Photodetachment near a metal surface

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We study the photodetachment cross sections of H[−] near a metal surface using closed-orbit theory. Formulas for cross sections are presented. We find the metal surface mainly modifies the photodetachment cross sections near threshold. It induces a strong oscillation in the photodetachment cross section between threshold and an energy $\frac{1}{4d}$ above threshold, where *d* is the distance between the negative ion and the metal surface. Below threshold the photodetachment cross section near a metal becomes finite because of quantum tunneling effect. The oscillation in the cross section is identified with a closed orbit and explained as an interference of the detached electron.

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 $[5,6]$ $[5,6]$ $[5,6]$ $[5,6]$. Our theoretical results show that the metal surface modifies the photodetachment cross sections near photodetachment threshold. Assume *d* is the distance between the negative ion and the metal surface. Then between threshold and an energy which is $\frac{1}{4d}$ above threshold the cross section becomes oscillatory. Effects of the metal on the photodetachment cross sections for high enough energy is small and ignorable. Below threshold, the photodetachment cross section is finite because the metal induces a quantum tunneling behavior similar to that in the photodetachment of a negative

In Sec. [II](#page-0-1) we will describe the Hamiltonian for the system of H[−] near a metal surface. In Sec. [III](#page-1-0) we first search and describe the closed orbits of the detached electron and then apply closed-orbit theory to calculate the photodetachment cross sections. We discuss in detail the physical effects induced by the metal surface. In Sec. [IV](#page-4-0) we describe the scaling relations and discuss their consequences in the cross sections. In Sec. [V](#page-5-0) we compare the photodetachment cross sections near a metal surface and the photodetachment cross sections in the presence of a static electric field. It is demonstrated that close to threshold and when the distance *d* between the metal surface and the negative ion is large, the effects of the metal surface can be approximated by a static

ion in the presence of a static electric field.

I. INTRODUCTION

It is now well established that a static electric field can induce interesting effects on the photodetachment cross sections of a negative ion. For the negative ion H−, Bryant *et al.* $\lceil 1 \rceil$ $\lceil 1 \rceil$ $\lceil 1 \rceil$ observed the "ripple" structure in the cross sections in the presence of a static electric field in contrast with the smooth cross sections in the absence of an electric field. Rau and Wong $[2]$ $[2]$ $[2]$ explained the "ripple" structure as an interference between the detached electron going up and down the electric potential hill. Du and Delos $\left[3,4\right]$ $\left[3,4\right]$ $\left[3,4\right]$ $\left[3,4\right]$ interpreted the "ripple" structure using closed-orbit theory $\lceil 5.6 \rceil$ $\lceil 5.6 \rceil$ $\lceil 5.6 \rceil$ and identified one special closed orbit of the detached electron that is responsible for the oscillation in the photodetachment cross section of H[−] in an electric field. Interests in photodetachment of negative ions in external fields can be traced to the work of Fabrikant some years ago $[7]$ $[7]$ $[7]$ and continue to attract both theoretical and experimental attentions $[8-19]$ $[8-19]$ $[8-19]$. On the other hand, a Rydberg atom near a metal surface constitutes a different system to study the atomic dynamics as well $[20-22]$ $[20-22]$ $[20-22]$. In this system the images of charged particles of the atom exert additional forces on the atomic electron. The classical motion of this system can be regular or chaotic depending on the energy and the distance between the atom and the metal surface $\lceil 21 \rceil$ $\lceil 21 \rceil$ $\lceil 21 \rceil$. Recent theoretical calculations using closedorbit theory show that the oscillations in the absorption spectra of an atom near a metal surface are also correlated to closed orbits of the system $\lceil 23 \rceil$ $\lceil 23 \rceil$ $\lceil 23 \rceil$.

