

# 1/n-expansion and scaling for the Stark effect in Rydberg atoms

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The Stark shifts and widths of atomic states in an intense electric field are calculated with the help of the 1/n-expansion. A previous theory is generalized to highly excited states of an arbitrary atom. The scaling relations for near-threshold ( $E \approx 0$ ) resonances are obtained which are in good agreement with experiment. The modification of the Bohr-Sommerfeld quantization rule due to the finite barrier penetrability is also considered.

## 1. Introduction

The energies and widths of Stark resonances in a hydrogen atom can be calculated by different methods (see, e.g. refs. [1-4] and references therein). Using the quantum defect method [5], we generalize the theory to Rydberg ( $n \gg 1$ ) states of an arbitrary atom in a strong electric field  $\varepsilon$  (up to values of  $\varepsilon \sim n^{-4}$  comparable with atomic field at the corresponding electron orbit). With the help of the 1/n-expansion [1] scaling relations for the near-threshold resonances have been obtained, which are in good agreement with experimental data for hydrogen, sodium and rubidium.

We use atomic units  $\hbar = m_e = e = 1$  (unless specified otherwise);  $n_1$ ,  $n_2$  and  $m$  are parabolic quantum numbers ( $m \geq 0$ ),  $n = n_1 + n_2 + m + 1$  is the principal quantum number of the level. Other notations are the same as in the preceding Letter [3].

## 2. Analytical theory

In calculating the energy of  $|n_1, n_2, m\rangle$  states with

$n \gg 1$  and  $n_2, m \sim 1$ , we use the WKB quantization conditions with allowance for the corrections of the order of  $\hbar^2$  [6], approximate separation of variables in the region  $r > r_a$ , and the "hidden" symmetry of the Coulomb field [7].

For atoms other than hydrogen the potential  $V(r)$  differs from the Coulomb potential  $-1/r$  at  $r \lesssim r_a$ <sup>#1</sup>. Since Stark shifts of the atomic levels in intense field  $\varepsilon$  considerably exceed the fine structure splitting,  $n_1$ ,  $n_2$  and  $m$  are good quantum numbers. In the Coulomb field there exists the well-known "accidental" degeneracy of states which is described by the hidden symmetry group [7]  $SO(4) = SO(3) \otimes SO(3)$ . Its generators are the angular momentum  $L = r \times p$  and the Runge-Lenz vector  $A = r/r + \frac{1}{2}(L \times p - p \times L)$ , while  $\mathcal{F}_{1,2} = \frac{1}{2}(L \pm A)$  are generators of  $SO(3)$  subgroups. Since  $L = \mathcal{F}_1 + \mathcal{F}_2$ , the quantum defect in parabolic basis  $|n_1 n_2 m\rangle$  is

$$\delta(n_1 n_2 m) = \frac{1}{n} \sum_{l=m}^{n-1} (2l+1) (C_{\mathcal{F}, M-m, lm}^{\mathcal{F}M})^2 \mu_l, \quad (1)$$

where  $\mathcal{F} = (n-1)/2$ ,  $M = (n_1 - n_2 + m)/2$ ,  $C_{\mathcal{F}, M-m, lm}^{\mathcal{F}M}$  are the Clebsch-Gordan coefficients for

<sup>#1</sup> Here  $r_a$  is the radius of atomic core, which is assumed to be small in comparison with the mean radius of the Rydberg states  $\langle r \rangle \sim n^2$ .

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the  $SO(3)$  group and  $\mu_l$  are quantum defects for a free ( $\epsilon=0$ ) atom. The values of  $\mu_l$  are tabulated and sharply decrease with growing  $l$ , so the sum in (1) actually retains several leading terms<sup>#2</sup>.

Let  $\beta_{1,2}$  denote the separation constants in the Schrödinger equation and  $\epsilon = \epsilon' - i\epsilon''$  and  $F$  are the reduced energy and reduced external field [3]. If  $m=0$ , we can determine  $\epsilon$ ,  $\beta_1$  and  $\beta_2$  from the equations

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

where  $z_i = (-1)^i 16\beta_i F \epsilon^{-2}$  for  $i=1$  or  $2$ ,  $\nu_i = [n_i + \frac{1}{2}(m+1)](1 - \delta/n)$ ,  $\delta = \delta(n_1 n_2 m)$  and the functions  $f(z)$ ,  $g(z)$  are expressed through the hypergeometric function<sup>#3</sup>. In the limit  $\epsilon \rightarrow 0$  the solution of (2) is in agreement with the perturbation theory up to the term of order  $\epsilon^3$  inclusively. Using eqs. (2) it is possible, however, to consider the case in which the field is strong,  $n^4 \epsilon \sim 1$ .

