The hydrogen atom in a strong electric field

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A calculation is reported of Stark shifts and widths of the ground and first excited states of the hydrogen atom in a strong electric field $\mathscr{E}$ up to values of $\mathscr{E}$ comparable with the field strength on an atomic orbit. Two independent methods are used, namely, summation of divergent perturbation-theory series and the $1/n$ expansion. The two methods have a wide region of overlap (in the parameters n_1, n_2, m, and $\mathscr{E}$). The calculations are confirmed by considering the Rydberg limit as $n \to \infty$.

1. The Stark effect is one of the classical but, at the same time, most difficult (part from the weak-field region) problems in quantum mechanics (see, for example, Refs. 1–20; a more detailed list of references is given in Refs. 1, 4, 10, and 15). When the external field $\mathscr{E}$ tends to zero, the energy of a level with parabolic quantum numbers n_1, n_2, m in the hydrogen atom can be expanded into a formal pertubation-theory series, as follows:

$$E^{(n_1 n_2 m)}(\mathscr{E}) = \frac{1}{2n^2}\sum_{k=0}^{\infty} \varepsilon_k^{(n_1 n_2 m)} F^k, \qquad (1)$$

where $n = n_1 + n_2 + m + 1$ is the principal quantum number ($m \geqslant 0$), k is the perturbation-theory order, $F = n^4\mathscr{E}$, $\varepsilon = 2n^2E$. The coefficients of the first few orders of pertubation theory are

$$\varepsilon_0 = -1, \quad \varepsilon_1 = 3(n_1 - n_2)/n,$$
$$\varepsilon_2 = -(1/8n^2)[17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19], \qquad (2)$$
$$\varepsilon_3 = [3(n_1 - n_2)/16n^3][23n^2 - (n_1 - n_2)^2 + 11m^2 + 39], \ldots;$$

and below we use atomic units for which $\hbar = m_e = e = 1$, so that the unit of the electric field strength is 1 a.u. $= m_e^2 e^5/\hbar^4 = 5.142 \times 10^9$ V/cm.

The first three perturbation coefficients have long been known.[1] The fourth-order coefficient for states with arbitrary n_1, n_2, m was calculated by Alliluev and Malkin,[4] using the dynamic symmetry group of the hydrogen atom. The explicit expressions[2)] for the perturbation-theory coefficients up to $k = 7$ were published by Silverstone[5] and up to $k = 9$ by Hoe *et al.*[6]

New perturbation-theory techniques, developed in the course of the last few years, can be used to calculate the coefficients ε_k of very high order. For example, calculations have been carried out[7,8] up to $k = 160$ for the ground state and up to $k = 100$ for $n = 2$ (Ref. 10). These coefficients carry significant information about the behavior of the atomic energy levels $E = E_0 - i\Gamma/2$ in a strong electric field. However, as $k \to \infty$, the higher perturbation-theory orders increases factorially (This is the Dyson phenomenon[11]):

$$\varepsilon_k^{(n_1 n_2 m)} \approx k!\alpha^k k^\beta c_0[1 + O(1/k)], \qquad (3)$$

where $\alpha = 3/2n$, $\beta = n + |n_1 - n_2| - 1$, and, for example, for states with $n_1 = n_2$,

$$c_0 = {}^1/_2[1 + (-1)^k]6^n/\pi n^3 n_1!(n - n_1 - 1)! \qquad (3')$$

The perturbation-theory series thus have a zero radius of convergence, and the energy $E^{(n_1 n_2 m)}(\mathscr{E})$ has an essential singularity at $\mathscr{E} = 0$ and a cut along the real axis. It follows that the use of perturbation theory in the evaluation of the Stark shifts and widths of atomic levels in a strong field cannot be carried out without the corresponding summing of convergent series.

The usual perturbation-theory polynomials

$$\sum_{k=0}^{N} \varepsilon_k F^k$$

determine $E_0(F)$ only in the weak-field region (in practice, for $\mathscr{E} \lesssim 0.03$ in the case of the ground state). The Padé approximants have been used[8] to extend this to $\mathscr{E} \simeq 0.1$. Numerical solution of the Schrödinger equation has been used[3,12] to calculate E_0 and Γ. We note at once that, for $F \gtrsim 0.2$, the results of Damburg and Kolosov[12] are significantly different from ours (and from other results;[3,13] see the detailed discussion in Sec. 5). In strong fields, the modified perturbation theory[13] appears to be valid (we note that this variant of perturbation theory was first proposed in Ref. 21 in the case of the anharmonic oscillator $V(r) = r^2 + gr^4$). However, the approximation used in Ref. 13 was of too low order, so that the convergence of the method could not be reliably judged. Moreover, the calculation was confined to the ground state of the hydrogen atom. Complex coordinates[14] and the Padé-Borel transformation[15] have been used to sum the perturbation theory series (1) with high precision, but these results were obtained up to $\mathscr{E} = 0.1$, and only for the ground state. At the same time, calculation of E_0 and Γ for strong fields ($F > 0.1$) and for a wide spectrum of states, including highly excited (or Rydberg[22]) states, are of considerable interest in view of advances in laser spectroscopy.

To solve this problem, we used the Padé-Hermite approximants[23] and the $1/n$ expansion.[24,25] These methods are briefly described below and then, in Sec. 3, we report the results of our calculations. In Sec. 4, we discuss the Rydberg limit ($n \to \infty$), which provides us with an independent verification of the validity of our method of summation of divergent perturbation-theory series.

2. Methods of calculation. The values of the Padé-Hermite approximant $y_{[L,M,N]}(F)$ were calculated from the known perturbation-theory coefficients ε_k using the equation

$$P_L - Q_M y + R_N y^2 = 0, \qquad (4)$$

where P_L, Q_M, and R_N are polynomials in F (of degree L, M,

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and N, respectively), whose coefficients are uniquely determined from the perturbation-theory coefficients, using the condition

$$P_L - Q_N E + R_N E^2 = O(F^{L+M+N+2}), \tag{5}$$

where $F \to 0$ and $E(F)$ is the pertubation-theory series (1). As a rule, we took $L = M = N$; this Padé-Hermite approximant will be denoted by $y_N(F)$. The usual Padé approximants $[L/M](F)$ are special cases of the Padé-Hermite approximant for $R_N \equiv 0$.

The Padé-Hermite approximants have an important advantage as compared with the Padé approximant that is particularly significant when the perturbation-theory series is summed for the Stark effect. Thus, it is clear from (4) that $y_N(F)$ can have an imaginary part even when all the coefficients of the polynomials P_N, Q_N, and R_N are real. We note that coefficients in (1) are real by perturbation-theory construction. Because of this, the polynomials P, Q, and R determined from (5) have only real coefficients. At the same time, the energy $E(F)$ has an imaginary part for any $F \neq 0$, which corresponds to the probability of ionization by the external field in this state. Hence, when we use the Padé approximant $[L/M](F)$ to sum the perturbation-theory series, the cut $0 < F < \infty$ is simulated by a higher density of Padé-approximant poles, and this leads to a numerical instability when E_0 and Γ are determined.

