Strong-field Stark effect: perturbation theory and $1/n$ expansion

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The Stark shifts and the widths of the ground and excited states of a hydrogen atom are calculated. Two independent calculation methods are used: a summation of divergent perturbation theory series and $1/n$ expansion. The results of the calculations for the Rydberg ($n \gg 1$) states are in agreement with the experiment.

1. Introduction

The Stark effect is one of the best known problems in quantum mechanics [1] but at the same time one of the most difficult (outside the weak-field region, see e.g. refs. [2–13]). For a level with parabolic quantum numbers n_1, n_2, m in a hydrogen atom, the perturbation theory (PT) series is

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

where [1] $\epsilon_0 = -1$, $\epsilon_1 = 3(n_1 - n_2)/n$, $\epsilon_2 = -(1/8n^2) \times [17n^2 - 9m^2 - 3(n_1 - n_2)^2 + 19]$, ..., ϵ and $F = n^4\varepsilon$ are convenient "reduced" variables,

$$\epsilon_{n_1,n_2,m} = 2n^2 E^{(n_1,n_2,m)} = \epsilon' - i\epsilon'',$$
$$\epsilon'' = n^2 \Gamma^{(n_1,n_2,m)}, \quad F = n^4\varepsilon, \qquad (2)$$

and $n = n_1 + n_2 + m + 1$ ($m \geqslant 0$) is the principal quantum number (we use atomic units, $\hbar = m_e = e = 1$; the electric field ε is measured in $\varepsilon_a = m_e^2 e^5/\hbar^4 = 5.142 \times 10^9$ V/cm).

The recent development of new PT methods has made it possible to calculate [2–7] a large number of PT coefficients ϵ_k, up to $k = 160$ in the case of the ground state [4], $k = 100$ for the states with $n = 2$ [5,6], see also refs. [2,3,7] (k is the PT order). Powerful algorithms have been developed for fast computation of arbitrary order in perturbation series (PS). However, PS has a zero convergence radius and the energy $E(\varepsilon)$ has an essential singularity at $\varepsilon = 0$ (see eq. (8′) below). It follows from the asymptotics of higher orders of PT:

$$E^{(n_1,n_2,m)} \underset{k\to\infty}{\simeq} k! a^k k^\beta \left(c_0 + \frac{c_1}{k} + \frac{c_2}{k^2} + \ldots\right), \qquad (3)$$

where $a = \frac{3}{2}n^3$, $\beta = n + |n_1 - n_2| - 1$ and c_j are some calculable constants. Such a situation is usually called Dyson's phenomenon [8].

For this reason, addition of partial sums of the PS (1) yields divergent results. The use of higher PT orders to calculate the shift and width, $E = E_r - i\Gamma/2$, of atomic levels in a strong ($F \sim 1$) electric field would be impossible without suitable methods for summing divergent series [#1]. Using Padé approximants (PA), one can determine E_r and Γ up to $\varepsilon \approx 0.1$ [4]. The complex coordinate method [9] and the Padé–Borel transformation [10] make it possible to sum PS highly accurately, but only the ground state

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[#1] Besides, summation of divergent PS is of principal importance because of the obvious analogy with the strong coupling problem in quantum field theory.

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was considered and $\varepsilon \leqslant 0.1$ [9,10]. Developments in lasers and atomic spectroscopy make it worthwhile to calculate E_r and Γ for intense fields and for highly excited (Rydberg) states also. The results are presented below.

2. Calculation methods

We used Hermite–Padé approximants (HPA) and $1/n$ expansion. The values of "diagonal" HPA $f_N(\varepsilon) = [N, N, N](\varepsilon)$ are calculated from the equation $P - Qf_N + Rf_N^2 = 0$, where P, Q and R are polynomials of ε of degree N, whose coefficients are determined from PT coefficients ϵ_k through the condition

$$P - QE + RE^2 = O(\varepsilon^{3N+2}), \quad \varepsilon \to 0, \tag{4}$$

where $E(\varepsilon)$ is PS (1). It is clear that HPA, in contrast with the usual PA, can have an imaginary part even when all the coefficients of the polynomials P, Q and R are real (which is the case in the Stark-effect problem). Therefore, HPA gives not only the value of the Stark shift, but also the width Γ.