At  $n \gg 1$  it is reasonable to use the  $1/n$ -expansion,

$$\begin{aligned} \epsilon_{n_1 n_2 m} &\equiv 2n^2 E^{(n_1 n_2 m)} \\ &= \epsilon^{(0)} + \frac{p}{n} \epsilon^{(1)} + \frac{1}{n^2} (p^2 \epsilon^{(2)} + \xi^{(2)} + m^2 \eta^{(2)}) + \dots, \end{aligned} \quad (3)$$

where  $p = 2n_2 + m + 1$  and  $\epsilon^{(k)}$ ,  $\xi^{(k)}$ ,  $\eta^{(k)}$  depend on  $F$ . In the limit  $n \rightarrow \infty$  system (2) reduces to the equation

$$(-\epsilon)^{1/2} = {}_2F_1\left(\frac{1}{4}, \frac{3}{4}; 2; -16F\epsilon^{-2}\right), \quad (4)$$

whose solution will be denoted as  $\epsilon_{cl} \equiv \epsilon^{(0)}(F)$ . It is easy to show that  $\epsilon_{cl}(F)$  increases monotonically along with  $F$ , crosses the boundary  $\epsilon=0$  at  $F=$

$F_* = 0.3834$  and remains real for all  $0 < F < \infty$ . The initial terms of the  $1/n$ -expansion can be expressed through the function  $\epsilon_{cl}(F)$  and its derivatives, e.g.,

$$\epsilon^{(1)} = \left(1 - 2F \frac{d}{dF}\right) \epsilon_{cl} + \left(1 - F \frac{d}{dF}\right) (-\epsilon_{cl})^{3/2}.$$

Using this formula, we find the scaling relations for the near-threshold resonances. Above the ionization threshold,  $E > 0$ ,

$$E_r^{(n_1 n_2 m)} = \frac{1}{2\tilde{n}^2} \epsilon_{cl}(\tilde{n}^4 \epsilon), \quad \Gamma^{(n_1 n_2 m)} = \frac{p}{\tilde{n}^3} \gamma_{cl}(\tilde{n}^4 \epsilon), \quad (5)$$

where<sup>#4</sup>  $n_* = n - \delta$ ,  $\tilde{n} = n_1 + \frac{1}{2}(m+1) - \delta$  and

$$\gamma_{cl}(F) = \theta(F - F_*) \left(F \frac{d}{dF} - 1\right) \epsilon_{cl}^{3/2}. \quad (4')$$

Note that at  $F \approx F_*$

$$\begin{aligned} \epsilon_{cl}(F) &= \alpha_1 f + \alpha_2 f^2 + \dots, \\ \gamma_{cl}(F) &= b_1 f^{1/2} + b_2 f^{3/2} + \dots, \end{aligned} \quad (6)$$

where  $f = (F - F_*)/F_* \rightarrow 0$  and the coefficients can be calculated analytically<sup>#5</sup>.

Below the threshold ( $E < 0$ ,  $F < F_*$ ) scaling relations acquire a somewhat different form,

$$\begin{aligned} E_r^{(n_1 n_2 m)} &= \frac{1}{2\tilde{n}^2} [\epsilon_{cl}(\tilde{n}^4 \epsilon) + \eta((\tilde{n}n_*)^2 \epsilon) \\ &\quad - (\tilde{n}/n_*)^2 \eta(n_*^4 \epsilon)], \\ \eta(F) &= [-\epsilon_{cl}(F)]^{3/2}. \end{aligned} \quad (7)$$

As usual, the value of  $\epsilon$  is fixed experimentally and a sequence of resonances near  $E=0$  is observed [8-12]. It follows from (5) that the  $|n_1 n_2 m\rangle$  states with given  $n_2$ ,  $m$  intersect the zero-field ionization limit  $E=0$  when

<sup>#4</sup>  $n_*$  is analogous to the effective principal quantum number  $n - \mu_b$ , which is used for the Rydberg states in the spherical basis  $|nlm\rangle$ .

