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The Stark shifts and widths for highly excited states, $n = 15 \div 30$, of hydrogen atom in strong electric field $\mathcal{E}$ are calculated (the $\mathcal{E}$ values exceed the classical ionization threshold $\mathcal{E}_*$ of the atom). The calculation method is summation of divergent perturbation series (PS) by means of Hermite-Padé approximants (HPA). The 1/n-expansion is also briefly discussed. The results of the calculation agree with the experimental data.

Fig. - 5 , ref. - 16

1. In the last few years investigation of highly excited, or Rydberg[1] states of atoms and molecules attracted a great interest and significant results were obtained in this field [1-5]. Recent experiments revealed resonances in atomic photoionization cross-sections in the presence of external electric field which correspond to $n \sim 15 \div 30$ and are narrow enough even at positive energy, $E > 0$ (first for Rb and then for hydrogen [2-5]). The existence of such states is absolutely inexplicable from the viewpoint of the classical ionization model, but can be explained using the WKB method which leads to approximate expressions for the energy E_0 and width Γ [6]. The relationship between resonances experimentally observed in hydrogen and Stark quasistationary states, their positions and widths obtained by numerical integration of the Schrödinger equation, were pointed out in refs.[4,7]. Using independent calculation methods [1)] we evaluated complex energies, $E = E_0 - i\Gamma/2$, of these states within a wide range of values of n and $\mathcal{E}$. The basic results of our calculations are discussed below.

2. Let $E^{(n_1 n_2 m)}$ be the energy of atomic level with parabolic quantum numbers n_1, n_2 and m $(m \geq 0)$, $n = n_1+n_2+m+1$ - the principal quantum number, $\mathcal{E}$ - the electric field strength (we use atomic units, $\hbar = m = e = 1$, and the same notations as in ref.[8]). The results of the calculation will be expressed through reduced variables,

$$\varepsilon^{(n_1 n_2 m)} = 2n^2 E^{(n_1 n_2 m)}, \quad F = n^4 \mathcal{E}, \quad \mu = \frac{m}{n}, \quad \nu_i = \frac{n_i + 1/2}{n} \qquad (1)$$

($\mu+\nu_1+\nu_2=1$), which are especially convenient in the case of Rydberg states, n >>1. The region of strong field corresponds to $F \gtrsim F_*$ where F_* is "the classical ionization threshold" (the values of F_* for different states of hydrogen atom range from 0.130 to 0.383, see ref.[8]). Of all n^2 states $|n_1 n_2 m\rangle$ with given n, which are degenerate at $\mathcal{E} = 0$, the states with minimal values of n_2 and m are the most stable (this is easily seen from the asymptotics [2] for the width $\Gamma^{(n_1 n_2 m)}$ at $\mathcal{E} \to 0$). Therefore, such states are of a particular interest for investigation.

The calculation results[3] are presented in Fig.1 (for the Stark shifts, $\varepsilon'_n = 2n^2 \,\mathrm{Re}\, E_0^{(n_1 n_2 m)}$) and Fig.2 (for the level widths, $\varepsilon''_n = n^2 \Gamma^{(n_1 n_2 m)}$). Here

$$\varepsilon_n \equiv \varepsilon'_n - i\varepsilon''_n = 2n^2(E_0 - i\Gamma/2)$$

The limiting curve, $n=\infty$, defined by the equation

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

is also shown in Fig.1 ("the Rydberg limit" corresponds to $\nu_1=1$, $\nu_2=\mu=0$, see ref.[8]). Note that F-dependence of ε'_n is almost linear at $0.3 < F < 0.8$. At $F = 0.4 \div 0.5$ the real part of the energy reverces its sign [4], yielding the quasistationary level with positive energy.

Fig.2 shows that for fixed n and F the $|n-1,0,0\rangle$ states have the smallest ionization probability. These are followed by $|n-2,0,1\rangle$ states, next come $|n-3,0,2\rangle$ and $|n-2,1,0\rangle$ states, etc.

The values of $\mathcal{E}_n''$ and especially $\mathcal{E}_n'$, for the latter states are very close to each other (see, in particular, Fig.3). This can be easily explained when considering the structure of PS:

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

where k is PT order,

$$\mathcal{E}_k = \begin{cases} P_k(\varkappa^2, \mu^2, 1/n^2), & \text{k is even} \\ \varkappa P_k(\varkappa^2, \mu^2, 1/n^2), & \text{k is odd} \end{cases} \tag{4}$$

$\varkappa = (n_1 - n_2)/n = \nu_1 - \nu_2$ and P_k is polynomial of degree $[k/2]$,

$$P_0 = -1, \quad P_1 = 3, \quad P_2(x,y,z) = -\frac{1}{8}(17 - 3x - 9y + 19z),$$

$$P_3 = \frac{3}{16}(23 - x + 11y + 39z), \ \ldots$$

(here $x = \varkappa^2$, $y = \mu^2$, $z = 1/n^2$).

The $|n-2,1,0\rangle$ and $|n-3,0,2\rangle$ states have the same value of $\varkappa = 1 - 1/n$ differing only by the parameter μ^2, i.e. by the terms of order $1/n^2$. On the other hand, $\varkappa = 1-(m+1)/n$ for $|n-m-1,0,m\rangle$ states with $m = 0,1,2\ldots \ll n$. Therefore, the coefficients $\mathcal{E}_k$ and the sums $\mathcal{E}^{(n_1 n_2 m)}(F)$ of the corresponding PS(3) differ already in the terms of order 1/n.

The values of $\mathcal{E}_n'$ and $\mathcal{E}_n''$ recalculated from the experimental data[4] according to photoionization of hydrogen atom are also shown in Figs.1,2 (note that for $\mathcal{E}$ = 6.5 and 8.0 kV/cm our results agree with the Kolosov's calculations[6] performed by different method). There is an obvious agreement between theory and experiment.

