

Stark effect exhibited by Rydberg atoms and the near-threshold resonances of the photoionization cross section

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The Stark shifts and the widths of the Rydberg states of atoms in a strong electric field are calculated in the vicinity of $E \approx 0$. The scaling relationships are obtained for above-barrier resonances. The theoretical results are compared with the experimental data on the photoionization of hydrogen and rubidium in the presence of a static electric field.

1. Extensive investigations of the Rydberg ($n \gg 1$) states of atoms and molecules, and of their properties in external fields, etc. have been made recently. Resonances of the photoionization cross section of atoms have been found experimentally (first for rubidium¹ and then for hydrogen²⁻⁴) in the presence of a static electric field \mathcal{E} ; these resonances correspond to $n \sim 15-40$ and they lie near $E = 0$ (which is the ionization limit for $\mathcal{E} = 0$). It follows from numerical calculations^{5,6} that the positions and (less accurately) the widths of these resonances coincide with complex energies $E = E_r - i\Gamma/2$ of quasistationary Stark states (in the case of the hydrogen atom). It is particularly interesting to consider the states¹ characterized by $n_1 \sim n \gg 1$, n_2 , and $m \sim 1$ which have the lowest decay probability in a field \mathcal{E} among all the n^2 sublevels with a given value of n . We shall confine ourselves to states of this type and develop an analytic theory for $E \approx 0$, valid for an arbitrary atom, and derive the scaling relationships [Eq. (10)] for above-barrier resonances. These relationships are in good agreement with the experimental results¹⁻⁴ and can be used to identify peaks of the ionization cross section.

2. The energy of quasistationary states of the hydrogen atom in an electric field \mathcal{E} are described (for $m = 0$ and $n \gg 1$) by the system of equations (4) given in Ref. 6. If we assume that $n_1 \gg n_2, m$, use the quantum defect method, and separate approximately the variables in the range $r > r_0$ (r_0 is the radius of the atomic core), we can generalize these equations to the case of an arbitrary atom. The "reduced" energy $\varepsilon = 2n^2 E^{(n, n_2, m)}$ and the separation constants $\beta_{1,2}$ are described by

$$\begin{aligned} \beta_1 (-\varepsilon)^{-1/2} f(z_1) - (F/8n^2) (-\varepsilon)^{-3/2} g(z_1) &= \nu_1, \\ \beta_2 (-\varepsilon)^{-1/2} f(z_2) + (F/8n^2) (-\varepsilon)^{-3/2} g(z_2) &= \nu_2, \\ \beta_1 + \beta_2 &= 1. \end{aligned} \quad (1)$$

Here, $F = n^4 \mathcal{E}$ is the effective field, $z_1 = -16\beta_1 F / \varepsilon^2$, $z_2 = 16\beta_2 F / \varepsilon^2$,

$$\nu_i = \frac{n_i + (m+1)/2}{n} \left(1 - \frac{\delta}{n} \right), \quad i=1, 2, \quad (2)$$

and the functions $f(z)$ and $g(z)$ are defined in the Appendix A. The parameter $\delta = \delta(n_1, n_2, m)$ can be expressed in terms of the quantum defects for a free atom:

$$\delta = \frac{1}{n} \sum_{l=m}^{n-1} (C_{J, M-m; l, m}^{J, M})^2 [(l+1)\delta_l^+ + l\delta_l^-], \quad (3)$$

where $J = (n-1)/2$; $M = (n_1 - n_2 + m)/2$; $\delta_l^\pm \equiv \delta_{jl}$ for

$j = l \pm \frac{1}{2}$; δ_{jl} is the quantum defect for the Rydberg states. The values of δ_{jl} decrease rapidly⁷ with l , so that in the sum of Eq. (3) we are left in fact with just the first few terms. In the case of the hydrogen atom, we find that $\delta_{jl} = \delta(n_1, n_2, m) \equiv 0$; in the case of rubidium, we have $\delta(n-1, 0, 0) = 0.768, 0.538$, and 0.414 , for $n = 20, 30$, and 40 , respectively. Calculation of $\delta(n_1, n_2, m)$ presents no difficulties since the quantum defects δ_{jl} are tabulated (in the spherical basis) in Ref. 7. When we pass from $(n_1, 0, 0)$ states to other series of states, the values of $\delta(n_1, n_2, m)$ decrease (Fig. 1).

