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Critical electric fields and Stark resonances in the hydrogen atom

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Abstract

The exact values of critical electric fields $\mathcal{E}_c$ for different states of a hydrogen atom, including its ground state, as well as the widths Γ_n of the Stark resonances at $\mathcal{E}=\mathcal{E}_c$, are calculated (at $\mathcal{E}=\mathcal{E}_c(n_1, n_2, m)$ the potential barrier for an electron in the (n_1, n_2, m) state disappears). Using the modified quantization condition with barrier penetrability included, we explain the dependence of Γ_n on the principal quantum number n.

1. In connection with experimental investigations of the near-threshold Stark resonances [1–4] the values of the electric field $\mathcal{E}=\mathcal{E}_c(n_1, n_2, m)$, where the (n_1, n_2, m) atomic level contacts the summit of a potential barrier, are of some interest (as in Refs. [5,6], we shall call $\mathcal{E}_c$ a "critical" field). The field $\mathcal{E}=\mathcal{E}_c$ separates two different regions: the weak field region, where atomic states are sub-barrier ones and their widths are exponentially small (tending to the quasiclassical asymptotics [7,8] at $\mathcal{E}\to 0$) and the strong field region, $\mathcal{E}>\mathcal{E}_c$, with the above-barrier resonances. Both experimental data and numerical calculations [9,10] show that the transition from one region to the other is rather sharp. So the critical fields $\mathcal{E}_c$, strictly defined in the quasiclassical limit $n\gg 1$, are meaningful for small quantum numbers as well.

The calculation of the critical fields $\mathcal{E}_c$ for a hydrogen atom is discussed briefly in Ref. [11]. Some new data are given in Section 1, in particular, for the (m, m, m) states with $m=\frac{1}{3}(n-1)=0, 1, 2, \ldots$ where $m(n)$ is the magnetic (principal) quantum number. Sections 2 and 3 contain entirely new results: The asymptotics of the Stark widths at $\mathcal{E}=\mathcal{E}_c$, when the atomic level contacts the barrier summit, see Eqs. (14)–(16) below, obtained with the help of the modified quantization condition with the barrier penetrability included [12–14]. Some properties of the above-barrier resonances are discussed in Section 3, where it is shown that these resonances are rather isolated in the energy region close to the barrier summit.

For the Stark problem in a hydrogen atom the variables are separated in parabolic coordinates [7], ξ, η, and φ $(0\leqslant\varphi\leqslant 2\pi)$, while a barrier exists for in the variable $\eta=r-z$. Since the wave function $\chi_2(\eta)$ is determined at the semi-axis $0<\eta<\infty$, $\eta=0$ is a singular point. The Langer transformation [15,16]

$$\eta=\exp(x),\quad \chi_2(\eta)=\exp(\tfrac{1}{2}x)\psi(x) \qquad (1)$$

moves this singularity to $-\infty$ and allows one to deal correctly with the boundary condition $\chi_2(0)=0$ in the quasiclassical approach. The Schrödinger equation is

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$$\frac{1}{n^2}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+p^2\psi=0\,,$$

$$p^2=-\tfrac{1}{4}\mu^2+\beta_2 y+\tfrac{1}{4}\epsilon y^2+\tfrac{1}{4}Fy^3\,, \qquad (2)$$

where $-\infty<x<\infty$, $y=n^{-2}\eta$ and β_2 is the separation constant. Here we use atomic units, $\hbar=e=m_e=1$, and "reduced" variables,

$$\epsilon=\epsilon'-\mathrm{i}\epsilon''=2n^2E_n(\mathscr{E}), \quad \epsilon''=n^2\Gamma_n, \quad F=n^4\mathscr{E}\,,$$

$$\mu=\frac{|m|}{n}, \quad \nu_i=(n_i+\tfrac{1}{2})/n\,, \qquad (3)$$

$E=E_r-\frac{1}{2}\mathrm{i}\Gamma$ is the complex resonance energy, n_1, n_2, m are parabolic quantum numbers and $n=n_1+n_2+|m|+1$.

