Structure of higher orders of the $1/n$ expansion

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The asymptote of higher orders of the $1/n$ expansion in quantum mechanical problems is found. It is shown that the coefficients $\varepsilon^{(k)}$ of the $1/n$ expansion grow factorially like $k!\,a^k$ as $k\to\infty$. The parameter a as a function of the coupling constant is studied. The derived analytic expressions agree with numerical calculations. As examples, the Yukawa, Hulthén and V funnel potentials are considered, as well as the Stark effect in the hydrogen atom and the molecular ion H_2^+.

1. The $1/n$ expansion occupies a special place among new quantum mechanical methods (see, e.g., Refs. 1–14). It is highly effective for highly excited (Rydberg) states of atoms and molecules, including effects in strong external fields.[3,5–7] In what follows we consider a version of this method suggested in Ref. 4, which can be applied both to a discrete spectrum and to quasistationary states (resonances). The energy values, which are complex in the latter case ($E_{nl}=E_r-i\Gamma/2$), are represented as a series in powers of a "small parameter" $1/n$:

$$\varepsilon\equiv\varepsilon'-i\varepsilon''=\varepsilon^{(0)}+\frac{\varepsilon^{(1)}}{n}+\ldots+\frac{\varepsilon^{(k)}}{n^k}+\ldots. \tag{1}$$

where $n=n_r+l+1$ is the principal quantum number, l is the orbital angular momentum, $\varepsilon=2n^2E_{nl}$ is the reduced energy of the level $\varepsilon''=n^2\Gamma_{nl}$, and k is the order of the $1/n$ expansion.

The behavior of the coefficients $\varepsilon^{(k)}$ for $k\gg 1$, apart from being interesting from the point of view of theory, is important when the energy is calculated to high accuracy on the basis of the expansion (1). As is known, the divergence of the perturbation theory (PT) series is due to the instability of the vacuum state when the sign of the coupling constant g is reversed (the so called Dyson phenomenon first considered in quantum electrodynamics[15] and later for the anharmonic oscillator,[16–18] Stark,[19–21] and Seeman[22] effects and other quantum mechanical problems[23–25]). It has turned out that the asymptote of higher PT orders has, as a rule, the form

$$E_k\approx(k_\alpha)!\;a^k k^\beta\left(c_0+\frac{c_1}{k}+\frac{c_2}{k^2}+\ldots\right),\quad k\to\infty, \tag{2}$$

$$E(g)=\sum_{k=0}^{\infty}E_k g^k, \tag{2a}$$

where $\alpha>0$, β, a, etc., are the constants which can be calculated.

When we pass from PT to the $1/n$ expansion (1), instead of g, we now have an expansion parameter $1/n$ which does not enter in the Hamiltonian explicitly. Contrary to higher PT orders, the coefficients $\varepsilon^{(k)}$ are complex functions of g. Therefore Dyson's arguments should be altered, as will be done below.

2. ASYMPTOTES OF HIGHER ORDERS OF THE $1/n$ EXPANSION (NUMERICAL CALCULATIONS)

Using recurrence relations (see Refs. 8 and 14), we have calculated 30 to 50 coefficients $\varepsilon^{(k)}$, checked that they follow the asymptote (2), and found the parameters of the latter. The calculations have been performed for the following problems: the V-funnel potential

$$V(r)=-r^{-1}+gr,\quad g>0, \tag{3}$$

its generalization

$$V(r)=-r^{-1}+(g/N)r^N, \tag{3a}$$

the screened Coulomb potential

$$V(r)=-r^{-1}f(x),\quad x=\mu r \tag{4}$$

(μ^{-1} is the characteristic screening radius and $\hbar=m=e=1$), and the Stark effect in the hydrogen atom and its spherical model [which corresponds to the change $g\to -g$ in Eq. (3)]. These examples embrace a wide class of potentials encountered in physics, including the short-range Yukawa and Hulthén potentials, the potential with confinement (3) often used in quantum chromodynamics, and potentials with a barrier.

In all cases, it has turned out that $\alpha=1$, i.e., the asymptote is factorial. The dependence of the number a in Eq. (2) on the problem parameters is of interest. For the potentials (4) the suitable parameters is $\nu=n^2\mu$ (see Ref. 4); in the case (3) $\mu=g^{1/2}$, and in the case (3a) $\mu=g^{1/(N+1)}$ and $f(x)=1-N^{-1}x^{N+1}$. Finally, for the Stark effect $\nu=n^2\mathscr{E}^{1/2}\equiv F^{1/2}$, where $\mathscr{E}$ is the constant electric field, and F is the "reduced" electric field[5,6] (we use here atomic units).