In Figs.4 and 5 the calculated energies of the Stark resonances are compared with experimental spectra taken from ref. [4]. It is seen that the positions of spectra maxima correspond to the values of $\mathcal{E}_n'$, while the peak widths qualitatively agree with $\mathcal{E}_n''$ (Fig.5 partly overlaps the Figure in ref.[7]). Thus, the theoretical calculations of the Stark resonances in a strong electric field agree with experiment, includimg the $E>0$ region, until the Stark resonances remain isolated. As is seen from Figs.4,5 the level width rapidly increases in the region $E > 0$, even for the $|n-1,0,0\rangle$ states which are the states with minimal ionization probability. Besides, the calculations show a decrease in the difference between energies of $|n_1,0,0\rangle$ and $|n_1,1,0\rangle$ states in this energy region. The above features readily allow one to understand the qualititative characteristics of the spectra measured[3-5] in the vicinity of $E \approx 0$.

3. Comments on the 1/n-expansion. We will consider here only states with magnetic quantum number m=0. In this case the integrals entering both the Bohr-Sommerfeld quantization rule and its correction term of order $\hbar^2$ can be calculated analytically (see Appendix A). We get the following equations for the energy and separation constants $\beta_{1,2}$:

$$\beta_1(-\varepsilon)^{-1/2} f(z_1) - \frac{F}{8n^2}(-\varepsilon)^{-3/2} g(z_1) = \nu_1 ,$$
$$\beta_2(-\varepsilon)^{-1/2} f(z_2) + \frac{F}{8n^2}(-\varepsilon)^{-3/2} g(z_2) = \nu_2 , \qquad (5)$$
$$\beta_1 + \beta_2 = 1$$

where $\nu_1 + \nu_2 = 1$, $\mu = 0$, $z_1 = -16\beta_1 F/\varepsilon^2$, $z_2 = 16\beta_2 F/\varepsilon^2$,

$$f(z) = F(\tfrac{1}{4}, \tfrac{3}{4}; 2; z)$$
$$g(z) = \tfrac{2}{3} F(\tfrac{3}{4}, \tfrac{5}{4}; 1; z) + \tfrac{1}{3} F(\tfrac{3}{4}, \tfrac{5}{4}; 2; z) \qquad (6)$$

and $F(\alpha,\beta;\gamma;z) \equiv {}_2F_1(\alpha,\beta;\gamma;z)$ is the hypergeometric function. The nonaccounted for in eq.(5) corrections do not exceed n^{-4} (see eq.(A.3)), therefore, in the case of Rydberg states, eqs.(5) are quite precise. Functions $f(z)$ and $g(z)$ are real for $-\infty < z < 1$ and have singularities at $z = 1$ (for further details see Appendix B). Note that $z_2 = 1$ corresponds to the classical ionization threshold, $F = F_*$.

At $F \to 0$, hence it follows from (5) that [5]

$$\varepsilon = -1 + 3\varkappa F - \tfrac{1}{8}(17 - 3\varkappa^2 + 19n^{-2})F^2 + \\ + \tfrac{3}{16}\varkappa(23 - \varkappa^2 + 39n^{-2})F^3 + \ldots \qquad (7)$$

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

(β_2 is obtained by replacing $\varkappa \to -\varkappa$, $F \to -F$) which coincides with PS in the weak field region. At an arbitrary value of F, equations (5) may be easily solved numerically. Until $F < F_* = F_*(\nu_1, \nu_2)$ the solution $\mathcal{E}(F)$ remains real and agree with the results of HPA for ε_n' thus confirming the chosen method of summation of divergent PS. At $F > F_*$, $\mathcal{E}(F)$ becomes complex [6] which makes it possible to calculate with this method not only the shift, but also the width of the level (compare with the case of the Yukawa potential[11]). Apart from its practical value [7], this fact is of essential importance for the 1/n-expansion itself. Such calculations are now in progress.

1/n-expansion follows from eqs.(5):

$$\mathcal{E} = \mathcal{E}^{(0)} + \frac{\mathcal{E}^{(1)}}{n} + \frac{\mathcal{E}^{(2)}}{n^2} + \dots \tag{8}$$

Let $n_1 >> n_2 \sim 1$. Then $\mathcal{E}^{(0)}$ is defined by eq.(2) and $\mathcal{E}^{(1)}$ - by (C.5). Note that $\mathcal{E}^{(0)}(F)=0$ at $F = F_0$, the function $\mathcal{E}^{(0)}(F)$ having no singularity at this point and remaining real in the region $F > F_0$ .The next coefficients $\mathcal{E}^{(k)}$ in (8) already have singularities at $F = F_0$:

$$\mathcal{E}^{(0)} = \alpha_1 f + \alpha_2 f^2 + \dots$$

$$\mathcal{E}^{(1)} = \frac{3\pi}{32}\left[1 - (-\alpha_1 f)^{1/2} + \dots\right], \quad \mathcal{E}^{(2)} \sim f^{-1}, \dots \tag{9}$$

where $f = (F - F_0)/F_0 \to 0$,

$$F_0 \equiv F_*(1,0) = (2\gamma/9\pi)^2 = 0.383\ldots,$$
$$\alpha_1 = \gamma^2/27\pi = 0.903\ldots, \qquad (10)$$
$$\alpha_2 = -0.0673\ldots$$

and $\gamma = [\Gamma(1/4)/\Gamma(3/4)]^2 = 8.754$ (for details see Appendix C). Thus, 1/n-expansion is not valid in the vicinity of $F = F_0$ 7) (as is the case for other quantum-mechanical problems [11]).

4. In the weak field region, the distance between neighbour levels grows linearly with $\mathcal{E}$. On the other hand, for strong fields

$$\Delta E = c\,\mathcal{E}^{3/4} \qquad (11)$$

where [4] $c = 7.47 \pm 0.2$ for states with $n \sim 20$ and energy E near zero 8) . This relationship can be easily explained by 1/n-expansion. If $n \to \infty$ and quantum numbers n_2, m are of the order of unity, then $\beta_1(F) \equiv 1$, $\beta_2(F) \equiv 0$ (see, e.g. eq.(7) at k=1 and 1/n = 0). Therefore, eqs.(5) are reduced to one equation (2), whence

$$\left.\frac{dE}{dn}\right|_{E=0} = c\,\mathcal{E}^{3/4}, \qquad c = c_0 + \frac{c_1}{n} + \frac{c_2}{n^2} + \ldots \qquad (12)$$

Here

$$c_k = \left[2F\,\varepsilon^{(k)\prime} - \tfrac{1}{2}(k+2)\varepsilon^{(k)}\right] F^{-3/4} \qquad (12')$$

and $\varepsilon^{(k)}$ are coefficients in expansion (8). Thus, $c_0 =$

= 3.708 (in atomic units). If energy E is measured in cm^{-1} and electric field $\mathcal{E}$ in kV/cm, then c_0 = 7.54 which is quite close to the above mentioned experimental value (see also Table 1).