Inspired by the studies of photodetachment of a negative ion in the presence of a static electric field and the dynamics of a Rydberg atom near a metal surface, we propose to study the photodetachment of a negative ion near a metal surface. This problem can be solved in a quantitative manner with solutions describing interesting physical effects. We will first apply the imaging method to determine the forces acting on the detached electron and specify the Hamiltonian for the detached electron. We will then search all the closed orbits of the detached electron in the system and calculate the photodetachment cross sections using standard closed-orbit theory

We consider the photodetachment of H[−] near a metal surface. A schematic diagram is shown for the detached electron and its interaction with other parts of the system in Fig. [1.](#page-1-1) We assume the negative ion is at the origin. *d* is the distance between the metal surface and the negative ion. The metal surface is perpendicular to the *z* axis and it intersects the *z* axis at −*d*. *r* is the position of the detached electron relative to the hydrogen atom which is represented by a positive charge and a negative charge in a circle. For our purpose here, H[−] is regarded initially as a one-electron system loosely *duml@itp.ac.cn bound by a short-range potential of the hydrogen atom.

electric field of strength $F = \frac{1}{4d^2}$. Finally we remark about the laser polarization dependence of the results and conclude. Atomic units are used throughout this work unless otherwise noted. **II. HAMILTONIAN**

FIG. 1. Schematic representation of a hydrogen atom and a detached-electron near a metal surface.

When the negative ion absorbs a photon, the active electron is detached and it moves away from the hydrogen atom.

Following the method of images $[20,24]$ $[20,24]$ $[20,24]$ $[20,24]$, each charge has an image inside the metal but the charge of the image has an opposite sign. The images of the hydrogen atom and the active electron are shown in the gray area in Fig. [1.](#page-1-1) There are three forces acting on the active electron. They come from the hydrogen atom, the image of the hydrogen atom, and the image of the active electron. The interaction between the active electron and the hydrogen atom can be neglected as done in the photodetachment of H[−] in a static electric field $[3,4]$ $[3,4]$ $[3,4]$ $[3,4]$.

The interaction between the active electron and the image of the hydrogen atom can be neglected for the same reasons. The distance between the detached electron and its image is $2(d+z)$. Following the previous approach [[20](#page-6-9)], we have the Hamiltonian governing the motion of the detached electron in cylindrical coordinates

$$
H = \frac{1}{2}(p_{\rho}^{2} + p_{z}^{2}) - \frac{1}{4(d+z)} + \frac{1}{4d},
$$
 (1)

where we have also added a constant and shifted the potential such that the value of the potential at the origin is zero.

III. CLOSED-ORBIT THEORY FOR PHOTODETACHMENT CROSS SECTION

We now apply closed-orbit theory to calculate the photodetachment cross sections of H[−] near a metal. Closed-orbit theory was originally developed to describe the oscillations in the absorption spectra of atoms in a magnetic field $[5,6]$ $[5,6]$ $[5,6]$ $[5,6]$. The theory has also been very effective in unveiling the oscillatory structures for photodetachment cross sections in a static electric field and in parallel fields $[4,14,15]$ $[4,14,15]$ $[4,14,15]$ $[4,14,15]$ $[4,14,15]$. Closedorbit theory gives the following physical picture for the photodetachment of a negative ion H[−] near a metal. When a laser is applied to the negative ion near a metal, it may absorb a photon. When it does, the active electron, which is initially in a loosely bound *S* state, goes into an outgoing *P* wave. This wave then propagates away from the hydrogen atom in all directions. Sufficiently far from the hydrogen atom, the wave propagates according to semiclassical mechanics and it is correlated with classical trajectories. If there are detachedelectron trajectories coming back to the hydrogen atom because of the force induced by the metal, they form closed orbits. The electron waves associated with the closed orbits also come back to the hydrogen and interfere with the outgoing detached electron. In Fig. [2](#page-2-0) we show the potential induced by the metal in Eq. (1) (1) (1) and the physical picture for the photodetachment process. Closed-orbit theory gives a prescription for calculating the oscillations in the photodetachment cross sections from the closed orbits once we have all the closed orbits of the detached electron of the system which start and end at the hydrogen atom.