Analysis of the convergence of the sequence $y_N(F)$ with increasing N shows that, when $N = 12$–15, numerical values of y_N are stabilized and the energy is obtained with a precision no worse than 10^{-4} (the calculation; then involves 60–80 orders of perturbation theory). We note that, in weak fields (in particular, for $F \lesssim 0.03$ when $n = 1$ and $F \lesssim 0.10$ when $n = 10$), the Stark shifts are calculated with higher accuracy. As far as the level widths are concerned, the values of $\mathrm{Im} y_N(F)$ become stabilized for $N \leqslant 15$ only in those cases for which $\Gamma > 10^{-8}$–10^{-9}. This limits, to some extent, the calculation of the widths $\Gamma^{(n_1 n_2 m)}(F)$ in weak fields. At this point, we confine our discussion to these brief remarks about the Padé-Hermite approximants. Further details, such as convergence precision of computed energy, and so on, can be found in Refs. 25 and 26.

Another approach, independent of that described above, is based on the $1/n$ approximation, which is being successfully used in different branches of theortical physics.[27,28] It has recently been shown that[24] the $1/n$ expansion can be used to calculate the energy not only in the discrete spectrum, but even for resonance levels. The energy expansion takes the form

$$\varepsilon_{nl} = \varepsilon^{(0)} + \varepsilon^{(1)}/n + \varepsilon^{(2)}/n^2 + \ldots, \tag{6}$$

where the first term represents, the classical particle at rest at the point corresponding to the minimum of the effective potential at $r = r_0$, and the higher-order terms correspond to the inclusion of zero-point oscillations and anharmonic effects. The Yukawa, Hulthen, and funnel potentials have been used[24] to show that the $1/n$ expansion, which is theoretical valid for $n \gg 1$, is accurate even for relatively small n. For example, for $n = 3$, the first three terms of (6) will suffice for a precision of 10^{-3}–10^{-4} in the level energy. We have applied this method to the Stark effect. For the nodeless $(0, 0, m)$ states, the first three coefficients in (6) can be calculated analytically and the result is

$$\begin{aligned}
\varepsilon^{(0)} &= -(1-\tau^2)^2(1+3\tau^2), \\
\varepsilon^{(1)} &= (1-\tau^2)^3[(1+3\tau)^{1/2} + (1-3\tau)^{1/2} - 2], \\
\varepsilon^{(2)} &= -\frac{(1-\tau^2)^4}{4(1-9\tau^2)^2}\{18 - 133\tau^2 + 3\tau^4 \\
&\quad - 12(1-9\tau^2)^{1/2}[(1+\tau)(1-3\tau)^{1/2} \\
&\quad + (1-\tau)(1+3\tau)^{1/2} - 1/2(1-\tau^2)]\},
\end{aligned} \tag{7}$$

whereas the higher-order coefficients are determined from recurrence relations. In these expressions, τ is a root of the equation

$$\tau(1-\tau^2)^4 = F, \tag{8}$$

that tends to zero for $F \to 0$ (see Appendix A for the derivation of these equations). All the coefficients $\varepsilon^{(k)}$ are real so long as $0 < \tau < 1/3$. For $\tau = 1/3$, which corresponds to fields

$$F = F_* = 2^{12} \cdot 3^{-9} = 0.208, \tag{9}$$

the two classical solutions[3] come into contact and the point of equilibrium moves into the complex plane. Thereafter, $\varepsilon^{(k)}$ become complex, so that not only the level shift but also its width can be described.

We note that the $1/n$ expansion is not valid for $F \simeq F_*$ because the coefficients $\varepsilon^{(k)}(F)$ have a singularity at this point. The remarkable fact is that, as F increases still further, the $1/n$ expansion again becomes valid for the determination of E_0 and Γ [the convergence of (6) in strong fields can be accelerated by summing it with the aid of the Padé approximant; this was used to obtain the results reported below].

The $1/n$ expansion converges rapidly for $F > F_*$ and $n \gtrsim 3$ (and especially for Rydberg states in which there has been increasing interest in recent years[22]), whereas the method involving the Padé-Hermite approximants has advantages for smaller n. It is significant that there is a region of overlap (in the parameters n and F), in which the two methods agree to a high precision and, for $F \leqslant 0.1$, with other calculations[14,15] (see Table II in Ref. 25). The $1/n$ expansion thus confirms the procedure that we have chosen for summing the divergent perturbation series.

3. Turning now to the results of our calculations, we begin with the $(0, 0, n-1)$ states which , in the classical limit $(n \to \infty)$, correspond to the motion of an electron on a circular orbit perpendicular to the direction of the field $\mathscr{E}$. In this case, all odd orders of perturbation theory vanish, i.e., $E = E(F^2)$. It is convenient to transform from $E, \mathscr{E}$ to the reduced variables

$$\varepsilon = 2n^2 E, \ \mathscr{F} = n^4 F, \ \mu = m/n, \ \nu_i = n_i/n. \tag{10}$$

The Stark shifts are shown in Fig. 1. of Ref. 16 (see also Ref. 25). We note that, in very strong fields, the Stark shifts of these levels change sign. We shall write the atomic level widths in the form

$$\Gamma^{(n_1 n_2 m)}(F) = \tilde{\Gamma}^{(n_1 n_2 m)}(F) \exp\{-n\delta_{n_1 n_2 m}(F)\}, \tag{11}$$

where the first factor, $\tilde{\Gamma}(F)$, corresponds to the quasiclassical formula

$$\begin{aligned}
\Gamma^{(n_1 n_2 m)} &= C_{n_1 n_2 m} F^{-(n-n_1+n_2)} \exp(-2n/3F), \\
C_{n_1 n_2 m} &= (4n)^{n-n_1+n_2} \exp[3(n_1-n_2)]/n_1!(n_2+m)!n^3;
\end{aligned} \tag{12}$$