<sup>#5</sup> From eqs. (4) and (4') one can obtain:  $\alpha_1 = \gamma^2/27\pi$ ,  $\alpha_2 = (\gamma^2/216\pi)(1 - \gamma^2/48)$ ,  $b_1 = \gamma^2/18(3\pi)^{3/2}$ , and so on, where  $\gamma = [\Gamma(\frac{1}{4})/\Gamma(\frac{3}{4})]^2 = 8.7538$  and  $F_* = (2\gamma/9\pi)^2 = 0.3834$ . Numerically we have  $\alpha_1 = 0.903$ ,  $\alpha_2 = -0.067$ ,  $\alpha_3 = 0.017$ ,  $\alpha_4 = -0.0063$ , ... Since  $\alpha_1 \gg |\alpha_2| > \alpha_3$ , the  $F$ -dependence of  $\epsilon_{cl}(F)$  is nearly linear at  $F \sim F_*$ , which is clearly seen in figs. 1 and 2. On the other hand,  $\gamma_{cl}$  has a square root singularity at  $F \rightarrow F_*$ , and  $\gamma_{cl}(F) \equiv 0$  as  $F < F_*$ .

<sup>#2</sup> Asymptotically  $\delta(n_1 n_2 m) \simeq 1/n$  as  $n \rightarrow \infty$ , but at  $n=20-40$  they are not yet small. In a rubidium atom, for example,  $\delta(24, 0, 0) = 0.633$ ,  $\delta(23, 1, 0) = 0.491$ ,  $\delta(22, 2, 0) = 0.386$ ,  $\delta(22, 1, 1) = 0.133$ ,  $\delta(23, 0, 1) = 0.092$ ,  $\delta(22, 0, 2) = 0.007$  ( $n=25$  for all these states). Naturally,  $\mu_l = \delta(n_1, n_2, m) \equiv 0$  for a hydrogen atom.

<sup>#3</sup> We have  $f(z) = {}_2F_1(\frac{1}{4}, \frac{3}{4}; 2; z)$ ,  $g(z) = \frac{1}{3} [{}_2F_1(\frac{3}{4}, \frac{5}{4}; 2; z) + 2 {}_2F_1(\frac{3}{4}, \frac{5}{4}; 1; z)]$ . At  $z \rightarrow 0$   $f(z) = 1 + \frac{3}{32}z + \frac{25}{1024}z^2 + \dots$ ,  $g(z) = 1 + \frac{25}{32}z + \frac{735}{1024}z^2 + \dots$ , while at  $z=1$  these functions have singularities.

$$n = k\epsilon^{1/4} + n_2 + \frac{1}{2}(m+1) + \delta(n_1 n_2 m), \quad (8)$$

where  $k = (2\gamma/9\pi)^{1/2} = 0.787$  in atomic units and  $k = 37.5$  if  $\epsilon$  is measured in kV/cm.

### 3. Comparison with experiment

The scaling (5) is verified in fig. 1. The experimental data points are:  $\circ$ : the  $|n_1, 0, 0\rangle$  states of the hydrogen atom [8] for  $\epsilon = 6.5$  and  $8.0$  kV/cm,  $\square$ : the  $|n_1, 0, 1\rangle$  and  $|n_1, 1, 0\rangle$  series in hydrogen [8],  $+$ : the data for Rb,  $\epsilon = 2.189$  kV/cm (the four left points) and also for  $\epsilon = 4.335$  and  $6.416$  kV/cm [9],  $*$ : the  $|n_1, 0, 0\rangle$  states for Na,  $\epsilon = 2.15$  and  $4.46$  kV/cm [10,11].

Fulfillment of scaling in the subthreshold region is illustrated in fig. 2. The experimental energies  $E_r^{(n_1 n_2 m)}$  taken from refs. [8-11] were recalculated in the following way:

$$\begin{aligned} \tilde{\epsilon}_{n_1 n_2 m} &= 2\tilde{n}^2 E_r^{(n_1 n_2 m)} - \eta((\tilde{n} n_*)^2 \epsilon) \\ &+ (\tilde{n}/n_*)^2 \eta(n_*^4 \epsilon). \end{aligned} \quad (9)$$