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Appendix A

The systematic derivation of higher orders of the WKB quantization rule has been elaborated by many authors , see refs. [12-14]. The one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi'' + V\psi = E\psi$$

is reduced by means of substitution $\psi(x) = \exp\{-\frac{i}{\hbar}\int^{x}\xi(x')\,dx'\}$ to the Riccati equation for the function $\xi(x)$.
Substituting into it the asymptotic series $\xi(x) = \sum_{k=0}^{\infty}(-i\hbar)^k\xi_k(x)$ Dunham[12] has obtained an explicit form corrections $\sim\hbar^2$ and $\sim\hbar^4$ to the Bohr-Somerfeld quantization rule:

$$\oint p\,dx\Big(1 - \frac{\hbar^2}{32}\Big[\frac{1}{p^3}(p^2)'\Big]^2 -$$

$$-\frac{\hbar^4}{2043}\Big\{49\Big[\frac{1}{p^3}(p^2)'\Big]^4 - \frac{16}{p^8}(p^2)'(p^2)'''\Big\} + O(\hbar^6)\Big) = 2\pi(n+1/2) \qquad (A.1)$$

where $p(x) = [2m(E - V(x))]^{1/2}$, $(p^2)' = d(p^2)/dx$ and the integration contour is to enclose the turning points in the complex plane of x (for more details see refs.[12-14]). Extension of eq.(A.1) to the Stark effect in a hydrogen atom was performed by Bek nstein and Krieger[10]:

$$\oint d\xi\, R\Big\{1 - \frac{1}{64R^6\xi^4}\Big[\frac{d}{d\xi}(R^2\xi^2)\Big]^2 + \ldots\Big\} = 2^{1/2}\pi(n_1+1/2),$$

$$R^2 = -\frac{1}{8}\mathcal{E}\xi + \frac{1}{4}E + \frac{\beta_1}{2\xi} - \frac{m^2}{8\xi^2} \qquad (A.2)$$

A similar quantization rule holds for the η variable except that $\mathcal{E}$ is replaced by $-\mathcal{E}$, β_1 by β_2 and n_1 by n_2.

Consider m = 0 states where the integrals entering eq.(A.2) are expressed through the hypergeometric functions. Performing the scaling transformation (1), $\xi = n^2 x$ and $\eta = n^2 y$, we get:

$$\oint \frac{dx}{x} Q_1^{1/2} \Big\{ 1 - \frac{1}{64 n^2 Q_1^3}\Big(x\frac{dQ_1}{dx}\Big)^2 - \\ - \frac{1}{8192 n^4}\Big[\frac{49}{Q_1^6}\Big(x\frac{dQ_1}{dx}\Big)^4 - \frac{16}{Q_1^{7/2}}\frac{dQ_1}{dx}\Big(x\frac{d}{dx}\Big)^3 Q_1\Big] + O(n^{-6})\Big\} = 2\pi \nu_1 \quad (A.3)$$

$$Q_1(x) = \beta_1 x + \tfrac{1}{4}\varepsilon x^2 - \tfrac{1}{4}F x^3, \\ Q_2(y) = \beta_2 y + \tfrac{1}{4}\varepsilon y^2 + \tfrac{1}{4}F y^3 \quad (A.4)$$

The possibility of evaluating integrals in eq.(A.2) at m = 0 to hypergeometric functions was indicated by Drukarev[15]. However, eqs.(A.6),(A.7) were not obtained and as a result the equations for $\varepsilon(F)$ in ref.[15] are more complicated than eqs. (5). As follows from eq.(A.3), the actual parameter of the WKB-expansion is $1/n^2$. We will restrict ourselves to only two terms of the expansion (A.3), assuming $\varepsilon < 0$ during the calculations. The final results will be applicable after analytic continuation for the case $\varepsilon > 0$ as well. The integration contour in eq.(A.3) encloses two turning points,

$$x_0 = 0, \qquad x_1 = \frac{1}{2F}\left[\varepsilon + (\varepsilon^2 + 16\beta_1 F)^{1/2}\right]$$

leaving the root $x_2 < 0$ of the function $Q_1(x)$ outside. The first term in (A.3) is

$$I_1 = \frac{1}{2} F^{1/2} \int_0^{x_1} [(x-x_1)(x_2-x)/x]^{1/2} dx = \frac{\pi}{4} F^{1/2} x_1 (x_2)^{1/2} {}_2F_1(-\tfrac{1}{2}, \tfrac{1}{2}; 2; \tfrac{x_1}{x_2})$$

where $x_1/x_2 = \frac{1-\sqrt{1-z}}{1+\sqrt{1-z}}$, $z = -16\beta_1 F/\varepsilon^2$. This expression can be simplified by means of the Kummer quadratic transformation[16]

$$F(2\alpha, 2\alpha-\beta+1; \beta; \tfrac{1-\sqrt{1-z}}{1+\sqrt{1-z}}) = \left(\frac{1+\sqrt{1-z}}{2}\right)^{2\alpha} F(\alpha, \alpha+\tfrac{1}{2}; \beta; z) \qquad (A.5)$$

In this case $\alpha = 1/4$, $\beta = 2$, $\frac{1}{2}(1+\sqrt{1-z}) = x_2 F/\varepsilon$, $x_{1,2} = [\varepsilon \pm (\varepsilon^2 + 16\beta_2 F)^{1/2}]/2F$. We get

$$I_1 = \pi\beta_1(-\varepsilon)^{1/2} F(\tfrac{1}{4}, \tfrac{3}{4}; 2; z_1), \quad z_1 = -16\beta_1 F/\varepsilon^2 \qquad (A.6)$$

