Classical autoionization of two-electron atoms

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The methods of stochastic dynamics are used to investigate the process of autoionization of a classical two-electron atom. The case when the outer-electron orbit has a radius much greater than the inner-electron orbit and is highly prolate is considered. The conditions determining the stochasticity threshold for the outer-electron motion are obtained. The rate of classical autoionization of two-electron atoms, which can be treated as a process of outer-electron diffusion over the highly excited orbits, is computed.

§ 1. INTRODUCTION

The description of the highly excited states in one-electron[1,2] and two-electron[3,4] atoms on the basis of classical mechanics has undergone intense development in the last few years. In particular, the use of the Kolmogorov-Arnold-Moser (KAM) theory[5] to describe the low-frequency ionization of the classical hydrogen atom allows us to obtain for the magnitude of the critical electromagnetic-wave field and the diffusional-ionization times values that agree with the experimental data.[6] Let us also note the recent papers by Belov and Khveshchenko,[7] Solov'ev,[8] and Belov *et al.*,[9] in which the planetary model of the two-electron atom is used. In Ref. 7 the classical two-electron atom in which the radius of the outer-electron orbit is large compared to that of the inner-electron orbit is considered. In that paper the effect of the interelectron interaction on the energy of these electrons is investigated. In Ref. 8 the classical two-electron atom with the electrons moving in equivalent orbits is considered, but autoionization is not investigated. A similar problem is considered in Ref. 9.

Doubly excited Rydberg states of atoms can now be experimentally produced.[10] An attempt to compute the autoionization widths Γ_A of such states by the traditional methods based on the quantum-mechanical perturbation theory (see, for example, Refs. 11 and 12) in terms of the interelectron interaction has failed. The point is that the condition for the applicability of the perturbation theory for the Coulomb interaction of highly excited electrons has, in atomic units, the form $1/v \ll 1$, where v is the relative velocity of the electrons. For electrons from shells with principal quantum numbers n_1 and n_2 ($n_2 \gg n_1$) the quantity v will be determined by the faster one, i.e., by the inner-shell electron: $v \approx v_1 = Z/n_1$, where Z is the charge of the atomic core. We find that the condition, $n_1/Z \ll 1$, for the applicability of the quantum-mechanical perturbation theory, as applied to the Rydberg state of the inner electron, is violated for small values of Z. Accordingly, some other method that takes more explicit advantage of the quasiclassical nature of the Rydberg states should be used to compute the Γ_A. The present paper is devoted to the investigation of the possibility of the autoionization of the classical two-electron atom by the methods of nonlinear dynamics.

How does the mechanism of the classical autoionization of an atom look like? First, we shall treat both the outer- and inner-shell electrons as moving along classical trajectories. As to the atomic core, which has a charge of $+2$, we shall not be interested in its structure here: we shall simply assume that its dimensions are small compared to the radii of the orbits of the two electrons, so that we can consider this atomic core to be a point formation. The mechanism of the classical autoionization is such that the Coulomb field of the inner electron is a classical periodic perturbation for the outer electron, which can, under the influence of the perturbation, make transitions into more highly excited orbits, and, ultimately, move away to infinity. The energy conservation law is not violated as a result of some decrease of the inner-electron energy. We shall essentially consider the case of electrons in orbits differing greatly in their radii. Thus, the change in the inner-electron orbit is quite insignificant, and our problem consists in the determination of the motion of the outer electron under the action of the Coulomb field of the point core and the inner electron's field, which can be assumed given. We assume that the frequency of revolution of the inner electron in its orbit is low compared to the electromagnetic-field frequency required for the single-photon ionization of the outer electron.

The problem of the classical two-electron atom is close to the celestial-mechanics problem of three gravitating bodies: a star and two planets. Indeed, the dependence on distance for the Coulomb forces is the same as for the gravitational forces, and the only difference is that the interaction potentials for the light particles have opposite signs. The interaction is in the case of planets attractive, and repulsive in the case of electrons. Furthermore, the planets of the solar system are characterized by small orbit eccentricities whereas in the case of electrons it is necessary to take an outer orbit with a sufficiently large eccentricity, if the autoionization probability is not to be vanishingly small.