A. Closed orbits

We now search for all the closed orbits. For the system described by the Hamiltonian in Eq. (1) (1) (1) , we find that the potential approaches a maximum value $E_m = \frac{1}{4d}$ as *z* increases to infinity. E_m divides the above threshold region into two. When the detached-electron energy E is greater than E_m , there is no closed orbit. When the detached-electron energy *E* is greater than zero but smaller than E_m , there is one and only one closed orbit in the system. This closed-orbit leaves the origin and moves initially in the z axis direction (away from the metal surface). It is slowed down, stopped, and attracted back to the origin (hydrogen atom) by the image charge inside the metal. Figure $3(a)$ $3(a)$ shows the family of detached-electron trajectories leaving the origin with energy *E* less than E_m . The closed orbit is marked by the darker line. Figure $3(b)$ $3(b)$ shows the detached-electron trajectories leaving the origin with energy E larger than E_m . No closed orbit is formed in this case.

We now describe in detail the closed orbit when the energy E is less than E_m . The initial momentum of the detached electron is $\sqrt{2E}$ at $z=0$ when it is detached and released by the hydrogen atom. As the electron moves in the *z* axis direction, its momentum decreases and reaches zero. It then moves toward and finally returns back to the hydrogen atom. The momentum of the outgoing detached electron along the closed orbit can be written as

$$
p_z = \sqrt{2\left(E - \frac{1}{4d} + \frac{1}{4(d+z)}\right)}.
$$
 (2)

By setting p_z to zero, we get the turning point of the closed orbit $z_m = \frac{4\vec{E}d^2}{(1-4Ed)}$.

We use $\overline{T(E, d)}$ to denote the time spent by the detached electron along the full closed orbit leaving from and returning to the hydrogen atom. It is given by

$$
T(E,d) = 2 \int_0^{z_m} \frac{1}{p_z} dz.
$$
 (3)

Insetting Eq. (2) (2) (2) into Eq. (3) (3) (3) , the result of the integral is $[25]$ $[25]$ $[25]$

FIG. 2. The metal-induced potential in Eq. (1) and a schematic illustration of the photodetach-
ment process of H⁻ near a metal surface. When a photon is absorbed by the negative ion, the de-
tached electron gains enough energy and moves away from the hydrogen atom. The detached-
electron moving to the right (away from the metal surface) is slowed down. If the detached-electron energy is less than
$$
\frac{1}{4d}
$$
, it is turned back to the hydrogen atom by the potential barrier on the right-hand side. The returning electron inter-
ferences with the outgoing electron, which leads to the oscillation in the photodetachment cross sections in Fig. 5.

$$
T(E,d) = \frac{4d^2\sqrt{2E}}{1 - 4Ed} + \frac{(2d)^{3/2}}{(1 - 4Ed)^{3/2}}\tan^{-1}\sqrt{\frac{4dE}{1 - 4Ed}}, \quad (4)
$$

$$
0 < E < E_m
$$

where the value of the inverse tangent function $tan^{-1}(x)$ is limited to the range $[-\pi/2,\pi/2]$.

The action along the full closed orbit is given by

$$
S(E,d) = 2 \int_0^{z_m} p_z dz.
$$
 (5)

Substituting p_z in Eq. ([5](#page-2-1)) by that in Eq. ([2](#page-1-3)), the result of the integral is $\lceil 26 \rceil$ $\lceil 26 \rceil$ $\lceil 26 \rceil$

$$
S(E,d) = \frac{1}{2} \sqrt{\frac{2d}{1 - 4Ed}} \cos^{-1}(1 - 8Ed) - 2d\sqrt{2E},
$$
 (6)

 $0 < E < E_m$

where the value of the inverse cosine function $cos^{-1}(x)$ is limited to the range $[0, \pi]$.

