Vol 17 No 8, August 2008
1674-1056/2008/17(08)/2932-06

Chinese Physics B

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Correspondence between classical dynamics and recurrence spectra of Rydberg hydrogen atom near a metal surface*

Li Hong-Yun(李洪云), Gao Song(高 嵩), Zhou Hui(周 慧),
Zhang Yan-Hui(张延惠), and Lin Sheng-Lu(林圣路)†

College of Physics and Electronics, Shandong Normal University, Jinan 250014, *China*

(Received 4 January 2008; revised manuscript received 30 January 2008)

The chaotic behaviours of the Rydberg hydrogen atom near a metal surface are presented. A numerical comparison of Poincaré surfaces of section with recurrence spectra for a few selected scaled energies indicates the correspondence between classical motion and quantum properties of an excited electron. Both results demonstrate that the scaled energy dominates sensitively the dynamical properties of system. There exists a critical scaled energy ε_c, for $\varepsilon < \varepsilon_c$, the system is near-integrable, and as the decrease of ε the spectrum is gradually rendered regular and finally turns into a pure Coulomb field situation. On the contrary, if $\varepsilon > \varepsilon_c$, with the increase of ε, the system tends to be non-integrable, the ergodic motion in phase space presages that chaotic motion appears, and more and more electrons are adsorbed on the metal surface, thus the spectrum becomes gradually simple.

Keywords: Poincaré surfaces of section, closed-orbit theory, recurrence spectra, chaos
PACC: 3450D, 0365S, 0545

1. Introduction

The hydrogen atom near a metal surface is a typical theoretical model which gives rise to rich dynamics and a variety of experimental responses in surface physics.[1] The photoabsorption and its dynamical properties have attracted much attention for many years.[2−4] The problem of a Rydberg hydrogen atom at a large distance from the metal surface has been considered in the approximation of the so-called instantaneous van der Waals interaction. Salas and Simonovic have represented quantum, classical and semiclassical dynamics of a Rydberg hydrogen atom in the instantaneous van der Waals potential.[4] When the Rydberg hydrogen atom approaches the surface, the interaction of atom with the surface cannot be considered simply as the instantaneous van der Waals interaction.

The closed-orbit theory developed by Du and Delos is one of the effective techniques to deal with the photoabsorption spectra involving chaotic classical dynamics.[5,6] The theory has been successfully applied to some atom and molecule systems in strong external fields.[7−14] In 2005, Du *et al* extended the electronic closed-orbit theory to that of radiated photon.[15] In 2006, Yang *et al* applied the closed-orbit theory to the approach to the photodetachment of H^- near an interface.[16] Wang *et al* first calculated the photoabsorption of the Rydberg hydrogen atom near a metal surface by using this theory,[17] but the contribution of the repetitive orbits induced by the Coulomb scattering was not considered. Moreover, the relation between the scaled energy and dynamical property of the system has not been analysed up to now. Although some of the previous investigations were devoted to analysing the structure of Poincaré surfaces of section,[18] the question is still opaque due to the lack of connection with corresponding quantum spectrum for the problem. In this paper, the accurate Hamiltonian has taken into account the entire atom–surface potential and the effect of the Coulomb scattering. In order to describe the correspondence between classical dynamics and quantum behaviours we analyse the structure of Poincaré surface of section and the recurrence spectra for several selected scaled energies. Comparing both numerical results, we present that the scaled energy dominates sensitively the dynamical properties of system. The electron motions that

*Project supported by the National Natural Science Foundation of China (Grant Nos 10774093 and 10374061).
†Corresponding author. E-mail: sllin@sdnu.edu.cn

are initial regular will, when subjected to an increase in the scaled energy step by step (it can be arrived by increasing the principal number n or decreasing the distance between the nucleus and the metal surface), gradually transform to a state of chaos, which corresponds to the case of adsorption of electrons to the metal surface. The paper is organized as follows: in Section 2, we discuss Hamiltonian of the hydrogen atom near a metal surface and give a rigorous formula for calculating the recurrence spectrum by using the closed-orbit theory. In Section 3 we investigate the dynamical behaviours based on the analysing of the Poincaré surface of section of phase space and the recurrence spectra at different scaled energies. Some concluding remarks and discussion are given in Section 4.

