Stark effect for the Rydberg states of the hydrogen atom

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The Stark shifts and the widths of highly excited ($n = 15$–30) states of a hydrogen atom in a strong electric field, which is higher than the classical ionization threshold of an atom, are calculated. The results of the calculations are in agreement with the experiment.

1. The study of highly excited (Rydberg) states of atoms and molecules has recently attracted considerable interest. Many important results have been obtained.[1–5] Resonances in the cross section for photoionization of atoms in an electric field have recently been observed experimentally, first in rubidium and later in hydrogen.[2–5] These resonances, which correspond to $n \sim 15$–30, are rather narrow even at $E > 0$. The existence of such (above-the-barrier) resonances is puzzling from the point of view of the classical ionization model, but it can be explained on the basis of the Wentzel-Kramers-Brillouin (WKB) method which can be used to obtain approximate equations for the energy E_0 and for the width[6] Γ. Glab *et al.*[4] and Kolosov[7] established a relationship between the resonances observed experimentally in hydrogen and the nearly steady Stark states, whose positions and widths were determined through a numerical solution of the Schrödinger equation. Using independent computation methods,[2)] we calculated complex energies $E = E_0 - i\Gamma/2$ of these states over a broad

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range of values of n and $\mathscr{E}$. The main results of these calculations are presented below.

2. Let us assume that $E^{(n_1 n_2 m)}$ is the energy of the level, $\mathscr{E}$ is the electric field strength, n_1, n_2, and m are parabolic quantum numbers ($m \geqslant 0$), and $n = n_1 + n_2 + m + 1$ (we use atomic units, $\hbar = m_e = e = 1$, and the same notation as in Ref. 8). We write the results of the calculations in "reduced" variables:

$$\epsilon^{(n_1 n_2 m)} = 2n^2 E^{(n_1 n_2 m)}, \quad F = n^4 \mathscr{E}, \quad \mu = m/n, \quad \nu_i = (n_i + 1/2)/n, \tag{1}$$

($\mu + \nu_1 + \nu_2 = 1$), which are very useful in the case of Rydberg states ($n \gg 1$). A strong-field region corresponds to $F \gtrsim F_*$, where F_* is the "classical ionization threshold" in the electric field (for various states of the hydrogen atom the values of F_* lie in the interval between[8] 0.130 and 0.383). Of all the n^2 states of the hydrogen atom $|n_1, n_2, m\rangle$ with a given principal quantum number n, the most stable states are those with the minimum values of n_2 and m (as can be seen from the asymptotic expression for the width $\Gamma^{(n_1 n_2 m)}$ in the limit $F \to 0$). These states are therefore of particular interest experimentally.

The results of the calculations[3)] are shown in Fig. 1 (for the Stark shifts we have $\epsilon_n' = 2n^2 \operatorname{Re} E^{(n_1 n_2 m)}$) and in Fig. 2 (for the "reduced" level widths we have $\epsilon_n'' = n^2 \Gamma^{(n_1 n_2 m)}$). Figure 1 also shows a limiting curve ($n = \infty$) which is calculated from the equation