The other approach is based on $1/n$ expansion:

$$\epsilon_{n_1,n_2,m}(F) \equiv 2n^2 E^{(n_1,n_2,m)} = \epsilon^{(0)} + \frac{\epsilon^{(1)}}{n} + \frac{\epsilon^{(2)}}{n^2} + \ldots \tag{5}$$

($\epsilon^{(k)}$ depend on F and quantum numbers n_1, n_2, m). The first term $\epsilon^{(0)}$ corresponds to the $n \to \infty$ limit and can be calculated with the help of the WKB approximation. For the $|0, 0, n-1\rangle$ states the first three coefficients in the expansion (5) were obtained analytically while $\epsilon^{(k)}$ with $k > 2$ were computed numerically with the help of recurrence relations [12]. For more details about these methods we refer to refs. [6,12].

On the other hand, for the $|n_1, n_2, 0\rangle$ states the integrals entering the Bohr–Sommerfeld quantization rule and corrections $\sim \hbar^2$ to it can be calculated analytically. In this case we arrive at the following equations for determining the energy ϵ and the separation constants β_i (see appendix):

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

$$\beta_2(-\epsilon)^{-1/2} f(z_2) + \frac{1}{8n^2} F(-\epsilon)^{-3/2} g(z_2) = \nu_2, \tag{6}$$

where $\beta_1 + \beta_2 = 1$, $\nu_i = (n_i + \frac{1}{2})/n$, $z_i = 16(-1)^i \beta_i F \times \epsilon^{-2}$, $i = 1$ or 2.

Table 1
Energies and widths of the hydrogenic states calculated by different methods. ϵ and ε are in atomic units; $\nu = (-2E_r)^{-1/2}$, $\nu = n$ for a free atom ($\varepsilon = 0$).

$|0, 0, n-1\rangle$ states

n	F	$-\epsilon_n$	computation method
1	0.1	1.05484 + i0.01454	HPA
		1.054836 + i0.014538	refs. [9,10]
1	0.5	1.25 + i0.55	HPA
		1.246 + i0.559	$1/n$
3	0.5	1.224 + i0.317	HPA
		1.22393 + i0.31685	$1/n$
1	1.0	1.248 + i1.294	$1/n$
		1.2487 + i1.2936	ref. [13]
3	1.0	1.27891 + i0.83875	$1/n$
10	1.0	1.2851 + i0.6739	HPA
		1.28520 + i0.67388	$1/n$

States with $n_1 = n_2 = (n-1)/2$, $m = 0$

n	ε (a.u.)	F	ν	$10^6\,\Gamma$	computation method
5	1.8×10^{-4}	0.1125	4.92402	2.283	HPA
			4.9239	2.22	$1/n$
			4.9240	2.282	ref. [11]
11	1.0×10^{-5}	0.1464	10.713	2.83	HPA
			10.7128	2.82	$1/n$
			10.688	2.815	ref. [11]
15	3.0×10^{-6}	0.1519	14.577	1.35	HPA
			14.5766	1.338	$1/n$
			14.5771	1.338	ref. [11]

$$f(z)=F(\tfrac{1}{4},\tfrac{3}{4};2;z),$$

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

and $F\equiv{}_2F_1$ is the hypergeometric function. In the limit $F\to 0$ we find from (6):

$$\epsilon=-1+3kF-\tfrac{1}{8}(17-3k^2+19n^{-2})F^2+\ldots,$$

$$\beta_1=\tfrac{1}{2}(1+k)+\tfrac{1}{8}[3(1-k^2)+n^{-2}]F$$
$$-\tfrac{1}{16}k(1-k^2+6n^{-2})F^2+\ldots \qquad (7)$$

($k=(n_1-n_2)/n$, β_2 is found through the substitution $k\to -k$, $F\to -F$), which is consistent with the PT expansions [1,2] in the weak field region. For an arbitrary F eqs. (6) can easily be solved numerically. Since the corrections disregarded in (6) are no larger than $\sim n^{-4}$, the system (6) is very accurate for Rydberg states, $n\gg 1$.