2. Theory and method

2.1. The Hamiltonian of the hydrogen atom near a metal surface

Figure 1 is a schematic diagram of the system. The hydrogen nucleus lies at the origin of the coordinates system with the electron at a distance r

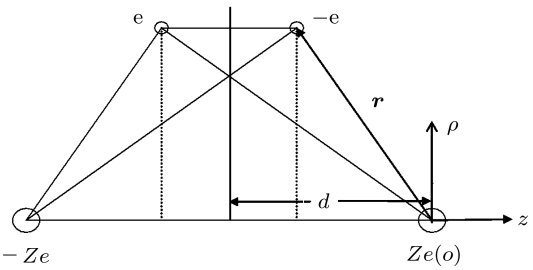


Fig.1. Diagram of the hydrogen atom near a metal surface.

from the nucleus and the z axis perpendicular to the metal surface which is sited in the $d = -z$ plane. Using electrical image potential method,[19] the Hamiltonian of the hydrogen atom takes the following form (we use atomic units in hereafter unless otherwise mentioned):

$$H = \frac{p^2}{2} - \frac{1}{r} + \frac{1}{\sqrt{\rho^2 + (2d+z)^2}} - \frac{1}{4(d+z)}, \quad (1)$$

where $r = (\rho^2 + z^2)^{1/2}$ and $p^2 = p_\rho^2 + \dfrac{l_z^2}{\rho^2} + p_z^2$. The last two terms on the right-hand side in expression (1) called electrical mirror image potential are induced by the metal surface. Because of the cylindrical symmetry, the z-component of angular momentum is conserved, therefore the φ-motion can be ignored. The system thus has two degrees of freedom. Here we consider only the case of $m = 0$ (i.e. $l_z = 0$) for convenience. Then the Hamiltonian is reduced to

$$H = \frac{p_\rho^2 + p_z^2}{2} - \frac{1}{\sqrt{\rho^2 + z^2}} + \frac{1}{\sqrt{\rho^2 + (2d+z)^2}} - \frac{1}{4(d+z)}. \quad (2)$$

To gain a correspondence between the quantum mechanics and classical dynamics, we introduce scaling variables according to the transformations $\tilde{r} = r/d$ and $\tilde{p} = p\sqrt{d}$. So Hamiltonian (2) can be rewritten as

$$Ed = \varepsilon = \frac{p^2}{2} - \frac{1}{\sqrt{\rho^2 + z^2}} + \frac{1}{\sqrt{\rho^2 + (2+z)^2}} - \frac{1}{4(1+z)}, \quad (3)$$

where the tildes have been omitted for simplicity. This scaled Hamiltonian (3) no longer depends on atom–surface distance d. Consequently, all the classical properties of the system do not depend on energy E or atom–surface distance d any longer but only on scaled energy ε. In addition, another crucial role in scaling transformation may be understood by noting that the position and the momentum comply with the commutation relation $[\tilde{r}, \tilde{p}] = \mathrm{i}d^{-1/2} = \mathrm{i}\hbar_{\mathrm{eff}}$ in scaling variables, which in turn introduces an effective Planck's constant $\hbar_{\mathrm{eff}}$ that can be used to comprehensibly incarnate the semiclassical limit by increasing the atom–surface distance d.

To eliminate the Coulomb singularity in the Hamiltonian, we adopt the semi-parabolic coordinates $u^2 = r + z$ and $v^2 = r - z$, and relative momentums $p_u = \mathrm{d}u/\mathrm{d}\tau$ and $p_v = \mathrm{d}v/\mathrm{d}\tau$, while the new time variable is defined as $\mathrm{d}\tau = \dfrac{1}{u^2 + v^2}\mathrm{d}t$.[10] This results in a regularized Hamiltonian as follows:

$$H = \frac{1}{2}(p_u^2 + p_v^2) - \varepsilon(u^2 + v^2) + \frac{2(u^2 + v^2)}{\sqrt{(u^2 + v^2)^2 + 8(u^2 - v^2) + 16}} - \frac{u^2 + v^2}{2(2 + u^2 - v^2)}. \quad (4)$$

By calculating expression (4), there is found a critical scaled energy value $\varepsilon_{\mathrm{c}} = -1.4922$ where the Coulomb interaction is comparable with the atom–surface interaction.