The following comments should be made about Eq. (3). The appearance of the Clebsch-Gordon coefficients $C_{J, M-m; l, m}^{J, M}$ is due to a hidden symmetry group of the hydrogen atom $SO(4)$, which explains what is known as the random degeneracy of levels in a discrete spectrum.⁸ It is known that this symmetry group can be decomposed, $SO(4) = SO(3) \otimes SO(3)$, so that passage from the parabolic basis $|n_1, n_2, m\rangle$ to the spherical one $|nlm\rangle$ in the subspace of states for a given value of n is equivalent to the addition of two moments⁹ $j_1 = j_2 = (n-1)/2$ in the $SO(3)$ group. The system of equations (1) is derived bearing in mind that a highly excited electron moves mainly in the Coulomb field of the atomic core and the deviation of the atomic field from the

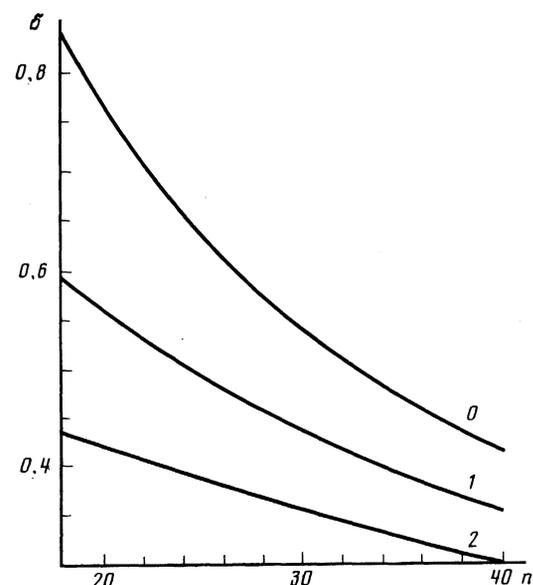


FIG. 1. Quantum defects [Eq. (3)] plotted for the $(n_1, n_2, 0)$ states of the rubidium atom; here, n is the principal quantum number of a level. The values of n_2 are given alongside each curve.

purely Coulomb one at $r \sim r_0 \ll n^2$ can be allowed for using the boundary condition. This has been employed frequently for the Coulomb systems with short-range forces^{10,11}; it should be compared with the semiclassical approach employed in dealing with the Zel'dovich effect.¹² We shall confine ourselves to just these brief comments and direct the reader to Ref. 13.

The system of equations (1) generally requires numerical calculations, but for $\varepsilon = 0$ (which corresponds to the crossing of the ionization limit $E = 0$ by a level in the absence of a field), they have the formal solution

$$F_0 = F_* (\nu_+^{1/2} - \nu_-^{1/2})^{-3}, \quad (4)$$

where $F_0 = n^4 \mathcal{E}_0$ is the reduced field corresponding to $\varepsilon = 0$,

$$\nu_+ = 1/2 [(\nu_1^2 + 1/6\pi n^2)^{1/2} + \nu_1], \quad \nu_- = 1/2 [(\nu_2^2 + 1/6\pi n^2)^{1/2} - \nu_2], \quad (4')$$

$$F_* = (2\gamma/9\pi)^2 = 0.3834, \quad \gamma = [\Gamma(1/4)/\Gamma(3/4)]^2,$$

and Γ is the gamma function. Ignoring in Eq. (4) small terms such as $1/6\pi n^2$, we obtain $F_0 = F_* \nu_1^{-4}$ or

$$\mathcal{E}_0 = 0.3834 [n_1 + (m+1)/2 - \delta]^{-4}. \quad (5)$$

This expression is in agreement with the numerical calculations of \mathcal{E}_0 carried out by the method of summation of perturbation theory series using the Padé-Hermite approximants (PHAs).⁶

It is usual to determine experimentally a series of Stark resonances in a fixed field \mathcal{E} . The energy $E = 0$ corresponds to the following principal quantum number:

$$n = n^{(0)} = k\mathcal{E}^{-1/4} + n_2 + (m+1)/2 + \delta(n_1, n_2, m), \quad (6)$$

where $k = (2\gamma/9\pi)^{1/2} = 0.787$ in the atomic system of units, but its value is $k = 37.5$ if \mathcal{E} is measured in kilovolts per centimeter. This simple expression is in good agreement with the results of numerical calculations.²⁾

Equation (1) can be used to derive the $1/n$ expansion for the energies of the levels:

$$e_{n_1 n_2 m} = 2n^2 E^{(n_1 n_2 m)} = e_0 + \rho e_1 + \rho^2 e_2 + \dots, \quad (7)$$

where $p = 2n_2 + m + 1$ and $\rho = p/n$ is a small parameter. The first term of the series $e_0 \equiv e_{cl}(F)$ is given by

$$(-e)^{1/2} = F^{1/4} \Gamma(3/4; 2; -16F/e^2), \quad (8)$$

and it corresponds to the classical limit $n \rightarrow \infty$. The corrections e_1 and e_2 can be expressed in terms of the function $e_0(F)$ and its derivatives:

$$e_1 = (1 - 2Fd/dF) e_0 + (1 - Fd/dF) (-e_0)^{1/2}, \quad (9)$$

$$\text{Im } e_2 = 3e_0^{1/2} [F^2 \ddot{e}_0 - 3/4 F \dot{e}_0 + (F \dot{e}_0)^2 / 2e_0 + 1/2 \dot{e}_0] \theta(F - F_*),$$