Note that the $1/n$ expansion converges rapidly at $n>5$–10, while HPA have advantages at small values of n. An important point is that there exists an overlap region (in parameters n and F), in which the two methods agree with each other quite closely (and at $\varepsilon\leqslant 0.1$ they agree with the results of other authors

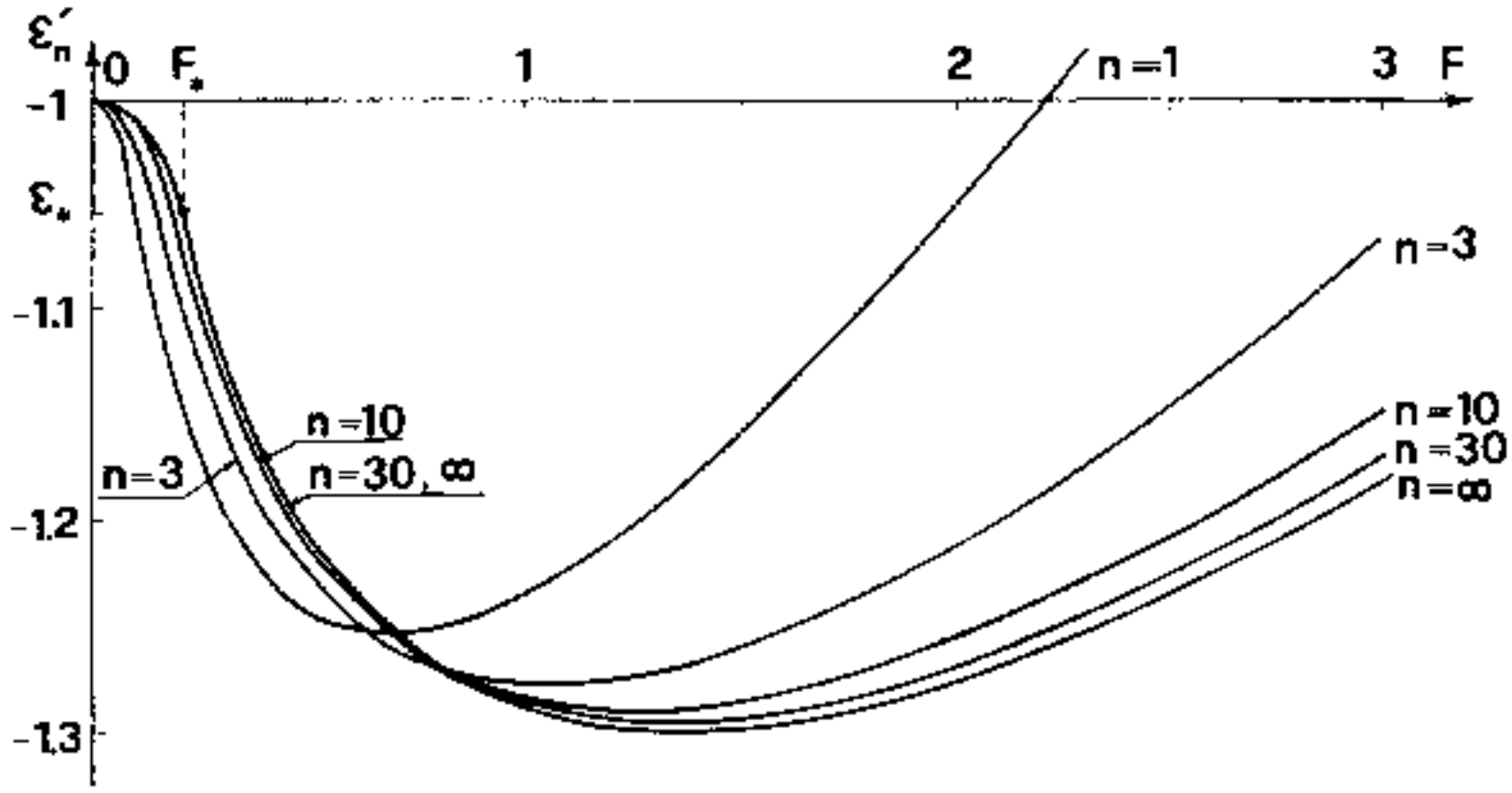

Fig. 1. The Stark shifts in a hydrogen atom (we use reduced variables (2)): (a) for the $|0, 0, n-1\rangle$ states, (b) for $|n-1, 0, 0\rangle$ states ($\varepsilon'=0$ corresponds to the ionization limit for a free atom).

[9–11,13]). See table 1 where we also compare the values of $\nu=(-2E_r)^{-1/2}$ and widths Γ obtained by our computations with the corresponding values from ref. [11]. The agreement is good enough, which, in particular, confirms the chosen summation procedure (HPA) of divergent PS for the Stark effect.

3. Results of computation

Fig. 1 shows the real part of the energy $\epsilon'_n=2n^2E_r^{(n_1,n_2,m)}$, for two series of states. Note that in very strong fields the Stark shift of the $|0, 0, n-1\rangle$ states changes sign.

The width of the levels is conveniently written in the form

$$\Gamma^{(n_1,n_2,m)}(\varepsilon)=\tilde{\Gamma}^{(n_1,n_2,m)}(\varepsilon)\exp(-n\delta_{n_1n_2m}), \qquad (8)$$

where $\tilde{\Gamma}$ corresponds to the semiclassical formula [1], which is asymptotically exact in the limit $\varepsilon\to 0$, and $\delta_{n_1n_2m}(\varepsilon)$ includes corrections to this limiting case. For instance,