The condition that the atomic level contacts the barrier summit (i.e., $E_r=U_m$) is expressed by the equations,

$$\mathrm{Re}\,p^2(y_m)=\mathrm{Re}\left.\frac{\mathrm{d}p^2}{\mathrm{d}y}\right|_{y=y_m}=0\,, \qquad (4)$$

which, with Eqs. (2) taken into account, have the form

$$\epsilon'+2Fy+\mu^2y^{-2}=0,$$

$$y=-\frac{\epsilon'}{3F}\left[1+(1-\zeta)^{1/2}\right]\,, \qquad (5)$$

where $y=y_m$ is the point of maximum of the effective potential in Eq. (2), $\zeta=12\beta_2' F/\epsilon'^2$, $\beta_2'=\mathrm{Re}\,\beta_2$ and $\epsilon'=\mathrm{Re}\,\epsilon<0$. The quantities ϵ' and β_2' depend on the reduced electric field F and the quantum numbers n_1, n_2, m of the state. They were calculated by summation of divergent perturbation theory series (PT) using Hermite–Padé approximants (a brief description of the method is given in Refs. [9,10]). In these calculations 60–80 PT orders were included [1], which provided for an accuracy $\sim 10^{-4}$ in ϵ and β_2, then the critical field $F_c(n_1, n_2, m)$ is calculated from Eq. (5).

The results of the calculations of F_c are given in Fig. 1. Curves 1–5 in this figure belong to the following states: $(0, n-1, 0)$, $(n_1, n_1, 0)$, (m, m, m), $(0, 0, n-1)$ and $(n-1, 0, 0)$, with $n_1=\frac{1}{2}(n-1)$ and $m=\frac{1}{3}(n-1)$. With the increase in the principal quantum number n, the F_c values approach the classical ionization threshold F_* [9], which depends only on the ratios ν_i. Here are some numerical values: $F_*=0.1298$, 0.1674, 0.1693, 0.2081 and 0.3834 for curves 1–5 in Fig. 1, respectively. For the Rydberg states [2], $n\gg 1$, we have