In Fig. [4,](#page-3-1) we show the energy dependence of time in Eq. (4) (4) (4) and action in Eq. (5) (5) (5) . When the energy *E* increases and approaches E_m , both $T(E,d)$ and $S(E,d)$ go to infinity. For small $(E_m - E)$, we have the following asymptotic expressions:

$$
T(E,d) \sim \frac{\pi\sqrt{2}}{8}(E_m - E)^{-3/2},
$$

$$
S(E,d) \sim \frac{\pi\sqrt{2}}{4}(E_m - E)^{-1/2}, \quad E \to E_m.
$$
 (7)

B. Photodetachment cross sections

According to closed-orbit theory $[5,6]$ $[5,6]$ $[5,6]$ $[5,6]$, the photodetachment cross section of our system can be written as

$$
\sigma(E,d) = \sigma_0(E) + \sigma_r(E,d), \tag{8}
$$

where $\sigma_0(E, d) = 16\sqrt{2}B^2\pi^2 E^{3/2}/3c(E_b + E)^3$ is the photodetachment cross section of H[−] without the metal surface, *B* =0.315 22 is related to the normalization of the initial bound state Ψ_i of H⁻ [[3](#page-6-2)], *c* is the speed of light and its value is approximately 137 a.u. $\sigma_r(E,d)$ is the oscillating part of the cross section corresponding to the electron closed orbit described above. Closed-orbit theory gives

$$
\sigma_r(E,d) = -\frac{4(E + E_b)\pi}{c} \operatorname{Im}\langle D\Psi_i|\Psi_{\text{ret}}\rangle,\tag{9}
$$

where Ψ_i is the initial bound state wave function of H⁻ and is given by $\Psi_i = Be^{\frac{ek_br}{r}}$ in the present one active electron approximation for photodetachment, $k_b = \sqrt{2E_b}$, E_b is the binding energy and it is approximately 0.754 eV, and *D* $= r \cos(\theta)$ is the dipole operator if we consider the polarization in the *z* axis. In closed-orbit theory the returning wave Ψ_{ret} in Eq. ([9](#page-2-3)) near the bound state of H⁻ is related to the initial outgoing detached electron as

$$
\Psi_{\text{ret}}(\vec{r}) = \sum_{j} \Psi_{\text{out}} A_j e^{i(S_j - \mu_j \pi/2)}, \qquad (10)
$$

where the sum runs over all the electron closed orbits going out from and returning to the hydrogen atom, S_i , A_i , and μ_i are, respectively, the action, amplitude, and Maslov index of the closed orbit *j*; $\Psi_{\text{out}}(r, \theta, \phi) = -\frac{4Bk^2i}{(k_b^2+k^2)^2}h_1^{(1)}(kr)\cos(\theta)$ is the initial outgoing electron wave from the negative ion $[4]$ $[4]$ $[4]$,

FIG. 3. Illustrating the difference for the family of outgoing detached-electron trajectories above and below the special energy $E_m = \frac{1}{4d}$, where *d* is the distance between the ion and the metal surface. (a) When detached-electron energy E is less than E_m , there is one closed-orbit (darker line) on the positive z axis. (b) When detached-electron energy E is larger than E_m , no closed-orbit is found. The solid line at $z=-60a_0$ represents the metal surface.

where $k = \sqrt{2E}$, and *E* is the energy of electron after detachment.

For the present system and when *E* is less than *Em*, because there is only one closed orbit, the sum in Eq. (10) (10) (10) includes only one term and the index *j* is dropped from now on. To calculate the returning wave function associated with the closed orbit, we draw a sphere of radius *R* large enough so that the asymptotic approximation $h_1^{(1)}(kr) = e^{i(\bar{k}r - \bar{\pi})}/kr$ is valid near the surface of sphere. The radius *R* must also be small enough so that the image potential term is much smaller than the kinetic energy of the detached electron inside the sphere, that is, $1/4d-1/4(d+R) \ll k^2/2$, which is $R/4d^2 \ll k^2/2$ if R/d is small. The direct outgoing wave for the detached electron on the surface of the sphere is then

$$
\Psi_{\text{out}}(R,\theta,\phi) = -i\frac{4Bk^2}{(k_b^2 + k^2)^2}\cos(\theta)\frac{e^{i(kR-\pi)}}{kR}.\tag{11}
$$

