Chaotic Autoionization of Molecular Rydberg States

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We investigate the energy exchange between a Rydberg electron and the molecular core in the regime where the Born-Oppenheimer approximation is violated. The theory developed allows the possibility for a strong energy exchange even for high orbital momentum of the electron when quantum defects are small. We establish the existence of a classical chaos border and of a quantum delocalization border above which diffusive autoionization of the electron takes place. The relevance of theory for autoionization of doubly excited Rydberg atoms is also discussed.

Recent experimental technique allows us to excite one electron in a molecular Rydberg state and to study the autoionization process caused by the interaction between the electron freedoms and the rotational and vibrational freedoms of the core [1-3]. From the physical viewpoint such a system represents an interesting example of a molecule in which the Born-Oppenheimer approximation is no more valid for the description of coupling between nuclear and electron motion. Indeed in this case the frequency of core motion is comparable with the frequency of the electron motion in the Rydberg state and new theoretical methods of investigation are required.

Because of the fast decrease of quantum defects with the increase of orbital momentum of the Rydberg electron, it is usually assumed that such interaction is important only when the electron passes near the molecular core. As a consequence only states with orbital momentum $l \leq 3$ could be involved in such interaction. The main idea is that for $l \geq 4$ quantum defects are negligible and therefore there should be no energy exchange between the electron and the molecular core [1-3]. In this paper we show the existence of a general mechanism of energy exchange between the molecular core and Rydberg electron which can take place for arbitrary large values of orbital momentum. We will show that such an interaction can lead to chaotic autoionization of the Rydberg electron and can be understood by constructing a simple area-preserving map which gives the change of electron energy after one orbital period.

Since we are interested in the case of large orbital momentum, the minimal distance $r_{min} \approx l^2/2$ between the electron and the core is always much larger than the size of the core a [4]. To understand the physical process we will describe the core as consisting of a positive Coulomb charge plus a rotating dipole. If the dipole moment of the core is zero then the interaction will take place due to the rotating quadrupole moment of the core.

For simplicity we will consider the case in which the electron orbit and the dipole rotation lie within the same plane so that the magnetic moment $m = l$ (the case of a

more general orientation of these planes qualitatively gives the same results). In this case the Hamiltonian, in atomic units, can be written in the form

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{L^2}{2I} - \frac{1}{r} + d\frac{x\cos\phi + y\sin\phi}{r^3}, \quad (1)$$

where d,L,I are, respectively, the dipole moment, the orbital momentum, and the moment of inertia of the core. The angle ϕ conjugate to L gives the angle between the x axis and the dipole direction.

We would like to remark that with the substitution $x = r\cos\varphi$, $y = r\sin\varphi$ in Hamiltonian (1) it is easy to see that $L + m = J$ is an integral of the motion; this corresponds to the conservation of the total momentum J of the molecule. This conservation law was extensively used in Refs. [1-3]; however, these authors assume that the electron momentum l is always less than 4 (due to small values of quantum defects for $l > 3$). Instead according to our considerations (see below) the change of l can be very large. Because of conservation of J, Hamiltonian (1) reduces to the system with 2 degrees of freedom:

$$H = \frac{p_r^2}{2} + \frac{m^2}{2r^2} + \frac{(J-m)^2}{2I} - \frac{1}{r} + \frac{d}{r^2}\cos\psi, \quad (2)$$

where $\psi = \phi - \varphi$ is the phase conjugated to m.

According to Hamiltonian (1) the phase ϕ rotates with frequency $\dot\phi = \omega = L/I$. If the energy of rotation of the core is larger than the change of electron energy after one orbital period, then the rotation frequency ω is approximately constant and system (1) can be reduced to the time-dependent Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) - \frac{1}{r} + d\frac{x\cos\omega t + y\sin\omega t}{r^3}. \quad (3)$$

Since we consider situations in which the dipole moment of the core is much less than the minimal distance r_{min} between the electron and the core, then Hamiltonian (3) can be approximately written as

$$H = \frac{1}{2}(p_x^2 + p_y^2) - [(x + d\cos\omega t)^2 + (y + d\sin\omega t)^2]^{-1/2}. \quad (4)$$

