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Correspondence Between Quantum and Classical Dynamics in Photodetachment Near Elastic Wall

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The photodetachment of H^- near an elastic wall was investigated and an analytical formula of the cross section was derived. It was found that the cross section is a superposition of a smooth background and sinusoidal oscillation, which depends on the distance between the ion and the elastic wall. The classical dynamics of the photo-detached electron and its quantum correspondence was analyzed. In this model, the semiclassical photodetachment cross section is exactly the same as the quantum result.

Key words: Photodetachment, Semiclassical theory, Negative ion

I. INTRODUCTION

The interactions of atoms and/or ions with a surface have long been investigated in different physical, chemical, and biological processes including adsorption and scattering from various surfaces [1]. Due to the high interest in nano-technological applications of atoms near surfaces and mesoscopic-scale atomic devices, there is a need for accurate characterization of atom-surface interactions. Recently, the interaction of Rydberg atoms [2], ions [3] and molecules [4] with metallic surfaces and thin metallic films have been investigated experimentally. It has been found that as the atoms, ions and molecules approach the surface, the Rydberg electrons are subject to fields caused by the presence of image charges in the metal, and thus the physics is closely related to the Stark effect behavior of the atoms, ions and molecules. The photodetachment of H^- in a static electric field has been studied at the quantum and semiclassical levels [5-9]. Photodetachments of H^- in other fields, such as in a gradient electric field [10], cross electric and magnetic fields [11] and in parallel electric and magnetic fields [12], have been also investigated theoretically. Inspired by these experimental and theoretical work, the authors considered the photodetachment of H^- near an elastic wall in the frame of semiclassical theory although a direct measurement of photodetachment of ions near a surface has not been achieved [13].

In the present work, the same system is investigated but by a quantum approach to gain insight into the correspondence between quantum and classical dynamics and to test the accuracy of semiclassical theory. The frame transformation method [14-17] was used to obtain the transition matrix element. It was found that the quantum photodetachment cross section is exactly the same as the semiclassical result, in contrast to the authors' analysis for the case in presence of a static electric field [18]. This coincidence is attributed to the simple form of the infinite potential wall. The cross section of H^- near an elastic wall is modulated by the elastic wall and shows oscillatory structure. The wavelength of the oscillation depends on the distance between the ion and the wall. Actually, a similar phenomena can be found in the spontaneous emission rate of atoms near a surface [19,20].

In this work, an analytical formula of photodetachment cross section of H^- near an elastic wall is derived by the frame transformation method, and compared with the semiclassical result.

II. PHOTODETACHMENT CROSS SECTION

To investigate the photodetachment of H^- near an elastic wall, we consider the following picture: A H^- sits at the origin and a z-polarized laser is applied for the photodetachment. An elastic wall perpendicular to z-axis is put at $-z_0$ (we take positive z_0). Therefore, the photodetached electrons are bounced back by the wall.

The H^- can be considered as, effectively, a one-electron system with the active electron loosely bound by a short-range, spherically symmetric potential $V_b(r)$, where r is the distance between the active electron and the origin where the nucleus is. The binding energy of the electron $E_b{=}{k_b}^2/2$ is approximately 0.754 eV, where k_b is related with the initial wave state $\Psi_i(r){=}B\exp(-k_b r)/r$. B is a normalization constant and is equal to 0.31552 [7,21]. The photon energy $E_p{=}E{+}E_b$, where E is the initial kinetic energy of the photo-detached electron.

In the formalism of quantum mechanics, the photodetachment cross section near an elastic wall at $-z_0$, $\sigma(E)$ is given in terms the dipole matrix elements by this ex-

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pression [17]

$$\sigma(E) = \frac{4\pi^2 E_p}{c} \int |\langle f_E| D |i\rangle|^2 \mathrm{d}E \quad (1)$$

where c is the speed of light, E_p is the photon energy, D is the dipole operator, $|i\rangle$ is the initial state of wave function of H^- which is given by Ψ_i, and $\langle f_E|$ is the final-state wave functions after the detachment. The final state is labeled by the energy E and is normalized according to $\langle f_E|f_{E'}\rangle=\delta(E–E')$. If we neglect the short range potential of the atomic core, the detached electron moves freely before the infinite potential wall at $-z_0$. In cylindrical coordinates, the normalized final state wave function can be obtained by solving the Schrödinger equation in free space with the boundary condition $\Psi(-z_0)=0$. The eigen solution is

