



CLASSICAL ADIABATIC THEORY OF THE ELECTRIC FIELD IONIZATION OF HYDROGEN ATOMS

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Abstract

Classical mechanics has been applied for the theoretical study of the ionization of hydrogen atoms by static electric fields. Under assumption that the ionizing field was adiabatically switched on, various threshold fields and ionization probabilities were calculated giving new insight in the electric field ionization of the Rydberg atoms.

1 Introduction

Ionization of Rydberg atoms by electric fields has been studied over years both experimentally and theoretically [1-6]. Various theories have been applied in determining ionization field thresholds: adiabatic and diabatic level transitions, saddle point analyses, quantum and classical numerical calculations. It has been repeatedly argued [3,4,6] that if the increase of the field is adiabatically slow, the ionization should occur in a narrow range of fields around $f_{th}(a.u.) = 1/16n^4$. This result has been supported by measurements on hydrogen-like atoms like Na, Li, Ar, but not on the hydrogen itself.

In this paper we shall use classical adiabatic theory in the calculation of the ionization threshold fields and probability functions in the case of the hydrogen atom. Although most natural for hydrogen, these calculations, based on the adiabatic theorem which states [7] that actions are adiabatic invariants, have never been performed. The results, presented in Section 4 and discussed in Section 5 give new insights in the problem of field ionization of Rydberg atoms. In Sections 1-3 we recall some basic facts concerning hydrogenic Stark effect. Atomic units ($m = 1, e = 1$) are used throughout this paper.

2 Separation of variables. Actions

We are studying the motion generated by the time-dependent Hamiltonian function

$$H = \frac{p^2}{2} - \frac{1}{r} + f(t)z, \quad (1)$$

assuming that $f(0) = 0$ and $0 < \dot{f}(t) \ll 1$, i.e. assuming that the static field is switched on adiabatically slow. We shall apply adiabatic theory which assures that actions are

adiabatic invariants. To do that we need to recall some basic facts concerning the static case when the field f is fixed and the Hamiltonian function is time-independent.

For $f(t) \equiv f$ fixed the Hamiltonian function Eq.(1) separates in the so-called semi-parabolic coordinates. Indeed if we introduce the canonical transformation

$$z = (u^2 - v^2)/2, \quad \rho = uv, \quad p_z = (up_u - vp_v)/(u^2 + v^2), \quad p_\rho = (vp_u + up_v)/(u^2 + v^2), \quad (2)$$

where $\rho, \phi, z, p_\rho, p_\phi, p_z$ are the standard cylindrical (canonical) coordinates, the transformed Hamiltonian functions reads

$$H = \frac{p_u^2 + p_v^2}{2(u^2 + v^2)} + \frac{p_\phi^2}{2u^2v^2} - \frac{2}{u^2 + v^2} + f \frac{u^2 - v^2}{2}. \quad (3)$$

After introducing the new time-like variable τ with:

$$\frac{dt}{d\tau} = u^2 + v^2, \quad (4)$$

it is easy to verify that the motion generated by H , Eq.(3), in time t and at energy $H = E$, is equivalent to the motion in time τ of the Hamiltonian function

$$K = \frac{p_u^2 + p_v^2}{2} + \frac{p_\phi^2}{2u^2} + \frac{p_\phi^2}{2v^2} - E(u^2 + v^2) + f \frac{u^4 - v^4}{2} \equiv 2. \quad (5)$$

The energy E is now a coefficient in the equivalent Hamiltonian function K , while the effective energy is fixed to 2. Obviously K is separable. Indeed, the projections of the orbits of K on the $u - p_u$ and $v - p_v$ planes can be seen as trajectories of the motions generated by the two one-dimensional Hamiltonian functions:

$$h_1 = \frac{p_u^2}{2} + \frac{p_\phi^2}{2u^2} - Eu^2 + \frac{f}{2}u^4 = 1 + c, \quad (6)$$

$$h_2 = \frac{p_v^2}{2} + \frac{p_\phi^2}{2v^2} - Ev^2 - \frac{f}{2}v^4 = 1 - c, \quad (7)$$

where c is the separation constant, i.e. it is the third independent integral of motion besides $H(= E)$ and p_ϕ . For $f = 0$ the constant c coincides with the z -projection of the Runge-Lenz vector A_z . We see that for any f both Hamiltonian functions h_1 and h_2 can generate bounded motions if $E < 0$. Moreover all trajectories of h_1 are closed if $f > 0$. Therefore, for any $f \geq 0$ there is a region in the phase space of the Hamiltonian function H , Eq.(3) which contains bounded trajectories. This (simply connected) region is foliated with three-dimensional invariant tori which are labelled by the corresponding values of integrals of motion. In order that the triplet (E, p_ϕ, c) corresponds to some invariant torus it is necessary that the following three inequalities are satisfied. The first one is

$$27p_\phi^2 f^2 + 8E^3 < 0. \quad (8)$$

Let, for $f > 0$, $x_1 \leq x_2 \leq x_3$ be the real roots of the cubic equation:

$$2fx^3 + 2Ex^2 + p_\phi^2 = 0. \quad (9)$$

Under the condition Eq.(8) this equation always has three real roots. Then the other two inequalities are

$$-1 - \frac{p_\phi^2}{2x_1} + Ex_1 + \frac{f}{2}x_1^2 \leq c \leq 1 - \frac{p_\phi^2}{2x_2} + Ex_2 + \frac{f}{2}x_2^2. \quad (10)$$