According to the Kramers-Henneberger transformation [5] the motion described by Hamiltonian (4) is the same as for a hydrogen atom in a circularly polarized monochromatic electric field with amplitude $\epsilon = d\omega^2$. This problem was studied in detail [6,7] where it was shown that the dynamics of the electron is described by the so-called Kepler map which gives the change of the electron energy after one orbital period:

$$\bar{N} = N + k\sin\Phi, \quad \bar{\Phi} = \Phi + 2\pi\omega(-2\omega\bar{N})^{3/2}, \quad (5)$$

where $N = E/\omega$ is the electron energy $E = -1/2n^2$ divided by the frequency of the dipole rotation (n is the principal quantum number). The bar indicates the new values of variables after one iteration of the map. The change of electron energy given by the first equation in (5) is defined by the rotating phase $\Phi = \omega t$ of the dipole at the moment when the electron passes near the perihelion. The second equation describes the change of the rotating phase of the dipole after one orbital period. The expression for

$$k = 2.6 d\omega^{1/3}\left[1 + \frac{l^2}{2n^2} + 1.09\omega^{1/3}l\right], \quad (6)$$

which gives the kick strength, was obtained in [6] and is correct in the regime where $\omega_0 = \omega n_0^3 > 1$ and when the orbital momentum $l < (3/\omega)^{1/3}$ (a different polarization orientation gives approximately the same k value [6]). Therefore the map (5) can be used only under the condition $d < a \ll r_{\min} \approx l^2/2 < 1/\omega^{2/3}$. From Eq. (6) it is seen that the kick strength k depends on l. However, according to [6], the change of l is small after one orbital period. The long time behavior of l can be understood by moving to the rotating frame in which the Hamiltonian of a hydrogen atom in the circular polarized field has the form [7]

$$H = \frac{p_r^2}{2} + \frac{m^2}{2r^2} - \frac{1}{r} - \omega m + d\omega^2 r\cos\psi. \quad (7)$$

Here ψ, conjugate to m, is the polar angle between electron and field direction in the rotating frame. Because of energy conservation, it is clear that during the ionization process the change of l is equal to the change of N (namely, to the number of absorbed photons). From the quantum viewpoint this relation is quite clear; indeed in circular polarized field, the momentum of photons is equal to 1, and therefore the change of the orbital momentum of the electron is equal to the number of absorbed photons, that is, $\Delta l = n_0/2\omega_0$ which, for $\omega_0 > 1$, leads only to a small change in k. Let us mention that the condition $l < (3/\omega)^{1/3}$ does not restrict the change of the energy since according to it the allowed change of energy is $(3\omega^2)^{1/3}$, which is bigger than the coupling energy of the electron if $\omega_0 \gtrsim 1$.

In order to check the validity of the map (5) we numerically integrated the classical equations of motion for the original Hamiltonian (3) and we plotted the change
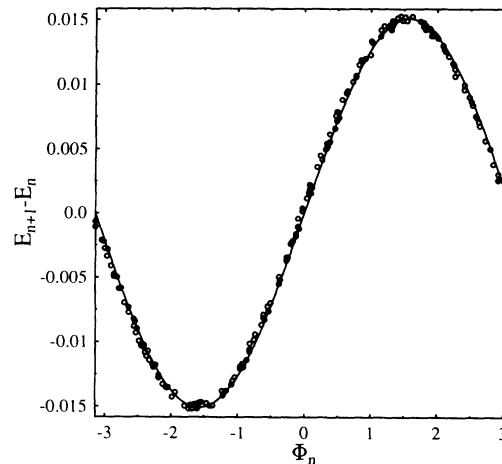

FIG. 1. Comparison of the numerically computed values $\Delta N = \bar{N} - N$ (dots) obtained by solving the system (3) for $dn_s^{-2} = 0.000\,625$, $\omega n_s^3 = 4$, $l/n_s = 0.3$, $n_0/n_s = 1.25$ and the theoretical curve $k\sin\Phi$ (full curve), with the value of k taken from (6). The value n_s fixes the classical scale.

$\Delta N = \bar{N} - N$ over one orbital period as a function of the dipole phase at perihelion. Figure 1 shows that the numerical results agree quite well with the theoretical curve $k\sin\Phi$, with the numerical value of k in agreement with expression (6), where for l we used the initial value, since its change was relatively small. A typical structure of the phase space is shown in Fig. 2(a) which is obtained from numerical integration of Hamiltonian (3). The comparison with the phase plot [Fig. 2(b)] obtained from the Kepler map (5) demonstrates that the map gives a good description of the dynamics.

The main interesting conclusion which can be drawn from our analysis is that the change of the energy after one orbital period, $k\omega$, is practically independent from the minimal distance $r_{\min} \approx l^2/2$ between the electron and the core. This result is certainly unexpected since, as can be seen from the Hamiltonian (3), the dipole interaction between the electron and the core sharply decreases with the increase of $r_{\min}$ approximately as l^4 (this corresponds to the rapid decrease of quantum defect with increasing l).