§ 2. DESCRIPTION OF THE MODEL

To simplfy exposition we assume that the two atomic electrons move in the same place. They are acted upon by the field of the point atomic core with charge $+2$ (everywhere below we use the system of units in which $e = m_e = 1$). Let us denote the radius vectors, the initial angular momenta and the energies of the electrons respectively by $\mathbf{r}_i$, $\mathbf{M}_i$, and $-E_i$ ($i = 1$ for the inner, and 2 for the outer, electron). As has already been noted in the Introduction, we shall assume that $r_2 \gg r_1$. The Hamiltonian of the two-electron atom has the form

$$H = T_1 - 2/r_1 + T_2 - 2/r_2 + 1/|\mathbf{r}_1 - \mathbf{r}_2|. \quad (1)$$

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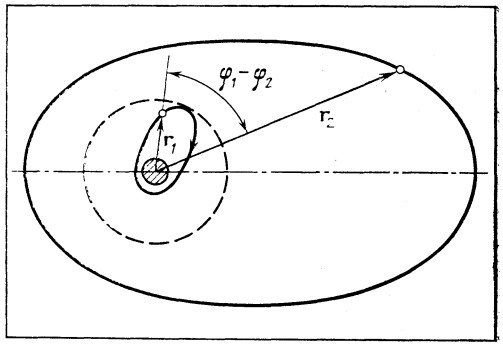

FIG. 1. Unperturbed orbits of the outer- and inner-shell electrons of a two-electron atom.

Here $T_i = (\dot{\mathbf{r}}_i)^2/2$ is the kinetic energy of the electron. The last term in (1) describes the interelectron repulsion. Let us, assuming that the inequality $r_1 \ll r_2$ always holds, simplify this last term in the expression on the right-hand side of (1):

$$|\mathbf{r}_1-\mathbf{r}_2|^{-1} \approx r_2^{-1}+\mathbf{r}_1\mathbf{r}_2 r_2^{-3}. \tag{2}$$

Here we assume that even when the outer electron is close to the atomic core (in the case of a large eccentricity) the radius of its orbit is large compared to that of the inner-electron orbit, so that the expansion (2) remains valid. Typical orbits satisfying these conditions are shown in Fig. 1.

Substituting the expansion (2) into the expression (1), we obtain

$$H=T_1-2/r_1+T_2-1/r_2+V. \tag{3}$$

Here the interaction potential V has the form

$$V=r_1 r_2^{-2}\cos(\varphi_1-\varphi_2), \tag{4}$$

where φ_1 and φ_2 are the azimuthal angles of the electrons in the plane of motion. As can be seen from (3), in the absence of the pertrubation V, the two electrons move in elliptic Kepler orbits independently of each other, but the inner electron moves in a Coulomb field with charge $+2$, while the outer electron moves in a screened field with charge $+1$. As already indicated above, we consider the motion of the inner electron as given, and are interested in the ionization of the outer electron under the action of the perturbation V. For simplicity we assume first that the inner electron moves in a circular orbit of radius r_1, i.e., that the eccentricity of the orbit of this electron is equal to zero. Denoting the inner-electron energy by $-E_1$, we obtain

$$r_1=1/E_1, \quad \omega_1=(2E_1)^{3/2}/2, \quad \varphi_1=\omega_1 t. \tag{5}$$