$e_0 \equiv de_0/dF$, etc.; θ is the Heaviside step function. We find that $e_0(F)$ remains real for all values in the range $0 < F < \infty$, whereas for $0.3 < F < 1.0$ it is a nearly linear function of F (Fig. 2). On the other hand, the coefficients $e_k(F)$ with $k \geq 1$ have an imaginary part in the range $F > F_*$. This makes it possible to use the $1/n$ expansion in describing the finite width of the Rydberg levels (this should be compared with a similar situation in the case of the Yukawa and Hulthén potentials¹⁵).

Using Eqs. (7) and (9), we can easily show that if

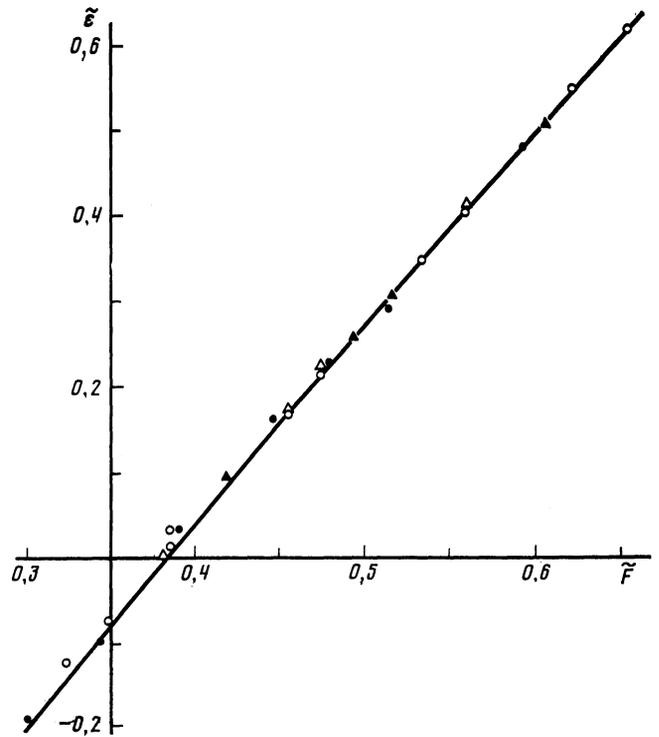


FIG. 2. Scaling relationships of Eq. (10) in the above-barrier region. The experimental points (O, ▲, Δ) for the hydrogen atom^{3,4} were obtained for $\mathcal{E} = 6.5$ and 8.0 kV/cm and three series of states: (O) $(n-1, 0, 0)$, $n = 23-28$; (▲) $(n-2, 0, 1)$, $n = 24$ or 25 ; (Δ) $(n-2, 1, 0)$, $n = 24$ or 25 . The data for rubidium (●) were obtained in fields $\mathcal{E} = 2.189$ kV/cm (four points on the left) and $\mathcal{E} = 6.416$ and 4.335 kV/cm (Ref. 1). The continuous line represents the dependence $\varepsilon_{cl}(\tilde{F})$.

$F > F_*$, the following scaling relationships (accurate to within terms of the order of $1/n^2$) are satisfied:

$$e'_{n_1 n_2 m} = \lambda^{-1/2} e_{cl}(\lambda F), \quad e''_{n_1 n_2 m} = \rho \lambda^{-1/4} \gamma_{cl}(\lambda F), \quad (10)$$

where

$$e_{n_1 n_2 m} = 2n^2 (E_r - i\Gamma/2) = e' - ie'',$$

$$\lambda = [1 - (2n_2 + m + 1 + 2\delta)/2n]^4,$$

$\Gamma = \Gamma^{(n_1 n_2 m)}(\mathcal{E})$ is the width of the level and $e_{cl}(F)$ can be found from Eq. (8) and from

$$\gamma_{cl}(F) = \theta(F - F_*) (Fd/dF - 1) e_{cl}^{1/2}. \quad (10')$$

The scaling relationships of Eq. (10) are easily checked experimentally: if we adopt the scaled variables

$$F' = \lambda F, \quad \varepsilon = \lambda^{1/2} e'_{n_1 n_2 m},$$

$$\tilde{\gamma} = p^{-1} (1 - \delta/n) (n_1 + (m+1)/2 - \delta)^3 \Gamma^{(n_1 n_2 m)}$$

we find that the experimental points fit universal curves $\varepsilon_{cl}(\tilde{F})$ and $\gamma_{cl}(\tilde{F})$. The values of these functions are listed in Table I.