As was shown in [6] the map (5) can be reduced to the celebrated standard map and, accordingly, a transition to chaotic diffusive excitation occurs when the parameter $K = 6\pi k\omega^2 n_0^5$ becomes larger than 1. Indeed in such a case the phases Φ in (5) become random and the orbit diffuses in N space with diffusion coefficient $D = k^2/2$. This process of chaotic diffusion excitation eventually leads to ionization. The ionization time measured in the number of orbital periods is approximately $t_D = N_I^2/D$ where $N_I = 1/2n_0^2\omega$ is the number of photons required for ionization. The possibility of diffusive excitation of the electron due to energy exchange with the molecular core during one orbital period had been also discussed in [8] in which, however, the orbital momentum is considered to
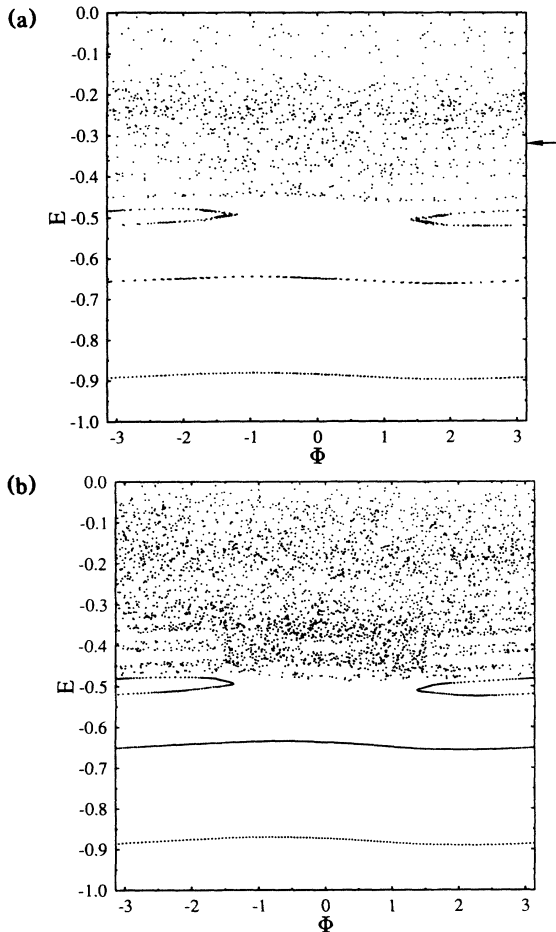
(a)

(b)

FIG. 2. (a) The phase plane (En_s^2,ϕ) for the system (3) with $dn_s^{-2}=0.000625$, $\omega n_s^3=4$, $l/n_s=0.3$. The arrow marks the initial energy of the trajectory of Fig. 1. (b) The phase plane obtained from the Kepler map (5) with the same parameters of case (a).

FIG. 3. The dependence of the energy change A on d for the quadrupole case with $\omega n_0^3=5$, $l/n_0=0.6$.

be small and the appearance of classical chaos as a necessary condition for diffusive excitation is not taken into account.

In the quantum case the situation is more complicated and two additional borders play a relevant role. First, in order that excitation can take place in the quantum

motion, it is necessary that the so-called Shuryak stability border [9] $k=1$ must be exceeded. This essentially means that the perturbation must be larger than the unperturbed level spacing; this is a pure quantum border and is not related to the nature of the classical motion. If both conditions $K>1$, $k>1$ are fulfilled, the quantum excitation takes place. However, as is now well known, quantum interference effects lead to the localization phenomenon, namely, the quantum distribution reaches a steady state which is exponentially localized in the number of photons N around the initial state, with the localization length $\ell_\phi \approx D=k^2/2$ [6]. This implies that ionization occurs if the localization length ℓ_ϕ is larger than the number of photons N_I necessary to reach continuum. The condition $\ell_\phi=1/2n_0^3\omega$ leads to the so-called quantum delocalization border $d \gtrsim 1/\omega^{5/6}n_0\sqrt{6}$. Notice that the Shuryak condition $k>1$ implies $d \gtrsim 1/5\omega^{5/3}$, and can be much more restrictive than the classical chaos border. For example, for $n_0=40$, $\omega_0=4$ we have $d \gtrsim 5$, much above the classical chaos border.

In the case where the dipole moment is equal to zero, we may consider the effect of quadrupole moment whose rotation will lead to a similar kind of mapping description. To investigate this case we consider the following model:

$$H = \tfrac{1}{2}(p_x^2+p_y^2)-0.5[(x-d\sin\omega t)^2+(y-d\cos\omega t)^2]^{-1/2}-0.5[(x+d\sin\omega t)^2+(y+d\cos\omega t)^2]^{-1/2}, \qquad (8)$$

which corresponds to the case of zero dipole moment and rotating quadrupole $Q \sim d^2$.