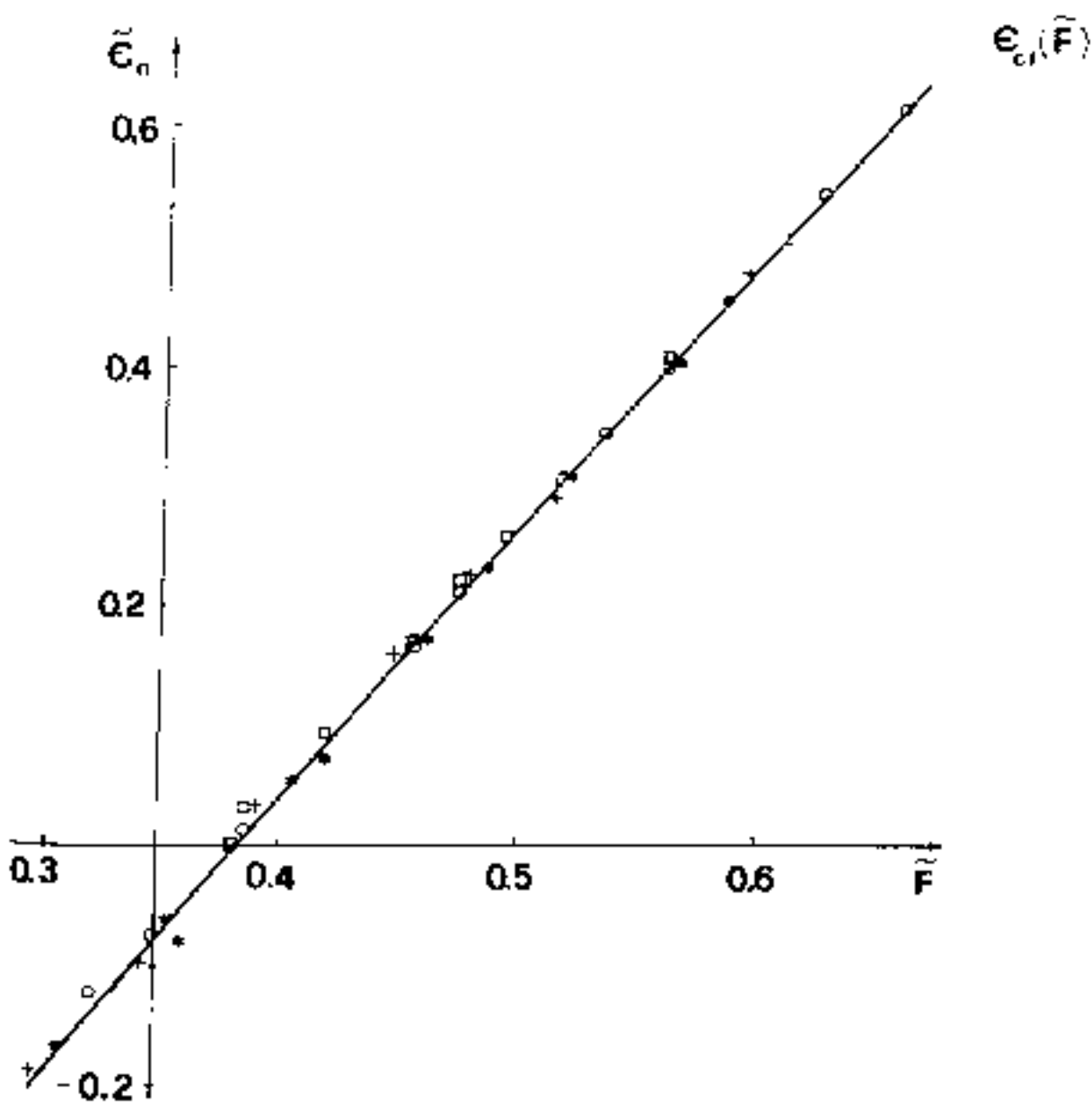


Fig. 1. Scaling (5) for the energies of the above threshold resonances. Solid curve is  $\epsilon_{cl}(\tilde{F})$ , the variables are  $\tilde{F} = \tilde{n}^4 \epsilon$ ,  $\tilde{\epsilon}_n = 2\tilde{n}^2 E_r^{(n_1 n_2 m)}$ . The experimental points are explained in the text.