$$\Psi_E(\rho,z,\Phi) = (2\pi)^{-1/2} \mathrm{e}^{im\Phi} J_m[(k^2-q^2)^{1/2}\rho] \cdot \frac{1}{\sqrt{\pi q}}[\sin(qz_0)\cos(qz) + \cos(qz_0)\sin(qz)] \quad (2)$$

where q is the momentum of the photodetached electron in z direction, thus $(k^2–q^2)^{1/2}$ is the momentum in ρ motion. To compute the dipole matrix element in Eq.(1), we have to transform the final wave function from cylindrical coordinates to spherical coordinates with the frame transformation method developed by Fano [14], Harmin [15] and Greene [16]. The energy normalized wave functions of a free electron with angular momentum quantum number l are given in spherical coordinates by

$$f_{lm}(r) = \left(\frac{1}{2\pi}\frac{2k}{\pi}\right)^{1/2} N_{lm} e^{im\Phi} P_{lm}(\cos\theta) j_l(kr) \quad (3)$$

$$N_{lm} = (-1)^{(|m|+m)/2} i^l \left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \quad (4)$$

By expansion of the zero-field wave functions in cylindrical coordinates in Eq.(3) in spherical function [17], we have

$$\Psi_E(\rho,z,\Phi) = \frac{1}{\sqrt{\pi q}}\sin(qz_0)\sum_l{}' U_{ql}(n,m) f_{lm}(r) + \sqrt{\frac{q}{\pi}}\cos(qz_0)\sum_l{}'' U_{ql}(n,m) f_{lm}(r) \quad (5)$$

where the summation $\sum_l{}'$ should include all the l's such that $(–1)^l=(–1)^m$, and the summation $\sum_l{}''$ includes all the l's such that $(–1)^l=(–1)^{m+1}$. In Eq.(5), the expansion coefficients

$$U_{ql}(n,m) = \left(\frac{2l+1}{kq}\right)^{1/2}\left[\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \cdot (-1)^{[(l-1-m)/2]} P_{lm}\frac{q}{k} \quad (6)$$

where the phase factor is $(–1)^{[x]}$, and $[x]$ denotes the smallest integer greater than or equal to x.

The photodetachment cross sections can now be calculated by substituting $\Psi_E(\rho,z,\Phi)$ in Eq.(5) for the final state in Eq.(1). Because of the dipole selection rule, only the l=1 term in Eq.(5) contributes to the cross section.

For photons polarized along the field direction, the l=1 term in $\sum_l{}''$ of Eq.(5) contributes to the cross section, $\sigma(E)$. The overlapping integral in Eq.(1) is

$$\langle f_E| D |i\rangle = -i\cos(qz_0)\frac{4B(2q)^{1/2}}{({k_b}^2+k^2)^2} \quad (7)$$

Inserting the expression into Eq.(1) and carrying out the integral, we obtain an analytical formula for the photodetachment cross section

$$\sigma(E,F) = \frac{16\sqrt{2}B^2\pi^2}{3c}\frac{E^{3/2}}{(E_b+E)^3} + \frac{2\pi^2}{c}\frac{4BE}{z_0(E_b+E)^3}\sin(2\sqrt{2}z_0E^{1/2}) \quad (8)$$

where the first term is just the field-free cross section.

III. RELATION TO THE SEMICLASSICAL PHOTODETACHMENT CROSS SECTION

The photodetachment of H^- near an elastic wall or in external fields can also be understood in the framework of closed orbit theory [22]. In the semiclassical theory, we have the following dynamical physical picture: The initial state Ψ_i is modified by the dipole operator related with the incident laser field to become the source wave function; Green's function propagates these waves outward to become the outgoing waves; and some of waves are turned back to the vicinity of the atomic core by external fields and/or other potential barriers; finally the waves overlap with the source wave to give the absorption spectrum. The exact Green's function can be obtained by a quantum approach for quite few simple cases. For many other cases, we can only obtain the Green's function approximately by means such as the semiclassical method.