According to simple estimates, the change in the electron energy after one orbital period $\Delta E=2k\omega$ is of the order ω^2Q, that is, of the order of the quadrupole rotation energy. Indeed from Eq. (8), after expansion in the small parameter d, one can compute the change of energy at the first order of perturbation in d^2:

$$\Delta E \sim \frac{d^2\omega_0}{n_0^6}\int_{-\pi}^{\pi}d\xi\frac{\cos[2\omega_0(\xi-e\sin\xi)]-1}{(1-e\cos\xi)^2} \sim d^2\omega^2, \qquad (9)$$

where $e=1-l^2/n_0^2$ is the eccentricity. The term -1 in the numerator, under the integral, takes out the contribution in ΔE not connected to the quadrupole rotation. The last relation in (9) is valid for $l<(3/2\omega)^{1/3}$ (otherwise the change of the energy, as in the dipole case, is exponentially small).
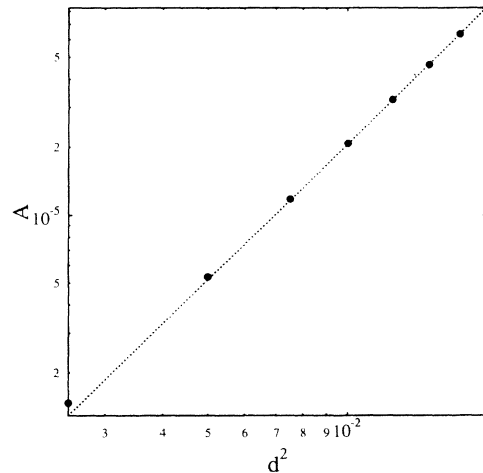
Numerical investigations show that the value of ΔE has weak dependence from orbital momentum l and can vary in the interval $\pm \omega^2 Q$. Figure 3 shows the dependence of the amplitude of the energy change $E_{n+1} - E_n = A \sin 2\Phi$ for the Rydberg electron after one orbital period as a function of the quadrupole moment $Q \sim d^2$. In agreement with the estimate (9) the dependence on Q is linear. Therefore the energy exchange between the Rydberg electron and the rotating molecule core with quadrupole moment, in the regime $r_{min}^2 \gg Q$, is described by the same kind of map (5) with $\sin 2\Phi$ in the first equation and with $k \sim Q\omega$. The main difference with the dipole case is that the Shuryak border $k > 1$ is more restrictive for the quadrupole since the interaction is weaker.

It is interesting to remark that the same types of problems arise for satellite motion around a gravitational body with rotating quadrupole moment. In this case the chaos border is given by $\Delta Q/R^2 \gtrsim 1/50\omega_0^3$ where ΔQ is the rotating part of the quadrupole of the body and R is the radius of the satellite orbit; ω_0 is the ratio between the quadrupole rotation frequency and the satellite frequency. The above border is obtained from the chaos border for a hydrogen atom with the substitution $\epsilon \sim Q\omega^{8/3}$. These considerations become relevant for deformed gravitating bodies (when $\Delta Q \sim a^2$ where a is the size of the body) with high rotation frequency (so that the frequency of this rotation is comparable with the frequency of satellites rotating close to the surface $\omega_0 \gtrsim 1$).

Another physical system in which the discussed phenomenon can play a relevant role is autoionization of alkaline earth atoms (for example, barium or strontium) with two highly excited electrons [10]. Indeed, in the case of "planetary states" when the principal quantum number n of the outer electron is much higher than that of the inner electron (n_1) the quantum defect μ leads to a precession of the Runge-Lenz vector b_1 of the inner electron with frequency $\omega = (4/n_1^3)\partial\mu_{l_1}/\partial l_1$ [10]. This precession gives the oscillating part of the dipole moment of the inner electron (with $d = n_1 b_1$) and makes this problem quite analogous to the problem of molecular Rydberg states considered above under the conditions that $\omega n^3 > 1$. To satisfy the condition that the outer electron does not touch the inner one $(n_1^2 \ll l^2)$ and the condition for the orbital momentum $l < (3/\omega)^{1/3}$ it is also necessary to have $\omega n_1^3 \ll 1$.

In conclusion, our classical analysis allows us to understand the physics of the energy exchange between the rotating molecular core and Rydberg excitation. We establish the critical value of interaction above which this ex-

change becomes chaotic, leading to diffusive autoionization of Rydberg electrons. Quantum effects can lead to suppression of this diffusive ionization, creating long living quasistationary states in the continuum spectrum of molecules. The investigation of this phenomenon in laboratory experiments will allow a better understanding of the phenomena of quantum chaos in molecular systems.

Finally, we remark that the model studied in this paper provides a simple example of a conservative system with 2 degrees of freedom in which quantum localization leads to nonergodic eigenstates on the energy surface. In particular this will imply Poisson statistics for energy levels in the localized regime.

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