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

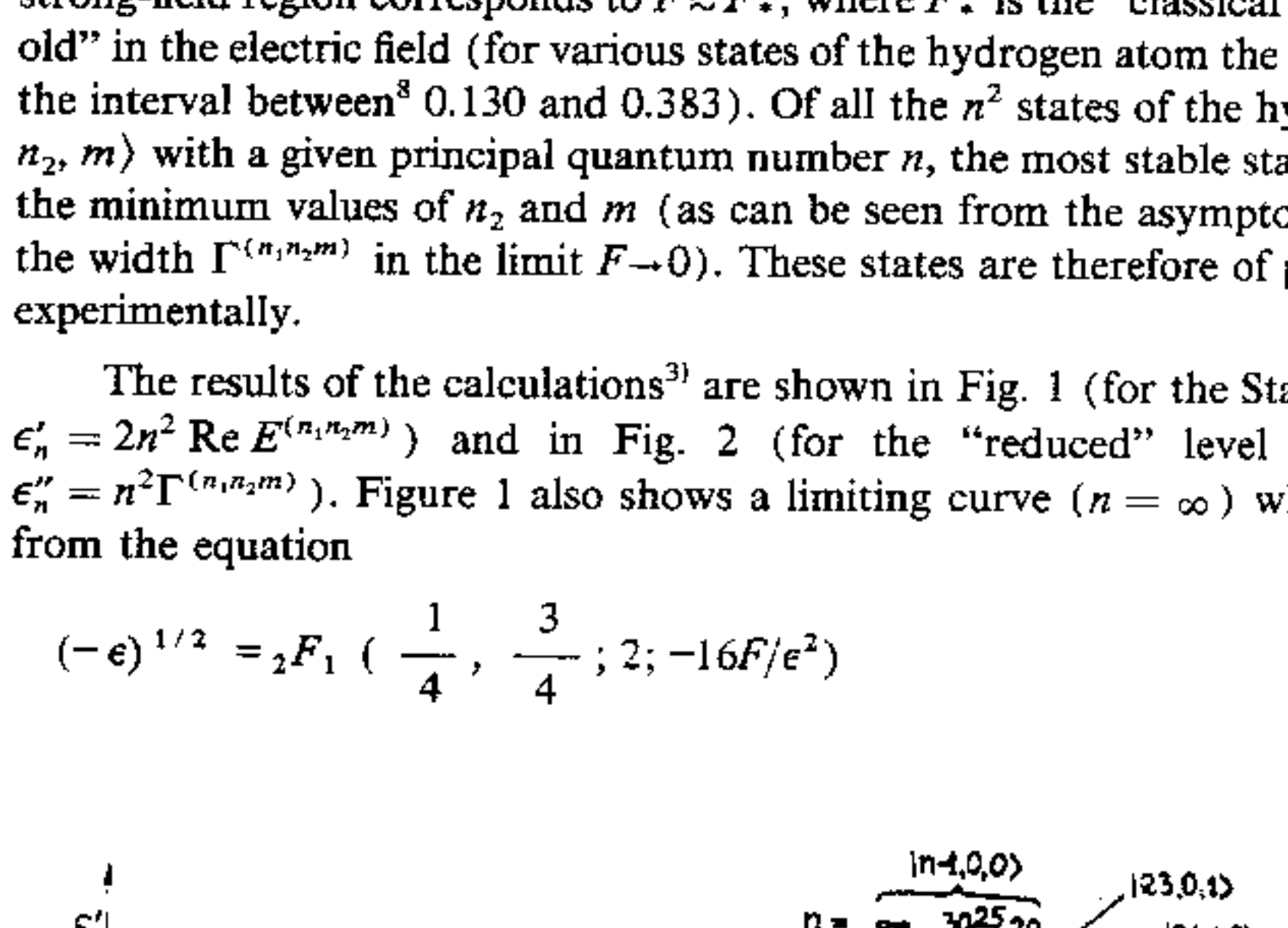

FIG. 1. Energies of the Stark resonances in the hydrogen atom. Curves—our calculations; ○—experimental data of Ref. 4 for $\mathscr{E} = 6.5$ kV/cm, $+$—for $\mathscr{E} = 8.0$ kV/cm, and $\triangledown$—for $\mathscr{E} = 14.4$ kV/cm. The energies of the states $|23, 1, 0\rangle$ and $|22, 0, 2\rangle$ are the same within an error of this plot.