For $f = 0$ (hydrogen atom) Eq.(8) becomes $E = E_0 < 0$, while Eq.(10) reduces to ($c = A_z$)

$$-1 + |p_\phi| \sqrt{-2E_0} \leq A_z \leq 1 - |p_\phi| \sqrt{-2E_0}. \quad (11)$$

The conditions (8) and (10) satisfied, the three actions $S_i = S_i(E, p_\phi, c)$, $i = 1, 2, 3$ corresponding to the invariant tori are determined with

$$S_1 = \frac{1}{\pi} \int_{u_1}^{u_2} (2(1+c) + 2Eu^2 - p_\phi^2/u^2 - fu^4)^{1/2} du, \quad (12)$$

$$S_2 = \frac{1}{\pi} \int_{v_1}^{v_2} (2(1-c) + 2Ev^2 - p_\phi^2/v^2 + fv^4)^{1/2} dv, \quad (13)$$

$$S_3 = p_\phi, \quad (14)$$

where $u_i, v_i, i = 1, 2$ are the positive roots of the corresponding integrands chosen in an obvious way. For $f = 0$ the first two of the above formulas simplify to give ($c = A_z, E = E_0$)

$$S_1 = \frac{1 + A_z}{2(-2E_0)^{1/2}} - \frac{|p_\phi|}{2}, \quad (15)$$

$$S_2 = \frac{1 - A_z}{2(-2E_0)^{1/2}} - \frac{|p_\phi|}{2}. \quad (16)$$

3 Evolution of tori

Consider now the slow increase from the zero value of the field f and choose some initial (for $f = 0$) invariant torus with E_0, p_ϕ, A_z . According to the adiabatic theorem [7], the actions S_i are approximate invariants, i.e. if f slowly increases they remain practically constant while other (for fixed f) integrals of motion E and c change arbitrarily with time (of course because of the axial symmetry, p_ϕ is exact integral of motion no matter what is the rate of change for f). In other words, the phase-space points that belonged to the same initial invariant torus will, at any given instant of time, all lie on the single torus defined with the constant values of actions S_i and changing values of $E(f(t))$ and $c(f(t))$. And this will hold until eventually the critical value of f is reached when the torus bifurcates into the cylinder, or physically, the atom ionizes. This bifurcational point obviously corresponds to the separatrix and unstable fixed point of the Hamiltonian function h_2 Eq.(7). Therefore, given E, p_ϕ and f , the corresponding critical value for c is defined with:

$$c_* = 1 + Ex_3 - \frac{p_\phi^2}{2x_3} + \frac{f}{2}x_3^2 \quad (17)$$

where x_3 is the largest real root of Eq.(9).

Now, suppose some initial (for $f = 0$) phase space point is chosen. To calculate the field intensity f_{ion} for which the corresponding trajectory of the Hamiltonian function H , Eq.(1), (with the slowly increasing field) will lead to the ionization, we have to equate the two expressions for the constant actions. One expression involves the initial values E_0 , A_z (and p_ϕ), Eqs.(15) and (16), and the other the critical ones, E , $c = c_*$ and f , Eqs.(12) and (13). In this way we obtain

$$\frac{1 + A_z}{2(-2E_0)^{1/2}} - \frac{|p_\phi|}{2} = \frac{1}{\pi} \int_{u_1}^{u_2} (2(1 + c_*) + 2Eu^2 - p_\phi^2/u^2 - fu^4)^{1/2} du, \quad (18)$$

$$\frac{1 - A_z}{2(-2E_0)^{1/2}} - \frac{|p_\phi|}{2} = \frac{1}{\pi} \int_{v_1}^{v_2} (2(1 - c_*) + 2Ev^2 - p_\phi^2/v^2 + fv^4)^{1/2} dv, \quad (19)$$

where c_* is given in Eq.(17).

Solving (for given E_0 , p_ϕ and A_z) these two equations in the unknowns E and f , we obtain the ionization function $f = f_{ion}(E_0, p_\phi, A_z)$. The ionization function completely describes the ionization process since it prescribes to any initial condition (i.e. initial torus) the field intensity for which the corresponding trajectory leads to ionization. From this function we can derive various probability functions depending on the preparation of the initial atomic state.