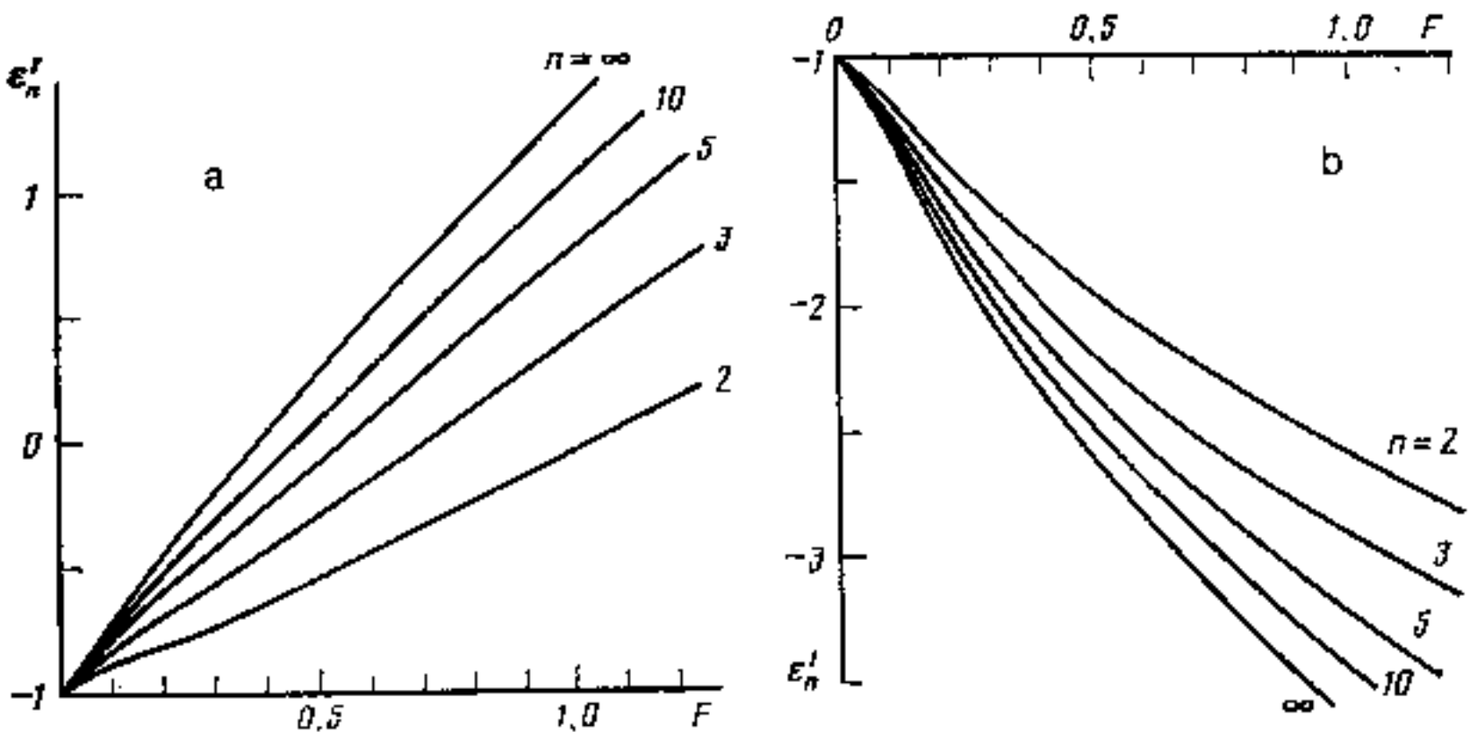

FIG. 1. Plots of $\varepsilon_n' = 2n^2 \mathrm{Re}E(F)$ for the states $(n-1, 0, 0)$—a and $(0, n-1, 0)$—b.

This formula is asymptotically correct in the limit as $F \to 0$ (cf. Refs. 17–19). Hence, $\delta_{n_1 n_2 m}(0) = 0$. We note that the exact form of the pre-exponential factor $C_{n_1 n_2 m}$ for a level with arbitrary quantum numbers was deduced by Slavyanov[18] and, later, by Yamabe and Tachibana.[19]

The widths $\Gamma^{(n_1 n_2 m)}$, calculated by the above methods, enable us to find the quantities $\delta_{n_1 n_2 m}$ in (11) (cf., Fig. 2 of Ref. 16). Similar calculations were performed for the two series of states $(n_1, 0, 0)$ and $(0, n_2, 0)$, of which the first corresponds to the smallest and the second to the largest widths among all the sublevels with given n. The results are shown in Fig. 1 (Stark shifts) and Fig. 2 (widths). The figures also show the limiting curves corresponding to $n = \infty$, calculated by independent methods (see also Sec. 4). It is clear from the figures that the limiting curves are in qualitative agreement with the results obtained by summing the perturbation-theory series and by the $1/n$ expansion.

For small F, only the factor $\tilde{\Gamma}$ is important in (11); it is very dependent on the field and varies by many orders of magnitude. However, the range of validity of (1) is relatively narrow: $\mathscr{E} \lesssim 0.1 n^{-4}$. As $F \to 0$,

$$\delta_{n_1 n_2 m}(F) = c_1 F + c_2 F^2 + \ldots, \tag{13}$$

where, for example,

$$c_1 = \frac{1}{12n^2} \begin{cases} 48n^2+9n+50 & \text{for } (n_1, 0, 0), \\ 42n^2+51n+14 & \text{for } (0, n_2, 0), \\ 33n^2+54n+20 & \text{for } (0, 0, m), \end{cases} \tag{14}$$

and, for the Rydberg states $(n \gg 1)$

$$c_1 = {}^1/_4 [11+13\nu_1+11\nu_2-8(\nu_1^2+\nu_1\nu_2+\nu_2^2)] + O(1/n) \tag{14'}$$

(these formuals follow from the results of Damburg and Kolosov[12]). The slope of the curves in Fig. 2 at $F = 0$ is in agreement with (13) and (14). However, the linear term in (13) is sufficient only for $F < 0.1$; in stronger fields, the function $\delta(F)$ becomes essentially nonlinear. In all the cases that we have considered, $\delta(F) > 0$, so that the ionization probability by a strong field in a given energy level is much lower than the probability predicted by the quasiclassical estimate (12). When $F > F_*$, the barrier in the effective potential $U_2(\eta)$ vanishes (see Appendix B) and the ionization process is no longer of the over-barrier type. In this region, the field dependence of the level width is approximately linear, as illustrated by Fig. 3 (this is also valid for other states). We note that the broken curves in Fig. 3 correspond to the inclusion of the first two terms in the $1/n$ expansion.

The perturbation theory coefficients for excited states with $n = 2$ and $n = 3$ were calculated previously.[10] Using these results and summing the corresponding perturbation theory series with the aid of the Padé-Hermite approximants, we obtain the Stark shift shown in Fig. 4 (see Ref. 26 for further details). The same method can be used for an arbitrary state $(n_1 n_2 m)$ for which the perturbation expansion is known to sufficiently high order.