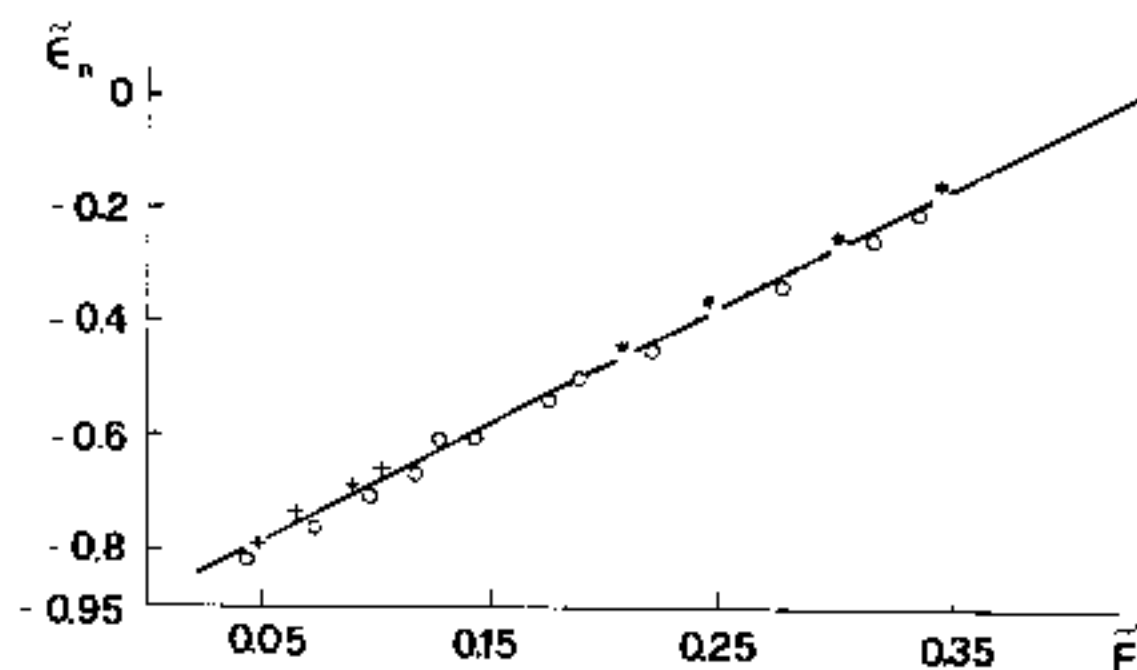


Fig. 2. Scaling (7) for the subthreshold resonances. The data for hydrogen (open circles) are taken from refs. [8,12].