In the case of subbarrier ($E < 0$, $F < F_*$) resonances, the scaling relationship becomes more complex:

$$e'_{n_1 n_2 m} = 2n^2 E_r^{(n_1 n_2 m)}$$

$$= \lambda^{-1/2} [e_{cl}(\lambda F) + \eta((\lambda/\mu)^{1/2} F) - (\lambda/\mu)^{1/2} \eta(\mu F)]. \quad (11)$$

where $\eta(F) = \{-e_{cl}(F)\}^{3/2}$ when $F < F_*$, $\mu = (1 - \delta/n)^4$, and the scaling factor λ has its previous value. Equa-

TABLE I.

F	ε_{cl}	γ_{cl}	F	ε_{cl}	γ_{cl}
0.1	-0.7144	-	0.55	0.3810	0.8977
0.2	-0.4499	-	0.6	0.4914	1.0384
0.3	-0.1999	-	0.65	0.6003	1.1675
0.35	-0.0792	-	0.7	0.7076	1.2884
0.4	0.0390	0.2700	0.8	0.9182	1.5126
0.45	0.1550	0.5498	0.9	1.1239	1.7200
0.5	0.2689	0.7396	1.0	1.3252	1.9153

tions (10) and (11) essentially contain just one universal function $\varepsilon_{cl}(F)$, which is deduced from Eq. (8).

The additional terms in Eq. (11), compared with the corresponding relationship in Eq. (10), originate as follows. For $F > F_*$, the first term in ε_1 [see Eq. (9)] is real, whereas the second is purely imaginary [this defines $\gamma_{cl}(F)$ and the width of the level]. For $F < F_*$, then $\varepsilon_{cl} < 0$ and, therefore, both terms in Eq. (9) make contributions (of the order of $1/n$) to the real part of the resonance energy.

The previous equations can be written in a physically clearer form if we replace the reduced energy ε with E_r and Γ , and if we introduce

$$n_* = n - \delta, \quad \tilde{n} = n_1 + \frac{m+1}{2} - \delta \quad (12)$$

($n_* - \tilde{n} = p/2 \gg \frac{1}{2}$), where n_* is the "effective" principal quantum number (similar to the number $n - \delta_1$, which is introduced for the Rydberg states in the spherical basis), whereas $\delta = \delta(n_1, n_2, m)$ is the quantum defect of Eq. (3). Then, in the case of above-barrier ($F > F_*$) resonances, we obtain

$$E_r^{(n_1, n_2, m)} = \frac{1}{2\tilde{n}^2} \varepsilon_{cl}(\tilde{n}^4 \mathcal{E}), \quad \Gamma^{(n_1, n_2, m)} = \frac{pn_*}{n\tilde{n}^3} \gamma_{cl}(\tilde{n}^4 \mathcal{E}), \quad (13)$$

whereas in the range $F < F_*$, we find that

$$E_r^{(n_1, n_2, m)} = \frac{1}{2\tilde{n}^2} [\varepsilon_{cl}(\tilde{n}^4 \mathcal{E}) + \eta((\tilde{n}n_*)^2 \mathcal{E}) - (\tilde{n}/n_*)^2 \eta(n_*^4 \mathcal{E})], \quad (14)$$

where E_r , Γ , and \mathcal{E} are all in atomic units. The above expressions are derived assuming $p \ll n$ and retaining only the first two (nonvanishing) terms of the $1/n$ expansion, so that the scaling relationships are accurate to within terms of order $1/n^2$. Note that Eq. (6) follows directly from Eq. (13).

For the hydrogen atom we have $\delta = 0$ and $n_* = n$, and also \tilde{n} is independent of n_2 . It is clear from Eq. (13) that the positions of above-barrier resonances (n_1, n_2, m) with fixed quantum numbers n_1 and m and different values of n_2 should be close to one another and their widths should be proportional to p (for example, $\Gamma^{(n_1, 0, 0)}(\mathcal{E}) : \Gamma^{(n_1, 1, 0)}(\mathcal{E}) \approx 1:3$). This conclusion is confirmed by numerical calculations (see Figs. 2 and 3 in Ref. 13).