In the case of circular motion, the energy and angular momentum M_1 of the inner electron are connected by the relation

$$E_1 M_1^2=2. \tag{6}$$

§ 3. REDUCTION OF THE PROBLEM TO THE PROBLEM OF THE HYDROGEN ATOM IN A PERIODIC FIELD

We assume that the oribt of the outer electron is highly prolate, i.e., that its eccentricity e_2 is close to unity:

$$e_2=(1-2E_2M_2^2)^{1/2}, \quad |e_2-1| \ll 1. \tag{7}$$

Indeed, because of the conservation of the angular momentum in the course of the escape of the outer electron from the atomic core, the energy E_2 tends to zero, and the trajectory of this electron becomes more and more enlongated. The minimum radius of the outer-electron orbit is equal to

$$r_2^{min}=(1-e_2)/(2E_2) \approx M_2^2/2. \tag{8}$$

Assuming that $r_2^{\min} \gg r_1$, and using the expressions (5), we obtain the inequality

$$M_2 \gg M_1, \tag{9}$$

at which the dipole expansion (2) is valid at all points of the trajectory of the outer electron.

For the subsequent analysis of the motion of the electrons, it is convenient to go over to the action-angle variables I_i and θ_i, where $i = 1,2$ (Ref. 13). In the case of circular motion of the inner electron, the introduction of these variables is trivial: $\theta_1 = \varphi_1$ and $I_1 = M_1$. For the description of the outer-electron motion along a highly prolate trajectory, let us introduce the additional regularizing variable ψ, viz, $\theta_2 = \psi - \sin\psi$, called the eccentric anomaly.[14] In this case the variables r_2 and φ_2 are connected with the action-angle variables for the Kepler trajectory by the relations

$$r_2=I_2^2[2\sin^2(\psi/2)+M_2^2/(2I_2^2)\cos\psi], \tag{10}$$

$$\varphi_2=2\,\mathrm{arctg}[2I_2/M_2\,\mathrm{tg}(\psi/2)]. \tag{11}$$

Let us point out that the second term in the right member of (10) is, on account of the condition (7), small: $a = M_2/I_2 \ll 1$; therefore, it counts only when the outer electron is close to the atomic core (when $\psi = 2\pi m$, $m = 0,1,2...$). For this reason we can set $\cos\psi = 1$ in (10).

For the same reason the function (11) is very close to being a step function, with steps of magnitude 2π and frequency $\omega_2 = 1/I_2^3$. Since the function $\varphi_2(t)$ is used only in the form of an argument of the cosine in (4), we shall simply drop it, and rewrite the perturbation (4) in the form

$$V=r_1(4I_2^4)^{-1}(\sin^2\psi/2+a^2/4)^{-2}\cos\omega_1 t. \tag{12}$$

In the case of unperturbed motion the quantity ψ is a slowly varying periodic function of the time:

$$\theta_2=\psi-\sin\psi=\omega_2 t. \tag{13}$$

Therefore, we can, on the basis of precisely the same arguments as in Ref. 6, expand the dipole moment $d = (\sin^2\psi/2 + a^2/4)^{-2}$ in a Fourier series:

$$d=\sum_{k=0}^{\infty} d_k\cos(k\theta_2). \tag{14}$$

The coefficients d_k for the case $k \gg a^{-3} \gg 1$ of interest to us here (see the Appendix) can be estimated with the aid of the formula

$$d_k \approx 26.3/(a^6 k^{5/3}). \tag{15}$$

Let us, using the value of the parameter $a = M_2/I_2$ and the formula (19), rewrite this expression in the form

$$d_k=2.6I_2I_1^5/M_2^6. \tag{16}$$

Thus, the final expression for the atomic Hamiltonian of the outer electron has the form

$$H=-1/(2I_2^2)+\mathscr{E}\cos(\omega_1 t)\sum_{k=0}^{\infty} d_k\cos(k\theta_2), \tag{17}$$

where we have set

$$\mathscr{E}=r_1/(4I_2^4). \tag{18}$$

The Hamiltonian (17) is equivalent to the Hamiltonian for the electron of a hydrogen atom located in an external electromagnetic field with electric field intensity $\mathscr{E}$ and frequency ω_1. This allows us to use for the solution of the problem the well-known methods reviewed in Ref. 6.

