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Photo-detachment cross section of H^- near two parallel interfaces*

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The photo-detachment cross section of H^- near two parallel elastic interfaces is derived and calculated by using the closed orbit theory. The photo-detachment cross section of H^- near two interfaces is shown to exhibit multi-periodic oscillations when the distance between the H^- and the interface is varied. Each peak in the Fourier transformed photo-detachment cross section corresponds to the length of a closed orbit, which is quite similar to the case of atomic spontaneous emissions in a dielectric slab. This study provides a new understanding of the photo-detachment process of H^- in the presence of interfaces.

Keywords: closed-orbit theory, photo-detachment cross section, Fourier transformation
PACC: 3450D, 3280F, 0365S

1. Introduction

The interactions of Rydberg atom,[1] ions[2] and molecules[3] with metallic surfaces and thin metallic films have attracted much attention in recent years. It is found that as the atoms, ions and molecules approach the surface, the Rydberg electron is subjected to fields caused by the presence of image charges in the metal, and therefore this physical phenomenon is closely related to the external field behaviour of atoms, ions and molecules. Most of these external field problems have been examined extensively using different methods. Among them, closed orbit theory (COT) has provided a useful theoretical framework to understand the oscillations in the complicated absorption spectra for atoms, molecules and negative ions in external fields.[4−6] The closed-orbit theory not only provides a physical picture for the oscillations in the photo-detachment or photo-absorption cross section, it is also a quantitative tool to calculate and analyse such an oscillation. Recently, much attention has been paid to the photo-induced electronic excitations of adsorbates on metal surfaces.[7] The resonant electronic states in adsorbed molecules are believed to be responsible for a variety of electron-induced dynamical processes at surfaces.[8] A very challenging topic in studying the surface chemical dynamics is how to control the lifetime of the resonant electronic states of the adsorbed molecules.[9] In 1999, Rous shows theoretically that the negative ions resonance can be controlled by the adsorption of the molecules onto an epitaxial metallic film.[10] In reality, the presence of a surface alters the resonance lifetime and the photo-detachment cross section of an adsorbed ion, because the barrier penetrability of the detached electron is modified.[11,12] Since H^- was proposed to use in probing adsorbate state lifetime and charge transfer during backscattering,[13] the photo-detachment of H^- near a surface has attracted much interest. In Ref.[14], Yang *et al* used an elastic wall model for the electron scattering surface. They derived and calculated the photo-detachment cross section of H^- near an interface by using the closed orbit theory. But as to the relation between the photo-detachment cross section and the closed orbits, they did not have a discussion. In this paper, we discuss the photo-detachment process of H^- near two parallel interfaces. For simplicity, we still use the elastic wall as the detached electron scattering surface. In this system, the classical motion of the detached electron is very similar to the case of the spontaneous emission process of an atom in dielectric interfaces.[15,16] The photo-detachment cross section of H^- near two interfaces is shown to exhibit

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multi-periodic oscillations when the distances between the H^- and the interfaces are varied. Therefore, this system can simulate the experiment of the photo-detachment of H^- in strong electric field.[17] In order to show the relation between the quantum photo-detachment cross section and the detached electron's classical closed orbits, we make a Fourier transformation of the cross section for this system. Each peak in the Fourier transformed cross section corresponds to the length of one detached electron's closed orbit going out from and returning to the nucleus. This result shows that the classical orbit can be revealed by examining the Fourier transform of the quantum cross section. It is another example to show the correspondence between the classical and quantum mechanics by using the closed orbit theory.

2. Photo-detachment cross section

The schematic of the system is shown in Fig.1. A hydrogen negative ion H^- sits at the origin and a z-polarized laser is used for the photo-detachment. Two parallel elastic interfaces perpendicular to z-axis are placed at $z = -d_1$ and $z = d_2$. So the photo-detachment electron is bounced back at the interfaces. The H^- ion can be considered effectively as a one-electron system, with the active electron loosely bound by a short-range, spherically symmetric potential $V_{\rm b}(r)$, where r is the distance between the active electron and the origin where the nucleus is situated. The photo-detached electron's wavefunction satisfies the Schrödinger equation with a source[18]

$$[E - H(r,p)]\psi_{\rm d} = D\psi_{\rm i}, \tag{1}$$

where E is the energy of the detached electron, D is the dipole operator, for z-polarized light, $D = Z$. H is the Hamiltonian of the detached electron and expressed as

$$H = \frac{P^2}{2} + V_{\rm b}(r); \tag{2}$$

$\psi_{\rm i}$ is the initial wavefunction of H^-. In the present study we take the one electron approximation.[19] The initial wavefunction in the configuration space is

$$\psi_{\rm i}(\boldsymbol{q}) = B\frac{{\rm e}^{-k_{\rm b}r}}{r}, \tag{3}$$

in which $B = 0.31552$ is a normalization constant; $k_{\rm b} = 0.2355883$, which is related to the binding energy $E_{\rm b}$ of H^- by $k_{\rm b} = \sqrt{2E_{\rm b}}$.