It would be of interest to calculate also the separations ΔE between consecutive Stark resonances in the vicinity of the ionization limit ($E \approx 0$), since the relevant experimental data are available for hydrogen.³

The use of the $1/n$ expansion gives the expression¹⁶

TABLE II. Energies and widths of the Stark states ($n_1, n_2, 0$) of the hydrogen atom ($\mathcal{E} = 16.8$ kV/cm).

n_1, n_2	n	$-E_r, \text{cm}^{-1}$			$\Gamma/2, \text{cm}^{-1}$	
		PHA	$1/n$	exp.	PHA	exp.
17.0	18	58.2	58.4	60.72	2.3	2.5
16.1	18	106.6	106.7	103.75	8.9	9.0
16.0	17	123.5	123.2	126.46	0.18	0.14
15.1	17	167.7	167.8	167.87	1.9	2.1
15.0	16	196.7	196.7	198.54	$< 10^{-2}$	$1.1 \cdot 10^{-4}$
14.2	17	211.6	212.1	210.09	5.7	6.6
14.1	16	235.3	235.2	238.12	0.012	0.016
13.2	16	274.3	274.2	275.81	0.28	0.23
13.1	15	315.2	315.2	314.81	0.003	-
12.3	16	314.8	315.0	314.81	1.3	1.6, 2.5
12.2	15	349.8	349.8	351.42	$< 10^{-3}$	$5 \cdot 10^{-5}$
11.4	16	353.2	353.8	351.42	3.3	3.0
11.3	15	384.4	384.4	386.35	0.002	0.018
10.4	15	419.2	419.1	419.23	0.03	0.032
0.13	14	781.8	781.9	781.64	0.57	0.62
1.12	14	750.9	750.9	751.7	0.27	0.25
2.11	14	720.0	720.0	721.0	0.11	0.11
3.10	14	689.1	689.1	689.1	0.033	0.04
5.8	14	627.3	627.3	629.0	-	0.002
6.7	14	596.3	596.3	597.7	0.003	0.003
7.6	14	565.2	565.2	566.0	$< 10^{-4}$	$1.5 \cdot 10^{-5}$
6.8	15	558.8	559.1	566.0	2.3	2.1, 3.2
8.6	15	488.9	488.1	490.92	0.44	0.38
9.5	15	453.9	453.8	455.5	0.11	0.13

Note. Here, PHA are the values of E_r and $\Gamma/2$ calculated by summing perturbation theory series using the Padé-Hermitian approximants⁶; $1/n$ is the numerical solution of the system (1); "exp." are the values taken from Ref. 4.

$$\Delta E = (dE/dn)_{E=0} = c\mathcal{E}^{3/4}, \quad c = c_0 [1 - \kappa n^{-1/2} + O(n^{-1/2})], \quad (15)$$

where $c_0 = 3.708$ and the coefficients $\kappa = \kappa(p)$ are numerically small. For example, we find that $\kappa = 0.043$ for the $(n-1, 0, 0)$ states; the general expression is derived in the Appendix B. The dependence $\Delta E \propto \mathcal{E}^{3/4}$ follows from a semiclassical treatment and it was found earlier in Refs. 17 and 18, but the coefficient c_0 obtained in Ref. 17 differs somewhat from that given above.

3. We shall begin our comparison with the experimental results of subbarrier resonances in the hydrogen atom and use the recently published positions and widths of these resonances.⁴ Table II gives two series of such resonances: those with $n_1 \gg n_2$ and those with $n_1 \lesssim n_2$ (in all cases we have $m = 0$, which is explained by the conditions of excitation of atoms by π -polarized laser radiation²⁻⁴). We used two numerical methods: PHAs and the $1/n$ expansion.^{6,14} The results obtained by these two methods agree with one another, thus confirming the procedure of summation of perturbation theory series (diverging for every value $\mathcal{E} \neq 0$) we used. The agreement between the theory and experiment can be regarded as good.³ The resonance widths are not yet known accurately (in the case of asymmetric resonances two possible values of $\Gamma/2$ are given in Ref. 4), but on the whole they also agree with our calculations.

Figure 2 shows that the scaling relationship of Eq. (10) is satisfied in the case of above-barrier resonances. The experimental points are converted from the photoionization spectra reported in Refs. 3 and 4. It should be pointed out that these points fit a universal curve $\varepsilon_{cl}(\bar{F})$ only if we include $\delta(n-1, 0, 0)$ in the scaling factor λ and increase by unity⁴ the values of n given in Ref. 1. Such a change in n is supported by a comparison of our calculations with the experimental photoionization spectrum¹ obtained near δ and reproduced in Fig. 3 [it should also be noted that Eq. (6) yields $n^{(0)} = 31.9$]. The reason for errors in Ref. 1 is clearly the use of fourth-order perturbation theory in the identification of peaks in the subbarrier range in the case of the hydrogen atom, whereas in the case of rubidium the correction for the quantum defect δ is important and must be allowed for. In the case of subbarrier resonances the relationship (14) is also confirmed well by the experimental results: see Fig. 2 in Ref. 19 (the number of experimental points in the figures could be increased quite readily). It therefore follows that the scaling relationships (13) and (14) are satisfied by all