To calculate the second term of eq.(A.3) we leave unchanged the first power of derivative dQ/dx under the integral sign, substitute the same second factor explicitly as $dQ/dx = \beta_1 + \frac{1}{2}\varepsilon x - \frac{3}{4}F x^2$ and integrate by parts

$$I_2 = \frac{1}{64 n^2} \oint \frac{x\,dx}{Q^{5/2}} \left(\frac{dQ}{dx}\right)^2 = \frac{1}{32 n^2}\left(\frac{2}{3}\beta_1 K_0 + \frac{2}{3}\varepsilon K_1 - \frac{3}{2} F K_2\right) \qquad (A.7)$$

where ($j = 0,1,2$)

$$K_j = 8F^{-3/2} \int_0^{x_1} [(x-x_1)(x_2-x)]^{-3/2} x^{j-3/2} dx =$$
$$= 8F^{-3/2} x_1^{j-2} (-x_2)^{-3/2} \frac{\Gamma(j-1/2)\Gamma(-1/2)}{\Gamma(j-1)} F(\tfrac{3}{2}, j-\tfrac{1}{2}; j-1; \tfrac{x_1}{x_2}) \qquad (A.8)$$

This expression appears to be indefinite at $j = 0$ and 1 and this obstacle is removed in a standard way:

$$\lim_{\gamma \to -n} \frac{1}{\Gamma(\gamma)} F(\alpha, \beta; \gamma; z) = \frac{\Gamma(\alpha+n+1)\Gamma(\beta+n+1)}{\Gamma(\alpha)\Gamma(\beta)(n+1)!} z^{n+1} F(\alpha+n+1, \beta+n+1; n+2; z)$$

Then applying transformation (A.5) to each K_j (with $\alpha = 7/4 - j$ and $\beta = 3 - j$) we obtain the correction of the order $1/n^2$,

$$I_2 = \frac{\pi F}{8 n^2 (-\varepsilon)^{3/2}} g(z_1), \tag{A.9}$$

$$g(z) = 3F(\tfrac{3}{4}, \tfrac{5}{4}; 1; z) - 2F(\tfrac{5}{4}, \tfrac{7}{4}; 2; z) + \\ + \frac{5}{32} z F(\tfrac{7}{4}, \tfrac{9}{4}; 3; z) \tag{A.10}$$

This expression can be further simplified. Indeed, the functions g_1, g_2 behave similarly at $z \to 1$:

$$g_1(z) \equiv 3F(\tfrac{3}{4}, \tfrac{5}{4}; 1; z) - 2F(\tfrac{5}{4}, \tfrac{7}{4}; 2; z) \approx c(1-z)^{-1}, \\ g_2(z) \equiv \frac{5}{32} z F(\tfrac{7}{4}, \tfrac{9}{4}; 3; z) \approx c(1-z)^{-1}, \tag{A.11}$$

$c = 2^{3/2}/3\pi$. Therefore, it can be assumed that $g_1(z)$ is a sum and $g_2(z)$ is the difference between two functions, one of which has a pole and the other has only logarithmic singularity. Suitable candidates are:

$$F(\tfrac{3}{4},\tfrac{5}{4};1;z) \underset{(z\to 1)}{=} \frac{2^{2/3}}{\pi}\left[\frac{1}{1-z}-\frac{1}{16}\ln(1-z)+\frac{3}{16}(2\ln 2-1)+\ldots\right]$$

$$F(\tfrac{3}{4},\tfrac{5}{4};2;z) \underset{(z\to 1)}{=} \frac{2^{2/3}}{\pi}\left[\ln(1-z)+(4-6\ln 2)+\ldots\right]$$

Using the Kummer quadratic transformation, we proceed to argument $u=(1-\sqrt{1-z})/(1+\sqrt{1-z})$:

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

$$F(\tfrac{3}{4},\tfrac{5}{4};2;z)=(1+u)^{3/2}\,F(\tfrac{1}{2},\tfrac{3}{2};2;u),\ \ldots$$

Then we come to

$$g_{1,2}(z)=(1+u)^{3/2}\,h_{1,2}(u)\quad,\qquad z=4u\,(1+u)^{-2}$$

$$h_1(u)=3F(\tfrac{3}{2},\tfrac{3}{2};1;u)-2(1+u)F(\tfrac{3}{2},\tfrac{5}{2};2;u)$$

$$h_2(u)=\frac{5}{16}\,u(1+u)\,F(\tfrac{3}{2},\tfrac{7}{2};3;u)$$

Further we use Gauss relations for contiguous hypergeometric functions[16]. After some simple, though lengthy calculations we get

$$h_1(u) = \frac{1}{3}\left[F\left(\tfrac{3}{2},\tfrac{3}{2};1;u\right) + 2F\left(\tfrac{3}{2},\tfrac{1}{2};2;u\right)\right]$$

$$h_2(u) = \frac{1}{3}\left[F\left(\tfrac{3}{2},\tfrac{3}{2};1;u\right) - F\left(\tfrac{1}{2},\tfrac{3}{2};2;u\right)\right]$$

Taking into account eq.(A.10), we finally obtain:

$$g(z) = \frac{2}{3}F\left(\tfrac{3}{4},\tfrac{5}{4};1;z\right) + \frac{1}{3}F\left(\tfrac{3}{4},\tfrac{5}{4};2;z\right) \qquad \text{(A.12)}$$

The quantization rules (5) follow from eqs.(A.6),(A.9) and (A.12).