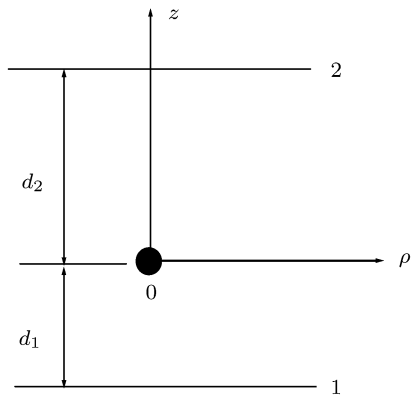


Fig.1. Schematic of the photo-detachment of H^- near two parallel elastic interfaces. H^- is denoted by a black dot at the origin. d_1 and d_2 represent the distances between the H^- and the elastic interfaces.

The physical solution of Eq.(1) requires only the outgoing wave present at large r. Once we have the wavefunction $\psi_{\rm d}(\boldsymbol{q})$ of the detached electron satisfying the correct outgoing boundary condition, the oscillator-strength density can be calculated by using the closed-orbit theory (COT). According to this theory, the photo-absorption cross section is related to the oscillator-strength density ${\rm D}f(E)$ by

$$\sigma(E) = \frac{2\pi^2}{c}{\rm D}f(E). \tag{4}$$

The oscillator strength for dipole transitions of an initial state $\psi_{\rm i}$ to final states at energy E is[4]

$${\rm D}f(E) = -\frac{2}{\pi}(E + E_{\rm b}){\rm Im}\langle D\psi_{\rm i}|\hat{G}^+|{\rm D}\psi_{\rm i}\rangle, \tag{5}$$

where $\hat{G}^+$ is the outgoing Green's function. The above equation has the following physical meaning: The initial state $\psi_{\rm i}$ is modified by the dipole operator associated with the laser field to give a 'source function' $|{\rm D}\psi_{\rm i}\rangle$. The Green's function $\hat{G}^+$ propagates these waves outward at fixed energy to become the outgoing waves. Due to the effect of the elastic interfaces, these waves cannot propagate to infinity, some of the waves are turned back by the interfaces and returns to the origin. Finally, the returning waves overlap with $|{\rm D}\psi_{\rm i}\rangle$, thus giving the interference pattern in the absorption spectrum.

According to the COT, the wavefunction $\psi_{\rm d}$ can be divided into a direct part and a returning part:

$$\begin{aligned}\psi_{\rm d} &= \hat{G}^+_{\rm dir}|{\rm D}\psi_{\rm i}\rangle + \hat{G}^+_{\rm ret}|{\rm D}\psi_{\rm i}\rangle \\ &= (\psi_{\rm d})_{\rm dir} + (\psi_{\rm d})_{\rm ret}.\end{aligned} \tag{6}$$

The direct part represents the detached electron wave initially going out from the nucleus after photo-detachment and never goes far from the core, and it satisfies the following equation:

$$\Big[E - \frac{P^2}{2}\Big](\psi_{\rm d})_{\rm dir} = z\psi_{\rm i}. \tag{7}$$

The solution of the above equation is[20]

$$(\psi_{\rm d})_{\rm dir}(q) = -\frac{4Bk^2}{(k_{\rm b}^2+k^2)^2} h_1^{(1)}(kr)\cos(\theta), \tag{8}$$

where $k = \sqrt{2E}$ is the momentum of the detached electron, $h_1^{(1)}(kr)$ is the outgoing spherical Bessel function.[21] The overlap integral of the direct part with the source gives the smooth background term in the cross section[14]

$$\begin{aligned} {\rm D}f_0(E) =& -\frac{2}{\pi}(E+E_{\rm b}){\rm Im}\langle D\psi_{\rm i}|(\psi_{\rm d})_{\rm dir}\rangle \\ =& \frac{8\sqrt{2}B^2E^{3/2}}{3(E_{\rm b}+E)^3}. \end{aligned} \tag{9}$$

The returning part of the detached electron wavefunction $(\psi_{\rm d})_{\rm ret}$ represents the electron wave that propagates outward into the external region first, then it is reflected by the elastic interface and finally returns to the vicinity of the core along all closed orbits to interfere with the steady outgoing waves. It is a sum over returning wave associated with each closed orbit. In Ref.[14], there is only one elastic interface, and accordingly, there is only one closed orbit which is travelling along the z-axis. But in our case, there are two elastic interfaces, the number of the primitive closed orbits is four and each closed orbits is still travelling along the z-axis. Some of the closed orbits are given in Fig.2.