The $1/n$ expansion is about a classical equilibrium point $x_0(\nu)$ in an effective potential which includes centrifugal energy. At sufficiently small ν this point and all the coefficients $\varepsilon^{(k)}(\nu)$ are real. When the parameter ν increases, for a certain value $\nu=\nu_*$ we have a collision of two classical solutions: stable (x_0) and unstable equilibrium points. The frequency ω of small-amplitude oscillations near the point x_0 vanishes (thus indicating the loss of stability):

$$\omega=C(1-\nu/\nu_*)^{1/4}+\ldots,\quad \nu\to\nu_*, \tag{5}$$

$$C=[6(1+xf'''/3f'')_{x=x_*}]^{1/4}. \tag{6}$$

The values of ν_* and $x_*=x_0(\nu_*)$ are found from the equations

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$$\nu = xf - x^2 f' \quad f - xf' - x^2 f'' = 0. \tag{7}$$

As far as calculations are concerned, it is worth noting that

$$C = (-2x^2\nu''/\nu|_{x=x_*})^{1/4} = [\varphi'(x_*)]^{1/4}, \tag{6a}$$

where the function $\nu(x)$ is given by the first of Eqs. (7), $\varphi(x) = -2x^2\nu'/\nu$, and all the values are taken at $x = x_*$.

For $\nu > \nu_*$ the equilibrium point becomes complex, as well as the coefficients $\varepsilon^{(k)}(\nu)$. Evidently, such a solution has no physical meaning in classical mechanics, but in quantum mechanics it does allow us to find (in the framework of the $1/n$ expansion) both E_r and the width Γ of the Breit–Wigner resonances of energy $E = E_r - i\Gamma/2$.

Let us discuss the results of our calculations. In Table I we list the coefficients of the $1/n$ expansion taken with opposite sign for the problem of the Stark effect in the hydrogen atom.[1)] For definiteness we have chosen the states with $n_1 = n_2 = 0$ and $m = n - 1$, where n_1, n_2, and m are parabolic quantum numbers. This table illustrates the behavior of $1/n$ expansion coefficients typical also of other quantum mechanical problems. For $F < F_* = 2^{12} \cdot 3^{-9} = 0.2081$ all coefficients $\varepsilon^{(k)}$ are real; for $F > F_*$, i.e., after the collision of classical solutions, they acquire an imaginary part. With increasing k, these coefficients first decrease (to $k = k_0 \sim 3$–5), and for $k > k_0$ they begin to grow. Such a behavior of $\varepsilon^{(k)}$ determines the advantage of the $1/n$ expansion in comparison, for example, with PT series (2a), where the factorial growth of higher orders, E_k, begins, as a rule, directly from $k = 1$.

Figure 1 shows the dependence of $|a|$ on the ratio ν/ν_* for the Stark effect in hydrogen, its spherical model, and the V-funnel potential. For $\nu \approx \nu_*$ the asymptote parameter $a \to \infty$, bringing about a drastic growth in $\varepsilon^{(k)}$, so that the expansion (1) ceases to be valid (this has been noted already, when the first attempts of summing the $1/n$ expansion have been made;[4,5] the cause is clear from Fig. 1). The V-

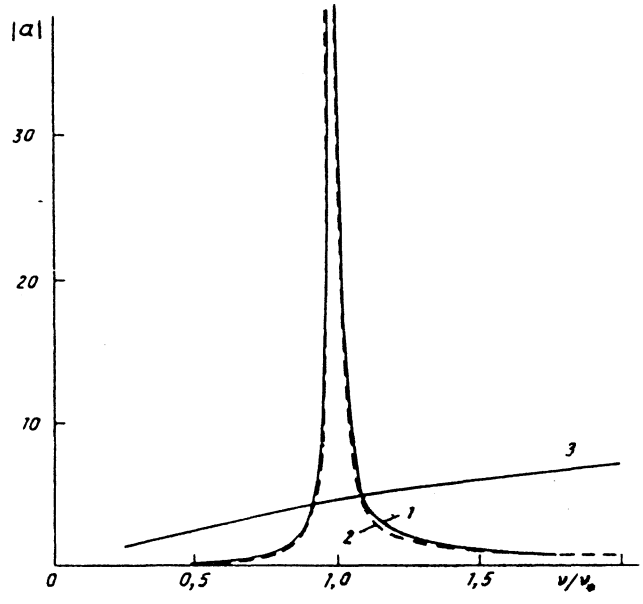

FIG. 1. The asymptote parameter $a(\nu)$ as a function of ν/ν_*. The curves *1*, *2*, and *3* relate to the Stark effect, its spherical model, and V funnel potential, respectively. In the last case $\nu_* = 2 \cdot 3^{-3/2}$ and the values of a are multiplied by 100.