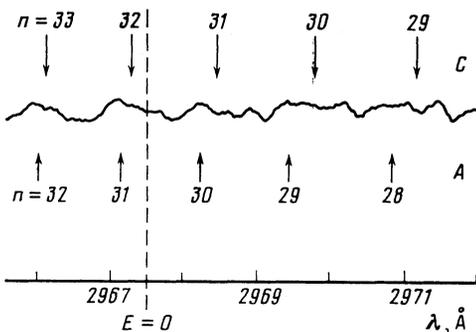


FIG. 3. Photoionization cross section of Rb obtained in a field $\mathcal{E} = 2.189$ kV/cm (Ref. 1). The value $E = 0$ corresponds to the ionization limit in the absence of an external electric field ($\mathcal{E} = 0$). The arrows identify the values of n in accordance with Ref. 1 (row A) and our values (row C).

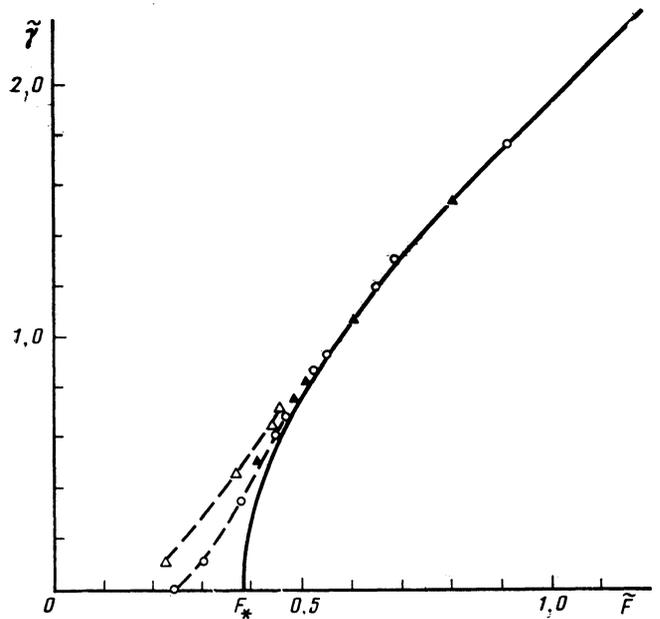


FIG. 4. Scaling based on Eq. (10) for the widths of the Stark states (hydrogen atom, $\delta = 0$). The ordinate represents the quantity $\gamma = (2n_2 + m + 1)^{-1} [n_1 + (m + 1)/2]^3 \Gamma^{(n_1, n_2, m)}$, where $\Gamma^{(n_1, n_2, m)}(\mathcal{E})$ is the width of the level in atomic units. The notation is the same as in Fig. 2. The continuous curve represents $\gamma_{cl}(\bar{F})$.

the atoms considered here (hydrogen, sodium, and rubidium) for different values of \mathcal{E} .

Figure 4 shows that the scaling relationship is obeyed by the Stark level widths. The experimental points were obtained for hydrogen. In the $F > 0.45$ range the relationship (10) is satisfied quite well. At values $F \sim F_*, \approx 0.4$ there are deviations from the scaling relationship; in this case it would be appropriate to calculate a correction of the order of $n^{-2/3}$ to Eq. (10).

Finally, we shall consider the separation ΔE between consecutive resonances. A comparison of Eq. (8) with the experimental results of Ref. 3 is made in Table III. A correction of order $n^{-2/3}$ to Eq. (15) is small ($\sim 1\%$), but it has the required sign and it improves the agreement between the theory and experiment.

4. On the whole the agreement between the theory and experiment is good and there is no doubt that the observed peaks of the photoionization cross sections of atoms correspond to the quasistationary Stark states (both in the range $E < 0$ and also in a certain range of energies $E > 0$, as long as $\Gamma \lesssim \Delta E$). Application of the $1/n$ expansion which is characterized by a high degree of precision in the case of the Rydberg states (see also Ref. 15) makes it possible to derive the scaling relationships of the type given by Eq. (10) for the positions and the widths of resonances near the ionization

TABLE III.

\mathcal{E} , kV/cm	ΔE , cm ⁻¹	
	from Eq. (15)	experiments (Ref. 3)
4.5	23.2	23.7±0.6
6.5	30.5	29.5±0.7
8.0	35.7	35.6±0.8
14.4	55.4	54.5±1.5
16.9	62.4	64.0±1.5

limit. These relationships and Eq. (6) can be used to identify the quantum numbers n_1, n_2 , and m .