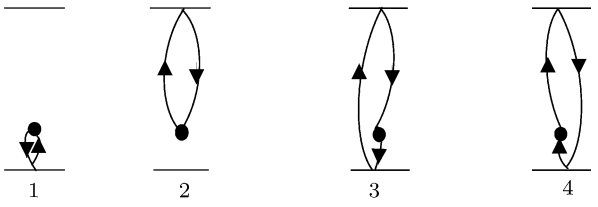


Fig.2. Four closed orbits of the detached electron between the two parallel elastic interfaces.

In order to obtain the returning wavefunction associated with each closed orbit, we draw a sphere of radius R, $R \approx 10a_0$. The outgoing wave on the surface of this sphere is then

$$\psi^0(q) = -\frac{4Bk^2}{(k_{\rm b}^2+k^2)^2}\cos\theta {\rm e}^{{\rm i}(kr-\pi)}/kr. \tag{10}$$

When this wave propagates out from the surface and travels along the closed orbit, it changes phase and amplitude. In the semiclassical approximation, the wave outside this sphere is a sum of the above outgoing waves:

$$\psi(q) = \sum_i \psi^0(q) A_i {\rm e}^{{\rm i}[S_i - \mu_i\pi/2]}, \tag{11}$$

where S_i is the action along the ith trajectory, μ_i is the Maslov index characterizing the geometrical properties of the ith trajectory and A_i is the amplitude. Due to the classical free motion of the detached electron, the amplitude is given by

$$A_i = \frac{R}{R+kt_i}, \tag{12}$$

where t is the time for going out from the source region and back to the origin.

If there are no elastic interfaces, the detached electron will propagate away from the source region near the nucleus as a spherical wave and never return. The photo-detachment cross section is only the smooth background term which can be obtained without any external field. But when there are elastic interfaces, as a group of outgoing waves hit the interfaces, some of the associated waves will be turned back by the interfaces. This orbit, initially going out from the nucleus, travelling in the z-direction, and finally returning to the nucleus is called a closed orbit. As it comes back close to the nucleus, each returning wave can be approximated by a plane wave travelling in the z-direction:

$$(\psi_{\rm d})^i_{\rm ret}(q \approx 0) = N_i {\rm e}^{\pm {\rm i}kz}, \tag{13}$$

in which '+' corresponds to the waves travelling in the negative z-direction; while '−' corresponds to the waves travelling in the positive z-direction. N_i is a constant. According to the general method given by Du and Delos,[4] we have

$$N_i = A_i {\rm e}^{{\rm i}(S_i-\pi/2)}(\psi_{\rm d})_{\rm dir}(R, \theta = 0), \tag{14}$$

where $S_i = \int p{\rm d}q = k^2 t_i = kL_i$ is the action of the closed orbit. L_i is the geometric length of the closed orbit in our case. For our systems, there are four basic closed orbits, and the lengths and amplitudes are as follows:

$$\begin{aligned} &L_1 = 2d_1, \quad L_2 = 2d_2, \quad L_3 = L_4 = 2(d_1+d_2), \\ &A_1 = \frac{R}{R+2d_1}, \quad A_2 = \frac{R}{R+2d_2}, \\ &A_3 = A_4 = \frac{R}{R+2(d_1+d_2)}. \end{aligned} \tag{15}$$

Substituting the above formulae into Eq.(14), we can obtain the constant N_i for each returning wave. The total returning waves are the sum of each returning wave:

$$(\psi_{\rm d})_{\rm ret} = \sum_{i=1}^{4} (\psi_{\rm d})^{i}_{\rm ret}(q \approx 0) = \sum_{i=1}^{4} N_i {\rm e}^{\pm {\rm i}kz}. \qquad (16)$$

The overlap integral of the returning waves with the source wavefunction $\langle D\psi_{\rm i}|$ gives the oscillation in the photo-detachment cross section,

$$\begin{aligned} {\rm D}f_1(E) = & -\frac{2}{\pi}(E+E_{\rm b}){\rm Im}\langle {\rm D}\psi_{\rm i}|(\psi_{\rm d})_{\rm ret}\rangle \\ = & \sum_{i=1}^{4} \frac{4BE}{d_i(E_{\rm b}+E)^3}\cos(\sqrt{2E}L_i) \\ = & \sum_{i=1}^{4} \frac{8BE}{L_i(E_{\rm b}+E)^3}\cos(kL_i). \end{aligned} \qquad (17)$$