2.2. Closed-orbit theory

In the closed-orbit theory, the photoabsorption rate is proportional to the oscillator strength density that is composed of a smooth back-ground term and the oscillating part involving a sum of contributions of all allowed closed orbits.[5] The oscillating part that needs emphatically considering can be written in a more explicit form as follows:

$$F(E) = \sum_j \sum_n C_j^n \sin[nS_j - \Phi_j^n], \tag{5}$$

where

$$C_j^n = \begin{cases} -E_{\rm i} 2^{19/4} \pi^{3/2} r_0^{-1/4} [\sin\theta_{\rm i}^j \sin\theta_{\rm f}^{j,n}]^{1/2} A_j^n y(\theta_{\rm i}^j) y^*(\theta_{\rm f}^{j,n}), & (\theta_{\rm i}^j \neq 0, \pi); \\ -E_{\rm i} 2^{9/2} \pi r_0^{-1/2} A_j^n y(\theta_{\rm i}^j = 0) y^*(\theta_{\rm f}^{j,n} = 0), & (\theta_{\rm i}^j = 0, \pi). \end{cases} \tag{6}$$

and

$$\Phi_j^n = \begin{cases} \frac{1}{2}\pi\mu_j^n + \frac{3}{4}\pi, & (\theta_{\rm i}^j \neq 0, \pi); \\ \frac{1}{2}\pi\mu_j^n + \frac{1}{2}\pi & (\theta_{\rm i}^j = 0, \pi). \end{cases} \tag{7}$$

Here, the subscript j runs over all the primitive closed orbits and n denotes their repetition times caused by the Coulomb nuclear potential. The recurrence amplitude C_j^n of the relevant closed orbit contains the information about its semiclassical amplitude A_j^n, the corresponding initial and final angles, $\theta_{\rm i}^j$ and $\theta_{\rm f}^{j,n}$, and the matrix element of the dipole operator between the initial state and the final state that is approximately represented as the zero-energy Coulomb scattering wave function. S_j is the action of the primitive closed orbit and Φ_j^n is an additional phase including the Maslov index μ_j^n and other geometrical considerations. Further details are given in Refs.[5,6].

After the scaling transformation, the scaled action is

$$S_j = w\tilde{S}_j, \tag{8}$$

where $w = 2\pi\sqrt{d}$. The sinusoidal oscillation terms in expression (5) are replaced by

$$F(w) = \sum_j \sum_n C_j^n \sin(wn\tilde{S}_j - \Phi_j^n). \tag{9}$$

In the interval $[w_1, w_2]$, we perform a Fourier transformation to obtain the recurrence spectrum

$$F(\tilde{S}) = \int_{w_1}^{w_2} F(w) {\rm e}^{-{\rm i}w\tilde{S}} {\rm e}^{-(w-w_0)^2/\delta} {\rm d}w \tag{10}$$

with $w_0 = (w_1 + w_2)/2$ and $\delta = (w_2 - w_1)^2$. In numerical computation the windowing function $\exp(-(w - w_0)^2/\delta)$ has been used to eliminate artificial side peaks in the recurrence strength. In this paper we choose the module $\left|F(\tilde{S})\right|$ for defining the recurrence spectrum and only concentrate our attention on the contributions of the shorter closed orbits in the hope of obtaining the spectrum in a definite resolution.

3. Results and discussion

3.1. Poincaré surface of section

The classical trajectories in phase space often have very involved global features which are apparent contradiction to the locally smooth flow. Poincaré proposed to deal with this problem by intercepting the flow at discrete times. The Poincaré surface of section is one of good tool to analyse the classical properties of dynamic system.[20] By numerically integrating the equations of motion associated with expression (4), the Poincaré surface of section can be built and chaotic or regular behaviours of the classical dynamics can be examined. For a Hamiltonian system with four-dimensional phase space for two degrees of freedom, the classical motion is restricted to a three-dimensional energy torus and the Poincaré surface of section is a two-dimensional cut of this torus, which consists of isolated points. Because the dimension of the section is one less than that of the flow, the map is easier to analyse and there are an infinite number of ways to specify the surface of section in general. In this paper we have set the phase space by using the surface of section with $p_v > 0$ and $u = 0$, thus we obtain Poincaré surface of section in v, p_v plane. Figure 2 presents the numerical computation at a critical scaled energy value ($\varepsilon_{\rm c}$) of -1.4922. The broken line in Fig.2 denotes the boundary of the section, i.e. the