$$\tilde{\Gamma}^{(0,0,n-1)}=\frac{2^{2n}}{n!n^{3n+2}}\varepsilon^{-n}\exp(-2/3n^3\varepsilon),$$

$$\tilde{\Gamma}^{(n-1,0,0)}=\frac{4e^{3(n-1)}}{n^6}\varepsilon^{-1}\exp(-2/3n^3\varepsilon). \qquad (8')$$

At weak fields, only the factor $\tilde{\Gamma}(\varepsilon)$, which depends very sharply on the field ε and varies by many orders of magnitude, is important in (8). Our calculations show, however, that the range of applicability of eqs. (8′) is quite narrow, $\varepsilon\lesssim 0.1n^{-5}$ – see fig. 2 (the behaviour of $\delta_{n_1n_2m}(F)$ for other states $|n_1n_2m\rangle$ is similar). The factor $\exp(-n\delta_{n_1n_2m})$ in eq. (8) would have to be taken into account for stronger fields, especially in the case of Rydberg states. Since $\delta_n>0$, the ionization probability in the region of intense fields is much smaller than the value that follows from the semiclassical estimate (8′). So, we have obtained the Stark shifts and level widths of hydrogen states up to $F=n^4\varepsilon\sim 2$. There is no difficulty in extending the calculations to greater values of F, but this is only of academic interest because the width Γ in fields $\varepsilon\gtrsim n^{-4}$ is already comparable with $|E_r|$. Such wide resonances are difficult to separate from the background due to the contribution of other states.