We regard it as our pleasant duty to thank B. M. Karnakov for discussing the results, and to A. V. Sergeev and A. V. Shchablykin for numerical calculations.

APPENDIX A

In the outer region where $r > r_0$ the variables in the Schrödinger equation are separable in parabolic coordinates $\xi = r + z$ and $\eta = r - z$. If the effective potentials²⁰

$$\begin{aligned} U_1(\xi) &= (m^2 - 1)/8\xi^2 - \beta_1/2\xi + \gamma/8\xi^3, \\ U_2(\eta) &= (m^2 - 1)/8\eta^2 - \beta_2/2\eta - \gamma/8\eta^3 \end{aligned} \quad (\text{A1})$$

are subjected to the Bohr-Sommerfeld quantization conditions with corrections of the order of \hbar^2 (Ref. 21), we obtain in the $m = 0$ case the system of equations (1), where

$$\begin{aligned} f(z) &= F(1/4, 3/4; 2, z), \\ g(z) &= {}_2F(3/4, 5/4; 1, z) + {}_1F(3/4, 5/4; 2; z) \end{aligned} \quad (\text{A2})$$

and $F(z) = {}_2F_1(\alpha, \beta, \gamma; z)$ is the hypergeometric function (for details of the calculations see Ref. 14). In the limit $z \rightarrow 0$, we find that

$$\begin{aligned} f(z) &= 1 + \frac{3}{32}z + \frac{35}{1024}z^2 + \dots, \quad g(z) \\ &= 1 + \frac{25}{32}z + \frac{735}{1024}z^2 + \dots, \end{aligned} \quad (\text{A3})$$

whereas at the point $z = 1$ these functions have a singularity:

$$\begin{aligned} f(z) &= c_0 [1 + 3/16 t \ln t + O(t)], \\ g(z) &= 1/2 c_0 [t^{-1} - 9/16 \ln t + O(1)], \end{aligned} \quad (\text{A4})$$

where $t = 1 - z \rightarrow 0$, and $c_0 = 2^{7/2}/3\pi$.

Using the ideas put forward in Refs. 22 and 23, we can readily show that the system of equations (1) is valid to within terms of order $1/n^2$ also when $m \neq 0$ (but provided $m \ll n$). The difference between the atomic field and the purely Coulomb field (at distances $r \lesssim r_0$) can be allowed for formally if we substitute $n_i \rightarrow n_i - \delta_i$ in the quantization conditions (see Ref. 12 and also Ref. 20). Since in the absence of a field ($\mathcal{E} = 0$) the effective charges in the potentials of Eq. (A1) are $\beta_1^{(0)}$ and $\beta_2^{(0)}$, it follows that $\delta_1 = \beta_1^{(0)}\delta$, and $\delta_2 = \beta_2^{(0)}\delta$ (for details see Ref. 13). Subject to these qualifications, the semiclassical quantization conditions assume the form given by Eqs. (1) and apply not only to the hydrogen atom but also to the Rydberg states of any atom. Numerical solution of these equations presents no problems: the results are given in Table II and in Fig. 3.

It was demonstrated by Drukarev²² that the semiclassical approximation needs refinement if the energy of a level is close to the top of the potential barrier in the effective potential $U_2(\eta)$. Applying the parabolic approximation and matching the semiclassical wave functions to the exact solutions, expressed in terms of the parabolic cylinder functions,²⁴ we can show that the first equation in the system (1) does not change, whereas in the second we have to make the substitution

$$v_2 \rightarrow v_2 - \frac{1}{2\pi n} \left[\varphi(a) + \frac{i}{2} \ln(1 + e^{-2na}) \right], \quad (\text{A5})$$

$$\begin{aligned} \varphi(a) &= \frac{1}{2i} \ln \left[\Gamma\left(\frac{1}{2} + ia\right) / \Gamma\left(\frac{1}{2} - ia\right) \right] \\ &\quad - a \ln a + a - \frac{1}{24a}, \end{aligned}$$

where ($\eta_{1,2}$ are the turning points)

$$a = \frac{1}{\pi} \int_{\eta_1}^{\eta_2} \left(\frac{m^2}{4\eta^2} - \frac{\beta_2}{\eta} - \frac{\mathcal{E}}{4} \eta - \frac{E}{2} \right)^{1/2} d\eta. \quad (\text{A6})$$

In the case of the states with $m = 0$, this integral can be calculated analytically:

$$a = \frac{n(-\varepsilon)^{1/2}}{2^{1/2}F} (1 - z_2) f(1 - z_2). \quad (\text{A7})$$