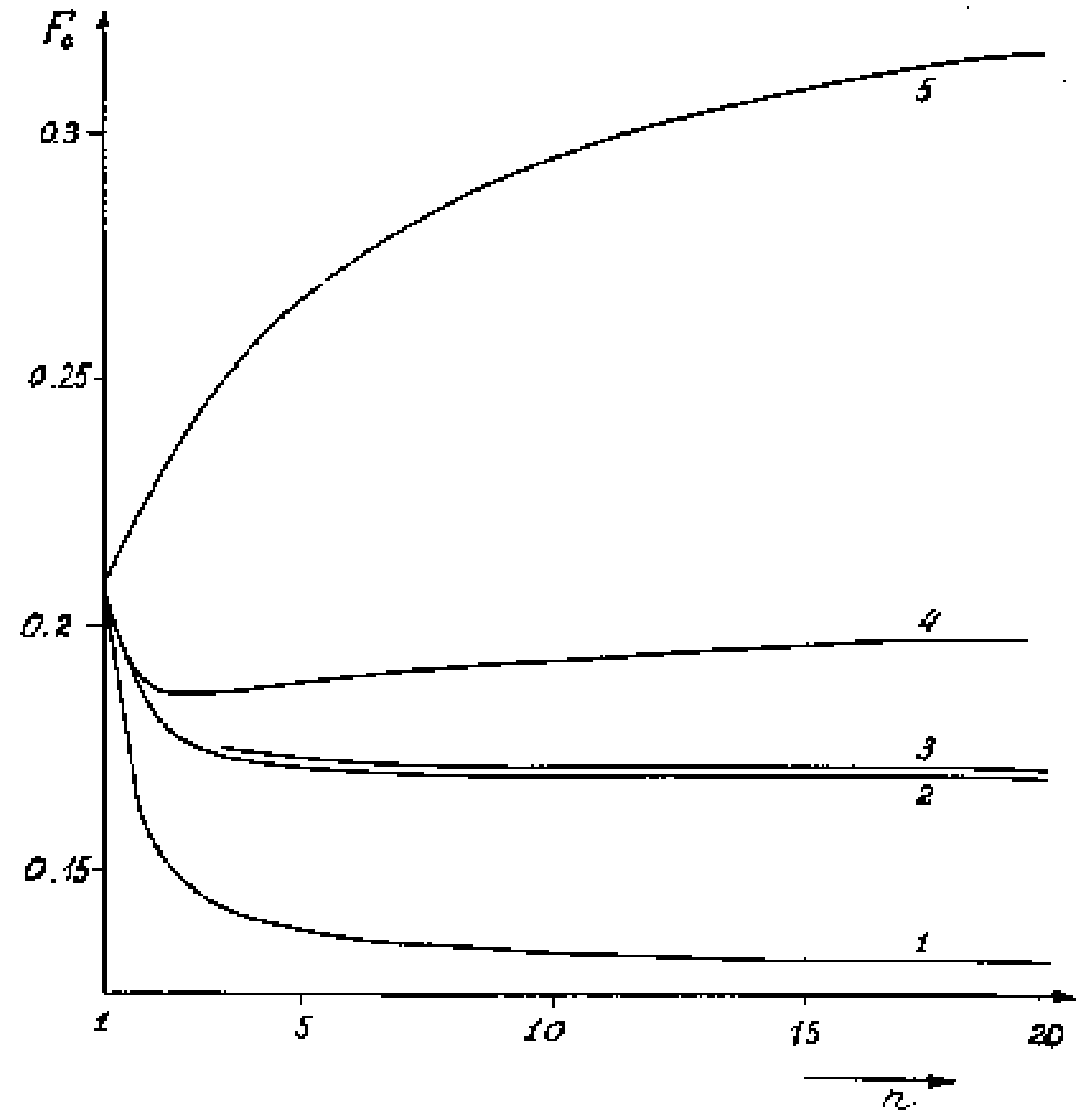

Fig. 1. The critical fields $F_c(n_1, n_2, m)$ for a hydrogen atom. Curves 1–5 correspond to different (n_1, n_2, m) states as explained in the text.

$$F_c/F_*=1+\frac{c_1}{n}+\frac{c_2}{n(\ln n+l_0)}+\dots\,, \qquad (6)$$

the parameters F_*, c_1 and c_2 depending on ν_1, ν_2 and μ ($\mu+\nu_1+\nu_2=1$). For example, $F_*=2^{10}(3\pi)^{-4}=0.1298$, $c_1=2-2^{5/2}\pi^{-1}=0.199$, $c_2=\frac{1}{2}\ln 2=0.347$ and $l_0=2.286$ for the $(0, n-1, 0)$ states ($\nu_1=\mu=0$, $\nu_2=1$ at $n\to\infty$). The asymptotics (6) with the above parameters is in good agreement with the results of numerical calculations at $n\geqslant 5$.

Let us compare the obtained values of F_c with other values available in literature. Consider the tunneling of an electron along the direction of the electric field $\mathscr{E}$ (one-dimensional model). The potential $V(z)=-z^{-1}-\mathscr{E}z$ has a maximum at $z_m=\mathscr{E}^{-1/2}$ with

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[1] We have compared the values of E_r and Γ, obtained by the above computational method, with the results of Refs. [6,17], in which the low-frequency ($\omega\ll 1$) theory of multiphoton ionization was developed. The results of the two approaches are in complete agreement at $\omega=0$. In particular, we reproduced the curve for the dc Stark shift in Fig. 3 of Ref. [16].

[2] Note that this asymptotics, as well as Eq. (14), is not valid for the $(0, 0, n-1)$ and $(n-1, 0, 0)$ states with $n_2=0$.

$V_m = -2\mathscr{E}^{1/2}$. Neglecting the Stark shift of the level, the disappearance of the barrier in $V(z)$ is determined by the condition $V_m = -1/2n^2$. It gives $F_c = \frac{1}{16}$, which is considerably less than the correct values of F_c. A similar approximation (i.e., $\epsilon' = -1$ and $\beta_2 = \frac{1}{2}$ in Eqs. (5)) gives $\zeta = \frac{3}{4}$, $F_c = 0.125$ for the ground state, $n = 1$. In Ref. [5] the value $\mathscr{E}_c(n=1) \approx 0.15$, obtained with only two PT orders, is quoted. Comparison with Fig. 1 and with the exact numerical value $\mathscr{E}_c(n=1) = 0.2082$ shows that all these approximations are insufficient.