The steady outgoing electronic wave produced in the photodetachment satisfies the inhomogeneous Schrödinger equation:

$$[E - H(r,p)]\,\psi_F^+(r) = D\Psi_i \quad (9)$$

where D is the dipole operator, which is z or $(x+iy)/\sqrt{2}$, for linear or circular polarized photons respectively and the Hamiltonian $H=–(1/2)\nabla^2+V_b(r)$. It has been shown that the photodetachment cross section can be written as [12,22]

$$\sigma(E) = -\frac{4\pi E_p}{c}\mathrm{Im}\,\langle D\Psi_i|\,\widehat{G}^+\,|D\Psi_i\rangle \quad (10)$$

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where $\widehat{G}^+$ denotes the outgoing Green's function and D is the dipole operator.

In the semiclassical picture, the Green function in Eq.(10) propagates the "source function" from the source point to the field point along two or more paths. The first path is associated with waves which propagate from the field point to the field point without ever leaving the atomic region. This is the direct path. Additionally, there are waves which propagate outward from the source point and enter the external region where they interact with the elastic wall and return to the vicinity of the atomic core where they arrive at the field point. Therefore, the returning wave in Eq.(9) can be divided into a direct part and a returning part,

$$\Psi_F^+ = \widehat{G}_{\rm dir}^+|D\Psi_i\rangle + \widehat{G}_{\rm ret}^+|D\Psi_i\rangle \equiv \Psi_{\rm dir} + \Psi_{\rm ret} \quad (11)$$

The direct part represents the detached electron wave initially going out from the core after photodetachment and never goes far from the core. The second part is known as the returning wave that propagates outward into the external region first, then is reflected by the elastic wall, and finally returns to the vicinity of the core to interfere with the steady outgoing wave. It is related with the so-called closed orbit along which the photo-detached electron returns to the origin. In the current case, only the outgoing electron going in $-z$ direction is bounced back by the wall and returns to the origin. This is only closed orbit which contributes to the returning part of the cross section. Accordingly, the cross section has two parts,

$$\sigma(E) = \sigma_{\rm dir}(E) + \sigma_{\rm ret}(E) \quad (12)$$

The first part is the contribution of the direct wave interfering with the source and is the cross section in free space. The second part is the contribution of the returning wave. The returning wave can be approximated by a plane wave traveling in the z-direction:

$$\Psi_{\rm ret} = N{\rm e}^{ikz} \quad (13)$$

where N is a proportional constant including the information of semiclassically propagating the electronic wave before its return. It can be written as

$$N = -\frac{4Bki}{2z_0(k_b^2+k^2)^2}{\rm e}^{i(2\sqrt{2}z_0E^{1/2}-\pi)} \quad (14)$$

The overlapping integral of the returning wave in Eq.(10) is the returning part of the cross section

$$\sigma_{\rm ret} = -\frac{4E_p}{c}{\rm Im}\int B\exp(-k_b r)\cos\theta N{\rm e}^{kr\cos\theta_{\rm ret}}r^2\sin\theta \, {\rm d}r{\rm d}\theta{\rm d}\phi \quad (15)$$

Completing the integral and adding the free-field cross section, we have the total photodetachment cross section. It has been shown that we obtain exactly the same cross section with Eq.(8) when the semiclassical method is used to propagate the returning wave function in the current case [13]. This coincidence can be explained by Eq.(10): the semiclassical Green's function is the same as its quantum counterpart for the case of free motion with a hard wall. Actually, the semiclassical approximation is accurate up to a quadratic potential. The authors previously investigated the same model but with a static electric field which is also exactly solvable and found that there was indeed a deviation of the semiclassical result in respect to the quantum one [13,23]. The deviation depends on the distance between the ion and the wall, and the electric field. The deviation is very small [23].

IV. RESULTS AND DISCUSSION

The photodetachment cross section can be calculated for different values of the distance between the ion and the elastic wall. The results are shown in Fig.1, which is similar to the one in Ref.[13] but with different distance parameters. We can see that the detachment spectrum consists of a smooth background and a sinusoidal oscillation, which is like the case in a static electric field. In Fig.1, we can see the pattern of photodetachment cross section alters with the increasing distance between the ion and the elastic wall. The free space case is shown in Fig.1(a) for comparison. When the distance is very large, the present system should revert to the case of the ion in free space. Taking z_0=1500a_0 in Eq.(8), the calculated cross section is shown in Fig.1(b). The spectrum is almost the same as the one in free space except for some very small ripples which appeared in the smooth background. When $z_0\to\infty$, the second term in Eq.(8) tends to zero. In semiclassical picture, this means that the only closed orbit vanishes. The closer the wall moves to the ion, the more electronic waves reflected by the elastic wall interfere with the outgoing source waves. Figure 1(c) shows the cross section when the wall is 300 a.u. away from the ion. The distance is 15.7 nm, and is quite typical in surface physics and cavity quantum dynamics. We can see the elastic wall significantly changes the cross section. If the wall approaches the ion further, the amplitude of oscillation in the spectrum increases, as seen in Fig.1(d).