TABLE I. The highest orders of $1/n$ expansion for Schottky effect.

k	$-\varepsilon^{(k)}$				$-\varepsilon^{(k)}$	
	$F=0.07$	0.10	0.15	0.18	0.25	0.50
0	1,0050	1,0103	1,0244	1,0368	1,0858+i·1,3918(−2)	1,2036+i·0,1896
1	1,148(−2)	2,454(−2)	6,384(−2)	1,099(−1)	0,1567+i·0,1935	7,110(−2)+i·0,3943
2	7,194(−3)	1,775(−2)	7,396(−2)	2,433(−1)	−0,1860−i·0,2188	−2,249(−2)−i·5,259(−2)
3	1,266(−3)	7,762(−3)	1,387(−1)	1,567	−0,6532+i·1,853	−5,665(−2)+i·4,565(−2)
4	9,072(−4)	9,647(−3)	5,707(−1)	2,061(1)	2,455(−1)−i·5,074	0,1437+i·6,741(−2)
5	6,711(−4)	1,547(−2)	3,3422	3,893(2)	−3,133(2)−i·3,329(2)	3,387(−2)−i·0,4657
6	7,066(−4)	3,249(−2)	2,515(1)	9,430(3)	−2,710(3)+i·1,036(4)	−1,7374+i·0,5207
7	8,673(−3)	8,230(−2)	2,294(2)	2,767(5)	2,897(5)−i·9,295(4)	5,2684+i·6,7720
8	1,260(−3)	2,443(−1)	2,452(3)	9,503(6)	−7,832(6)−i·6,448(6)	2,448(1)−i·4,106(1)
9	2,085(−3)	8,301(−1)	3,001(4)	3,737(8)	−4,390(7)+i·3,856(8)	−3,023(2)−i·4,990(1)
10	3,887(−3)	3,1761	4,138(5)	1,655(10)	1,497(10)−i·7,504(9)	4,655(2)+i·2,170(3)
15	0,3597	1,078(4)	8,572(11)	1,170(19)	2,435(18)+i·1,027(19)	−9,420(7)−i·1,639(8)
20	1,982(2)	2,193(8)	1,068(19)	4,975(28)	−4,034(28)+i·4,669(26)	7,299(13)+i·6,618(13)
25	2,165(3)	1,669(12)	4,987(26)	7,934(38)	1,196(38)−i·5,680(38)	−1,765(20)−i·7,961(19)
40	–	–	1,376(52)	8,719(71)	−3,069(71)−i·3,571(71)	3,497(41)−i·1,975(41)

Note. The table contains the coefficients $-\varepsilon^{(k)}$ for the states $(0,0,n-1)$ in the hydrogen atom, k is the order of the $1/n$ expansion, $F = n^4\mathscr{E}$, $\hbar = m = e = 1$ (the electric field unit is $\mathscr{E}_{at} = 5.142 \cdot 10^9$ V/cm). In the parentheses the order of magnitude is indicated, i.e., $(m) \equiv 10^m$. For example, $1.148(-2) = 0.01148$.

funnel potential (3) has only discrete spectrum (for $0<g<\infty$), therefore no collision of classical solutions occurs here. According to this, the parameter a remains finite for all ν (see curve 3).

Similar calculations have been performed for the Yukawa [$f(x)=e^{-x}$ in (4)] and Hulthén [$f(x)=x/(e^x-1)$, see Fig. 2] potentials. Note that in these two cases the asymptote of $\varepsilon^{(k)}(\nu)$ has, along with (2), oscillating terms corresponding to the singularities in the complex plane of the Borel variable z [see (A3)]. These terms are important for large $k=20$–30, which makes the numerical calculation of the parameter a much more complicated (the details are discussed in Appendix A).

3. The behavior of the asymptote parameter $a=a(\nu)$ for small ν and $\nu\to\nu_*$ can be found analytically. In the first case[2)]

$$\varepsilon^{(k)}=(-1)^k\frac{f_{k+1}}{2^{k-1}(k+1)}\nu^{k+1}+\dots, \tag{8}$$

where $k\geqslant 1$, and f_k are the expansion coefficients of the screening function

$$f(x)=\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}f_k x^k. \tag{4a}$$