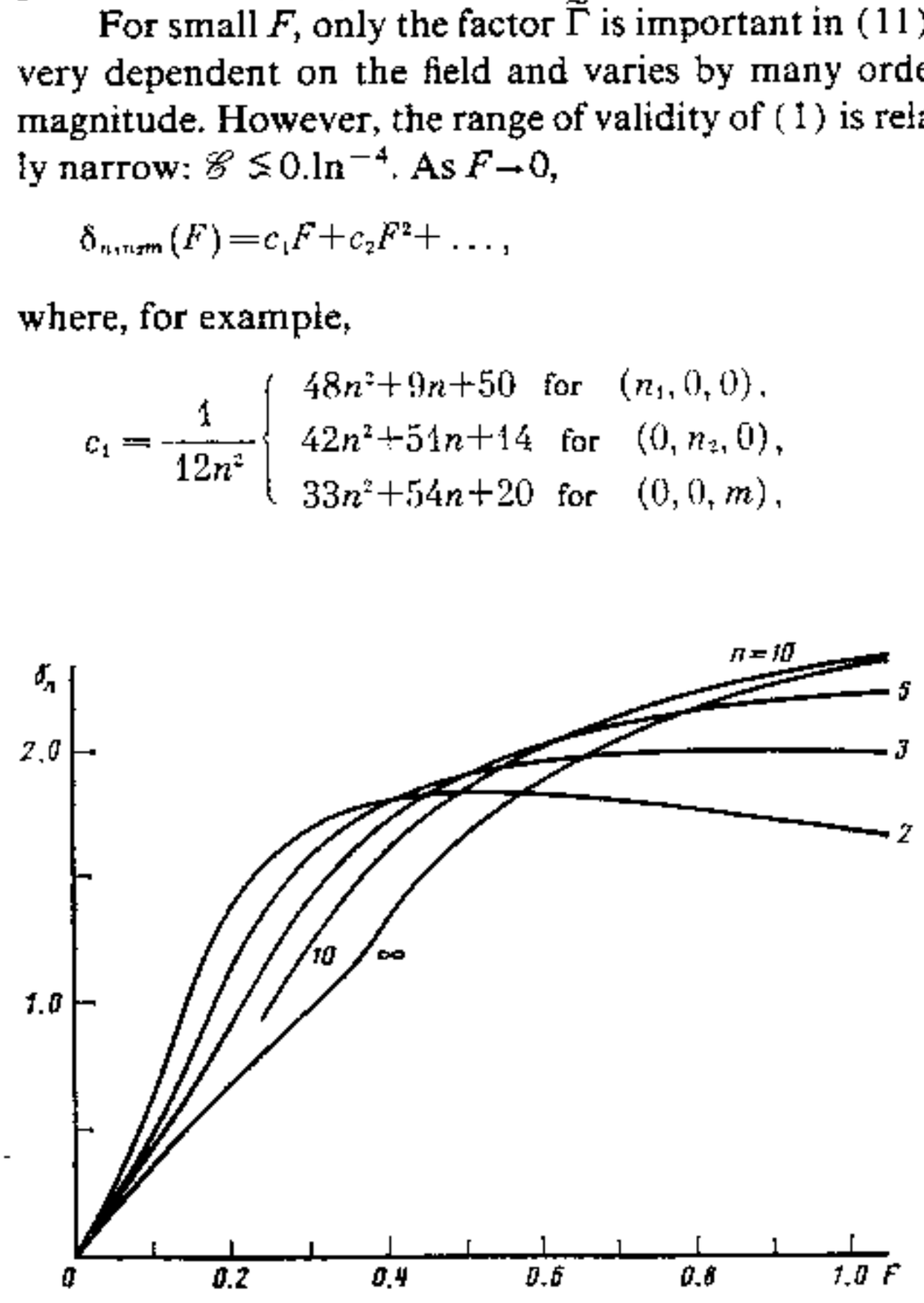

FIG. 2. The function $\delta_n(F)$ for the $(n-1, 0, 0)$ states [cf. Eq. (11)].

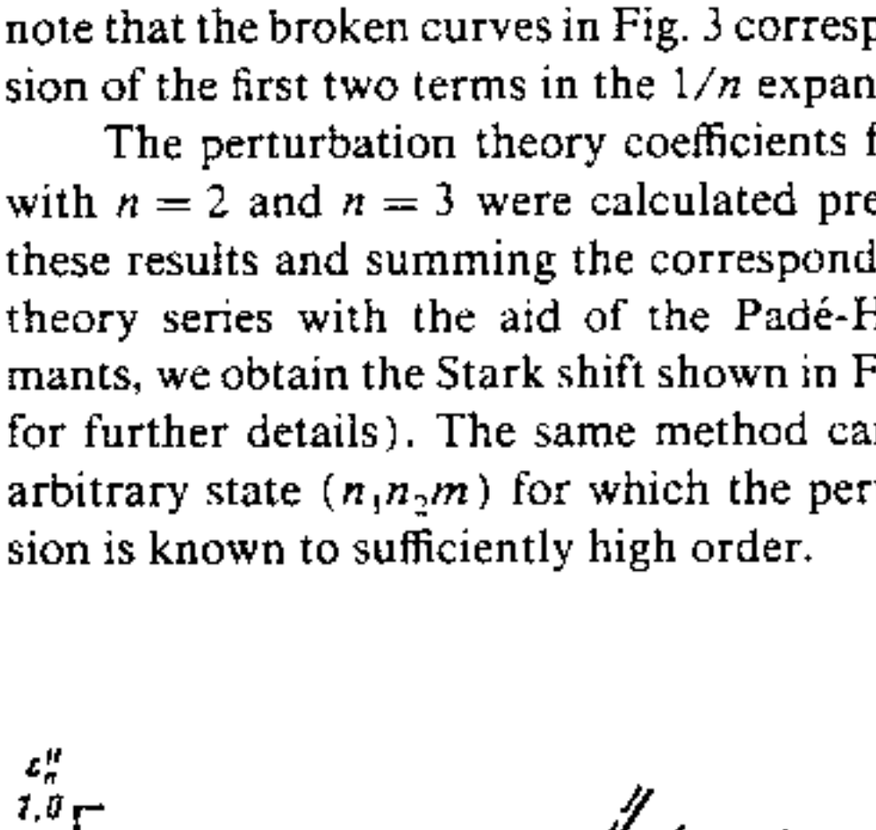

FIG. 3. $\varepsilon_n'' = n^2\Gamma_n$ as a function of the external field for the $(0, 0, n-1)$ states. The difference between the broken curves [first two terms in (6)] and the solid curves is a measure of the precision of the $1/n$ expansion.