In the above equation, $d_3 = d_4 = d_1 + d_2$. L is the geometric length of the closed orbit. Combining Eqs.(9) and (17), we obtain the total photo-detachment cross section of H^- in the presence of two parallel elastic interfaces:

$$\begin{aligned} {\rm D}f(E) = & \frac{8\sqrt{2}B^2E^{3/2}}{3(E_{\rm b}+E)^3} \\ & + \sum_{i=1}^{4} \frac{4BE}{d_i(E_{\rm b}+E)^3}\cos(\sqrt{2E}L_i). \end{aligned} \qquad (18)$$

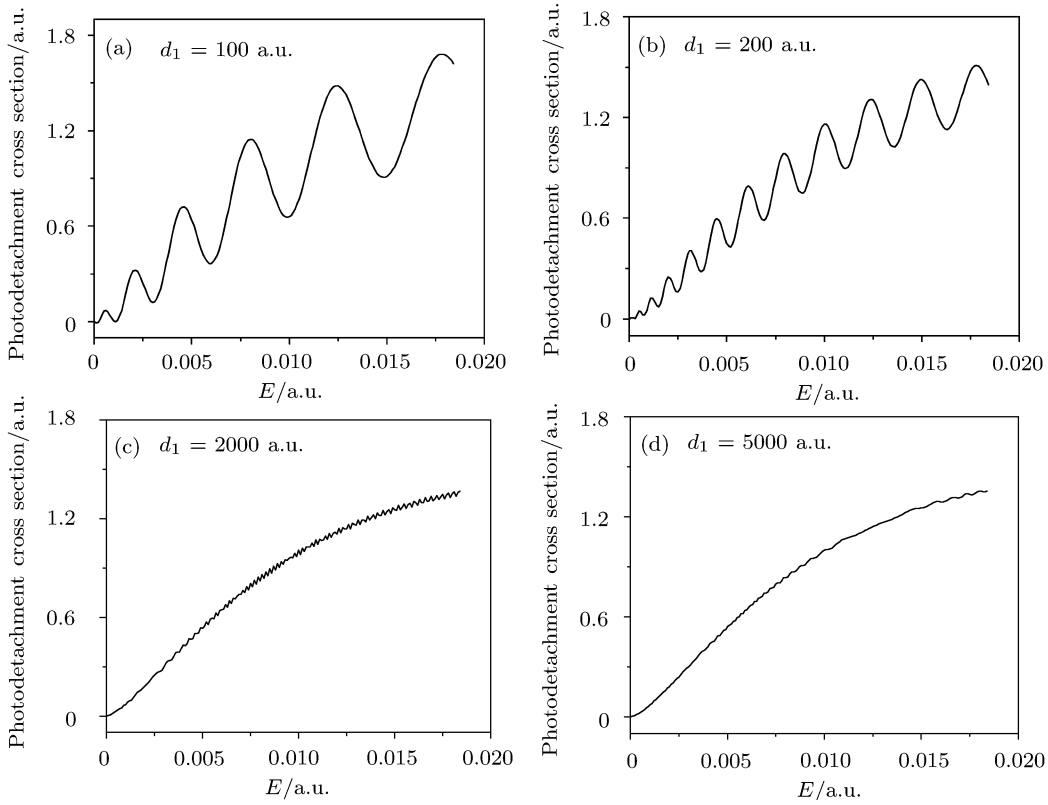


Fig.3. Photo-detachment cross section of H^- near two elastic interfaces. The upper interface locates at infinity $d_2 \to +\infty$. The distances between the H^- and the lower interface are (a) d_1=100a.u.; (b) d_1 = 200 a.u.; (c) d_1 = 2000 a.u.; (d) d_1 = 5000 a.u. This case equals the photo-detachment cross section of H^- near one elastic interface.[14] The horizontal axis is the energy of the detached electron in atomic unit and the vertical axis is the photo-detachment cross section.