The asymptotes of the $1/n$ expansion coefficients are determined here by the nearest singularity of the function $f(x)$ in the complex plane. If this singularity is at a finite distance b from zero, then

$$|\varepsilon^{(k)}|\approx k!(\nu/2b)^k,\quad k\to\infty. \tag{9}$$

Thus, even for small $\nu\ll\nu_*$ [when the potential (4) is close to the Coulomb potential for which the series (1) is cut off at the first term] the coefficients of the $1/n$ expansion grow factorially. For example, for the Hulthén potential we have

$$f(x)=x/(e^x-1),$$
$$f_0=1,\ f_1=1/2,\ f_k=B_k\ (k\geqslant 2),$$

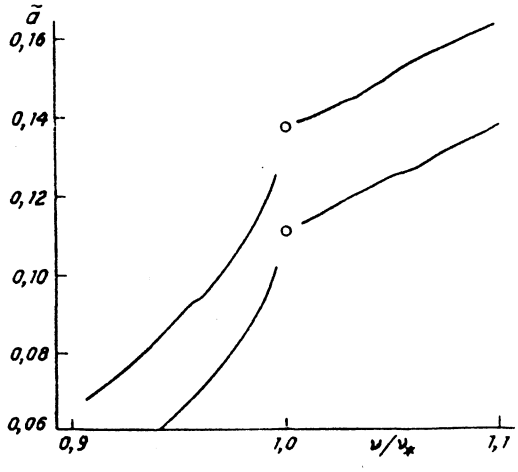

FIG. 2. The verification of Eq. (12) for ν close to ν_*. The upper curve corresponds to the Hulthén potential, and the lower to the Yukawa potential. The ordinates are the values of $\tilde a=|(1-\nu/\nu_*)^{5/4}a(\nu)|$. The parameter $a(\nu)$ was found numerically by using the higher orders of the $1/n$ expansion. Theoretical values $\tilde a(\nu_*)=A$ are denoted by points.

where B_k are the Bernoulli numbers. Therefore

$$\varepsilon^{(k)}=(-1)^{(k+1)/2}k!\left(\frac{\nu}{4\pi}\right)^k\left[\frac{2\nu}{\pi}+O\left(\frac{1}{k}\right)\right] \tag{10}$$

(k is odd) which agrees with the Eq. (9).

In the second case ($\nu\to\nu_*$), passing from $x=\mu r$ to ξ: $x=x_0(1+n^{-1/2}\xi)$ and expanding all the quantities in the Schrödinger equation in the powers of ξ, we find[3)] the anharmonic oscillator equation in which the nonlinearity ξ^s enters with a factor proportional to $n^{-(s-2)/2}$ ($s\geqslant 3$). Thus, as $n\to\infty$ we have a weak-coupling regime. Using the well-known results for asymptote of the higher PT orders for the anharmonic oscillator,[16,18] we easily find that the corresponding contribution to the coefficient $\varepsilon^{(k)}$ is of order $(k-1)!\omega^{-(s+2)/(s-2)}$. For finite $\omega>0$ all these contributions are, generally speaking, of the same order. If, however, the frequency $\omega\to 0$ [i.e., $\nu\to\nu_*$, see (5)], then the contribution from the smallest value $s=3$ prevails. Taking into account the results of Ref. 18 for the cubic oscillator, we find that

$$\varepsilon^{(k)}(\nu)\approx\text{const}\cdot k!\ a^k k^{-5/4},\quad k\to\infty, \tag{11}$$

where $a(\nu)$ has a power-law singularity for $\nu=\nu_*$:

$$a\approx A(1-\nu/\nu_*)^{-5/4},$$
$$A=\frac{5}{96}C^3=0{,}1997[1+(xf'''/3f'')_{x=x_*}]^{3/4}. \tag{12}$$

Here C is the same coefficient as in Eq. (5). In Table II we have listed the values of the coefficients A and C, and also ν_{cr} and ν_* for some short-range potentials (including the Yukawa and Hulthén potentials often used in nuclear physics and the Tietz potential which is a good approximation for the Thomas-Fermi model in neutral atoms[27,28]) and also for the Stark effect in its spherical model (3). The quantities ν_*, A and C were defined above. As for ν_{cr}, this value of the parameter $\nu=n^2\mu$ corresponds to $\varepsilon^{(0)}=0$, i.e., to the instant when the levels with $n\gg 1$ and $l\sim 1$ merge into the continuum.[4]

4. PARAMETERS OF THE $\varepsilon^{(k)}$ ASYMPTOTE

We now find the expressions for an arbitrary potential, limiting ourselves for simplicity to the states with $l=n-1\gg 1$. The quasi-classical momentum is[4)]

$$p(r)=\frac{1}{n}[-\varphi(y,\nu)]^{1/2},\quad \varphi=y^{-2}-2y^{-1}f(\nu y)-\varepsilon^{(0)}, \tag{13}$$

where $y=n^{-2}r$ and $\varepsilon^{(0)}(\nu)$ is the classical energy corresponding to a particle immobile at the point $x_0=\nu y_0$. The level width, to exponential accuracy, is

$$\Gamma_n\approx\exp\left(-2\int_{r_1}^{r_2}|p|\,dr\right)=\exp(-2nQ).$$

This gives for $\lambda=1/n\to 0$ energy jump the behavior which corresponds to the function $\varepsilon=\Sigma_k\varepsilon^{(k)}\lambda^k$ with factorially growing coefficients. The $\varepsilon^{(k)}$ asymptote for $k\to\infty$ is given by the dispersion relation in the variable λ:

$$\varepsilon^{(k)}(\nu)=\frac{1}{\pi}\int_0^{\infty}\frac{d\lambda}{\lambda^{k+1}}\varepsilon''(\lambda,\nu)=\frac{1}{\pi}\int_0^{\infty}\frac{d\lambda}{\lambda^{k+3}}\Gamma_n(\nu). \tag{14}$$

TABLE II.