4. The classical ionization threshold

It is well known [1] that only the potential $U_2(\eta)=-\beta_2/2\eta+m^2/8\eta^2-\frac{1}{8}\varepsilon\eta$ has a barrier while

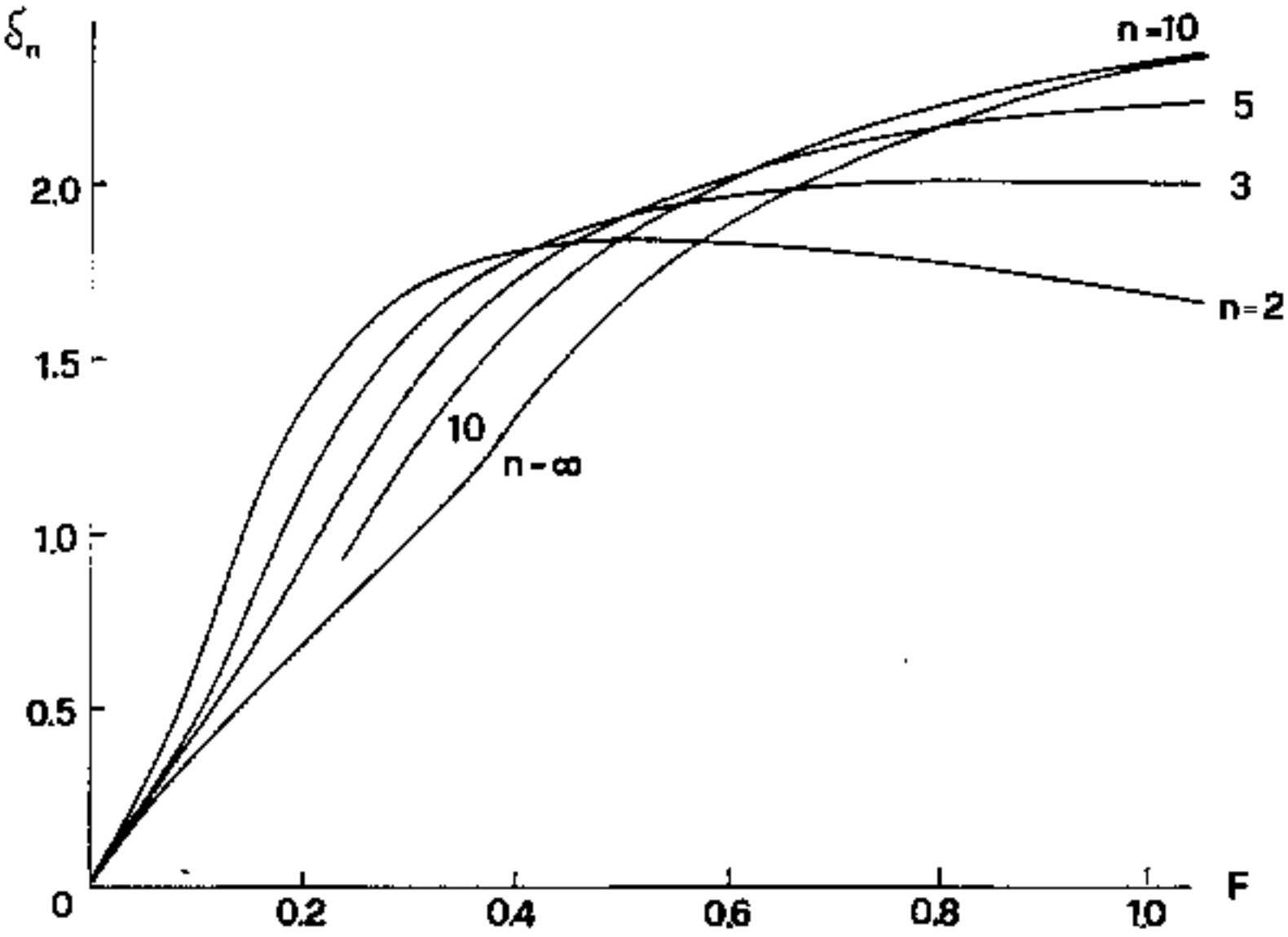

Fig. 2. The function δ_n, eq. (8), for $|n_1, 0, 0\rangle$ states, $n_1=n-1$.

