations reflect the interference between the different quantum states. The structure of the 2PPE intensity corresponds well with the time evolution of the autocorrelation function composed of the same quantum states (Fig. 4(c)).

In conclusion, we study the wave packet dynamics of the photodetachment of H^- on dielectric surface by using

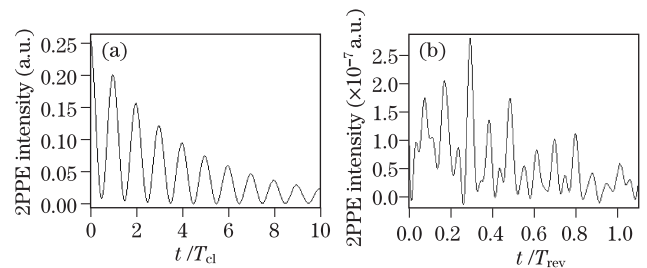


Fig. 5. Quantum beat spectra for the coherent excitation of the photodetached electron state with different quantum numbers. (a) Quantum numbers $n = 3$ and 4 for ten classical periods and (b) quantum numbers $n = 5-9$ for one revival period.

the wave packet evolution and the autocorrelation function. The evolutions of the wave packet and the autocorrelation function for different superpositions of the photodetached electron's eigenstates are obtained. The results show that the initial momentum of the laser pulse and the lifetime of the surface state affect the revival structure of the wave packet evolution. For small initial momentum of the laser pulse, the eigenstates it can excite are few. The wave packet's revival structure is exact. After one period, it regains its initial structure. While for the large initial momentum of the laser pulse, many eigenstates are included in the wave packet. The wave packet's revival structure is not very good. After a short period of time, the wave packet collapses. Numerical calculations show that the photodetached electron wave packet involving many surface states displays more dramatic spatial dynamics. Besides, the evolutions of the photodetached electronic wave packet near the dielectric surface and the 2PPE intensity of surface electron exhibit some similar properties. Our result is helpful to understand the time-resolved surface spectroscopy for adsorbed ions or atoms near surfaces.

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