Using the above equation, we calculate the photo-detachment cross section of H^- near two parallel elastic interfaces for different values of the distance between the ion and the elastic interfaces (see Fig.3). In order to show the correspondence between the cross section and the detached electron's closed orbits, we perform the Fourier transform (FT) of the photo - detachment cross section ${\rm D}f(E)$. The quality of the FT can be improved if we first remove the background term and then multiply by $(E_{\rm b}+E)^3/E$ before FT. We define

$${\rm D}f'(L) = {\rm D}f_1 \times \frac{(E_{\rm b}+E)^3}{E} = \sum_{i=1}^{4} \frac{4B}{d_i}\cos(kL_i). \qquad (19)$$

The FT of the above equation is

$$F(L) = \int_{k_1}^{k_2} \mathrm{D}f' \times \mathrm{e}^{-\mathrm{i}kL}\mathrm{d}k, \qquad (20)$$

where L is the geometric length of the orbit. Therefore, the Fourier transform of the photo-detachment cross section will show its features at L corresponding to the length of the classical closed orbit. For a finite length of the orbit, $F(L)$ are complex numbers. We have calculated $|F(L)|^2$ in our calculation.

3. Results and discussions

In Fig.2 we plot the four basic closed orbits of the detached electrons in the presence of two parallel elastic interfaces. The first two closed orbits describe the detached electrons that leave the ion, and returns to it after they are reflected back by the upper or lower interface. These two closed orbit have the lengths $L_1 = 2d_1$, $L_2 = 2d_2$. The third closed orbit describes the detached electron departing from the H^- and travelling down toward the lower interface, it is bounced back by the lower surface and then travels up to the upper surface; it is reflected again and returns to the H^-; the fourth closed orbit describes the detached electron that moves in the opposite direction of the third orbit, therefore the length for the third and the fourth closed orbits is identical and is given by $L_3 = L_4 = 2(d_1 + d_2)$. In Fig.3, we plot the photo-detachment cross section of H^- in the presence of two parallel elastic interfaces, in which one interface is located at infinity from the origin ($d_2 \to +\infty$), and the other interface at $z = -d_1$. This case is equivalent to the photo-detachment of H^- near one interface as given in Ref.[14]. The photo-detachment cross section is shown to exhibit a damping oscillation as the distance between the H^- and the elastic interface d_1 is increased. In order to show the relation between this oscillation and the closed orbit, we calculate the FT of Fig.3. The FT cross section is given in Fig.4. In this case, there is only one closed orbit of the detached electron, with its length $L = 2d_1$. From this figure we also find: if d_1 is very large, the length of the closed orbit is very long. Longer length of the electron's closed orbit usually corresponds to small amplitude of oscillations, thus its contribution to the photo-detachment cross section is very small (see Figs.4(c) and 4(d)). This case is quite similar to the spontaneous emissions of the atom in a single dielectric interface.[15]