2. To obtain the Stark resonances at $\mathscr{E} = \mathscr{E}_c$, we use the modified Bohr–Sommerfeld quantization condition with the barrier penetrability included [12–14],

$$J = \frac{1}{\pi}\int_{x_0}^{x_1} p\,\mathrm{d}x = n + \tfrac{1}{2} - \frac{1}{2\pi}\varphi(a)\,, \tag{7}$$

where J is the quantization integral, $p(x, E) = \{2[E - U(x)]\}^{1/2}$ the quasiclassical momentum,

$$a = \frac{1}{\pi}\int_{x_1}^{x_2} [-p^2(x, E)]^{1/2}\,\mathrm{d}x\,, \tag{7'}$$

$$\varphi(a) = \frac{1}{2\mathrm{i}}\ln[\Gamma(\tfrac{1}{2} + \mathrm{i}a)/\Gamma(\tfrac{1}{2} - \mathrm{i}a)(1 + \mathrm{e}^{-2\pi a})] + a(1 - \ln a)\,, \tag{7''}$$

x_i are the turning points and $x_1 < x < x_2$ is the sub-barrier region. If the energy is close to the barrier summit, $E \approx U_m \equiv U(x_m)$, the potential $U(x)$ can be approximated by the "upturned oscillator",

$$U(x) \approx U_m - \tfrac{1}{2}\omega^2(x - x_m)^2,$$

$$a = (U_m - E)/\omega\,, \tag{8}$$

$|a| \ll 1$. Expanding all the quantities in Eq. (7) at $a \to 0$ and taking into account that $a = \mathrm{i}\Gamma/2\omega$ at $E_r = U_m$, one can solve the resultant equations in the logarithmic approximation, $\ln(n + \frac{1}{2}) \gg 1$,

$$\bar{\Gamma}_n = \frac{\omega \ln 2}{\ln(n + \frac{1}{2}) + l_0}\,, \tag{9}$$

where

$$J_0 = \frac{1}{\pi}\int_{\bar{x}_0}^{x_m} \bar{p}\,\mathrm{d}x\,,$$

$$l_0 = \ln\left(\frac{8\omega(x_m - \bar{x}_0)^2}{J_0}\right) + C + 2\int_{\bar{x}_0}^{x_m}\left(\frac{\omega}{\bar{p}} - \frac{1}{x_m - x}\right)\mathrm{d}x\,, \tag{9'}$$

$\bar{x}_0$, x_m and $\bar{p} = p(x, U_m)$ are the turning points and the momentum at $E = U_m$, $C = 0.5772$ is the Euler constant and we denote $\bar{\Gamma}_n \equiv \Gamma_n(E_r = U_m)$.

It should be noted that the oscillator frequency ω depends on n, which can be easily seen from the following example ($l = 0$),

$$V(r) = -\frac{g}{\alpha r^{\alpha}} - \mathscr{E}r, \quad 0 < \alpha < 2\,. \tag{10}$$

If $\mathscr{E} \to 0$, the energy levels with $E \sim U_m$ get into the region of highly excited states, where

$$|E_n| \sim n^{-2\alpha/(2-\alpha)}, \quad \langle r_n \rangle \sim n^{2/(2-\alpha)}\,,$$

$$\omega_n \sim |E_n|^{1/2}/\langle r_n \rangle \sim n^{-(2+\alpha)/(2-\alpha)}\,, \tag{11}$$

whence the estimation follows,

$$\bar{\Gamma}_n \approx \mathrm{const} \times (n^{(2+\alpha)/(2-\alpha)}\log n)^{-1}, \quad n \gg 1\,. \tag{12}$$

For the Stark problem in hydrogen with two degrees of freedom (ξ and η variables), the calculations become more complicated. From Eqs. (2), (5) it follows that

$$\omega_n(\mathscr{E} = \mathscr{E}_c) = \frac{c_3(1 - \zeta)^{1/4}}{n^3[1 + (1 - \zeta)^{1/2}]}(-\epsilon_c')^{-1/2}F_c, \tag{13}$$

where $c_3 = \frac{3}{2}$ and ζ is defined in Eq. (5). So, $\omega_n \propto n^{-3}$, which is related to the impact frequency of an electron with the wall of the potential barrier in the Coulomb field and corresponds to the Gamow formula (see also Eq. (11) at $\alpha = 1$).

The final expression for the widths $\bar{\Gamma}_n$ can be written as

$$\bar{\Gamma}_n = \gamma n^{-3}(\ln n + l_0)^{-1}, \quad \mathscr{E} = \mathscr{E}_c, \quad n \gg 1\,, \tag{14}$$