§ 4. CRITERION FOR THE OVERLAP OF THE RESONANCES

The Hamiltonian (17) has been written in a form equivalent to the formula (32) in Ref. 6 (although here the Fourier coefficients d_k have a different form). In the review given in Ref. 6 the classical low-frequency ionization of the hydrogen atom by a monochromatic electro-magnetic field is considered. Let us, following Ref. 6, carry out a standard investigation of the conditions for the stochastic behavior of the solution to the problem described by the Hamiltonian (17).

Let us separate from the perturbation only the resonance term with number $k=\omega_1/\omega_2$ $(k\gg 1)$, where $\omega_2=1/I_2^3$ and $\omega_1=4/I_1^3$ are the unperturbed frequencies of the motion of the outer and inner electrons, as expressed in terms of the action variables. Let us recall that, in these variables, the radius of the inner orbit is equal to $r_1=I_1^2/2$. Using the relation (5), we obtain

$$k=4(I_2/I_1)^3. \tag{19}$$

Further, retaining only the slowly varying part of the Hamiltonian, we arrive at the standard form of the Hamiltonian[5]:

$$H_r=-3/(2I_2^4)I^2+(^1/_2)\mathscr{E}d_k\cos\theta. \tag{20}$$

Here the quantity I_2 is fixed at the resonance point (19), the new phase θ is equal to $\theta=\theta_2-\omega_2 t$, and the quantity I is a new action variable introduced in the vicinity of the resonance.

The width of the action separatrix turns out in this case to be equal to

$$\Delta I_k=(^2/_3 d_k r_1)^{1/2}. \tag{21}$$

We shall also need the width of the frequency separatrix, which differs from (20) by a constant factor:

$$\Delta\omega=(6d_k r_1)^{1/2}/I_2^4. \tag{22}$$

We obtain the distance between the resonances by differentiating the expression $\omega=\omega_1/k$ with respect to the quantity k:

$$\delta\omega\approx\omega_1/k^2. \tag{23}$$

The degree of overlap of the resonances is given by the expression

$$s=\Delta\omega/\delta\omega;$$

we use the Chirikov criterion for the overlap of the resonances in the form

$$2.5s^2>1. \tag{24}$$

In the notation used in (4)–(6) and (18), the condition (24) has the form

$$120d_k(I_2/I_1)^4>1. \tag{25}$$

Let us, using the estimate (16) for the coefficient d_k, rewrite the inequality (25):

$$313I_2^5I_1/M_2^6>1. \tag{26}$$

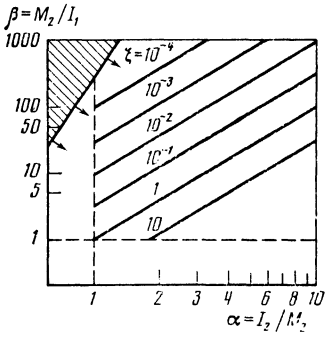

FIG. 2. The boundary, corresponding to the inequality (28), of the stochasticity region for the outer-electron orbit is hatched. The arrows indicate the direction of enhancement of the resonance overlap. The dashed lines indicate the limits $(\alpha\sim 1, \beta\sim 1)$ of applicability of the model under consideration. The continuous lines correspond to the constant values of the ratio $\xi=\alpha^4/\beta^8$.

Two parameters arise in the problem:

$$\alpha=I_2/M_2\gg 1, \quad \beta=M_2/I_1\gg 1. \tag{27}$$

Instead of the intensity of the critical field in the case of low-frequency ionization of the hydrogem atom,[6] i.e., the intensity of the field in which the process of electron diffusion over the orbits begins, there arises in the present case an inequality involving the parameters of the electron orbits:

$$\alpha^5>\beta/313. \tag{28}$$

It can be seen (see Fig 2) that, for the real situation, the boundary $(\alpha\sim 1, \beta\sim 1)$ of the region of applicability of our model lies deep inside the stochasticity region. The overlap of the resonances increases [i.e., the criterion (27) for it is fulfilled more and more conservatively] as the outer electron's "principal quantum number" I_2 (or the paramter α) increases, but ceases when we go over to the deeper-lying shells on which the inner electron is localized (i.e., when the paramter β is increased). This occurs when

$$I_1<I_2/313. \tag{29}$$

The estimate (29) is valid at values of $\alpha\sim 1$.