Appendix B

Let us give expansions for functions $f(z)$ and $g(z)$ defined by eq.(6). At $z \to 0$

$$f(z) = \sum_{k=0}^{\infty} f_k z^k = 1 + \frac{3}{32}z + \frac{35}{1024}z^2 + \dots ,$$

$$g(z) = \sum_{k=0}^{\infty} g_k z^k = 1 + \frac{25}{32}z + \frac{735}{1024}z^2 + \dots , \qquad \text{(B.1)}$$

where

$$f_k = \frac{(4k-1)!!}{k!(k+1)!\,2^{4k}}, \qquad f_0 = 1 \qquad \text{(B.2)}$$

$$g_k = \frac{1}{3}(2k+3)(4k+1) \qquad \text{(B.3)}$$

At $z = 1$ these functions have singularities (besides $f(z)$ remains finite):

$$f(z) = A\left(1 + b_0 t \ln t + b_1 t + O(t^2 \ln t)\right),$$

$$g(z) = \frac{A}{2}\left(t^{-1} + c_0 \ln t + c_1 + \cdots\right) \qquad \text{(B.4)}$$

where $t = 1 - z \to 0$,

$$A = 2^{7/2}/3\pi = 1.2004$$

$$b_0 = 3/16, \qquad b_1 = \frac{1}{16}(13 - 18 \ln 2) = 0.0327\ldots,$$

$$c_0 = -9/16, \qquad c_1 = \frac{1}{16}(54 \ln 2 - 35) = 0.1519\ldots$$

Finally,, at $z \to -\infty$

$$f(z) = \alpha(-z)^{-1/4} + O(z^{-3/4}), \quad g(z) = \beta(-z)^{-1/4} + \cdots \qquad \text{(B.5)}$$

where

$$\alpha = \frac{2}{3}\left(\frac{2}{\pi}\gamma\right)^{1/2}, \quad \beta = 4\left(\frac{2}{\pi\gamma}\right)^{1/2}, \quad \gamma = 8.7537\ldots \; (eq.(10))$$

Appendix C

For states with $n_1 \to \infty$, n_2 and $m \sim 1$, the first term of 1/n-expansion $\mathcal{E}^{(0)}$ is defined by eq.(2). Making use of the Kummer quadratic transformation it can be re-written in a more convenient form:

$$(\mathcal{E}^2+16F)^{1/4}={}_2F_1\left(\tfrac{1}{2},\tfrac{5}{2};2;w\right),\quad w=\tfrac{1}{2}\left(1+\frac{\mathcal{E}}{\sqrt{\mathcal{E}^2+16F}}\right) \quad (C.1)$$

With $F=n^4\mathcal{E}$ increasing, $\mathcal{E}\equiv\mathcal{E}^{(0)}$ changes from -1 to ∞, while variable w changing from 0 to 1. Substituting $\mathcal{E}=0$ into (C.1) we get

$$F_0=\left\{\tfrac{1}{2}\,{}_2F_1\left(\tfrac{1}{2},\tfrac{5}{2};2;\tfrac{1}{2}\right)\right\}^4 \quad (C.2)$$

It follows from (B.1) that $\mathcal{E}^{(0)}$ as a function of F is not singular at $F=F_0$ and therefore may be expanded in series (9) in integer powers of f. Coefficients $\alpha_1, \alpha_2, \dots$ may be calculated successively, substituting expansion (9) into eq.(C.1):

$$w=\tfrac{1}{2}+\tfrac{1}{8}F_0^{-1/2}\left[-\alpha_1 f+(\alpha_2-\tfrac{1}{2}\alpha_1)f^2+\dots\right]$$

$$\alpha_1=\left\{F\left(\tfrac{1}{2},\tfrac{5}{2};2;\tfrac{1}{2}\right)\right\}^3\Big/2F'\left(\tfrac{1}{2},\tfrac{5}{2};2;\tfrac{1}{2}\right) \quad (C.3)$$

This leads to values (10) for F_0 and α_1 provided the following identities are taken into account

$$F\left(\alpha,\beta;\tfrac{\alpha+\beta+1}{2};\tfrac{1}{2}\right)=F\left(\tfrac{\alpha}{2},\tfrac{\beta}{2};\tfrac{\alpha+\beta+1}{2};1\right)=$$
$$=\pi^{1/2}\,\Gamma\left(\tfrac{\alpha+\beta+1}{2}\right)\Big/\Gamma\left(\tfrac{\alpha+1}{2}\right)\Gamma\left(\tfrac{\beta+1}{2}\right),$$
$$F'\left(\alpha,\beta;\tfrac{\alpha+\beta+1}{2};\tfrac{1}{2}\right)=4\pi^{1/2}\,\Gamma\left(\tfrac{\alpha+\beta+1}{2}\right)\Big/\Gamma\left(\tfrac{\alpha}{2}\right)\Gamma\left(\tfrac{\beta}{2}\right) \quad (C.4)$$

(α = 1/2, β = 5/2). From the system of eq.(5) we also obtain the next term of 1/n-expansion

$$\varepsilon^{(1)} = (2n_2+1)\,\varepsilon^{(0)} \cdot \frac{1 + (-\varepsilon^{(0)})^{1/2}(1+\frac{1}{4}\psi)}{1-\psi} ,$$

$$\psi = \frac{3}{16} F^{-1/4} x^{5/4} F(\tfrac{5}{4},\tfrac{7}{4};3;-x) = \begin{cases} 6F - 25F^2 + \dots, & F \to 0 \\ 1 + \frac{1}{2} f - \frac{5}{16}\left(1 - \frac{\pi^2}{240}\right) f^2 + \dots & F \to F_0 \end{cases} \qquad (C.5)$$

$$x = 16F/(\varepsilon^{(0)})^2, \quad f = (F - F_0)/F_0$$

Hence

$$\varepsilon^{(1)} = -(2n_2+1)\left(3F + \tfrac{3}{4}F^2 + \dots\right), \quad F \to 0 \qquad (C.6)$$

(this is in an agreement with PT series (7) if we take into account that $\varkappa = 1-(2n_2+1)/n)$, and at $F \to F_0$ we come to (9).

In conclusion let us clarify the origin of eq.(12). Differentiating $E = \frac{1}{2n^2}\sum \varepsilon^{(k)} n^{-k}$ with respect to n and taking into account that $\varepsilon^{(k)} = \varepsilon^{(k)}(n^4 \mathcal{E})$ we get

$$\frac{dE}{dn} = (\mathcal{E}/F)^{3/4} \sum_{k=0}^{\infty}\left(2F\varepsilon^{(k)\prime} - \frac{k+2}{2}\varepsilon^{(k)}\right) n^{-k} \qquad (C.7)$$

At k = 0 and $F = F_0$ we have $\varepsilon^{(0)} = 0$, $F\varepsilon^{(0)\prime} = \alpha_1$, hence

$$C_0 = 2\alpha_1 F_0^{-3/4} = (\pi\gamma/2)^{1/2} \qquad (C.8)$$

where γ is a constant introduced in eq.(10).