$U_1(\xi)$ is a confining potential for all $\varepsilon>0$ ($\xi=r+z$, $\eta=r-z$ are parabolic coordinates). The field $F=F_*$, for which the barrier in $U_2(\eta)$ disappears, will be referred to as the classical ionization threshold. When $m=0$, the potential $U_2(\eta)$ has a maximum at $\eta_0=2(\beta_2/F)^{1/2}$ and $U_2(\eta_0)=-\frac{1}{2}(\beta_2 F)^{1/2}$. The barrier disappears when $\epsilon=U_2(\eta_0)$, i.e., $z_2=16\beta_2 F/\epsilon^2=1$, which corresponds precisely to the singular point of the hypergeometric function in eq. (6).

Assuming in (6) that

$$z_2=1, \quad \beta_1=\frac{\beta}{1+\beta}, \quad \beta_2=\frac{1}{1+\beta},$$

we can reduce (6) to the single equation

$$\beta F(\tfrac{1}{4},\tfrac{3}{4};2;-\beta)=\frac{2^{7/2}}{3\pi}\frac{2n_1+1}{2n_2+1}, \tag{9}$$

where the classical ionization threshold is given by

$$F_*=\frac{1024}{(3\pi)^4}\frac{1}{(1+\beta)^3\nu_2^4}. \tag{10}$$

Eq. (9) was solved numerically and it was found that F_* increased monotonically with ν_1 between 0.1298 ($\nu_1=0$) to 0.3834 ($\nu_1=1$). The values of F_* for some states with $n_1\gg 1$, n_2 and $m\sim 1$ are given in ref. [17].