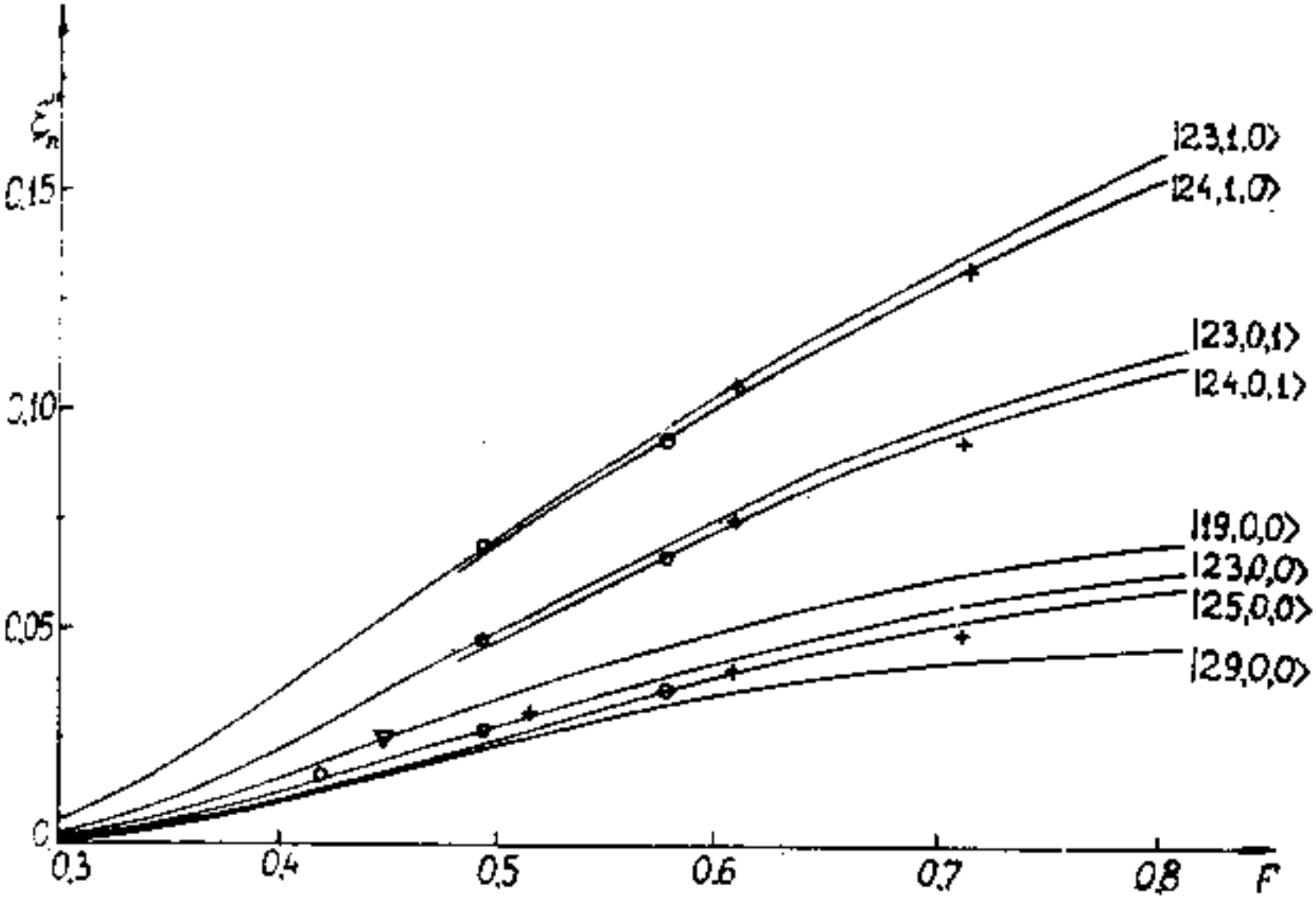

FIG. 2. Widths of the Stark resonances, $\epsilon_n'' = n^2\Gamma^{(n_1 n_2 m)}$. The parabolic quantum numbers appear next to the curves (the rest of the notation is the same as in Fig. 1).