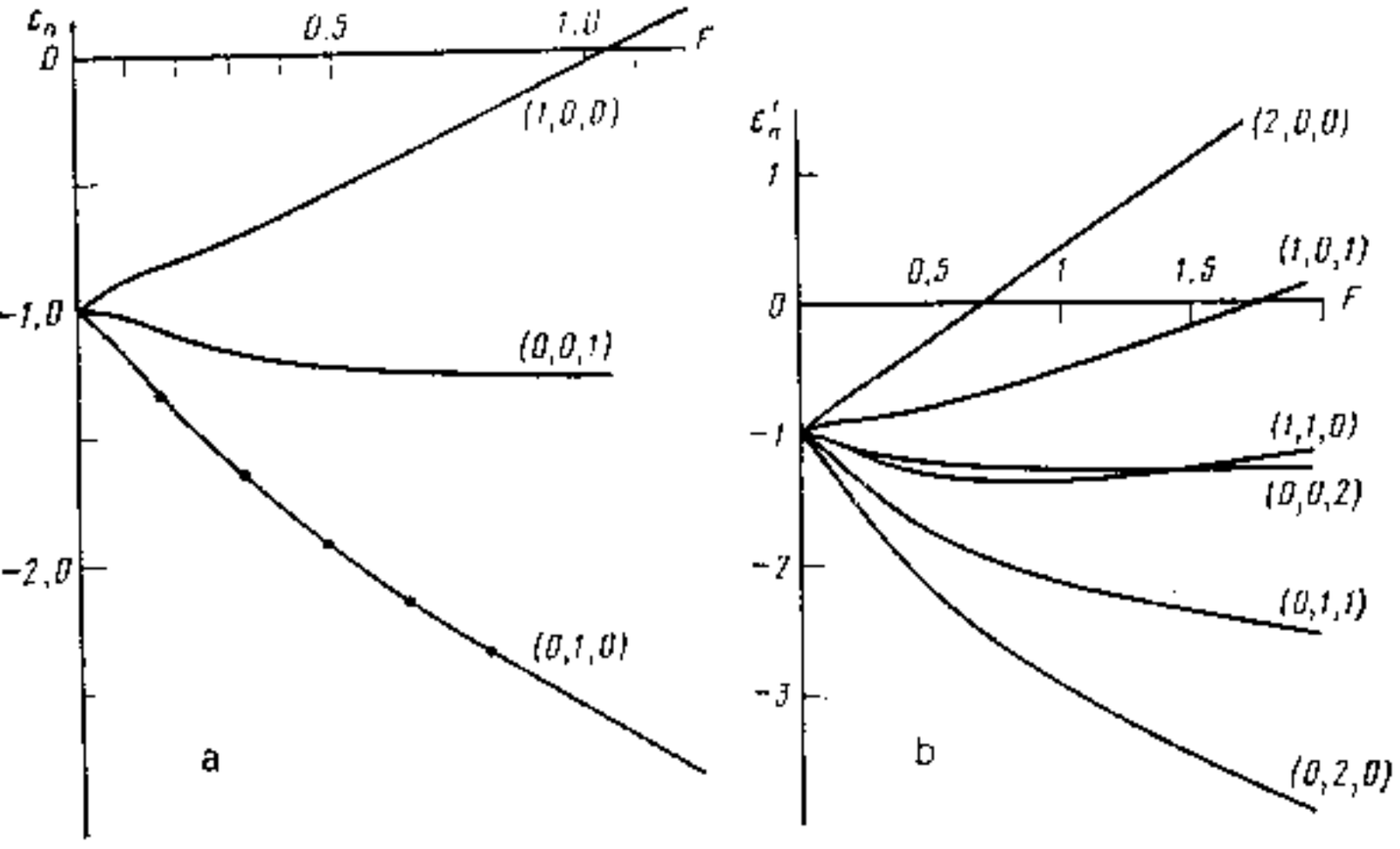

FIG. 4. Stark shifts of the $n = 2$ (a) and $n = 3$ (b) levels. The parabolic quantum numbers (n_1, n_2, m) are indicated against the curves. The points are taken from Ref. 20.

4. Rydberg limit. The excited-state energies are determined from the quasiclassical quantization condition of Bohr and Sommerfeld. In the limit as $n \to \infty$, we have

$$\int_{\xi_1}^{\xi_2} d\xi \left(\frac{4\beta_1}{\xi} - \frac{\mu^2}{\xi^2} - F\frac{\xi}{2} + \varepsilon \right)^{1/2} = 2\pi\nu_1,$$

$$\int_{\eta_1}^{\eta_2} d\eta \left(\frac{4\beta_2}{\eta} - \frac{\mu^2}{\eta^2} + F\frac{\eta}{2} + \varepsilon \right)^{1/2} = 2\pi\nu_2, \quad \mu + \nu_1 + \nu_2 = 1 \quad (15)$$

where $\mu = m/n \geqslant 0$, ξ_i, η_i are the turning points. The integrals in these expressions are, in general, relatively complicated elliptic integrals. The situation becomes simpler when $m = 0$. The integrals can then be evaluated analytically and (15) assumes the form

$$\beta_1 {}_2F_1(1/4, 3/4; 2; -16\beta_1 F/\varepsilon^2) = (-\varepsilon)^{1/2}\nu_1,$$
$$\beta_2 {}_2F_1(1/4; 3/4; 2; 16\beta_2 F/\varepsilon^2) = (-\varepsilon)^{1/2}\nu_2, \ \beta_1 + \beta_2 = 1, \ \nu_1 + \nu_2 = 1, \quad (16)$$

where ${}_2F_1(\alpha, \beta; \gamma; z)$ is the hypergeometric function [the unknowns are ε and the separation constants, β_1, β_2; see Appendix B for details of the calculations leading to (16)]. As $F \to 0$, we obtain

$$\begin{aligned} \beta_1 &= \nu_1[1 + 3/2\nu_2 F + 1/4(\nu_1 - \nu_2)\nu_2 F^2 + \dots], \\ \beta_2 &= \nu_2[1 - 3/2\nu_1 F - 1/4\nu_1(\nu_1 - \nu_2)F^2 + \dots], \\ \varepsilon &= -1 + 3(\nu_1 - \nu_2)F - 1/8[17 - 3(\nu_1 - \nu_2)^2]F^2 + \dots \end{aligned} \quad (17)$$

Let us now consider some limiting cases.

(1) When $\nu_1 = 0$ [states of the form $(0, n_2, 0)$], we have $\beta_1 \equiv 0$ for any F, and (16) reduces to the single equation

$$(-\varepsilon)^{1/2} = {}_2F_1(1/4, 3/4; 2; 16F/\varepsilon^2). \quad (18)$$

The root of this equation remains real so long as $z = 16F/\varepsilon^2 < 1$. When $z = 1$, the hypergeometric function has a branch point; the corresponding values of F and ε are labeled with an asterisk:

$$F_* = 1024/(3\pi)^4 = 0.129782, \ \varepsilon_* = -128/9\pi^2 = -1.441012. \quad (19)$$

As $F \to F_*$, the solution of (18) has a singularity:

$$\varepsilon = \varepsilon_* \left\{ 1 - \frac{1}{2} f - \frac{2}{3} \frac{f}{\ln f} + O\left(f \frac{\ln \ln f}{(\ln f)^2} \right) \right\}, \quad (20)$$

where $f = (F_* - F)/F_*$ and $F > F_*$ the function $\varepsilon(F)$ acquires an imaginary part. When $F > F_*$, the quantity $\varepsilon(F)$ moves into the complex plane; this enables us to describe not only the level shift, but also the level width (as in the case of the $1/n$ expansion[24,25]). The corresponding curve ($n = \infty$) obtained by numerical solution of (18) is shown in Fig. 1b [formula (20) was used as the initial approximation for the iterations]. It is clear from the figure that (18) provides a qualitative description of E_0 and Γ for Rydberg states ($n \gg 1$).