4 Ionization. Thresholds and probability functions

First, let us assume that only the initial energy E_0 of the hydrogen atom is specified, i.e., that the atom is prepared in the state described with the microcanonical ensemble of uniformly distributed phase space points on the energy hypersurface E_0 . In other words, the probability distribution of the phase space points is

$$dw_{E_0}(\vec{r}, \vec{p}) = const. \times \delta(E_0 - H_{st}(\vec{r}, \vec{p}, f = 0)) d\vec{r} d\vec{p}, \quad \int dw = 1. \quad (20)$$

The energy hypersurface is foliated with the tori defined with the corresponding values of p_ϕ and A_z and it is not hard to see that the above distribution function leads to the uniform distribution over tori i.e.

$$dw_{E_0}(p_\phi, A_z) = (-E_0/2)^{1/2} dp_\phi dA_z. \quad (21)$$

Given some field intensity f we can ask what is the probability of the ionization $w_{E_0}(f)$. To answer that, first we have, for given E_0 and f , to solve the equation

$$f = f_{ion}(E_0, p_\phi, A_z) \quad (22)$$

in the unknowns p_ϕ and A_z which additionally satisfy the conditions Eq.(11). The solution, if it exists, defines a curve in the $p_\phi - A_z$ plane. An example of such solution is given in Fig.1 for the case $E_0 = -1.272$ and $f = 1$. The parallelogram in the figure is the border of the region of possible values of p_ϕ and A_z for given E_0 (Eq.(11)). Clearly the points that belong to the solution curve correspond to those initial invariant tori that bifurcate when the field intensity reaches the given value. This curve divides the set of pairs (p_ϕ, A_z) into two subsets one of which, as indicated in Fig.1, corresponds to the initial conditions for

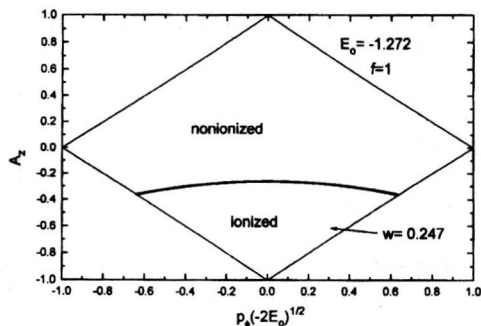


Fig 1. The solution of the equation $f = f_{ion}(E_0, p_\phi, A_z)$ in the case $E_0 = -1.272$ and $f = 1$.

which the ionization has already occurred for smaller field intensities, while for the rest of the initial tori ionization will occur for larger field intensities.

As follows from the Eq.(20), the volume of this "ionized" subset, $p_{E_0}(f)$, is proportional to the ionization probability $w_{E_0}(f)$, i.e.,

$$w_{E_0}(f) = (-E_0/2)^{1/2} p_{E_0}(f). \tag{23}$$

Due to the scaling properties (when the canonical coordinates are rescaled $q \rightarrow qf^{1/2}$, $p \rightarrow pf^{-1/4}$, the energy scales as $E \rightarrow Ef^{-1/2}$) of the Hamiltonian function H , Eq.(1), we have that the ionization probability depends on E_0 and f only through single parameter f/E_0^2 or fn_0^4 where n_0 is the principal quantum number ($E_0 = -1/2n_0^2$).

The ionization probability function $w = w(fn_0^4)$ is given in Fig.2. From this curve one can extract various threshold fields depending on the definition of the threshold. If, as in the experiment [g91], the threshold is defined as the field intensity for which the half of the initial ensemble is ionized, we find that $f_{th}(n_0) = 1/5.783n_0^4$. However, the formal threshold corresponds to the field intensity for which the initial microcanonical ensemble starts to ionize. From Fig.1 we see that this corresponds to the field for which the initial conditions $p_\phi = 0$ and $A_z = -1$ lead to ionization. Such initial conditions correspond, in quantum case, to (maximally) red shifted states in the Stark manifold. In this case Eqs.(18) and (19) can be solved analytically and the resulting threshold field $f_0(n_0)$ reads

$$f_0 = \frac{32^2}{81\pi^4} \frac{1}{n_0^4} \approx \frac{1}{7.7n_0^4}. \tag{24}$$

The opposite situation is when the initial microcanonical ensemble is completely ionized. The corresponding field intensity f_1 is that for which the initial conditions $p_\phi = 0$ and $A_z = 1$ lead to ionization. Such initial conditions correspond, in quantum case, to (maximally) blue shifted states in the Stark manifold. f_1 is also calculated analytically with the result

$$f_1 = \frac{64}{\pi^4} \left(\int_0^1 \sqrt{1-t^4} dt \right)^4 \frac{1}{n_0^4} \approx \frac{1}{2.6n_0^4}. \tag{25}$$

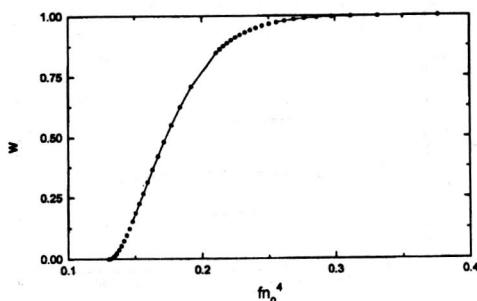


Fig. 2 The ionization probability function $w(f n_0^4)$.