No.	$f(x)$	ν_{cr}	ν_*	C	A	Notes
1	e^{-x}	0,73576	0,83996	1,289	0,1116	Yukawa potential
2	$x(e^x-1)^{-1}$	1,29522	1,52344	1,381	0,1371	Hulthén potential
3	$\exp(-x^2/2)$	1,21306	1,58650	1,682	0,2478	–
4	$(1+x)^{-2}$	0,5	0,52815	1,033	0,0574	Tietz potential
5	xe^{-x}	1,08268	1,34425	1,565	0,1997	–
6	$x\exp(-x^2)$	0,73576	1,08268	2,000	0,4167	Gaussian
7	$1+x^2$	–	0,38490	1,565	0,1997	Spherical model
8	–	–	0,45618	0,8660	0,2406	Stark effect

Note. Here A and C are the coefficients in Eqs. (12) and (5).

Here we regard λ as a continuous variable (which is natural for $n \gg 1$) and assume that the energy is analytic in λ, after which the dispersion relations are derived in a standard manner [see, e.g., Ref. 17 devoted to the asymptote of higher PT orders for an anharmonic $(gx^4/4)$ oscillator].

Equation (14) yields the relation between the asymptotes of the $1/n$-expansion coefficients and the widths of highly excited states:

$$\varepsilon^{(k)} \approx k!\, a^k k^{\sigma+1}(c_0+c_1/k+\ldots),\ k\to\infty,$$
$$\Gamma_n \approx \pi c_0 a^{-(\sigma+2)} n^\sigma \exp(-n/a),\ n\to\infty, \tag{15}$$

where

$$a^{-1}=2^{1/2}\int_{r_0}^{r_2}[U(r)-U(r_0)]^{1/2}dr=2Q(\nu), \tag{16}$$

$$Q(\nu)=\int_{y_0}^{y_2}[\varphi(y,\nu)]^{1/2}\,dy, \tag{16a}$$

and y_0 and y_2 are the turning points (see Fig. 3). This formula gives the parameter $a(\nu)$ for $\nu<\nu_*$ and can be analytically extended to the region $\nu>\nu_*$. Other asymptote parameters $(\sigma, c_0, \ldots)$ are easily found with the help of (14), if the pre-exponential factor in the formula for Γ_n is known. In the case of the Stark effect and spherical model (3) the function $Q(\nu)$ is calculated analytically (see Appendix B).

Consider now the values of ν close to ν_*. Taking it into account that as $y\to y_0$ we have $\varphi=\omega^2 y_0^{-4}(y-y_0)^2+\cdots$, where ω is the dimensionless oscillation frequency, we get

$$\varphi(y,\nu)\approx\frac{\omega^2}{y_0^4(y_2-y_0)}(y-y_0)^2(y_2-y),\quad y_0<y<y_2, \tag{17}$$

where

$$y_{0,1}=y_*[1\mp h(1-\nu/\nu_*)^{1/2}+\ldots],$$
$$y_2=y_*[1+2h(1-\nu/\nu_*)^{1/2}+\ldots], \tag{18}$$
$$h=[{}^3/_2(1+xf'''/3f'')_{x=x_*}]^{-1/2}$$

($x=\mu r=\nu y$). Substituting (17) into (16) and calculating the integral, we find

$$Q(\nu)={}^4/_{15}\omega(y_2/y_0-1)^2, \tag{19}$$

which, together with (18) and (5), yields the formula (12).

Thus, at the point of collision of classical solutions the parameter $a(\nu)$ has a power-law singularity whose exponent does not depend on the form of the potential $V(r)$. As numerical calculations show (see Appendix C), it retains the same value, $-5/4$, also for the two-dimensional (the variables $\xi=r+z$ and $\eta=r-z$ are parabolic coordinates) problem of the Stark effect in the hydrogen atom.

5. SUMMATION OF THE $1/n$ EXPANSION

We have found thus that in quantum mechanics the asymptotes of higher orders of the $1/n$ expansion are, as a rule, factorial.[5)] This explains why in some cases (e.g., the Stark effect[5,6]), in order to find the energy to an accuracy necessary for the experiment, we have to calculate several tens of coefficients $\varepsilon^{(k)}$ and sum the series (1). At present this procedure is developed well enough and does not present any fundamental difficulties.