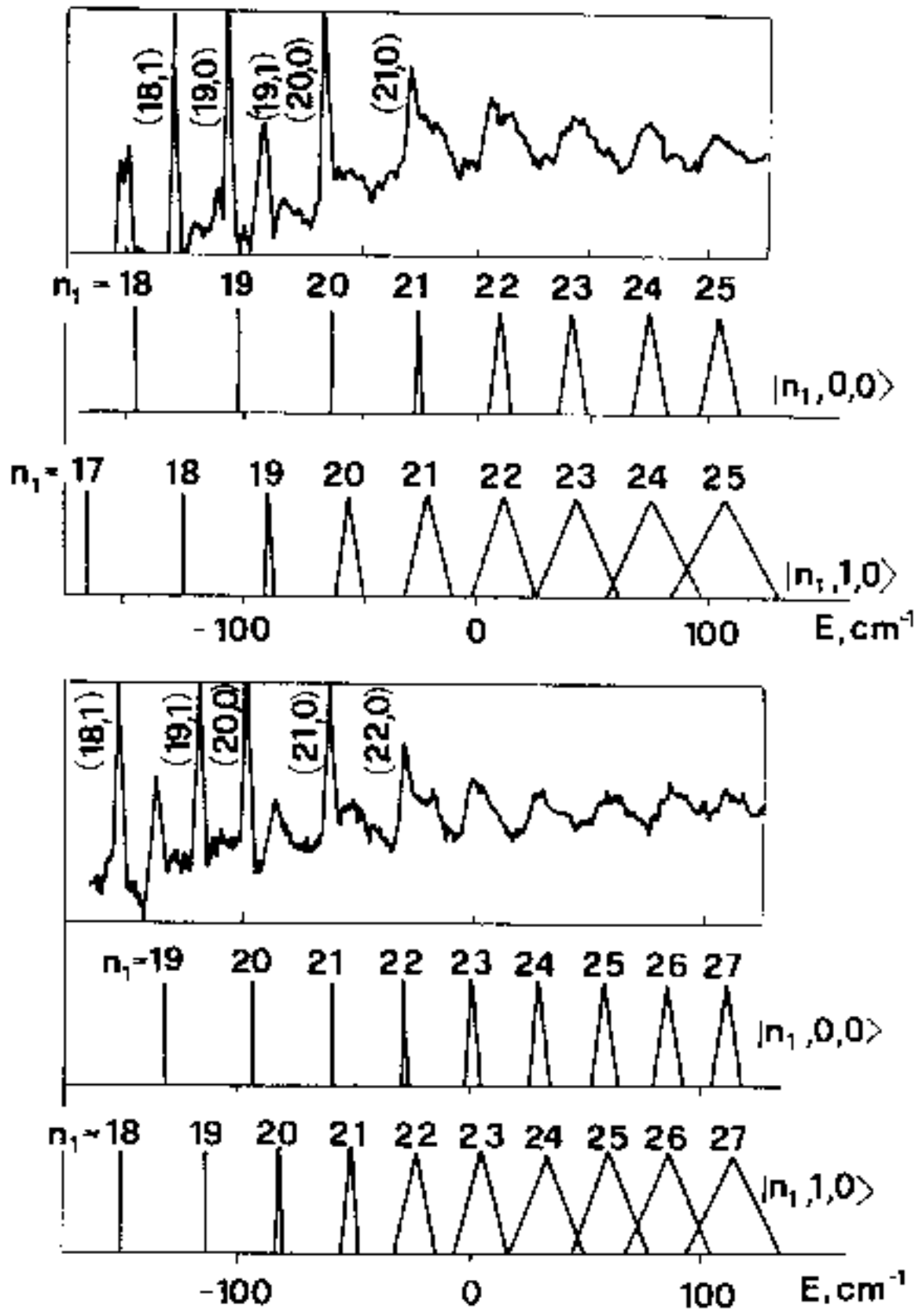

Fig. 3. Experimental spectrum [14] of the photo-ionization of a hydrogen atom with $\varepsilon=8.0$ kV/cm. The results of calculations for two series of states are also shown (the vertex of the triangle denotes E_r and its base represents the width Γ). Note that 100 $\mathrm{cm}^{-1}=9.113\times10^{-4}$ Ry $=0.0124$ eV.

5. Comparison with experiment

The study of Rydberg states of atoms and molecules has recently attracted considerable interest. Resonances in the cross sections for photo-ionization of atoms in the presence of an electric field have been discovered (see refs. [14,15] and references therein). Glab et al. [14] and Kolosov [16] established a relationship between the resonances in hydrogen and the Stark quasistationary states, whose positions and widths were determined through a numerical solution of the Schrödinger equation.

Using the methods described above, we calculated the complex energies of these states over a broad range of values of ε and n_1, n_2, m. As an example, the Stark resonance energies near $E=0$ which we calculated are compared in fig. 3 with the experimental spectrum taken from ref. [14]. We see that the positions of the maxima correspond to the values ϵ_n' obtained from eqs. (6) and that the width of the peaks is in qualitative agreement with ϵ_n''. A more detailed comparison is made in table 2, which contains the resonance energies E_r (taken with an opposite sign) and $\Gamma/2$ for the subthreshold ($E<0$) resonances [#2], the values of the variable $f=(F-F_*)/F_*$ are also given in table 2. This quantity shows the proximity of the resonance energy $E_r^{(n_1,n_2,m)}$ to the top of the potential barrier $U_2(\eta_0)$ and qualitatively explains the seeming irregularity in the values of resonance widths.

[#2] Similar results were obtained for other data reported in refs. [13,14]. Table 3 in ref. [17] contains about 50 resonances, whose positions and widths agree with the theoretical computations within the limits of experimental errors (which is 1–2 cm^{-1} for E_r).