§ 5. COMPUTATION OF THE PROBABILITY OF AUTOIONIZATION TREATED AS A DIFFUSION PROCESS

Let us write down the expression for the diffusion coefficient in much the same way as is done in Ref. 6:

$$D=\frac{\pi}{2}(k\mathscr{E}d_k/\omega_2)^2. \tag{30}$$

Let us, substituting for the quantities entering into (30), rewrite this expression in the form

$$D=2{,}67I_1^8I_2^6/M_2^{12}. \tag{31}$$

We compute the diffusion time from the formula (59) in Ref. 6:

$$\tau_D\approx I_2^2/(2D). \tag{32}$$

The reciprocal quantity $\Gamma_A=\tau_D^{-1}$ can be interpreted as the autoionization probability per unit time (Fig. 3):

$$\Gamma_A=2D/I_2^2=5{,}34I_1^8I_2^4/M_2^{12}. \tag{33}$$

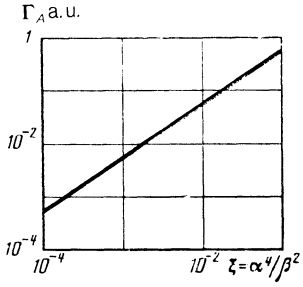

FIG. 3. Diffusional autoionization probability Γ_A per unit time, plotted as a function of the parameter $\xi = \alpha^4/\beta^8$ in accordance with the formula (34). The charge of the atomic core is equal to + 2.

In the notation introduced in (27) the autoionization probability per unit time will have the following form:

$$\Gamma_A = 5.34\alpha^4/\beta^8. \tag{34}$$

This expression has meaning when the computed diffusion time is long compared to the period of the outer-electron motion:

$$T_2\Gamma_A \ll 1, \tag{35}$$

where $T_2 = 2\pi I_2^3$.

§ 6. CONCLUSION

The principal result of the foregoing investigation is the conclusion that classical autoionization of two-electron atoms does occur, and that its probability per unit time is given by the expression (34). Let us note that the present theory cannot be applied to negative ions, since in this case autoionization should be determined by essentially quantum laws.

Let us specify the conditions under which the above-presented classical-autoionization model is valid. The first one is the condition (35) for the power-law increase of the autoionization rate in the course of the process. The second condition requires that the perturbation (4) be a low-frequency one, i.e., that $\omega_1 \ll E_2$ at

$$I_2 \ll I_1^{3/2}/2, \tag{36}$$

and is a condition that imposes limitations on the outer- and inner-electron orbit parameters.

Let us note that the transition to noncircular inner-electron orbits offers no fundamental difficulties. All the calculations carried out above will be valid if we replace r_1 by $r_1^{(m)}$ and ω_1 by $m\omega_1$, where $r_1^{(m)}$ is the Fourier coefficient with number m in the expansion of the periodic function $r_1(t)$. In this case we can consider a situation of the type of the Jupiter-Saturn resonance in celestial mechanics.[15]

APPENDIX

In this Appendix we compute the Fourier coefficients of the perturbation that are used above in the present paper. These coefficients are introduced by the relation (14), from which we find

$$d_k = \frac{1}{T}\,\mathrm{Re}\int_0^T d(\psi)\exp(ik\omega t)\,dt. \tag{A.1}$$