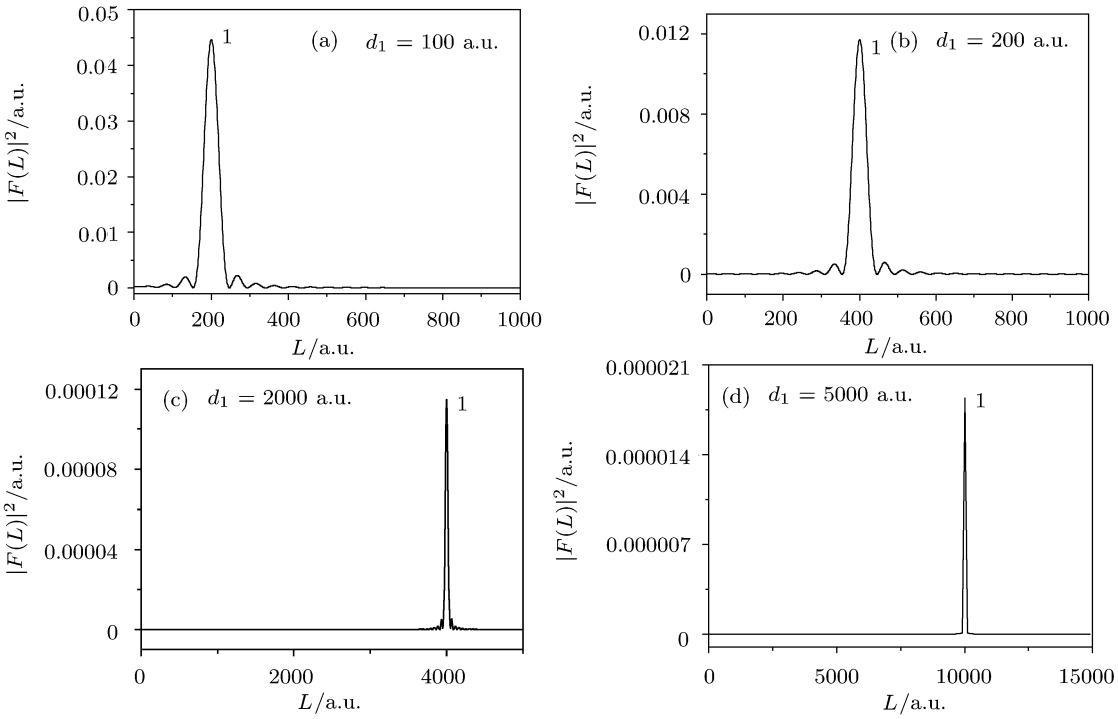


Fig.4. Fourier transform of the corresponding photo-detachment cross section of H^- near one elastic interface in Fig.3. Each peak in the plot corresponds to one electron's closed orbit. The number 1 beside each peak denotes the first closed orbit in Fig.2. The horizontal axis is the length of electron's orbit and the vertical axis is the FT photo-detachment cross section.

Figure 5 displays the photo-detachment cross section of H^- near two parallel elastic interfaces, with one interface located at $z = -d_1$ and the other interface at $z = d_2$. The photo-detachment cross section is shown to exhibit a multi-periodic oscillations. From this figure, we can see if we locate the first interface at $z = d_1 = 200$ a.u. (atomic unit), this distance from H^- is 10.6nm and is quite typical in surface physics and cavity quantum dynamics. Then we change the distance of the second interface d_2 from H^-. We find when the distance d_2 is very large, about 5000a.u. from the origin, it has only little effect on the photo-detachment cross section. But as we move the interface 2 closer to the H^-, the influence of this interface on the photo-detachment cross section of H^- becomes significant (see Figs.5(d–a)). This can be interpreted as follows: the closer the second interface from H^-, the more the returning waves bounced back by this interface, therefore, their contribution to the cross section becomes greater. Furthermore, if we put the two interfaces all far away from the H^-, one is at 5000a.u. and the other is at 10000a.u., the effect of the interfaces on the cross section is very small, and the present system should recover to the case of H^- in free space, which is a smooth background term without external field, as we can see from Fig.5(f).