Footnotes

1) Namely, summation of divergent Rayleigh-Schrödinger perturbation series (PS) and 1/n-expansion. (More details about these methods are contained in refs. [8,9]).

2) At $F \to 0$

$$\Gamma^{(n_1 n_2 m)} \approx \frac{e^{3n}}{n_2!\,(n_2+m)!\,n^3}\left(\frac{4n}{e^3 F}\right)^{2n_2+m+1} \exp\left\{-\frac{2n}{3F}\right\}$$

3) When summing PS we use quadratic Hermite-Padé approximants (HPA), see eq.(5) in ref.[9]. In these calculations 50÷60 orders $\mathcal{E}_k$ were used which provided an accuracy of $\sim 0.1\%$ for the energy eigenvalue (in the region $F \sim 0.5$).

4) In particular, the limiting curve corresponding to $n=\infty$ traverses zero at $F = F_0 = 0.3834$ ... (see eqs.(9),(10)).

5) If the variables

$$t_i = \beta_i\,(-\varepsilon)^{-1/2}$$

are introduced, the quantization conditions (5) take the form which is more convenient for iteration:

$$\begin{cases} t_1 f(z_1) - \frac{F}{8n^2}(t_1+t_2)^3 g(z_1) = \nu_1 \\ t_2 f(z_2) + \frac{F}{8n^2}(t_1+t_2)^3 g(z_2) = \nu_2 \end{cases}$$

where $z_i = \mp 16\, F\, t_i (t_1 + t_2)^3$, i = 1 and 2 while

$$\mathcal{E} = -(t_1 + t_2)^{-2}$$

whence one can easily obtain expansions (7) from these expressions: $t_1 = \nu_1 + (\frac{3}{2}\nu_1^2 + \frac{1}{8n^2})F + \ldots$, $t_2 = \nu_2 - (\frac{3}{2}\nu_2^2 + \frac{1}{8n^2})F + \ldots$,...

6) See, for example, eq.(9) for coefficient $\mathcal{E}^{(1)}$.

7) 1/n-expansion is the most appropriate method in the case of n >>1.

8) Here E is measured in cm^{-1}, $\mathcal{E}$ - in kV/cm. Note that
$\mathcal{E} = 0.9113 \cdot 10^{-5}\, n^2 E(cm^{-1})$,
$100\ cm^{-1} = 4.56 \cdot 10^{-4}$ a.u. = 0.0124 eV

9) See ref.[10]. We have corrected here a misprint in eq.(15) of this paper.

10) It should be emphasized that the possibility of reducing integrals entering eq.(A.2) at m = 0 to hypergeometric functions was indicated in the work[15] by Drukarev. But expressions (A.6) and (A.9) were not obtained in that case owing to which the equations for $\mathcal{E}(F)$ in[15] are more complicated than eq.(5).

Table 1

Spacings of the Stark resonances at the threshold ($E \gtrsim 0$) as a function of the electric field $\mathcal{E}$.

$\mathcal{E}$, kV/cm	ΔE, cm^{-1} exp.	theor.
4.5	23.7±0.6	23.3
6.5	29.5±0.7	30.7
8.0	35.6±0.8	35.9
14.4	54.5±1.5	55.8
16.9	64.0±1.5	62.9

Footnote: Experimental values of ΔE are taken from ref. [4], theoretical values correspond to eq.(11) with $c = c_0 = 7.543$.

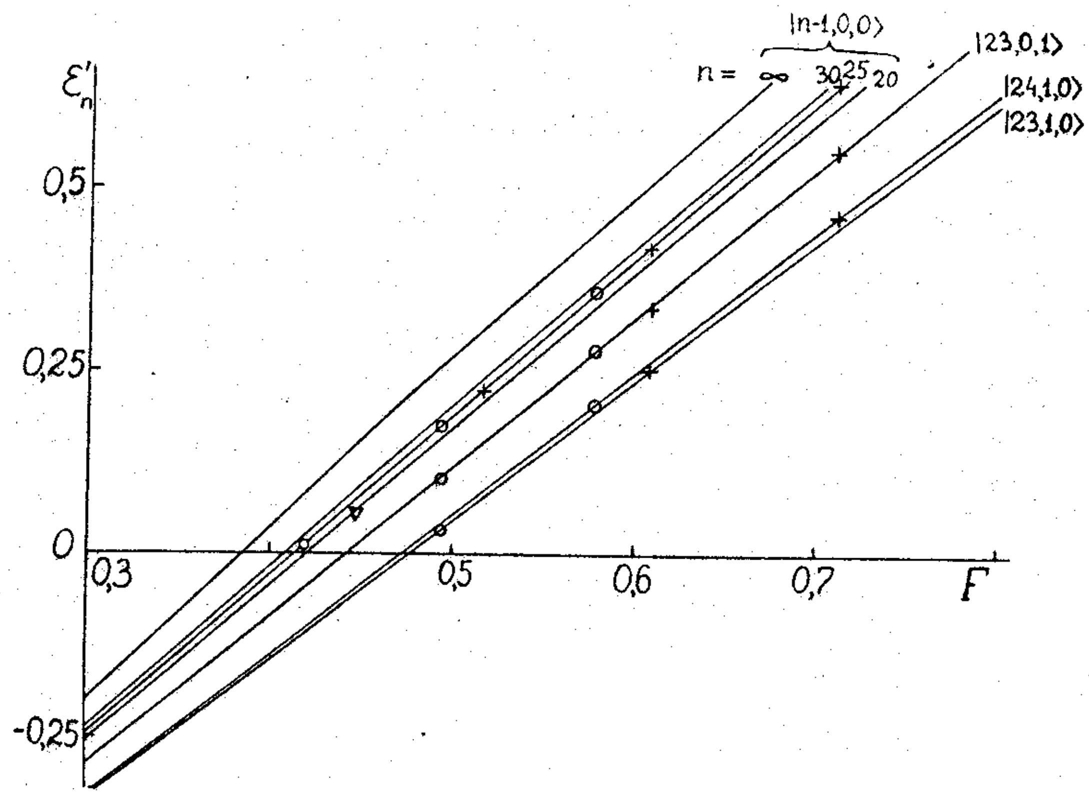

Fig.1. The energies of the Stark resonances in hydrogen atom. Solid curves are the calculation results, o - experimental data /4/ at $\mathcal{E}$ = 6.5 kV/cm, + - at = 8.0 kV/cm and ∇ at = 14.4 kV/cm. The curves for $|23, 1, 0\rangle$ and $|22, 0, 2\rangle$ states coincide within the accuracy of figure.