Here $T = 2\pi/\omega$, and the integrand contains the periodic function

$$d(\psi) = [\sin^2(\psi/2) + a^2/4]^{-2}, \tag{A.2}$$

with

$$\psi - \sin\psi = \omega t. \tag{A.3}$$

The quantity d_k means here the complex value of the integral (A.1). Differentiating (A.3), we obtain

$$d_k = \frac{2}{\pi}\int_0^{\pi} \exp[ik(\psi - \sin\psi)]\frac{\sin^2(\psi/2)}{[\sin^2(\psi/2)+a^2/4]^2}\,d\psi. \tag{A.4}$$

Let us estimate this integral with the aid of the well-known stationary-phase method. The stationary phase point is located at the left end of the integration range; therefore, let us expand the argument of the exponential function in a Taylor series around zero:

$$\psi - \sin\psi \approx \frac{\psi^3}{6} + \sum_{m=2}^{\infty}\frac{(-1)^{m+1}\psi^{2m+1}}{(2m+1)!}. \tag{A.5}$$

Let us retain the first term of the series (A.5) in the index of the exponential function and reduce the remaining terms to a pre-exponential function, using the formula $\exp(x) \approx 1 + x$. It then becomes clear that the characteristic values of ψ have the magnitude $\psi \approx (6/k)^{1/3} \ll 1$. This allows us to expand the pre-exponential power function in the integral (A.4) in a Taylor series in the small ratio $(\psi/a) \ll 1$. Indeed, from the relations (7), (9), and (19) we have $I_2 \gg M_2 \gg I_1$, whence it follows that

$$ka^3 \sim (M_2/I_1)^3 \gg 1. \tag{A.6}$$

Replacing the upper limit of integration by infinity, we obtain

$$d_k = \frac{8}{\pi a^2}\int_0^{\infty}\exp(ik\psi^3/6)\left[C_1 + \sum_{m=2}^{\infty}C_m\psi^{2m+1}\right]\sum_{n=1}^{\infty}P_n\psi^{2n}\,d\psi, \tag{A.7}$$

where we have set

$$C_1 = 1, \quad C_m = (-1)^{m+1}ik/(2m+1)!, \quad m = 2, 3, \ldots, \qquad P_n = (-1)^{n+1}na^{-2n}, \quad n = 1, 2, 3, \ldots. \tag{A.8}$$

Let us expand the series product in (A.7) in order to estimate the quantity d_k by the first nonvanishing term. Let us label the result of term by term multiplication of the series by two indices, equal to the numbers m and n of the terms to be multiplied:

$$d_k = \sum_{m,n=1}^{\infty} d_k^{(m,n)}. \tag{A.9}$$

There will then arise integrals of the form

$$I_p(k) = \int_0^{\infty}\exp(ik\psi^3/6)\,\psi^p\,d\psi, \quad p \geqslant 2. \tag{A.10}$$

The integral (A.10) reduces to a gamma function after we have made the change of variable $s = k\psi^3/6$, and closed the integration contour with the aid of a quadrant and the ordinate axis:

$$I_p(k) = 2\cdot 6^{(p-2)/3}\Gamma[(p+1)/3]\exp[i\pi(p+1)/6]k^{-(p+1)/3}. \tag{A.11}$$

Using the formula (A.11), we find that the first real terms of the series (A.9) are:

$$d_k^{(1,1)}=0, \quad d_k^{(2,1)}=-1{,}1/(a^4k^{5/3}), \quad d_k^{(1,2)}=26.3/(a^6k^{5/3}). \tag{A.12}$$

A comparison of the moduli of these terms in the case when $a=M_2/I_2\ll 1$ shows that

$$d_k^{(2,1)}/d_k^{(1,2)}\approx a^2/24\ll 1. \tag{A.13}$$

The higher-order terms of the seris (A.9) are clearly smaller than those written out above. Furthermore, as the estimate shows, the contribution of the right end of the integration range to the value of the integral (A.4) is insignificant; therefore, the value of the Fourier coefficient is equal to

$$d_k\approx 26.3/(a^6k^{5/3}). \tag{A.14}$$

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