Table 2
Energies and halfwidths of the subthreshold Stark resonances in a hydrogen atom. $\varepsilon = 16.8$ kV/cm, magnetic quantum number $m=0$ for all the states considered, $f=(F-F_*)/F_*$. For more details see ref. [17].

n_1	n_2	$-E_r$ (cm^{-1})		$\Gamma/2$ (cm^{-1})		f
		theor.	exp. [15]	theor.	exp. [15]	
17	0	58.1	60.7	2.21	2.5	0.10
16	1	106.6	103.8	8.93	9.0	0.29
16	0	123.3	126.5	0.15	0.14	−0.12
15	1	167.6	167.9	1.84	2.1	0.04
14	2	211.5	210.1	5.64	6.6	0.16
14	1	235.3	238.1	0.020	0.016	−0.18
13	2	274.2	275.9	0.27	0.23	−0.08
12	3	313.8	314.8	1.29	1.6	−0.001
12	2	349.8	351.4	1.1×10^{-4}	10^{-4}	−0.28
11	4	352.2	351.4	3.29	3.0	0.07
11	3	384.4	386.3	1.9×10^{-3}	1.8×10^{-3}	−0.21
10	4	419.1	419.2	0.025	0.032	−0.16

The theoretical predictions of the Stark resonances in a strong electric field are in good agreement with the experimental data [14,15], including those in the above-barrier region (as long as the resonances remain isolated, see fig. 3). It shows that the peaks in photo-ionization cross sections correspond to the Stark quasistationary states and, on the other hand, demonstrates that summation of divergent PS in quantum mechanics can give valuable physical information far beyond the region of weak coupling.

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Appendix

The systematic derivation of higher orders of the WKB quantization rule in the case of the Stark effect in a hydrogen atom was performed by Bekenstein and Krieger [19]:

$$\oint \mathrm{d}\xi R\left[1-\frac{1}{64\xi^4R^6}\left(\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi^2R^2)\right)^2+\ldots\right]$$
$$=2^{1/2}\pi(n_1+\tfrac{1}{2}),$$
$$R=\left(\frac{\beta_1}{2\xi}-\frac{m^2}{8\xi^2}+\tfrac{1}{4}E-\tfrac{1}{8}\varepsilon\xi^2\right)^{1/2}, \qquad (A.1)$$

and a similar equation for the η variable, in which $\varepsilon\to-\varepsilon$, $\beta_1\to\beta_2$ and $n_1\to n_2$.

For $m=0$ states the integrals entering eq. (A.1) can be expressed through the hypergeometric functions. The first term in (A.1) is

$$\oint R\,\mathrm{d}\xi=\frac{n\pi}{2^{3/2}}F^{1/2}x_1(-x_2)^{1/2}$$
$$\times F(-\tfrac{1}{2},\tfrac{1}{2};2;x_1/x_2), \qquad (A.2)$$

where $\xi=n^2x$, $x_{1,2}=(1/2F)[\epsilon\mp(\epsilon^2+16\beta_1F)^{1/2}]$. This expression can be simplified considerably by means of the Kummer quadratic transformation

$$F\left(\alpha,\alpha-\beta+1;\beta;\frac{1-(1-z)^{1/2}}{1+(1-z)^{1/2}}\right)$$
$$=\left(\frac{1+(1-z)^{1/2}}{2}\right)^{\alpha}F\left(\frac{\alpha}{2},\frac{\alpha+1}{2};\beta;z\right)$$

(in this case $\alpha=\frac{1}{2}$, $\beta=2$, $z=-16\beta_1F/\epsilon^2$). Finally,

$$\oint R\,\mathrm{d}\xi = 2^{1/2}\pi\beta_1(-\epsilon)^{1/2}$$

$$\times F(\tfrac{1}{4},\tfrac{3}{4};2;-16\beta_1 F/\epsilon^2). \qquad (A.3)$$

The calculation of the second term in (A.1) is similar, but more cumbersome. As a result, we arrive at eqs. (6).

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