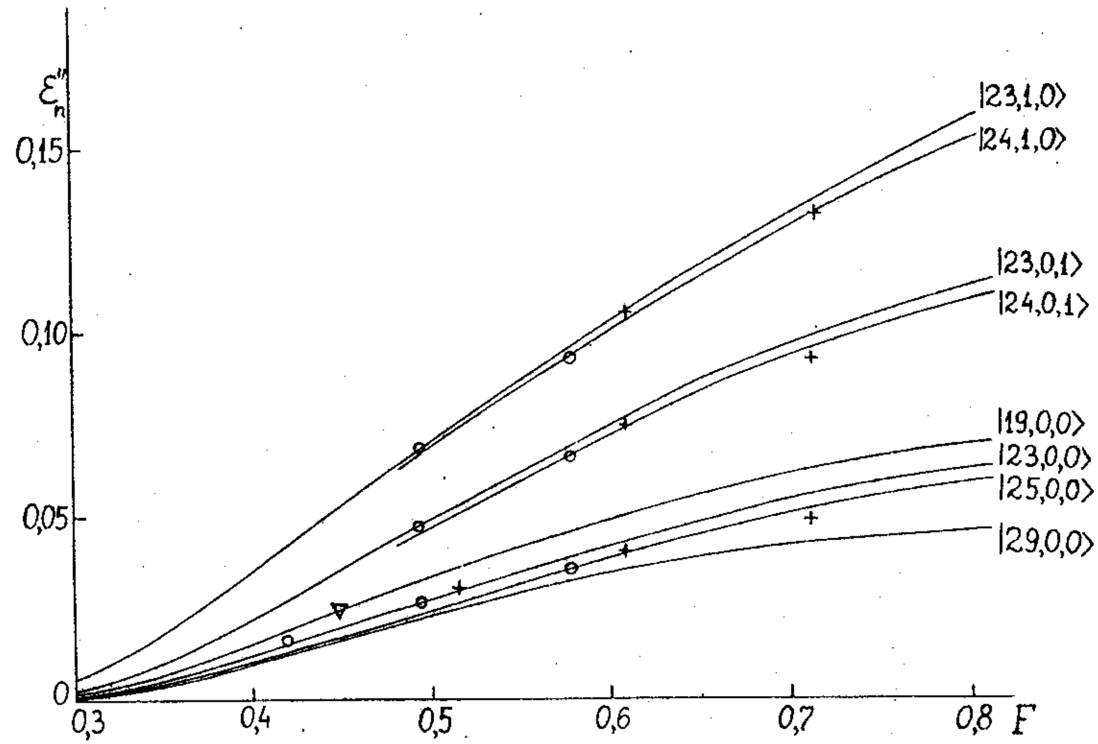

Fig.2. The widths of the Stark resonances, $\mathcal{E}_n'' = n^2\,\Gamma^{(n_1 n_2 m)}$. Parabolic quantum numbers n_1, n_2, m are given at the curves (notations are the same as in Fig.1).

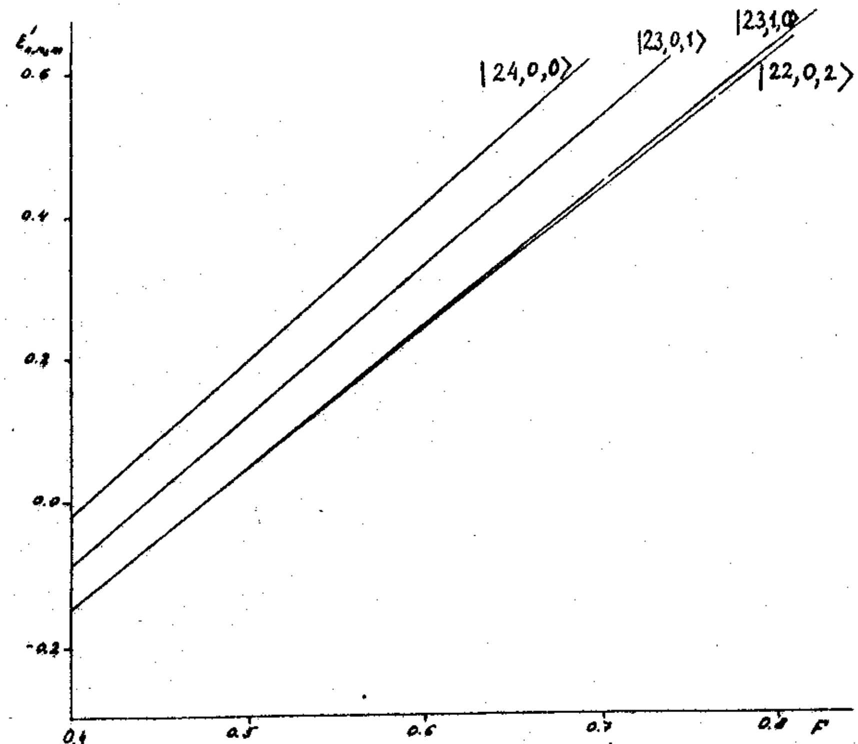

Fig.3. The Stark shifts ($\varepsilon'_{n_1 n_2 m} = 2\,\mathrm{Re}\,E^{(n_1 n_2 m)}$) for the n = 25 states. The curves were calculated by PS summation using HPA, 52 orders of perturbation theory being used.