(the "Rydberg limit" is $\nu_1 = 1$, $\nu_2 = \mu = 0$; see Ref. 8). In the interval $0.3 < F < 0.8$, the ϵ_n' versus F dependence is approximately linear. At $F \approx 0.4$–0.5 the real part of the energy changes sign,[4)] and the result is that we have a (quasistationary) level with a positive energy.

It can be seen in Fig. 2 that the least likely to be ionized (with a fixed n and F) are the states $|n-1, 0, 0\rangle$. They are followed by the states $|n-2, 0, 1\rangle$ and then by the states $|n-3, 0, 2\rangle$ and $|n-2, 1, 0\rangle$. In this case the quantities ϵ_n'', and especially ϵ_n', are approximately equal to each other for the given pair of states. This approximate equality can easily be explained by examining the perturbation-theory series:

$$E^{(n\ n_2 m)} = \frac{1}{2n^2} \sum_{k=0}^{\infty} \epsilon_k^{(n_1 n_2 m)} F^k , \tag{3}$$

where k is the perturbation-theory order,

$$\epsilon_k = \begin{cases} P_k(\kappa^2, \mu^2, 1/n^2), & k - \text{even}, \\ \kappa P_k(\kappa^2, \mu^2, 1/n^2), & k - \text{odd}, \end{cases}$$

$\kappa = \nu_1 - \nu_2 = (n_1 - n_2)/n$, and P_k is a polynomial of degree $[k/2]$ of its arguments. The states $|n = 2, 1, 0\rangle$ and $|n-3, 0, 2\rangle$ have the same $\kappa = 1 - 3/n$ and they differ only in the parameter μ^2, i.e., the terms $\propto 1/n^2$. On the other hand, for the states of the type $|n-m-1.0, m\rangle$ with $m = 0, 1, 2 \ldots \ll n$ the parameter $\kappa = 1 - (m+1)/n$, so that the coefficients ϵ_k differ even in the terms on the order of $1/n$.