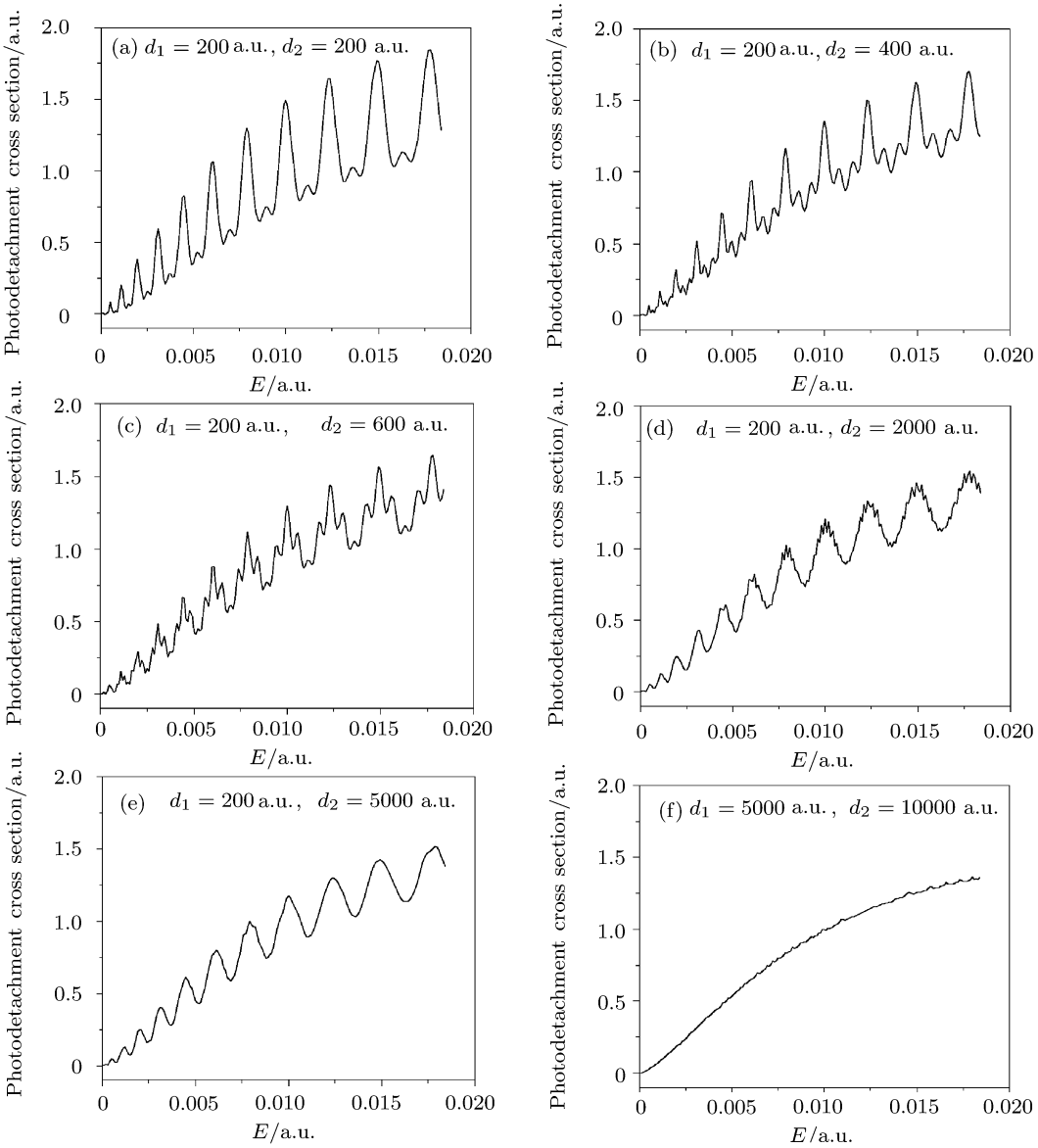


Fig.5. Photo-detachment cross section of H^- near two elastic interfaces. The distances between the H^- and the two interfaces are (a) $d_1 = 200$ a.u., $d_2 = 200$ a.u.; (b) $d_1 = 200$ a.u., $d_2 = 400$ a.u.; (c) $d_1 = 200$ a.u., $d_2 = 600$ a.u.; (d) $d_1 = 200$ a.u., $d_2 = 2000$ a.u.; (e) $d_1 = 200$ a.u., $d_2 = 5000$ a.u.; (f) $d_1 = 5000$ a.u., $d_2 = 10000$ a.u.

In order to show the contribution of the closed orbits to the multi-periodic oscillation in the photo-detachment cross section, we calculate the FT cross section of Fig.5 (see Fig.6). Each peak in the Fourier transformed photo-detachment cross section corresponds to the length of one closed orbit. When $d_1 = d_2$, the lengths of the first two closed orbits are equal, thus they correspond to one peak in Fig.6(a). But if $d_1 \neq d_2$, the lengths of the first two closed orbits are not the same, so they correspond to different peaks in Figs.6(b–d). Besides, the lengths of the third and the fourth closed orbits of the detached electron are identical, therefore these two closed orbits correspond to one peak in Fig.6(a–d). This phenomenon is similar to the case of atomic spontaneous emissions in a dielectric slab.[16]