More detailed information on ionization one obtains under assumption that the initial state is defined by specifying both energy E_0 and angular momentum p_ϕ . Then the initial state of the atom is described by the ensemble of uniformly distributed points on the four-dimensional surface in the phase space defined with E_0 and p_ϕ . This surface is foliated with the family of three-dimensional invariant tori parameterized with A_z and the initial state is described with the uniform distribution over tori:

$$dw(A_z) = dA_z / (2 - 2 |p_\phi| \sqrt{-2E_0}). \quad (26)$$

Given some field intensity f we can ask what is the ionization probability $w_{E_0, p_\phi}(f)$ of the initial state. To answer that, we have to solve the equation $f = f_{ion}(E_0, p_\phi, A_z)$ in the unknown A_z . If the solution is denoted by $A_z^{ion}(f; E_0, p_\phi)$, the ionization probability is

$$w_{E_0, p_\phi}(f) = \frac{A_z^{ion}(f; E_0, p_\phi) + 1 - |p_\phi| \sqrt{-2E_0}}{2 - 2 |p_\phi| \sqrt{-2E_0}}. \quad (27)$$

Due to the scaling properties of the Hamiltonian function Eq.(1) the probability function depends only on two arguments, i.e.: $w_{E_0, p_\phi}(f) = w_{|p_\phi|/n_0}(f n_0^4)$, where $E_0 = -1/2n_0^2$. In Fig.3 we give the dependence of the ionization probability on the scaled field intensities $f n_0^4$ for several values of the parameter $|p_\phi|/n_0$.

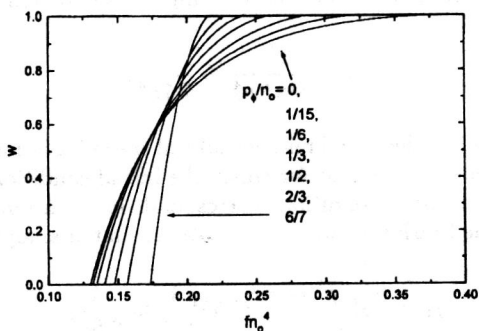


Fig 3. The ionization probability function $w_{|p_\phi|/n_0}(f n_0^4)$ for various values of the parameter $|p_\phi|/n_0$.

5 Discussion

Our calculations are in qualitative accordance with the previous results [3,6]. They also predict that those states which are Stark shifted to greater binding energies (red shifted) will ionize at lower fields than those which are shifted to lower binding energies (blue shifted), see Eq.(24) and (25), Fig.(3) and Eq.(27). However, our ionization fields $1/7.7n_0^4 \leq f \leq 1/2.6n_0^4$ are much higher than the previous result $f = 1/16n_0^4$ observed, e.g. on sodium. The reason for this discrepancy is the following [8]. In experiments, the initial atomic states always possess small angular momentum p_ϕ , almost zero in the classical limit. For small p_ϕ the dynamics in the case of hydrogen and other Rydberg atoms differ dramatically. The electron is allowed to come close to the proton (in the case of hydrogen) or atomic core (in the case of Rydberg atoms). In the case of the Rydberg non-hydrogenic atoms, the Hamiltonian function is nonintegrable (due to the additional term describing influence of the atomic core), and the motion becomes highly irregular in contrast to the case of hydrogen. This chaotic motion significantly lowers the ionization fields for $p_\phi \approx 0$, compared to those in the hydrogenic case. Therefore we expect that the measurements performed on hydrogen atom should give in the adiabatic limit the ionization fields close to our results, Figs.2 and 3.

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KLASIČNA ADIJABATSKA TEORIJA JONIZACIJE VODONIKOVIH ATOMA ELEKTRIČNIM POLJEM

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Sadržaj Klasična mehanika je primenjena za teorijsko ispitivanje jonizacije vodonikovih atoma statičkim električnim poljem. Pod pretpostavkom da je jonizaciono polje adijabatski uključivano, različiti pragovi polja i verovatnoće jonizacije su računane dajući nov doprinos razumevanju problemu jonizacije Rydbergovih atoma električnim poljem.