In weak fields we have $z_2 \rightarrow 0$ and $a = n/3\pi F \gg 1$ [see Eq. (A4)]; therefore,

$$\varphi(a) + \frac{i}{2} \ln(1 + e^{-2na}) = \frac{7}{2880} a^{-3} + \dots + \frac{i}{2} e^{-2na}. \quad (\text{A8})$$

Hence, we obtain

$$\Gamma(n_1, n_2, m) \approx \frac{1}{2\pi n^3} e^{-2na} \propto F^{-p} \exp\left(-\frac{2n}{3F}\right), \quad (\text{A9})$$

which agrees with the familiar threshold behavior²⁰ of the level width. It is clear from Eq. (A8) that in this case the difference between the refined equations and the system (1) is unimportant when we calculate the positions of the Stark levels. However, for $n\varepsilon^{3/2} \sim 1$ (i.e., in the range $|F - F_*| \lesssim n^{-2/3}$ near $F = F_*$) the parameter a becomes of order unity and in solving the system (1) we have to allow for the correction to v_2 described by Eq. (A5). We can also calculate the correction of order $n^{-2/3}$ to the scaling relationships of Eq. (10). These calculations are under way at present.

APPENDIX B

We shall consider the separation between consecutive resonances in the vicinity of the ionization limit: $\Delta E = (dE/dn)_{E=0}$. Bearing in mind that $E = \varepsilon/2n^2$, applying the scaling relationships of Eq. (10) to the real part of the energy, and expanding Eq. (B3), we obtain Eq. (15) where

$$c_0 = (\pi\gamma/2)^{1/2} = 3.708, \quad (\text{B1})$$

$$\kappa = c_1 \{ p [1 - (1 + 2/3\pi p^2)^{-1/2}] \}^{1/2}, \quad (\text{B2})$$

$c_1 = \gamma^z / (2^{16/3} \cdot 9) = 0.211$ and $p = 2n_2 + m + 1$. It should be pointed out that terms of the order of $1/n$ in Eq. (15) cancel out and the appearance in this expansion of fractional powers of n is due to the "collision" of two classical solutions at $F = F_*$ and $\varepsilon = 0$ (see Ref. 15). The coefficients are numerically small and decrease with p , so that for $p > 3$ we can ignore corrections of the order of $n^{-2/3}$ in Eq. (15). These expressions are derived using the expansion

$$e_{cl}(F) = \alpha_1 f + \alpha_2 f^2 + \alpha_3 f^3 + \dots, \quad f = (F - F_*)/F. \quad (\text{B3})$$

which follows from Eq. (8). Here,

$$\alpha_1 = \frac{\gamma^2}{27\pi} = 0.9034, \quad \alpha_2 = \frac{1}{8}(1 - \gamma^2/48)\alpha_1 = -0.0674, \quad (B4)$$

$$\alpha_3 = \frac{3}{32}(-1 + \gamma^2/216 + \gamma^4/6912) = 0.0173$$

and γ is a constant introduced in Eq. (4'). The rapid fall of the values $|\alpha_k|$ explains the approximate "linearity" of the graph $\varepsilon_{cl}(F)$ in the range $0.3 < F < 1$, as demonstrated clearly in Fig. 2. The values of the functions $\varepsilon_{cl}(F)$ and $\gamma_{cl}(F)$, which occur in the scaling relationships of Eq. (10), are listed in Table I (for details of this table see Ref. 13).

¹Here, n_1 , n_2 , and m are the parabolic quantum numbers ($m \geq 0$) related by $n = n_1 + n_2 + m + 1$. We shall use (unless specifically stated) atomic units and the same notation as in Ref. 6.

²In the case of quantum number n_1 of Eq. (6) we obtain $n_1^{(0)} = n^{(0)} - n_2 - m - 1 = 23.0, 21.8, \text{ and } 18.0$ for $\mathcal{E} = 6.5, 8.0, \text{ and } 16.8$ kV/cm in the case of the $(n_1, 0, 0)$ states of the hydrogen atom. These values of $n_1^{(0)}$ (corresponding to $E = 0$) are in full agreement with the numerical calculations reported in Fig. 3 of Ref. 6 and in Ref. 14.

³The experimental values of the energy E are subject to an error⁴ of the order of 2 cm^{-1} , so that the last two figures of the values of E_{exp} in Table II are not very significant. According to Eq. (6), $n^{(0)} = 19$ for the $(n - 1, 0, 0)$ states.

⁴However, if the peaks in the photoionization spectrum of rubidium are assigned the values of n from Ref. 1, we obtain points which deviate from the ε_c curve in Fig. 2 by more than the experimental error (see Ref. 13). Therefore, the scaling relationships allow us to determine the quantum numbers of the resonances.

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