(2) Similarly, $\beta_2 \equiv 0$ when $\nu_2 = 0$ [cf. (17)]. For the $(n_1, 0, 0)$ states, we therefore obtain the equation

$$(-\varepsilon)^{1/2} = {}_2F_1(1/4, 3/4; 2; -16F/\varepsilon^2). \quad (21)$$

The energy $\varepsilon(F)$ vanishes for $F \to F_0$, where

$$F_0 = 1/16\{{}_2F_1(1/4, 5/4; 2; 1)\}^4 = 0.3834.$$

In the numerical solution of (21), it is convenient to use identities to transform it to the form

$$(\varepsilon^2 + 16F)^{1/4} = {}_2F_1(1/2, 3/2; 2; 1/2 + \varepsilon/2(\varepsilon^2 + 16F)^{1/2}). \quad (21')$$

Hence, it is clear that $F = F_0$ is not a singular point of $\varepsilon(F)$ and ε remains real for all $0 < F < \infty$. Therefore, for $(n_1, 0, 0)$ states, the level width vanishes in the limit as $n \to \infty$. Actually, the first equation in (16) is the quantization condition in the funnel potential $U_1(\xi) = -1/2\xi + \mathscr{E}\xi/8$ (the energy spectrum is exclusively discrete) and the second reduces to the identity $0 = 0$.

For all other states, the quasiclassical description gives a finite level width in the region above the threshold, $F > F_*$.

(3) We also calculated[26] the series of states $(n_1, n_1, 0)$ for which, as for the $(0, 0, m)$ states, the linear Stark effect is not present in a weak field. We also calculated[26] the energies and widths of states with $n_1 = 20$–30 and $n_2, m = 0$, 1, and 2, which have the lowest decay probability among all the states with given n.

(4) It is well known[1,2] that only the potential $U_2(\eta)$ has a barrier (for sufficiently small F). The field $F = F_*$, for which the barrier on $U_2(\eta)$ disappears, will be referred to as the classical ionization threshold. When $m = 0$, the potential $U_2(\eta)$ has a maximum at $\eta_0 = 2(\beta_2/F)^{1/2}$:

$$U_2(\eta_0) = -4(\beta_2 F)^{1/2}.$$

The barrier disappears when $\varepsilon = U_2(\eta_0)$, i.e., $\beta_2 F/\varepsilon^2 = 1/16$, which corresponds precisely to the singular point of the hypergeometric function in (16).

Analysis of (16) shows that

$$F_*(n_1, n_2, 0) = \begin{cases} 0.130+0.052\nu_1+\ldots, & \nu_1 \to 0, \\ 0.383-1.259(1-\nu_1)^{1/2}+\ldots, & \nu_1 \to 1, \end{cases} \quad (22)$$

where F_* monotonically increases with increasing $\nu_1 = n_1/n$ (see Appendix C).

For $F > F_*$, the width Γ becomes practically a linear function of F (up to $F \sim 5$, cf. Fig. 3).

(5) Comparison with other calculations. The Stark effect in the hydrogen atom in strong fields was considered in Refs. 3, 12, 13, and 20 mostly for the ground state. The Weyl method was used in Ref. 3 to calculate E_0 and Γ, a numerical solution of the Schrödinger equation was used in Ref. 12, the modified perturbation theory was employed in Ref. 13, and the Borel summation of the perturbation-theory series for the separation constants, β_1, β_2 was used in Ref. 20. For $F \leqslant 0.1$, all these results agree with the exception of Ref. 13 (the level width obtained in Ref. 13 has an incorrect behavior for $F \to 0$). The values of E_0 and Γ for $n = 1$ and $F \leqslant 0.25$, calculated by Hehenberer *et al.* in Ref. 3, are in agreement with our calculations. The calculations of Damburg and Kolosov[12] for states with $n = 1$ and $n = 2$ disagree sharply with our calculations for $F \gtrsim 0.2$ (see Sec. 4 of Appendix B for further details), but the results of Ref. 20 are in agreement with our own (see Fig. 4). However, we note that the calculations of E_0 and Γ were reported in Ref. 20 for only two states, namely, (0, 0, 0) and (0, 1, 0), and for a small number of F points.

(6) Let us now summarize. Summation of divergent perturbation-theory series in the Stark-effect problem can be used to find the complex energy $E = E_0 - i\Gamma/2$ of the Breit-Wigner resonance that transforms into a discrete level (n_1, n_2, m) as $F \to 0$. The significant point here is the choice of a suitable procedure for summing the perturbation-theory series, which becomes clear if we compare the effectiveness of the two methods, i.e., those based on the Padé approximants and the Padé-Hermite approximants. To calculate E_0 and Γ to 4–5 significant figures, we have to go to at least order 50 in perturbation theory (see Sec. 2). The exact perturbation-theory coefficients corresponding to such values of k are by then[8,10] given by the asymptotic formula (3) associated with the Dyson singularity in the energy $E(\mathscr{E})$ as $\mathscr{E} \to 0$. This singularity is thus reproduced by summing the perturbation-theory series with the aid of the Padé-Hermite approximant, which appears to be the necessary condition for a successful summation of divergent series. It follows that the number of higher perturbation-theory orders calculated exactly must be quite large if we do not wish to confine our attention to the weak-binding region.

The $1/n$ expansion, which is particularly efficient for the Rydberg states (and for $n_1, n_2 \ll n$), and completely confirms the results obtained by summing the perturbation-theory series, is an independent method of calculating E_0 and Γ.

We have reproduced above the Stark shifts and level widths of the hydrogen atom up to $\mathscr{E} \sim 1.5n^{-4}$. There is no difficulty to extending the calculations to greater values of $\mathscr{E}$, but this is only of academic interest because the level width Γ in fields $F = n^4\mathscr{E} \sim 1$ is already comparable with $|E_0|$. Such wide resonances are difficult to separate from the background due to the contribution of other states.

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APPENDIX A
1/*n*-expansion for the Stark effect

We begin with nodeless states ($n_1 = n_2 = 0$, $m = n - 1$), for which there are no "radial excitations". By analogy with Ref. 24, in the limit as $n \to \infty$, the classical equilibrium point ξ_0, η_0 and the level energy E are determined by the set of equations

$$\frac{d}{d\xi} U_1(\xi) = \frac{d}{d\eta} U_2(\eta) = 0,$$
$$U_1(\xi_0) = U_2(\eta_0) = {}^1/_4 E, \quad \beta_1 + \beta_2 = 1 \quad (A1)$$

where $U_{1,2}$ are the effective potentials in the coordinates ξ and η, and $\beta_{1,2}$ are the separation constants.[2] Direct analysis of these equations is quite difficult. We shall simplify it by exploiting the fact that the Bohr theory of the atom is valid for $n \gg 1$. In the absence of the field $\mathscr{E}$, the (0, 0, m) state corresponds to a circular electron orbit, perpendicular to the z-axis (the direction of the external field $\mathscr{E}$). When the electric field is turned on, the classical orbit shifts and changes its radius, but remains circular (Fig. 5). Hence, we find that

$$\mathscr{E} = -zr^{-3}, \quad \rho r^{-3} = v^2\rho^{-1}, \quad \rho = (r^2 - z^2)^{1/2},$$
$$E = {}^1/_2 v^2 - 1/r + \mathscr{E}z, \quad \rho v = m \approx n \quad (A2)$$

where the first two equations correspond to the equilibrium of forces acting on the electron in its own rest frame (cf. Fig. 5). If we apply the scale transformation (10), and assume that $r = (1 - \tau^2)^{-2}$, we obtain (8). In this procedure, $\varepsilon^{(0)}$ is given by (7) and we can verify that all the equations in (A1) are satisfied identically. A correction of arbitrary order, $\varepsilon^{(k)}$, in (6) can be calculated from the recurrence relations given in Ref. 25, which are very convenient in computer calculations. When $\tau = 1/3$, the potential $U_2(\eta)$ ceases to have a barrier. The corresponding field is given by (9), and the reduced energy and radius and electron orbit are given by

$$\varepsilon_* = -2^8 \cdot 3^{-5} = -1.0535, \quad r_* = {}^{81}/_{64} = 1.265. \quad (A3)$$