As the wave in Eq. (11) (11) (11) propagates out from the sphere along the closed orbit, its amplitude and phase change. The change is counted for by $A_j e^{i(\bar{S}_j - \mu_j \pi/2)}$. For the closed orbit on the *z* axis described above, the Maslov index is equal to 1.

FIG. [4](#page-2-2). Typical energy dependence of time $T(E,d)$ in Eq. (4) and the action $S(E,d)$ in Eq. ([6](#page-2-5)) for the closed-orbit discussed in the text. In the figures $d=60a_0$, where a_0 is the Bohr radius. See text and Fig. [3](#page-3-0) for *Em*.

The action $S(E,d)$ is given in Eq. ([6](#page-2-5)). The amplitude *A* is calculated by $\lceil 4 \rceil$ $\lceil 4 \rceil$ $\lceil 4 \rceil$

$$
A = \left| \frac{\det J^{(2)}(\rho, z, 0)}{\det J^{(2)}(\rho, z, T)} \right|^{1/2} \left| \frac{\rho(0)}{\rho(T)} \right|^{1/2}, \quad (12)
$$

where T is the time of the closed orbit evaluated in Eq. (4) (4) (4) . $J^{(2)}(\rho, z, t)$ is a 2 × 2 Jacobian matrix given by

$$
J^{(2)}(\rho, z, t) = \begin{pmatrix} \frac{\partial \rho}{\partial t} & \frac{\partial z}{\partial t} \\ \frac{\partial \rho}{\partial \theta} & \frac{\partial z}{\partial \theta} \end{pmatrix},
$$
(13)

where the elements of the 2×2 Jacobian matrix are calculated with respect to the closed orbit. If the detached electron is initially on the sphere of radius *R* and moves out with velocity *k* in the direction of θ , for the ρ coordinate we have $\rho(t, \theta) = R \sin \theta + tk \sin \theta$. For the closed orbit the initial outgoing angle $\theta=0$, and it gives $\partial \rho / \partial t=0$ and $\partial \rho / \partial \theta = R + tk$. Thus, we have det $J^{(2)}(\rho, z, t) = -\dot{z}(t)(R + tk)$. For the closed

orbit we also have $\dot{z}(0) = k$ and $\dot{z}(T) = -k$. Using these results in Eq. (13) (13) (13) and Eq. (12) (12) (12) we obtain

$$
A = \left| \frac{kR}{-k(R + tk)} \right|^{1/2} \left| \frac{R}{R + tk} \right|^{1/2} = \frac{R}{R + tk},
$$
 (14)

which is valid for the propagation from the sphere of radius *R* out and back to the sphere of radius *R*. Inside the sphere, the wave function can be approximated by an incoming plane wave. The returning wave must match the plane wave on the sphere. In the present case, the returning wave can be well approximated by a plane wave traveling in the negative *z* direction,

$$
\Psi_{\text{ret}}(\mathbf{q}) = g_{\text{metal}}e^{-ikz},\tag{15}
$$

where g_{metal} is independent of z and is calculated by the matching procedure. The result is

$$
g_{\text{metal}} = \frac{1}{kT} e^{i(S-\pi/2)} \frac{4iBk}{(k_b^2 + k^2)^2},\tag{16}
$$

where *T* and *S* are the time and action of the closed orbit in Eq. (4) (4) (4) and Eq. (6) (6) (6) . Substituting Eq. (16) (16) (16) and Eq. (15) (15) (15) in Eq. (9) (9) (9) and carrying out the overlap integral, we obtain the oscillatory part of the cross sections

$$
\sigma_r(E,d) = \frac{8\pi^2 B^2 \sqrt{2E}}{c(E_b + E)^3 T(E,d)} \cos[S(E,d)],
$$
 (17)

where the detached-electron energy *E* is greater than zero but less than the energy *Em*.