In conclusion, let us consider the problem of summation of the $1/n$ expansion in the interval $\nu_{cr}<\nu<\nu_*$. That this problem is not trivial is seen from the fact that all the coefficients $\varepsilon^{(k)}(\nu)$ are real, whereas the sum of the series (1) is complex (since the level now belongs to continuum, having become a Breit–Wigner resonance). To sum the series (1), we have used the method of Padé–Hermite approximants (PHA) whose brief description is given in Refs. 6 and 8. We have restricted ourselves to quadratic PHA, $[L, M, N](\lambda)\equiv F(\lambda)$, where $\lambda=1/n$ is the expansion parameter, and $F(\lambda)$ is found from the equation

$$P_L-Q_M F+R_N F^2=0,$$

that is

$$F(\lambda)=\frac{1}{2R_N}[Q_M\pm(Q_M^2-4P_L R_N)^{1/2}], \tag{20}$$

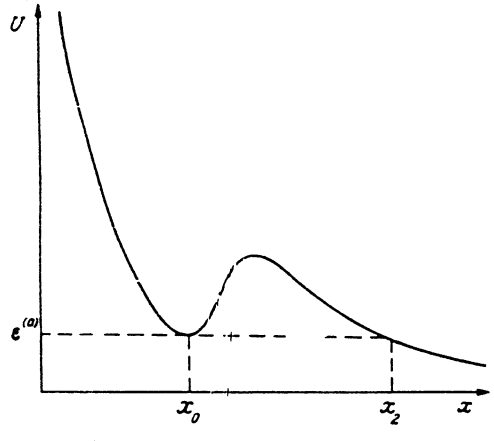

FIG. 3. The effective potential U (in the qualitative form).

where $P_L(\lambda)$, $Q_M(\lambda)$ and $R_N(\lambda)$ are polynomials of degree L, M, and N, respectively, and whose coefficients are found from the relation

$$P_L(\lambda)-Q_M(\lambda)\varepsilon+R_N(\lambda)\varepsilon^2=O(\lambda^{L+M+N+2}),\ \lambda\to 0, \quad (21)$$

while $\varepsilon(\lambda)$ is the formal power series (1). Substituting it into (21) we obtain a system of linear equations for the coefficients of the polynomials mentioned above. Using a computer, we can easily find the numerical solution of this system.

It is easy to understand that, since the coefficients $\varepsilon^{(k)}$ are real for all $k=0, 1, 2, \ldots$, the polynomials P_L, Q_M and R_N also have only real coefficients. As seen from (20), the PHA, unlike ordinary PA $[L/M](\lambda)$, can have an imaginary part, therefore the summation of the $1/n$ expansion by the PHA method is adequate for quasistationary states.

This method has been applied to two problems: to the Yukawa potential and Stark effect. In the first case we have compared the calculated values of E_r and Γ with those from Ref. 25, and in the second case with the results of summing PT series in powers of electric field $\mathscr{E}$.[6] The values of the quasistationary state energy found by independent methods agree well with each other.

Consider, as an illustration, the Stark effect in the hydrogen atom for the states $(0, 0, n-1)$. In Table I we have listed the $1/n$ expansion coefficients in the region of interest, $F<F_*=0.2081$, i.e., before the collision of classical equilibrium points (here $F=n^4\mathscr{E}$). It is seen that $\varepsilon^{(k)}$ has for $k\gtrsim 10$ a rapid growth which becomes especially noticeable as $F\to F_*$. The results of summing the series (1) for $n=3$, 10, and 20 are given in Table III, where the values of the Stark shift $\Delta\varepsilon_n$ and level width are also listed:

$$E^{(0,0,n-1)}=-\frac{1}{2n^2}(1+\Delta\varepsilon_n+i\varepsilon_n'') \quad (22)$$

(these values are denoted in Table III by $1/n$). As a rule, we have used diagonal PHA [i.e., $L=M=N$ in Eqs. (21)] and $N\sim 15$. Thus, we have taken into account 30–40 orders of the $1/n$ expansion, which ensures an energy-calculation accuracy of order 10^{-4}–10^{-5} (in Table III we have given only the established figures of the PHA sequence). The accuracy of the $1/n$ expansion drops at $F\approx F_*$, which is quite understandable in light of the results above. As seen from Table III, the values of E_r and Γ found upon summing the $1/n$ expansion agree fully with the results of independent calculations.[6] Similar results have been found also for other states.