where γ and l_0 are constants, depending on n_1, n_2 and m. For instance,

$$\gamma = 2^8(3\pi)^{-3}\ln 2 = 0.212\,,$$

$$l_0 = C - 4 + \ln 96\pi = 2.286\,, \tag{14'}$$

in the case of the $(0, n-1, 0)$ states. The values of γ

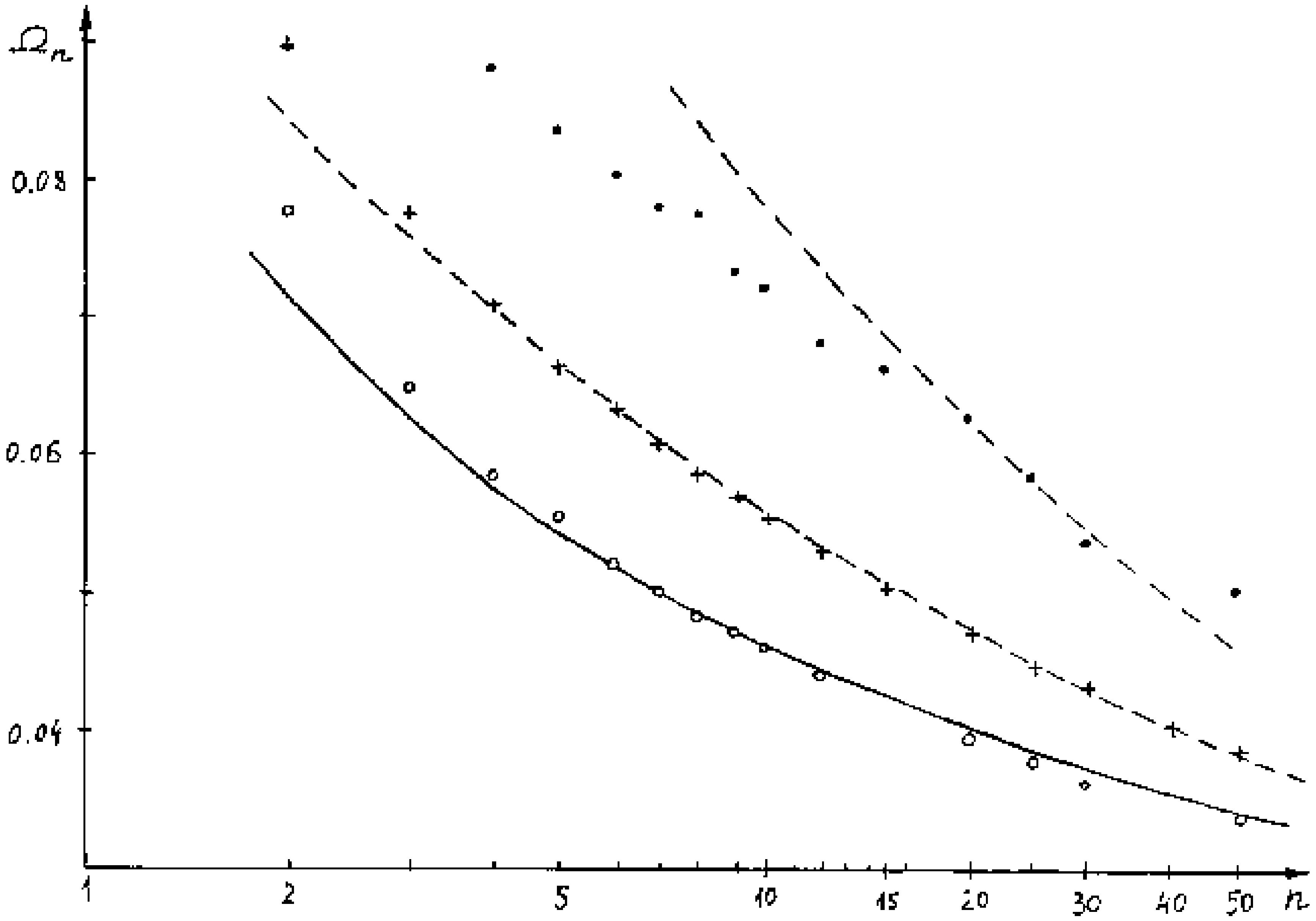

Fig. 2. The dependence of $n^3\bar{\Gamma}(n_1 n_2 m)=\Omega_n$ on the principal quantum number n. The values of $\ln n$ are plotted at the abscissa. The solid curve is calculated by Eq. (14) with the values of the parameters γ and l_0 given in (14′), the dotted ones correspond to Eqs. (15) and (16).

and l_0 for an arbitrary state can be calculated numerically, see Appendix.