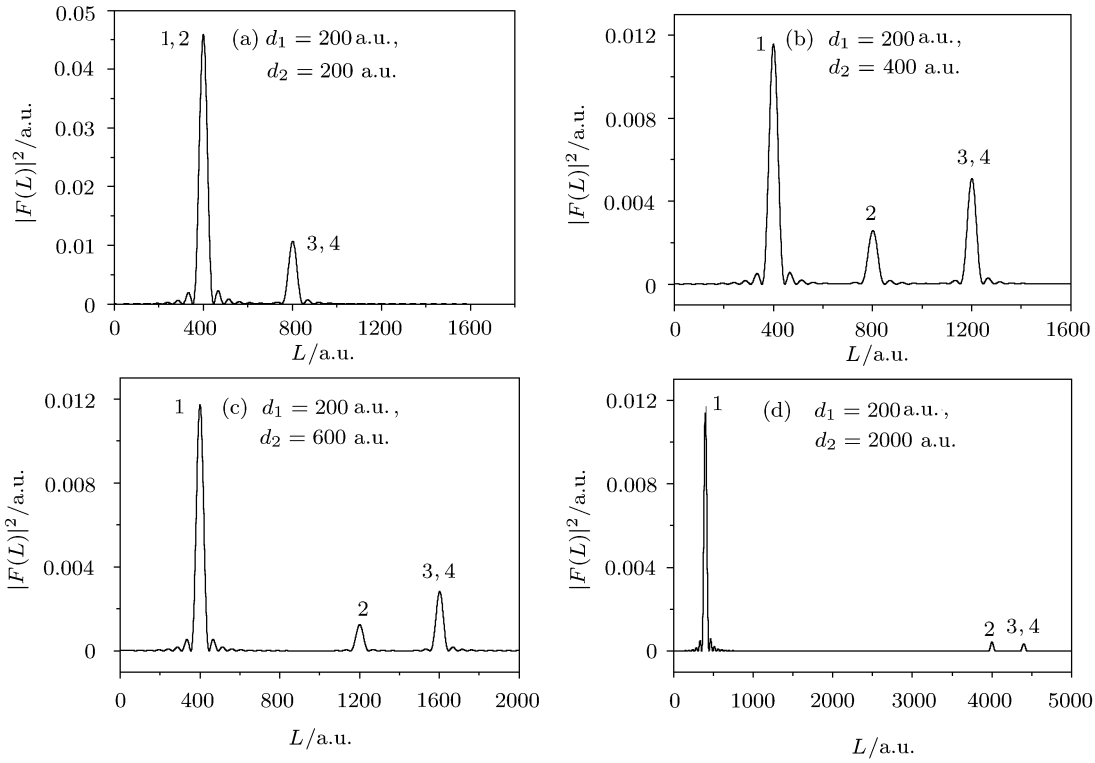


Fig.6. Fourier transforms of the corresponding photo-detachment cross section of H^- near two elastic interfaces in Fig.5. Each peak corresponds to one closed orbit of the detached electron. The number beside each peak corresponds to the closed orbit given in Fig.2.

4. Conclusion

In summary, we have studied the oscillation of the photo-detachment cross section of H^- near two parallel interfaces by the COT. The calculated photo-detachment cross section exhibits multi-periodic oscillations when the distances between the H^- and the interfaces are varied. An analytical formula of the cross section is derived. We find that the elastic interfaces have significant influence on the photo-detachment process. Each peak in the FT cross section corresponds to the contribution of one closed orbit. This study provides a general framework for the understanding of the photo-detachment process of H^- in the presence of two interfaces. In this paper, we consider the interface as an elastic wall, therefore this is only a simple model. As to the metal interface, the method we used in this paper cannot be directly applied to these real systems. The theoretical calculation and analysis of the photo-detachment or photo-absorption process of atoms or ions near a metal surface is in progress. We hope that our results will be useful for understanding the photo-detachment processes of ions in the vicinity of interfaces, cavities and ion traps.[22]

References

[1] Hill S B, Haich C B and Zhou Z 2000 *Phys. Rev. Lett.* **85** 5444

[2] Wethekam S, Mertens A and Winter H 2003 *Phys. Rev. Lett.* **90** 037602

[3] Lloyd G R, Procter S R and Softley T 2005 *Phys. Rev. Lett.* **95** 133202

[4] Du M L and Delos J B 1988 *Phys. Rev.* A **38** 1896

[5] Wang D H and Ding S L 2003 *Phys. Rev.* A **68** 023405

[6] Wang D H and Ding S L 2004 *Chin. Phys.* **13** 30

[7] Petek H, Weida M J, Nagano H and Ogawa S 1999 *Science* **288** 239

[8] Borisov A G, Kazansky A K and Gauyacq J P 2001 *Phys. Rev.* B **64** 201105

[9] Gadzuk J W 1999 *Annu. Rev. Phys. Chem.* **39** 395

[10] Rou P J 1999 *Phys. Rev. Lett.* **83** 5086

[11] Rou P J and Hartley D M 1995 *Chem. Phys.* **236** 299

[12] Hartley D M and Rou P J 1995 *Surf. Sci.* **341** 213

[13] Sjakste J, Borisov A G and Gauyacq J P 2004 *Phys. Rev. Lett.* **92** 1561015

[14] Yang G C, Zheng Y Z and Chi X X 2006 *J. Phys.* B **39** 1855

[15] Wang F H, Jin Y P，Gu B H, Zhou Y S, Wang X H and Du M L 2005 *Phys. Rev.* A **71** 044901

[16] Du M L, Wang F H, Jin Y P, Zhou Y S, Wang X H and Gu B H 2005 *Phys. Rev.* A **71** 065401

[17] Bryant H C, Mohagheghi A, Stewart J E, Donahue J B, Quick C R, Reeder R A and Yuan V 1987 *Phys. Rev. Lett.* **58** 2412

[18] Gibson N D, Davis B J and Larson D J 1993 *Phys. Rev.* A **48** 310

[19] Du M L and Delos J B 1988 *Phys. Rev.* A **38** 5609

[20] Du M L 1989 *Phys. Rev.* A **40** 4983

[21] Abramowitz M and Stegun I A *Handbook of Mathematical Functions* 1987 (New York: Dover) pp34–100

[22] Ma X G, Sun W G and Cheng Y S 2005 *Acta Phys. Sin.* **54** 1149 (In Chinese)