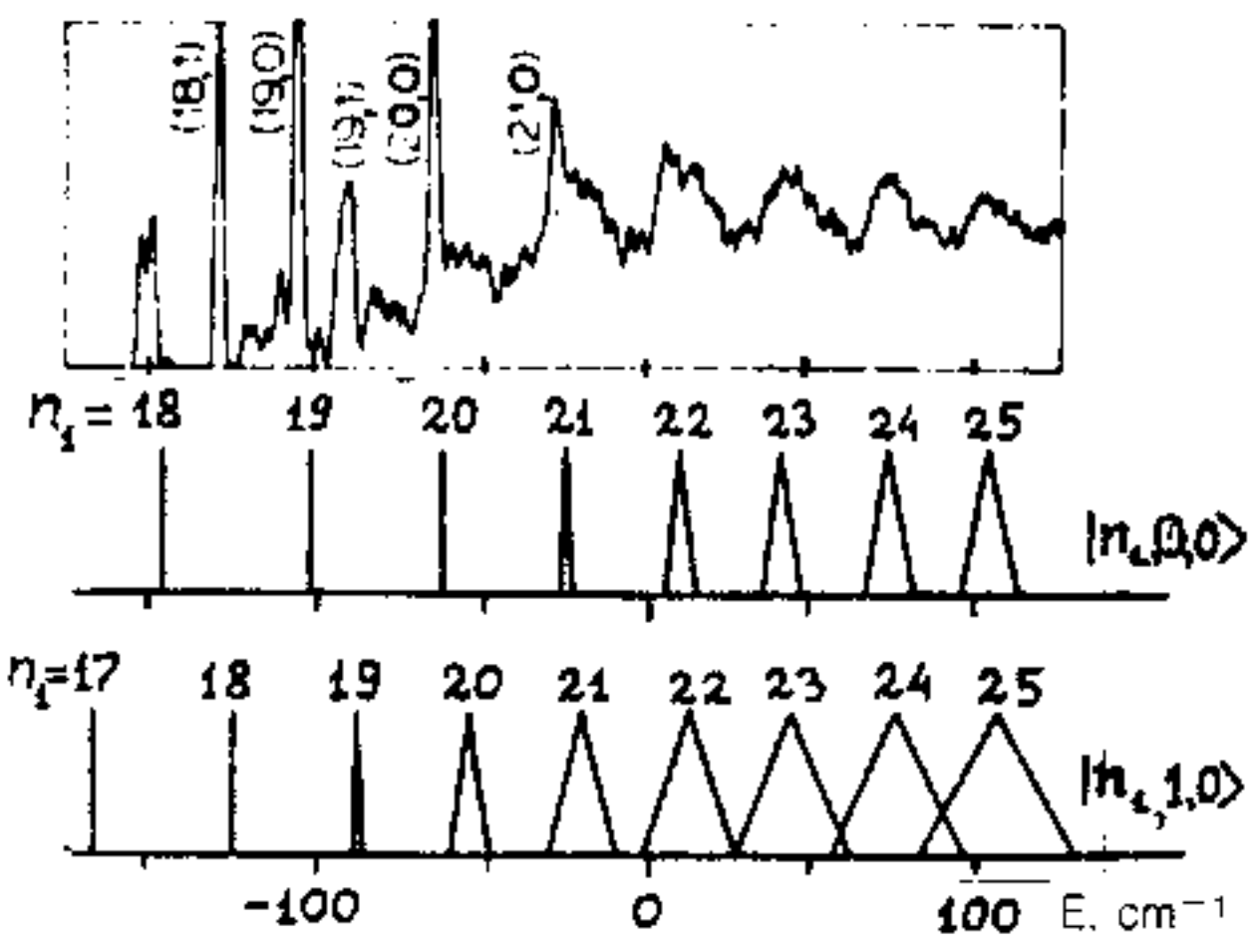

FIG. 3. Experimental spectrum[4] of the photoionization of a hydrogen atom with $\mathscr{E} = 8.0$ kV/cm. The results of calculations for two series of states are also shown (the vertex of the triangle denotes E_0 and its base represents the level width Γ).

Figures 1 and 2 show curves for ϵ_n' and ϵ_n'', scaled from the experimental data[4] on the photoionization of hydrogen atoms (for the fields $\mathscr{E} = 6.5$ and 8.0 kV/cm our calculations are in agreement with Kolosov's[7] calculation which was carried out using a different method). There is clearly an agreement between theory and experiment.

The Stark resonance energies which we calculated are compared in Fig. 3 with the experimental spectrum taken from Ref. 4. We see that the positions of the maxima correspond to the values of ϵ_n' and that the width of the peaks is in qualitative agreement with ϵ_n''. Similar results were also obtained for other data which were reported in Refs. 2–5. The theoretical predictions of the Stark resonances in a strong electric field are thus in agreement with the experimental results, including those for the region $\epsilon_n' > 0$ (as long as the resonances remain isolated).

3. A remark concerning the $1/n$ expansion. We restrict the discussion here to the states with $m = 0$. The integrals contained in the Bohr-Sommerfeld quantization rule and in the correction on the order of $\hbar^2$ to this rule[10] in this case can be calculated analytically. We find the following equations for determining the energy and the separation constants $\beta_{1,2}$:

$$\beta_1 (-\epsilon)^{-1/2} f(z_1) - \frac{1}{8n^2} F(-\epsilon)^{-3/2} g(z_1) = \nu_1 ,$$

$$\beta_2 (-\epsilon)^{-1/2} f(z_2) + \frac{1}{8n^2} F(-\epsilon)^{-3/2} g(z_2) = \nu_2 , \qquad (4)$$

$$\beta_1 + \beta_2 = 1,$$

where

$\nu_1+\nu_2=1$ $(\mu=0)$, $z_1=-16\beta_1F/\epsilon^2$, $z_2=16\beta_2F/\epsilon^2$, $f(z)=F\left(\frac{1}{4},\ \frac{3}{4};\ 2;z\right)$,