It should be noted that the asymptotics (14) may be modified, $n_2=0$. For example, we obtained for the circular states $(0, 0, n-1)$ that [3]

$$\bar{\Gamma}_n=\gamma_1 n^{-16/5} \tag{15}$$

and for the $(n-1, 0, 0)$ states [4]

$$\bar{\Gamma}_n=\gamma_2 n^{-10/3}, \quad n\to\infty . \tag{16}$$

The widths $\bar{\Gamma}_n$ for different states of a hydrogen atom, calculated by summation of PT series, are shown in Fig. 2. As can be seen from Fig. 2, the asymptotics (14) is in good agreement with numerical calculations already at $n>3$.

3. A resonance can be observed without ambiguity, if $\Gamma \ll \Delta E$, where ΔE is the spacing between the adjacent resonances. In the one-dimensional case from the modified quantization condition (7) it follows that $(n\gg 1)$

$$\eta_n=\frac{\bar{\Gamma}_n}{\Delta E_n}=\frac{\ln 2}{2\pi}\approx 0.110 , \tag{17}$$

$$\bar{\Gamma}_{n+1}/\bar{\Gamma}_n=1+\frac{c_4}{\ln(n+\frac{1}{2})+c_5}+\dots , \tag{18}$$

with $c_4=2\pi^2/\ln 2\approx 28.5$ and $c_5=C+\ln 16\pi\approx 4.50$ (in the parabolic approximation). These asymptotics are valid, within the frame of the parabolic approxima-

tization integrals J_i near the top of the barrier, $F\to F_c$. It is easy to obtain that

$$\mathrm{Im}\,\beta_2 = -\tfrac{1}{4}s\epsilon'', \quad a = \mathrm{i}\,\frac{n}{8\omega}\,(1+s/y_{\mathrm{m}})\epsilon'' , \tag{A.4}$$

where $\epsilon'' = -\mathrm{Im}\,\epsilon \to 0$,

$$s = \int\limits_{x_0}^{x_1} \frac{\mathrm{d}x}{k_1(x)} \bigg/ \int\limits_{x_0}^{x_1} \frac{\mathrm{d}x}{x k_1(x)} \tag{A.5}$$

and the reduced variables (3) are used. The expansion of J_2 is analogous, but much more complicated, since the derivaties $\partial J_2/\partial\epsilon$ and $\partial J_2/\partial\beta_2$ are logarithmically divergent, as $F\to F_c$.

Finally, we obtain Eqs. (6) and (9), where

$$y = \frac{4\omega \ln 2}{(1+s/y_{\mathrm{m}})} , \tag{A.6}$$

$$l_0 = C + \ln[8\omega(y_m - \bar{y}_0)^2] + \frac{2(\tau_0 + s\tau_1)}{1+s/y_{\mathrm{m}}} , \tag{A.7}$$

$$\tau_j = \int\limits_{\bar{y}_0}^{y_m} \mathrm{d}y \left(\frac{\omega}{y^j \bar{k}_2(y)} - \frac{1}{y_m^j (y_m - y)} \right), \quad j = 1, 2 , \tag{A.8}$$

and the frequency ω of the "upturned oscillator" is given by Eq. (13). Here we denote by overbars (e.g., $\bar{y}_0$, $\bar{y}_1 \equiv y_{\mathrm{m}}$, $\bar{k}_2(y)$, etc.) the values of the corresponding variables at $E_r = U_{\mathrm{m}}$, or $\mathcal{E} = \mathcal{E}_{\mathrm{c}}$. Since $\bar{k}_2(y) = \omega(y_{\mathrm{m}} - y) + \dots$ at $y \to y_{\mathrm{m}}$, the integrals τ_j are convergent and can be calculated numerically. For $m=0$ states it is possible to obtain σ_i, τ_j in analytic form. In particular, in the case of the $(0, n-1, 0)$ states with $n \gg 1$ we have $\mu = \beta_1 = 0$, $\beta_2 = 1$, then

$$F_c \to F_* = \frac{2^{10}}{(3\pi)^4} \approx 0.130, \quad \epsilon_* = -\frac{2^7}{(3\pi)^2} \approx -1.441 ,$$

$$y_m = \omega^{-2/3} = (3\pi/4)^2 \approx 5.552 , \tag{A.9}$$

$$s = 0, \quad \tau_0 = -2(1 - \ln 2), \quad \tau_1 = \frac{2\ln 2}{y_{\mathrm{m}}} , \tag{A.10}$$

and Eqs. (14), (14′) immediately follow.

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