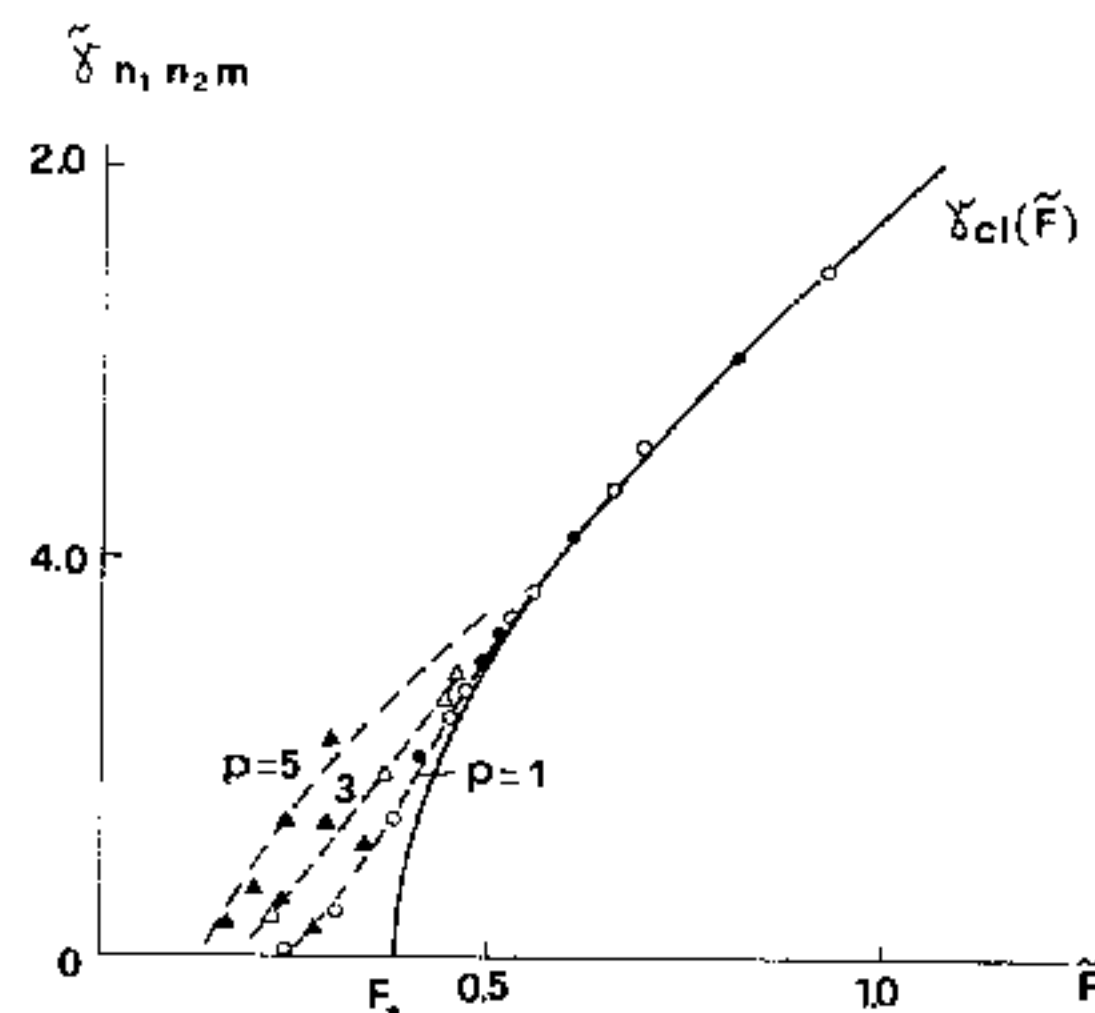


Fig. 3. Scaling for the widths of the Stark resonances. The values of  $p = 2n_2 + m + 1$  are shown at the curves.

According to (7), the points  $\tilde{\epsilon}_{n_1 n_2 m}$  for an arbitrary atom must set onto the universal curve  $\epsilon_{cl}(\tilde{F})$ , which is the case indeed.

With regard to the resonance widths  $\Gamma^{(n_1 n_2 m)}$ , at  $F \geq 0.5$  eq. (5) is fulfilled. See fig. 3, where the variables

$$\tilde{F} = \tilde{n}^4 \epsilon, \quad \tilde{\gamma}_{n_1 n_2 m} = \frac{\tilde{n}^3}{p} \Gamma^{(n_1 n_2 m)}(\epsilon) \quad (10)$$

are used. Notations are:  $\circ$ ,  $\bullet$  and  $\Delta$ : the  $|n_1, 0, 0\rangle$ ,  $|n_1, 0, 1\rangle$  and  $|n_1, 1, 0\rangle$  states in hydrogen at  $\epsilon = 6.5$  and  $8.0$  kV/cm [8,12],  $\blacktriangle$ : the  $|n_1, n_2, 0\rangle$  states in Na at  $\epsilon = 3.59$  kV/cm [10,11].

In all the cases considered the agreement between

theory and experiment is good. The scaling relations can be used to identify the quantum numbers ( $n_1, n_2, m$ ) of the peaks in photo-ionization cross sections, as well as to control computations performed by more precise numerical methods.

However, there are some deviations from scaling for  $\Gamma^{(n_1 n_2 m)}$  at lower values of the field,  $F < 0.4$  (fig. 3). Here the correction to the Bohr-Sommerfeld quantization rule due to the barrier penetration should be taken into account. In the problem at hand, only the potential

$$U_2(\eta) = \frac{m^2}{8\eta^2} - \frac{\beta^2}{2\eta} - \frac{1}{8}\epsilon\eta$$

has a barrier, while  $U_1(\xi)$  is the confining potential for  $0 < F < \infty$ . The Schrödinger equation near the barrier  $\eta = \eta_m$  allows an exact solution in parabolic cylinder functions, which is matched with the quasiclassical wave function at  $\eta < \eta_m$ , while at  $\eta \rightarrow \infty$  the solution goes over into an outgoing wave (which corresponds to a quasistationary state). As a result, in the second of eqs. (2) we must make the substitution

$$\nu_2 \rightarrow \nu_2 - \frac{1}{2\pi n} \varphi(a), \tag{11}$$

where

$$\begin{aligned} \varphi(a) &= \frac{1}{2i} \ln \left[ \Gamma\left(\frac{1}{2} + ia\right) / \Gamma\left(\frac{1}{2} - ia\right) (1 + e^{-2\pi a}) \right] \\ &\quad + a(1 - \ln a), \\ a &= \frac{1}{\pi} \int_{\eta_1}^{\eta_2} (-p_\eta^2)^{1/2} d\eta, \end{aligned} \tag{12}$$

and  $n_1 < \eta_1 < \eta_2$  is the subbarrier region. If  $\epsilon \rightarrow 0$ , the parameter  $a \rightarrow \infty$  and

$$\varphi(a) = \frac{1}{24a} + \frac{7}{2880a^3} + \dots + \frac{1}{2}i \exp(-2\pi a). \tag{13}$$

Taking into account an exponentially small imaginary part of  $\varphi(a)$ , one can obtain from (2) the correct weak-field behaviour,

$$\begin{aligned} \Gamma^{(n_1 n_2 m)} &\simeq \epsilon^{-p} \exp(-2/3n^3\epsilon), \quad \text{as } \epsilon \rightarrow 0 \\ (p &= 2n_2 + m + 1). \end{aligned}$$

A numerical solution of the system (2) with the substitution (11) gives a correct interpolation between the weak-field region and the scaling region  $F \gtrsim F_*$  (fig. 4). We will compare the calculations with experimental data on the Stark resonance widths in a more detailed paper.