When the energy E is greater than E_m , the detached electron will never return to the hydrogen atom and there is no closed orbit. Consequently, the oscillatory term $\sigma_r(E,d)$ is zero according to closed-orbit theory. Therefore, the abovethreshold photodetachment cross section of H[−] near a metal surface for a laser polarized perpendicular to the metal surface can be written as

$$
\sigma(E,d) = \frac{16\pi^2 \sqrt{2}B^2 E^{3/2}}{3c(E_b + E)^3} + U(E_m - E)
$$

$$
\times \frac{8\pi^2 B^2 \sqrt{2E}}{c(E_b + E)^3 T(E,d)} \cos[S(E,d)], \quad E \ge 0,
$$
 (18)

where $U(E_m - E)$ is the unit step function,

$$
U(E_m - E) = \begin{cases} 1 & \text{if } E_m - E > 0, \\ 0 & \text{if } E_m - E < 0. \end{cases}
$$
 (19)

For energy below photodetachment threshold $E \le 0$, the cross section is finite because of quantum tunneling effect. The case is similar to that in the static electric field $\left[27\right]$ $\left[27\right]$ $\left[27\right]$. The formula can be written as

$$
\sigma(E,d) = \frac{\pi^2 B^2}{c d^2 (E_b + E)^3} \exp[-2S_t(E,d)], \quad E \le 0, \tag{20}
$$

where

$$
S_t(E,d) = \int_{z_t}^{0} \sqrt{2\left(\frac{1}{4d} - \frac{1}{4(d+z)} - E\right)} dz, \qquad (21)
$$

where z_t is given by the same expression as z_m right after Eq. (2) (2) (2) except the energy *E* is less than zero. The above integral can be worked out $[28]$ $[28]$ $[28]$. The result is

$$
S_t(E,d) = -d\sqrt{-2E} + \frac{1}{2}\sqrt{\frac{2d}{1-4dE}}\ln[\sqrt{(1-4dE)} + \sqrt{-4Ed}], \quad E \le 0.
$$
 (22)

In Fig. [5](#page-5-1) we show the cross section described by Eq. (18) (18) (18) , Eq. (19) (19) (19) , Eq. (20) (20) (20) , and Eq. (22) (22) (22) as a function of photon energy $E_{\text{photon}} = E + E_b$ (solid line) for $d = 60a_0$. The photodetachment cross section without the metal surface is shown as the dotted line for comparison. For this *d* value, we have $E_c = E_b + E_m = 0.867$ eV. The vertical dashed lines indicate the photodetachment threshold where the photon energy is equal to E_b and the vertical dashed-dotted lines mark the position where the photon energy is equal to E_c . The whole energy range is divided into three regions. In the region on the lefthand side of the vertical dashed lines, which is below photodetachment threshold, the photodetachment cross section of free negative ion is zero. But when a metal surface is nearby, the detached electron can tunnel through the potential barrier induced by the metal. Consequently the photodetachment cross section becomes finite in the presence of a metal surface. The most interesting change caused by the metal surface is in the region with photon energy between threshold and the energy E_c . When the metal surface is nearby, the photodetachment cross section becomes oscillatory. The oscillation corresponds to the closed orbit of the detached electron and is the signature of the interference between the returning electron and the initial outgoing electron. For a fixed distance *d* between the negative ion and the metal surface, as the photon energy increases and approaches E_c , the oscillation frequency increases but the oscillation amplitude decreases. Finally in the third region on the right-hand side of the vertical dashed-dotted lines, the cross section with the metal surface is the same as the cross section without the metal surface.