area that the electron can reach, which is just closed. The boundary of the section can be obtained from the following equation:

$$p_v^2 = 4 + 2\varepsilon v^2 - \frac{4v^2}{4 - v^2} + \frac{v^2}{2 - v^2}. \qquad (11)$$

Several isolated fixed points in surface of section are the centres of concentric closed loops that are defined as a basin or a mountain as shown in a topographic map. Between these mountains and basins, there are separating lines with self-intersection which correspond to the librating or rotating closed orbits.

As is known, each periodic orbit generates a fixed point in the section. Elliptic fixed point is linearly stable, while hyperbolic fixed point is unstable. A quasiperiodic orbit generates an invariant curve, whereas chaotic orbits densely fill a finite volume and the chaotic regions usually appear around hyperbolic fixed points. There are five fixed points and a lot of invariant curves in Fig.2, which imply that no chaos appears. In Fig.3, we depict three periodic orbits which lead to three elliptic fixed points and two hyperbolic fixed points. The elliptic fixed point at the centre of the figure corresponds to the periodic stable orbit $u = v$, i.e. $z = 0$ (perpendicular to the metal surface), which is shown in Fig.3(a), the other two elliptic fixed points correspond to the periodic stable orbit shown in Fig.3(b), which is elliptical in shape, and the hyperbolic fixed points correspond to the periodic unstable orbit indicated in Fig.3(c).

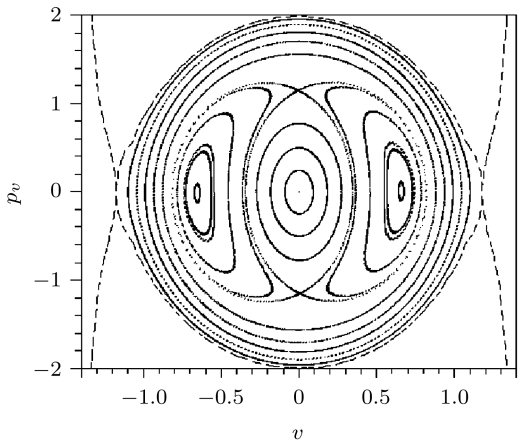


Fig.2. Poincaré surface of section of the Rydberg hydrogen atom near a metal surface at a critical scaled energy value (ε_c) of −1.4922.

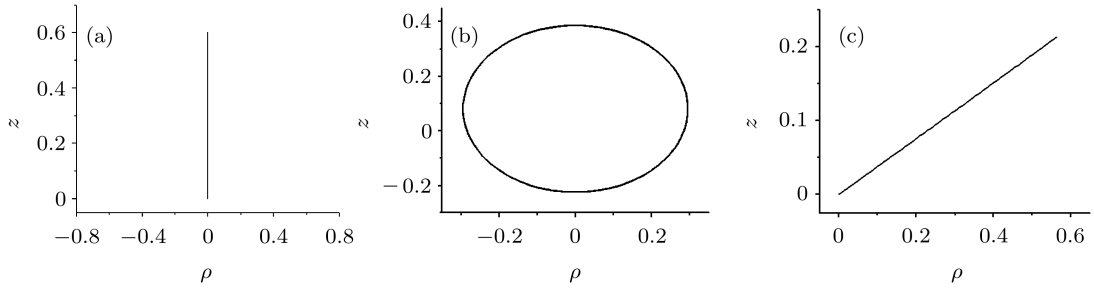


Fig.3. Three periodic orbits corresponding to different fixed points for a critical scaled energy value (ε_c) of −1.4922.