When $F > F_*$, the root of (8) becomes complex, i.e., the equilibrium point ξ_0, η_0 moves into the complex plane. This

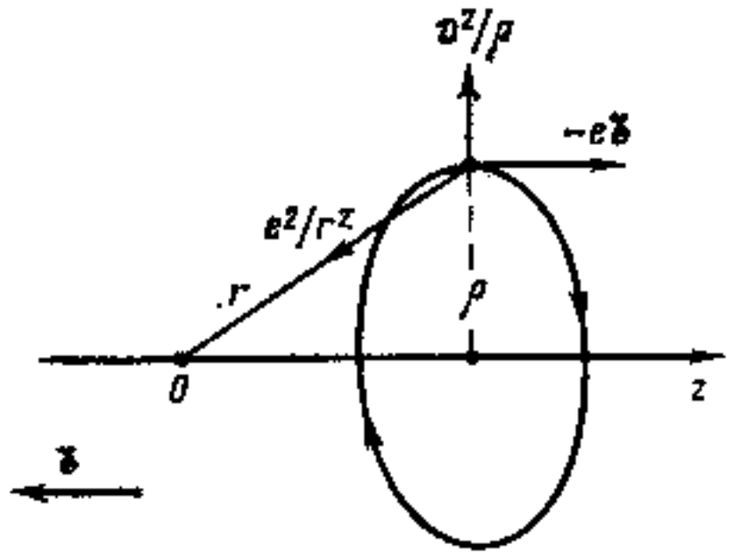

FIG. 5. Classical electron orbit of the hydrogen atom corresponding to the (0, 0, m) state for $m = n - 1 \gg 1$.

solution is not meaningful to classical mechanics but, in quantum mechanics, it determines the energy and width of highly-excited states (cf. the Yukawa potential[24]).

When $F > F_*$, we assume in (8) that

$$\tau^2 = 1 - se^{-i\theta} \tag{A4}$$

and take into account the fact that F remains real. This leads to the following equations that specify $\varepsilon(F)$ in parametric form:

$$F = (\sin\theta)^{1/2}(\sin 8\theta)^{4}(\sin 9\theta)^{-9/2},$$
$$\varepsilon^{(0)} = 3s^3 e^{-3i\theta} - 4s^2 e^{-2i\theta}, \quad s = \sin 8\theta/\sin 9\theta \tag{A5}$$

where $0 < \theta < \pi/9$. We note that

$$\frac{d\varepsilon^{(0)}}{dF} = \begin{cases} -2\tau(1-\tau^2)^{-2}, & F < F_*, \\ -2\dfrac{(\sin\theta)^{1/2}(\sin 9\theta)^{1/2}}{(\sin 8\theta)^2} e^{4i\theta}, & F > F_*. \end{cases} \tag{A6}$$

Hence, it follows that $\varepsilon'' = -\mathrm{Im}\varepsilon$ increases monotonically with the field F, and $\varepsilon' = \mathrm{Re}\varepsilon$ at first decreases (up to $\theta = \pi/12$) and then begins to increase. The minimum of $\varepsilon'(F)$ lies near the strong-field region: $F_{\min} = 9.2^{-5/2}(3^{1/2} - 1)^{1/2} = 1.361$.

Assuming that $\theta \to 0$, we find from (A5) that $F \to F_* = 2^{12} \times 3^{-9}$ and $\varepsilon'' \sim (F - F_*)^{3/2}$. Further increase in F results in a practically linear dependence of the level width on the field (cf. Fig. 3). This also occurs for other states (n_1, n_2, m) and continues up to $F \simeq 5$. On the other hand, when $F \to \infty$,

$$\varepsilon^{(0)} = 1.5(1 - 3^{1/2}i)F^{1/3}[1 + O(F^{-1/3})], \tag{A7}$$

but this asymptotic formula is only for theoretical interest (it sets in for $F \gtrsim 50$).

So far, we have assumed that $n_1 = n_2 = 0$. The $1/n$ expansion can also be obtained for other states when $n_1, n_2 \ll n$. The first term of (6) remains the same as before whereas, for example, the first-order correction is given by

$$\varepsilon^{(1)} = (1-\tau^2)^{-1}[(2n_1+1)(1+3\tau)^{1/2} + (2n_2+1)(1-3\tau)^{1/2} - 2], \tag{A8}$$

where $\tau = \tau(F)$ has the same meaning as before.

APPENDIX B

The limiting curves $\delta_n(F)$ corresponding to $n = \infty$ were calculated on the basis of the following considerations. For fields $\mathscr{E}$ smaller than the classical ionization thresholds $\mathscr{E}_*$, the width of a level in an electric field is determined by the barrier transmission factor

$$\Gamma^{(n_1 n_2 m)}(\mathscr{E}) \approx \exp\left\{-2\int_{\eta_1}^{\eta_2} d\eta \left[2\left(U_2(\eta) - \frac{1}{4}E\right)\right]^{1/2}\right\}, \tag{B1}$$

where η_1, η_2 are the turning points and, when the Langer correction is included,

$$U_2(\eta) = -\beta_2/2\eta + m^2/8\eta^2 - 1/8\mathscr{E}\eta.$$

Assuming that $n \gg 1$, and using the scaling

$$\eta = -n^2\varepsilon F^{-1}x, \quad E = \varepsilon/2n^2, \quad \mathscr{E} = Fn^{-4}$$

we obtain

$$\Gamma^{(n_1 n_2 m)} \approx \exp[-2n(-\varepsilon)^{3/2}J(F)/3F],$$
$$J(F) = \frac{3}{2}\int_{x_1}^{x_2} \frac{dx}{x}\left(a - \frac{1}{4}bx + x^2 - x^3\right)^{1/2}, \tag{B2}$$
$$a = -\mu^2F^2/\varepsilon^3, \quad b = 16\beta_2 F/\varepsilon^2, \quad \mu = m/n.$$

From (11) and (12), we have

$$\delta_{n_1 n_2 m}(F) = (2/3F)[(-\varepsilon)^{3/2}J(F) - 1] - (1 - \nu_1 + \nu_2)\ln F - c_{\nu_1\nu_2}, \tag{B3}$$

where

$$c_{\nu_1\nu_2} = (1-\nu_1)\ln(1-\nu_1) + \nu_2 \ln \nu_2 - (1 - \nu_1 + \nu_2)(1 + 2\ln 2) - 3(\nu_1 - \nu_2).$$

We recall that $\mu + \nu_1 + \nu_2 = 1$, so that each of the numbers ν_1, ν_2 lies between zero and unity. The function $J(F)$ is, in general, a relatively complicated elliptic integral. We now consider a few cases for which the calculations become simpler.