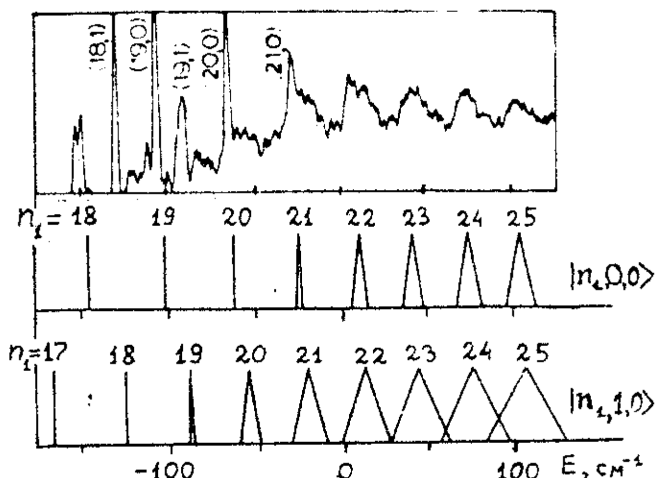

Fig.4. The experimental spectrum[4] of hydrogen atom photoionization at $\mathcal{E}$ = 8.0 kV/cm. The results of our calculations for $|n_1, 0, 0\rangle$ and $|n_1, 1, 0\rangle$ states are presented below (the apex of triangle indicates the resonance energy E_r and its base represents the width Γ).

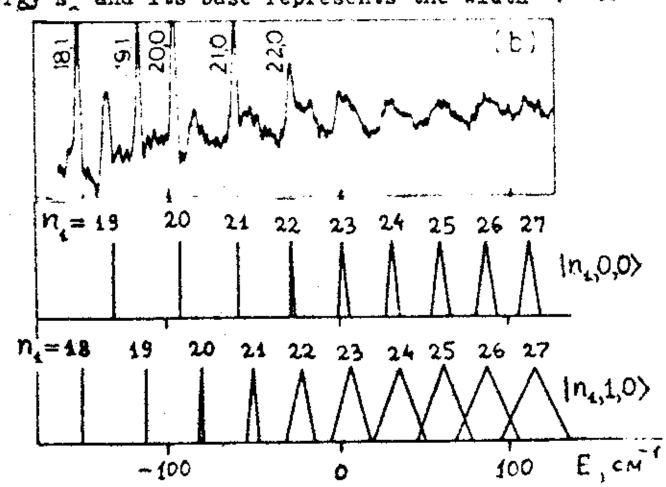

Fig.5. The same as in Fig.4 at $\mathcal{E}$ = 6.5 kV/cm (100 cm^{-1} = = 0.0124 eV).

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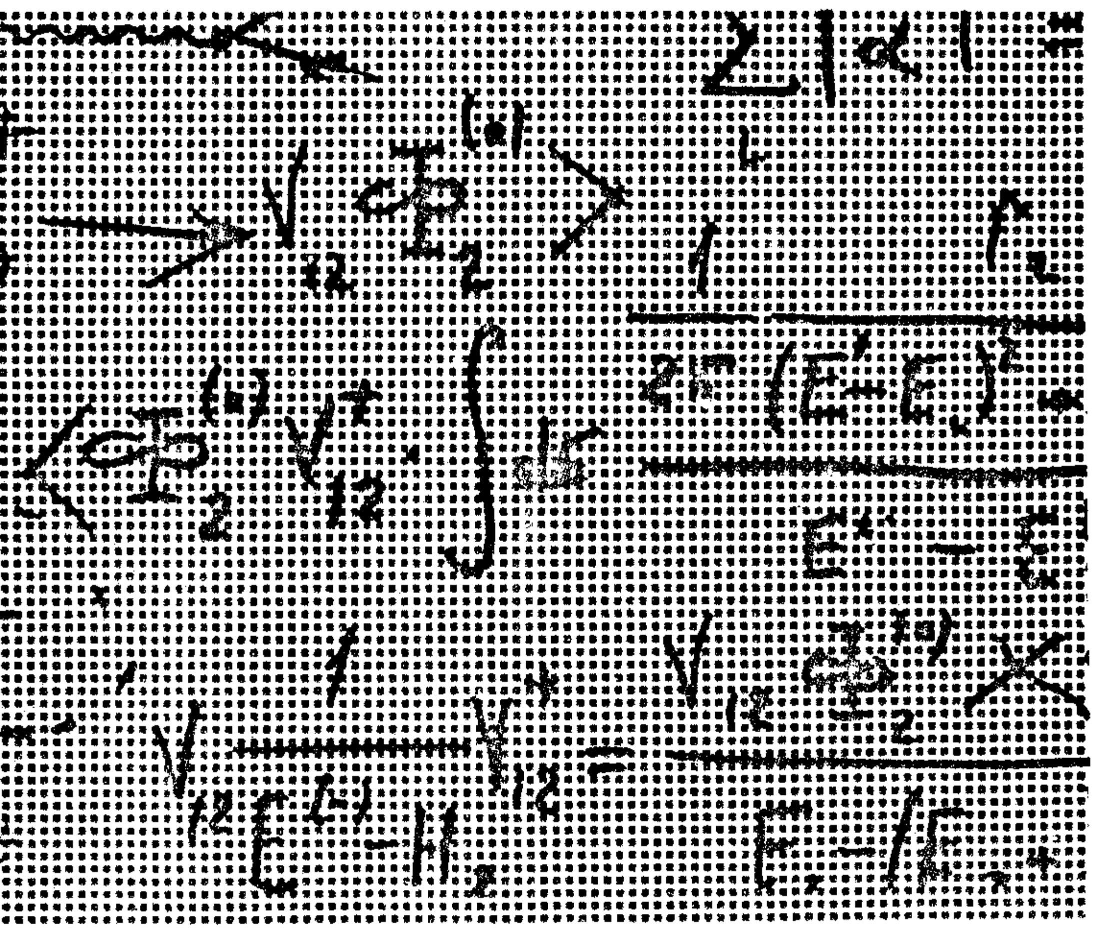

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