The evolution of chaos with scaled energy is illustrated as Poincaré surface of section in Fig.4. Surfaces of section are computed for the values of scaled energy ranging from −1.8 to −0.2. The five fixed points, i.e. the periodic orbits, always exist with scaled energy varying, but the number of the quasiperiodic orbits changes. For $\varepsilon < \varepsilon_c$, the image potential is less important than the Coulomb term, electron motion is regular and its classical orbits are always quasiperiodic. The boundary of section is closed at all times, and electrons can never be captured by the metal surface. When the scaled energy decreases within a definite interval, the structure of Poincaré surface of section does not change obviously except that the boundary of section becomes small. For $\varepsilon > \varepsilon_c$, the boundary of section is not closed due to the role of the image potential, the electron–surface interaction becomes strong enough to capture the electron of the orbits and chaos begins to appear. With the increase of scaled energy, the boundary of section becomes more open, meanwhile the area that electron can reach diminishes and the capture scope increases. More and more electrons reach the capture scope and are adsorbed on the metal surface. The number of quasiperiodic orbits decreases, which implies that the ergodic domain obviously increases. At $\varepsilon = -0.2$, most of the phase space is chaotic except small regions that remain regular motion.

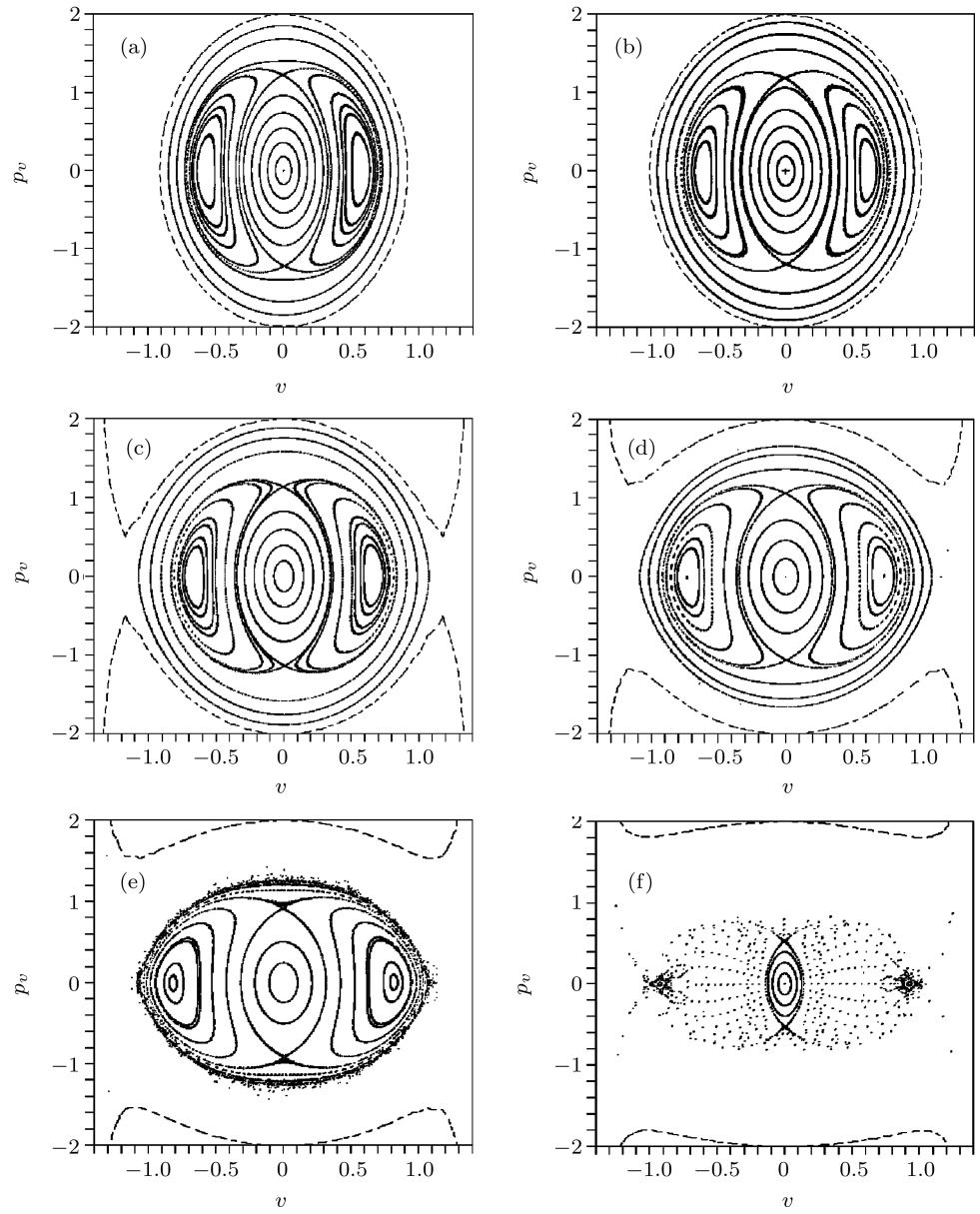


Fig.4. Poincaré surfaces of section of the Rydberg hydrogen atom near a metal surface for different values of scaled energy ε: -2.2 (a), -1.8 (b), -1.4 (c), -1.0 (d), -0.6 (e) and -0.2 (f).

3.2. The recurrence spectra of the Rydberg hydrogen atom near a metal surface

In order to obtain further insight into how the dynamical properties of the Rydberg electron near a metal surface depend on scaled energy of the system, we compute the recurrence spectra in Fig.5 at the same selected scaled energies as those in Fig.4 by using the closed-orbit theory. We choose the atomic initial state to be $2s_{m=0}$ and final state excited by Laser irradiating as $np_{m=0}$. These transitions require that the light should be polarized along the z axis. The vertical axis and the horizontal axis in Fig.5 represent the modulus of the recurrence spectrum $\left|F(\tilde{S})\right|$ and the scaled action $\tilde{S}$, respectively. Each peak in the figure corresponds to a primitive closed orbit