$$g(z)=\frac{2}{3}F\left(\frac{3}{4},\ \frac{5}{4};\ 1;z\right)+\frac{1}{3}F\left(\frac{3}{4},\ \frac{5}{4};\ 2;z\right)$$

and $F\equiv{}_2F_1$ is a hypergeometric function. Since the corrections disregarded in (4) are no larger than about n^{-4}, system (4) is very accurate for Rydberg states. In the limit $F\to 0$ we find the following expressions from (4):

$$\begin{aligned}\epsilon&=-1+3\kappa F-\frac{1}{8}(17-3\kappa^2+19n^{-2})F^2+\ldots,\\ \beta_1&=\frac{1}{2}(1+\kappa)+\frac{1}{8}[3(1-\kappa^2)+n^{-2}]F-\frac{\kappa}{16}(1-\kappa^2+6n^{-2})F^2+\ldots\end{aligned}\tag{5}$$

(β_2 is found through the substitution $\kappa\to-\kappa$, $F\to-F$), consistent with the perturbation-theory expansions in the weak-field region. For an arbitrary F Eqs. (4) can be solved numerically. As long as $F<F_*$ (ν_1,ν_2), the solution of $\epsilon(F)$ is real and is consistent with the results of the APE method for ϵ_n' (and therefore supports the procedure which we chose for summing the diverging perturbation-theory series). At $F>F_*$ the solution becomes complex, allowing this method to be used to calculate not only the level shift but also the level width.[5)] Apart from purely practical value, this circumstance is of fundamental importance for the $1/n$ expansion. Such calculations are now being carried out.

4. In weak fields the distance between the adjacent levels, ΔE, increases linearly with $\mathscr{E}$. On the other hand, for a strong field we have

$$\Delta E=c\mathscr{E}^{3/4};\tag{6}$$

here[4] $c=7.51\pm0.02$ for the states with $n\sim20$ and energy E approximately equal to zero (here E is given in cm^{-1}, and $\mathscr{E}$ is in kV/cm). This relation can easily be explained in terms of the $1/n$ expansion.

$$\left.\frac{dE}{dn}\right|_{E=0}=c\mathscr{E}^{3/4},\quad c=c_0+\frac{c_1}{n}+\frac{c_2}{n^2}+\ldots.\tag{7}$$

If $n_1\to\infty$ and the quantum numbers n_2 and m are on the order of unity, then system (4) reduces to Eq. (2), from which at $E=0$ we find

$$F_0=F_*(1,\ 0)=(2\gamma/9\pi)^2=0.383\ldots,\quad c_0=(\pi\gamma/2)^{1/2}=3.708\ldots\tag{8}$$

(in atomic units) where $\gamma=[\Gamma(1/4)/\Gamma(3/4)]^2$. If the energy E is measured in cm^{-1} and $\mathscr{E}$ is measured in kV/cm, we have $c_0=7.54$, in approximate agreement with the experimental value.

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[2)]Specifically, the summation of the divergent series of the Rayleigh-Schrödinger perturbation theory and the $1/n$ expansion. These methods are discussed in detail in Refs. 8 and 9.

[3)]The quadratic Padé-Hermite approximations were used to sum the perturbation-theory series for the energy of the levels [see Eq. (5) in Ref. 9].

[4)]In particular, the limiting curve corresponding to $n = \infty$ crosses zero at $F = F_0 = 0.3834\ldots$ [see Eq. (8)].

[5)]The $1/n$ expansion gives a clear explanation for the occurrence of the nearly steady, above-the-barrier states. In the limit $F \to F_*$, there is a clashing between two classical ($n \to \infty$) solutions. As a result, they reach the complex plane. In this case $\epsilon(F)$ acquires an imaginary part, which is attributable to the width of above-the-barrier resonances. The solution of $\epsilon(F)$ in system (4) has the same type of singularity at the point $F = F_*$ as that in the other quantum-mechanical problems (in a Yukawa potential,[11] for example).

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