IV. SCALING RELATIONS

Scaling relations are important in the analysis of photoionization cross sections $[29]$ $[29]$ $[29]$. For the present system, scaling relations also exist and can be explored. In Eq. (1) (1) (1) if we transform variables according to $r = dr'$, $p = d^{-1/2}p'$, then we find the scaled Hamiltonian is

$$
h = \frac{1}{2} (p_{\rho}^{\prime 2} + p_{z}^{\prime 2}) - \frac{1}{4(1+z')} + \frac{1}{4}.
$$
 (23)

If we define the value of h as the scaled energy ε , then the time $T(E,d)$ in Eq. ([4](#page-2-2)) and the action in Eq. ([6](#page-2-5)) of the closed orbit can be written as

$$
T(E,d) = \left(\frac{\varepsilon}{E}\right)^{3/2} \hat{T}(\varepsilon),\tag{24}
$$

FIG. 5. The photodetachment cross section of H[−] at a distance $d=60a_0$ away from a metal surface as a function of photon energy (solid line). The laser polarization is perpendicular to the metal surface. The dotted lines represent the photodetachment of a free negative ion. The vertical dashed lines at E_b =0.754 eV is the photodetachment threshold and the dashed-dotted lines mark the special energy $E_c = E_b + \frac{1}{4d}$ above threshold. The metal surface induces an oscillation in the region sandwiched between the vertical dashed lines and the dashed-dotted lines. The metal surface also makes the cross section below threshold finite because of quantum tunneling effect. Above E_c the photodetachment cross section is not affected by the metal surface according to closed-orbit theory. Note the energy scale below threshold is different.

$$
S(E,d) = \sqrt{\frac{\varepsilon}{E}} \hat{S}(\varepsilon),
$$
\n(25)

where $\hat{T}(\varepsilon)$ and $\hat{S}(\varepsilon)$ are, respectively, the time and action of the closed orbit of the scaled system in Eq. (23) (23) (23) calculated at energy $\varepsilon = Ed$. The expressions for $\hat{T}(\varepsilon)$ and $\hat{S}(\varepsilon)$ can be obtained from $T(E,d)$ in Eq. ([4](#page-2-2)) and $S(E,d)$ in Eq. ([6](#page-2-5)) by setting *d* to 1 and *E* to ε . For $S_t(E,d)$ we also have the scaling relation $S_t(E,d) = \sqrt{\frac{\varepsilon}{E}} \hat{S}_t(\varepsilon)$ except the energy *E* and ε are both less than zero. Similarly $\hat{S}_t(\varepsilon)$ can be obtained from $S_t(E,d)$ in Eq. ([22](#page-4-6)) by setting *d* to 1 and *E* to ε .

Using the scaling relations for $T(E,d)$ and $S(E,d)$ in Eq. (24) (24) (24) and Eq. (25) (25) (25) , one can write the oscillatory term in the photodetachment cross sections in Eq. (18) (18) (18) in an alternative way. Let us fix a scaled energy ε and then vary both E and d of the original system in Eq. ([1](#page-1-2)) such that $Ed = \varepsilon$. Define a new variable $w = \sqrt{\frac{e}{E}}$. The oscillatory term in Eq. ([18](#page-4-3)) can be turned to

$$
\sigma_r = \frac{8\pi^2 B^2 \sqrt{2\varepsilon}}{c(E_b + \varepsilon/w^2)^3 w^4 \hat{T}(\varepsilon)} \cos[w\hat{S}(\varepsilon)].
$$
 (26)

Equation ([26](#page-5-3)) shows that $w^4 \sigma_r$ is an oscillation with a phase linear in the new variable *w* and a constant amplitude if E_b $\geq \varepsilon/w^2$ or $E_b \geq E$.

V. COMPARISONS WITH THE STATIC ELECTRIC FIELD CASE

Near threshold the photodetachment cross sections near a metal surface look similar to the photodetachment cross sections in a static electric field. As the energy increases, the differences of the two cross sections also increases. When the energy is larger than E_c , the oscillation of the cross section near a metal vanishes, but the oscillation in the other system is still present.