In summary, the photodetachment of H^- near an elastic wall was analyzed, and an analytical formula of the cross section was derived. It was found that the cross section is a superposition of a smooth background and sinusoidal oscillation, which depends on the distance between the ion and the elastic wall. The physical origin of the oscillation in quantum cross section can be attributed to the only classical closed orbit which goes out in $-z$ direction and returns to the atomic core. In this model, the semiclassical photodetachment cross section is exactly the same as the quantum result. Therefore, environment such as potential walls or cavities can significantly influence the photodetachment of

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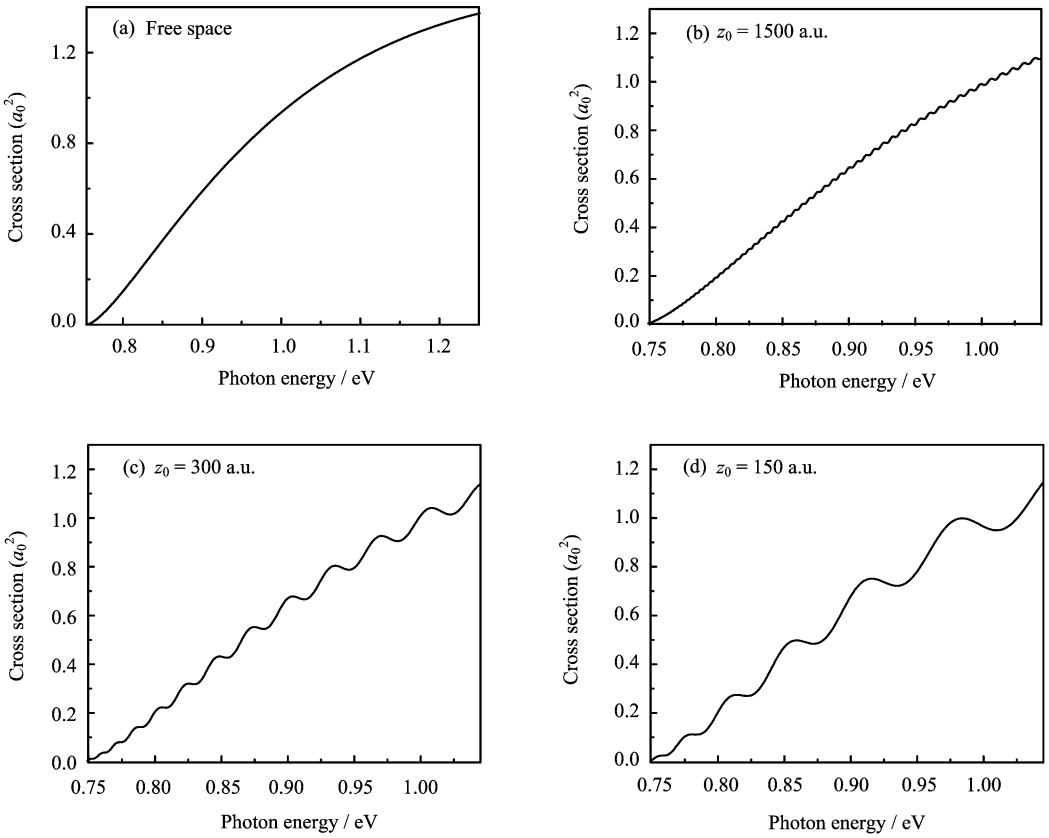

FIG. 1 The dependence of the photodetachment cross section on the distance between the negative hydrogen ion and the elastic wall. The result is similar to Ref.[13] but with different distances. The distances are: (a) z_0=∞, (b) z_0=1500 a.u., (c) z_0=300 a.u., and (d) z_0=150 a.u.

ions and/or absorption spectra of atoms. We can extend our model system to a real system such as a metal surface where we have an image potential.

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