or its repetition. We can see from Fig.5 that the spectral structure at $\varepsilon = -1.4$ is most complicated, which can refer to the significant increase of the number of closed orbits. If $\varepsilon < \varepsilon_c$, the system becomes near integrable. With the decrease of the scaled energy, the action of the electrical image potential weakens, therefore, the number of the closed obits reduces and the spectrum also becomes regular step by step finally is the same as that in the situation of pure Coulomb

field. Whereas for $\varepsilon > \varepsilon_c$, the system will tend to be non-integrable, the electron–surface interaction becomes strong enough to capture the electron of the orbits in an outer region. With the further raise of the scaled energy, more and more electrons possibly touch the metal surface and are adsorbed on it, which results in the number of the closed orbits decreasing dramatically and makes the structure of the recurrence spectrum simpler. These phenomena accord with those reflected in Poincaré surfaces of section above, which indicate that the same dynamical properties of system are displayed.

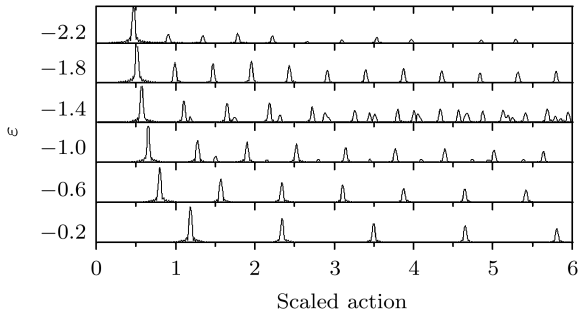


Fig.5. Recurrence spectra of the Rydberg hydrogen atom near a metal surface at the same selected scaled energies as those in the above figure.

4. Conclusion

The Poincaré surface of section of phase space together with the closed-orbit theory for investigating the dynamical impacts of the Rydberg hydrogen atom near a metal surface is a very effective method and provides a theoretical model for studying the escape and transform problem of the active particles. The scaled energy controls the structure of Poincaré surface of section and the recurrence spectral patterns, and therefore the electron motions. There exists a critical scaled energy value ε_c, on which the dynamical properties depend sensitively. At present, the interactions of Rydberg atoms and ions with metal surfaces and medium surfaces has received much attention and been widely investigated,[21] but no experimental spectrum of the hydrogen atom near a metal surface is available. This paper provides remarkable evidence that clearly reveals the correspondence between classical dynamics and quantum behaviours and therefore is useful for understanding the photoabsorption process of atoms in the vicinity of metal surface and the theoretical calculation might be used to simplify some more difficult problems.

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