The modification of the Bohr-Sommerfeld quantization condition for an arbitrary potential is

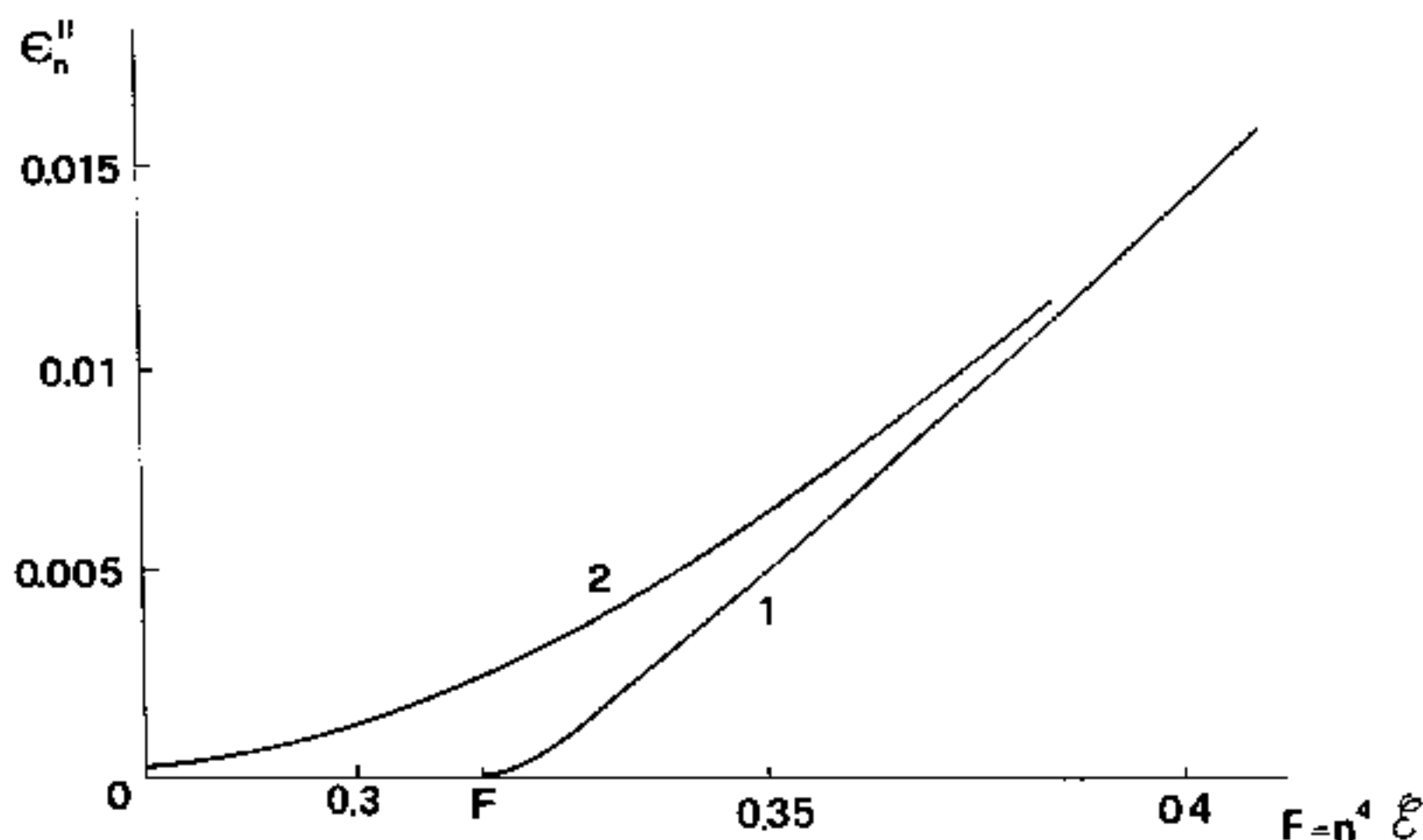


Fig. 4. Effect of barrier penetrability on the calculation of the level width,  $\epsilon_n'' = n^2 \Gamma^{(n_1, 0, 0)}$ , for the  $|n-1, 0, 0\rangle$  states,  $n=20$ . Curve 1: solution of eqs. (2) without the function  $\varphi(a)$ , i.e.,  $\nu_2 = \frac{1}{2}n$ , in this case  $\epsilon_n'' \equiv 0$  at  $F < F_*$ . Curve 2: solution of (2) with the substitution (11).