For $\nu>\nu_*$ the coefficients of the $1/n$ expansion become complex and the calculation of the level width Γ is simplified. Instead of (20) it is sufficient to use, for example, partial sums of the series (1):

$$s_k=\sum_{j=0}^{k}\varepsilon^{(j)}n^{-j}. \quad (23)$$

In doing this, we can use fewer coefficients $\varepsilon^{(j)}$. In this manner we have found the values of $\Delta\varepsilon_n$ and ε_n'' from Table III belonging to the region $F>F_*$. Earlier the partial sums (23) were used in other quantum-mechanical problems.[3-5,7]

The accuracy of the $1/n$ expansion grows with the principal quantum number n, therefore this method is most suitable for Rydberg ($n\gg 1$) states.

6. THE $1/n$ EXPANSION AND THE PROBLEM OF TWO COULOMB CENTERS

The nonrelativistic problem of two Coulomb centers

$$V(\mathbf{r})=-\frac{Z_1}{r_1}-\frac{Z_2}{r_2},\quad r_{1,2}=\left[\rho^2+\left(z\pm\frac{R}{2}\right)^2\right]^{1/2}, \quad (24)$$

is encountered in various branches of physics;[29] the application of the $1/n$ expansion to this problem has been considered in Refs. 12, 30, and 31. In this case the coefficients $\varepsilon^{(k)}$ of the series (1) depend on the internuclear distance R. The first term $\varepsilon^{(0)}(R)$ corresponds to the energy of a particle moving along a classical orbit, and is determined by the condition of equilibrium of the forces acting upon an electron in its rest system. We restrict ourselves to the symmetric case

TABLE III. The Stark shift and width of the states $(0,0,n-1)$ in a strong electric field.

F	$\Delta\varepsilon_n$	ε_n''	Calculation method	F	$\Delta\varepsilon_n$	ε_n''	Calculation method
	$n=3$				$n=3$		
0,07	9,663(−3)	1,2(−7)	$1/n$	0,20	9,2(−2)	–	$1/n$
	9,6627(−3)	1,186(−7)	PT		9,157(−2)	3,469(−2)	PT
0,10	2,1020(−2)	1,231(−4)	$1/n$, PT	0,25	0,1244	7,283(−2)	$1/n$, PT
0,15	5,394(−2)	8,145(−3)	»	0,30	0,1519	0,1170	»
0,18	7,691(−2)	2,223(−2)	»	0,40	0,1941	0,2143	$1/n$
0,19	8,437(−2)	2,817(−2)	$1/n$		0,1942	0,2144	PT
	8,434(−2)	2,820(−2)	PT	0,50	0,2239	0,3169	$1/n$
					0,224	0,317	PT
	$n=10$				$n=20$		
0,10	1,2966(−2)	–	$1/n$, PT		1,15982(−2)	–	$1/n$, PT
0,15	3,1755(−2)	7,379(−5)	»		2,77719(−2)	1,1(−7)	»
0,18	5,0356(−2)	2,5162(−3)	»		4,32324(−2)	2,969(−4)	»
0,20	6,4866(−2)	7,877(−3)	$1/n$		5,7258(−2)	2,971(−3)	$1/n$
	6,4881(−2)	7,870(−3)	PT		5,7258(−2)	2,970(−3)	PT
0,25	9,9766(−2)	3,2154(−2)	$1/n$, PT		9,3186(−2)	2,3222(−2)	$1/n$, PT
0,30	0,12967	6,5272(−2)	»		0,12399	5,3783(−2)	»
0,40	0,17637	0,14340	»		0,17199	0,12775	»
0,50	0,21044	0,22859	»		0,20709	0,20923	»

Note. The quantities $\Delta\varepsilon_n$ and ε_n'' are defined in (22); atomic units are used.

$Z_1 = Z_2 = 1$, which corresponds to the molecular hydrogen ion H_2^+. For the states with $m = n-1$, $n \to \infty$ the equations can be written in a parametric form

$$\begin{aligned} \varepsilon^{(0)} &= -2(1-\tau)^2(1+\tau), \\ \varepsilon^{(1)} &= 2(1-\tau)^3[(1+3\tau)^{1/2}+(1-3\tau)^{1/2}-2], \\ \omega_{1,2} &= 4(1-\tau)^3(1\pm 3\tau)^{1/2}, \quad \widetilde{R} = \tau^{1/2}(1-\tau)^{-2}, \end{aligned} \tag{25}$$

where $0 < \tau < \frac{1}{3}$, $\varepsilon = n^2 E$, $\widetilde{R} = n^{-2} R$, and $E(R)$ is the term energy. These equations give the dependence of the $1/n$ expansion coefficients on R and easily follow from the formulas of Ref. 30. Here $\omega_{1,2}$ are the frequencies of normal electron modes about the equilibrium point in the effective potential $U(\rho,z)$, $\rho = (x^2+y^2)^{1/2}$, and the variable τ has a simple geometric meaning: $\tau = \cos^2\alpha$ where α is the angle at the vertex Z in the triangle (Z, Z, e).