The similarity in the cross sections of the two systems near threshold can be further quantified. We now show that for energy near threshold the photodetachment cross sections near a metal surface can be approximated by the photodetachment cross sections in a static electric field with field strength $1/4d^2$. To do this, we note when the energy is close to threshold, the motion of the closed orbit for the detached electron is limited to a small region of space near the hydrogen atom, the potential in the Hamiltonian in Eq. (1) (1) (1) can be approximated by

$$
-\frac{1}{4(d+z)} + \frac{1}{4d} \approx \frac{1}{4d^2}z.
$$
 (27)

When this approximation is used in Eq. (1) (1) (1) , the Hamiltonian becomes identical to that in a static electric field with strength $1/4d^2$. The returning time $T(E,d)$ and the action $S(E,d)$ for small *E* can be approximated as

$$
T(E,d) \sim 8\sqrt{2}d^2\sqrt{E},
$$

$$
S(E,d) \sim \frac{16}{3} \sqrt{2} d^2 E^{3/2}, \quad E \to 0. \tag{28}
$$

Using $F = \frac{1}{4d^2}$ and the above approximations for $T(E,d)$ and $S(E,d)$ in Eq. ([18](#page-4-3)), one immediately finds the cross sections near a metal surface are the same as the photodetachment cross sections in a static electric field with field strength *F* $=\frac{1}{4d^2}$ $=\frac{1}{4d^2}$ $=\frac{1}{4d^2}$ [4].

VI. CONCLUSIONS

We have proposed a model for the photodetachment of H[−] near a metal surface based on the image method and studied the cross sections using closed-orbit theory. We found that the metal surface modifies the photodetachment cross section below and above photodetachment threshold. Below photodetachment threshold, the cross section becomes nonzero because of quantum tunneling of a detached-electron crossing a potential barrier induced by the metal. Above photodetachment threshold, the cross section becomes oscillatory. As the photon energy increases, the oscillation frequency increases but the oscillation amplitude decreases. When the photon energy reaches and exceeds a special energy E_c , the oscillation disappears completely. If *d* is the distance between the negative ion and the metal surface, then E_c is $\frac{1}{4d}$ above threshold. In closed-orbit theory the oscillation above threshold is associated with a closed orbit of the detached electron. The disappearance of the oscillation above E_c reflects the disappearance of closed orbits. Scaling relations suggest the

best way to study the above threshold oscillation is to vary both the energy *E* and the distance *d* in such a way that the product $Ed = \varepsilon$ is a constant. As a function of $w = \sqrt{\frac{\varepsilon}{E}}$, the oscillation phase is linear and the oscillation amplitude multiplied by $w⁴$ is also approximately constant. We found close to threshold the effects of the metal surface on the cross section is equivalent to a static electric field with field strength $F = \frac{1}{4d^2}$. Finally we note that the formulas for the cross sections in Eq. (18) (18) (18) and Eq. (20) (20) (20) are derived for laser polarization perpendicular to the metal surface. When the laser polarization is at an angle θ_L with the perpendicular direction of the metal surface, closed-orbit theory can still be applied $\lceil 27 \rceil$ $\lceil 27 \rceil$ $\lceil 27 \rceil$. The results are simple: The cross sections with a laser polarization angle θ_L are obtained by multiplying $cos^2(\theta_L)$ to Eq. ([20](#page-4-5)) and to the oscillatory term (second term) in Eq. ([18](#page-4-3)).

Like the collisions of Rydberg atoms and metal surface [[30,](#page-6-21)[31](#page-6-22)], photodetachment near a metal surface provides a sensitive probe of the interactions between the atoms and the surface. For example, the distance *d* between the ion and the metal surface can be extracted from the oscillatory photodetachment cross section. We hope the present theoretical results will encourage experimental investigations of photodetachment process near a metal surface.

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