$$\int_{r_1}^{r_2} p(r) dr = [n + \frac{1}{2} - \varphi(a)/2\pi]\pi, \quad n=0, 1, \dots, \quad (14)$$

where  $\varphi(a)$  is given in (12),

$$a = \frac{1}{\pi} \int_{r_1}^{r_2} (-p^2)^{1/2} dr,$$

$$p^2 = 2(E - V) - (l + \frac{1}{2})^2 r^{-2}.$$

Note that the function  $\varphi(a)$  has singularities at the points

$$a = a_n = (n + \frac{1}{2})i, \quad (15)$$

which correspond to the poles of the scattering amplitude for a parabolic barrier. If  $a \gg 1$ , eq. (14) is reduced to the well-known Gamow formula for the level width. However, this equation can be applied also in the cases when the level energy  $E$  is close to the barrier summit, or is above it. It can be checked by considering some exactly solvable model potentials (see appendix).

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### Appendix

Here we consider a model potential

$$V(r) = -\frac{1}{2}\omega^2(r-R)^2, \quad 0 < r < \infty, \quad (A.1)$$

for which the Schrödinger equation with  $l=0$  can be solved analytically. It makes it possible to compare the exact results with our approximation. The substitution

$$x = (2\omega)^{1/2} e^{-i\pi/4} (r-R)$$

transforms the Schrödinger equation into the standard form

$$\frac{d^2\chi}{dx^2} + (p + \frac{1}{2} - \frac{1}{4}x^2)\chi = 0,$$

where

$$p = -\frac{1}{2} - ia,$$

$$a = \frac{1}{\pi} \int_{r_1}^{r_2} (-p^2)^{1/2} dr = -E/\omega$$

( $r_{1,2} = R(1 \mp \epsilon^{1/2})$  are turning points). The spectrum of the quasistationary states is defined by the equation  $\chi(0) = 0$ , or

$$D_{-1/2-ia}(-2e^{-i\pi/4}s^{1/2}) = 0, \quad (A.2)$$

where  $s = \frac{1}{2}\omega R^2 = V_0/\omega$ ,  $V_0 = -V(0)$ . Supposing  $n \gg 1$ ,  $s \gg a$  and using the asymptotics of  $D_p(z)$ , we obtain from the exact equation (A.2):

$$s - \frac{1}{2}a[\ln(s/a) + 1 + 2\ln 2] + \frac{1}{2}\varphi(a) = (n + \frac{3}{4})\pi, \quad (A.3)$$

$\varphi(a)$  is defined by eq. (12). On the other hand, in this case  $\int_0^{r_1} p dr = \frac{1}{2}sf(\epsilon)$ ,

$$\begin{aligned} f(\epsilon) &= (1-\epsilon)^{1/2} - \epsilon \operatorname{arth}(1-\epsilon)^{1/2} \\ &= 1 + \frac{1}{2}\epsilon \ln \epsilon - (\frac{1}{2} + \ln 2)\epsilon + \frac{1}{8}\epsilon^2 + \dots, \quad \epsilon \rightarrow 0, \\ &= \frac{2}{3}(1-\epsilon)^{3/2} + \dots, \quad \epsilon \rightarrow 1, \end{aligned}$$

and  $\epsilon = -E/V_0$  (note that  $a = s\epsilon$ ).

Thus, the usual Bohr-Sommerfeld quantization condition gives

$$sf(\epsilon) = (n + \frac{3}{4})\pi, \quad (A.4)$$

which corresponds to eq. (A.3) in the case  $\epsilon \ll 1$ . However, an additional term  $\frac{1}{2}\varphi(a)$  is present in (A.3), in accordance with the substitution (11).

When neglecting the barrier penetration, the region of the discrete spectrum corresponds to  $0 < \epsilon < 1$ . The full number of bound states is

$$n_0 = s/\pi - \frac{3}{4} + O(s^{-1}), \quad (A.5)$$

as immediately follows from eq. (A.4) at  $\epsilon=0$ .

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