1. $\mu = 1$, $\nu_1 = \nu_2 = 0$. This case corresponds to a classical particle at rest at the minimum $\eta = \eta_0$ of the effective potential $U_2(\eta)$. We then have

$$p^2(\eta) = 1/2E - 2U_2(\eta) = \mathscr{E}(\eta - \eta_0)^2(\eta - \eta_2)/4\eta^2,$$
$$\eta_0 = -n^2\varepsilon^{(0)}[1 - (1-q)^{1/2}]/3F, \quad \eta_2 = -n^2\varepsilon^{(0)}[1 + 2(1-q)^{1/2}]/3F. \tag{B4}$$

where $\varepsilon^{(0)} < 0$ and $q = 3b/4$, and the values of $\varepsilon^{(0)}$ and β_2 correspond; to the first term in the $1/n$ expansion:

$$\varepsilon^{(0)} = -(4-3u)u^2, \quad \beta_2 = 1/2\left[1 + \left(u^{-1} - \frac{3}{2}u^{-3}\right)F\right] \tag{B5}$$

where $u = 1 - \tau^2$. Since $p^2(\eta)$ has a repeated root, the integral $J(F)$ can be expressed in terms of elementary functions:

$$J(F) = 3^{-1/2}(1 - 2/3z^2)^{-1/2}[z - 2/3z^3 - (1-z^2)\,\mathrm{arth}\, z],$$
$$z = \left[\frac{3(1-q)^{1/2}}{1 + 2(1-q)^{1/2}}\right]^{1/2} = \begin{cases} 1 - 1/2F - 13/8F^2 + \ldots, & F \to 0, \\ cf^{1/2}, & F \to F_*, \end{cases} \tag{B6}$$
$$f = (F_* - F)/F_*, \quad c = 3^{1/2}2^{-1/2} = 1.456.$$

Hence,

$$\delta_\infty(F) = \begin{cases} 11/4F + \ldots, & F \to 0, \\ a_0 - a_1 f + a_2 f^{3/2} + \ldots, & F \to F_*, \end{cases} \tag{B7}$$
$$a_0 = 9\ln 3 - 10\ln 2 - 4513/2048 = 0.7524, \quad a_1 = 2.204, \quad a_2 = 1.748.$$

We note that the expansion $\delta_\infty(F)$ becomes identical with (13), (14) as $F \to 0$, $n \to \infty$.

2. $\mu = 0$. In this case, $U_2(\eta)$ does not have a centrifugal barrier, so that $J(F)$ reduces to a hypergeometric function. If we use the quadratic Kummer transformation, we can simplify the answer and finally obtain

$$J(F) = 3\pi \cdot 2^{-7/2}(1-b)\,{}_2F_1(1/4, 3/4; 2; 1-b). \tag{B8}$$

Since (as $b \to 0$)

$${}_2F_1(1/4, 3/4; 2; 1-b) = k_0\{1 + 3/16\, b(\ln b + k_1) + 105/512\, b^2 \ln b + O(b^2)\},$$
$$k_0 = 2^{7/2}/3\pi, \quad k_1 = 13/3 - 6\ln 2,$$

we find that

$$\delta_{n_1 n_2 0}(F) = (4 + 3/2\nu_2 - 2\nu_2^2)F + O(F^2), \quad F \to 0, \tag{B9}$$

which agrees with (13).

3. The $\delta_{n_1 n_2 m}$ have a particularly simple form for the $(n_1, 0, 0)$ states. Here, $\beta_2 \equiv 0$ [cf. (17)], $a = b = 0$, and $J(F) = 1$, so that

$$\delta_{n,00}(F) = (2/3F)[(-\varepsilon)^{3/2} - 1] + 3, \tag{B10}$$

where $\varepsilon(F)$ is determined from (21). In particular,

$$\delta_{n,00}(F) = 4F - {}^{16}/_{3}F^2 + \ldots, \quad F \to 0.$$

We must now make some remarks in relation to Ref. 12. The results reported there for strong fields do not agree with our results (cf., in particular, Figs. 5 and 6 in Ref. 15). A possible reason for this discrepancy may be as follows. The values of E_0 and Γ given in Ref. 12 were determined from the passage of the scattering phase through $\pi/2$ (for real E), which corresponds to the scattering of an electron by a proton in an external field $\mathscr{E}$. In our calculations (see also Refs. 3 and 13), we use the radiation condition (divergent wave at infinity), which corresponds to the decay of a quasistationary state. Actually, when the formal perturbation-theory series (1) is constructed, we use the exponential decrease of the wave function for $r \to \infty$, which, in the analytic continuation $\lambda = (-2E)^{1/2} = -ik$, becomes the radiation condition. For narrow resonances, the two approaches are, of course, equivalent.

APPENDIX C

Assuming in (16) that

$$16\beta_2 F/\varepsilon^2 = 1, \quad \beta_1 = \beta/(1+\beta), \quad \beta_2 = (1+\beta)^{-1},$$

we can reduce this system to the single equation for the variable $\beta = \beta(\nu_1)$:

$$\beta_2 F_1({}^1/_4, {}^3/_4; 2; -\beta) = 2^{7/2}\nu_1/3\pi(1-\nu_1), \tag{C1}$$

where the classical ionization threshold F_* and the corresponding energy ε_* are given by

$$F_* = \frac{2^{10}}{(3\pi)^4}\beta_2^2\nu_2^{-4}, \quad \varepsilon_* = -\frac{128}{(3\pi)^2}\left(\frac{\beta_2}{\nu_2}\right)^2. \tag{C2}$$

Equation (C1) was solved numerically and it was found that F_* increased monotonicaly with ν_1 between 0.1298 ($\nu_1 = 0$) and 0.3834 ($\nu_1 = 1$). At ($\nu_1 = 1$), it has a power-type singularity:

$$F_* = F_0(1 - a\nu_2^{2/3} + \ldots), \tag{C3}$$

where

$$\nu_2 = 1 - \nu_1 \to 0, \quad F_0 = {}^{16}/_{81}\pi^2[\Gamma({}^3/_4)]^{-8} = 0.383411, \quad a = 6\pi^{-1}[\Gamma({}^3/_4)]^{8/3} = 3.284\ldots. \tag{C4}$$

The values of $F_*(\nu_1, \nu_2, 0)$ are almost constant in the range $0 \leqslant \nu_1 \lesssim 0.5$, but vary relatively rapidly near $\nu_1 = 1$. This is due to the fact that the coefficient a is numerically large.

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[2)]It is important to note that analytic formulas for ε_k become exceedingly unwieldy even for $k = 7$. In practice, it is more convenient to calculate the higher orders numerically for each particular state (n_1, n_2, m), using the recurrence relations (see, for example, Refs. 7–9).

[3)]An analogous phenomenon occurs in other problems, i.e., for resonance levels ($l > 1$) in the Yukawa and Hulthen potentials.[24]

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