Explicit expressions were obtained[30] for the first three orders of the $1/n$ expansion; subsequent coefficients are more conveniently found by recurrence relations. A relevant algorithm realized on a computer has made it possible to calculate effectively tens of coefficients $\varepsilon^{(k)}(R)$ in the problem of two Coulomb centers. Numerical analysis shows that they grow factorially as $k \to \infty$, and the asymptote parameter $a(R)$ increases drastically for $\widetilde{R} \to R_* \approx 1.3$ (see Fig. 8 in Ref. 30). We shall list below some of the analytic results.

With the help of calculations similar to described above (see Sec. 4), we find

$$\begin{aligned} a(R) &= -\tfrac{1}{2}(\operatorname{arth}\zeta - \zeta)^{-1}, \\ \zeta &= (1+\tfrac{1}{2}\widetilde{R}^2\varepsilon^{(0)})^{1/2} = (1-3\tau)^{1/2}(1-\tau)^{-1}. \end{aligned} \tag{26}$$

The frequency $\omega_2 \propto f^{1/2} \to 0$ as $\tau \to \frac{1}{3}$, and the corresponding classical orbit loses its stability. This happens for $\widetilde{R} = R_* = 3^{3/2}\cdot 2^{-2} = 1.299$. For $\widetilde{R} \to R_*$ we have

$$\begin{aligned} \tau &= \tfrac{1}{3} - \tfrac{2}{9}f - \tfrac{1}{9}f^2 + \ldots, \quad \zeta = (\tfrac{3}{2}f)^{1/2}(1 - \tfrac{1}{12}f + \ldots), \\ \varepsilon^{(0)} &= \varepsilon_*(1 + \tfrac{1}{2}f + \tfrac{1}{4}f^2 + \ldots), \\ \varepsilon^{(1)} &= \varepsilon_*(1 - 2^{-1/2} - (f/6)^{1/2} + \ldots), \end{aligned}$$

where $\varepsilon_* = -32/27$, $f = 1 - \widetilde{R}/R_*$, and as $R \to 0$:

$$\begin{aligned} \tau &= t - 4t^2 + \ldots, \quad \zeta = 1 - \tfrac{1}{2}t + \tfrac{3}{8}t^2 + \ldots, \\ \varepsilon^{(0)} &= 2(-1 + t - 3t^2 + 13t^3 + \ldots), \\ \varepsilon^{(1)} &= \tfrac{9}{2}(-t^2 + 11t^3 + \ldots), \quad t = \widetilde{R}^2 = R^2/n^4, \end{aligned}$$

whence

$$a(R) = \begin{cases} -\tfrac{1}{2}[\ln(n^2/R) - (1-\ln 2)]^{-1}, & R \to 0, \\ -(\tfrac{2}{3})^{1/2} f^{-1/2}(1 - \tfrac{13}{20}f + \ldots), & R \to n^2 R_*. \end{cases} \tag{27}$$

Thus, $a(R) < 0$ for $0 < R < n^2 R_*$. This agrees with numerical calculations[30] which show that in this range of R the series (1) is oscillating and can be summed by PA. The PA convergence becomes worse when R reaches $n^2 R_*$, since $a(R) \to \infty$ and the coefficients $\varepsilon^{(k)}(R)$ increase drastically.

A more detailed analysis shows[30] that three classical trajectories merge at $\widetilde{R} = R_*$. One of them, S_0, given by the equations above, is stable whereas the other two, S_1 and S_2, are complex. For $\widetilde{R} > R_*$ the orbit S_0 loses stability ($\omega_2^2 < 0$), and S_1 and S_2 become real and determine the $1/n$ expansion coefficients (for $R \gg 1$ each of them corresponds to electron localization near one of the nuclei Z_1 or Z_2). For $\varepsilon^{(0)}(R)$, $a(R)$, etc., we can find, in this case, formulas similar to (25) and (26). In particular,

$$a(R) = \frac{1}{4}|\zeta(1-\zeta^2)^{-1} - \operatorname{arth}\zeta|. \tag{28}$$

The variable ζ is related now to R by the equations

$$\zeta = \left(\frac{3\tau - 1}{3\tau - \tau^2}\right)^{1/2}, \quad \widetilde{R} = \frac{R}{n^2} = \frac{8\tau^{3/2}}{(1-\tau)(\tau+1)^2}, \tag{29}$$

where $\frac{1}{3} \leqslant \tau < 1$ (note that $\widetilde{R} = R_*$ for $\tau = \frac{1}{3}$ and $\tau \to 1$ corresponds to $R \to \infty$). The formulas (26) and (28) are derived on the basis of Eq. (16) with allowance for variable separation in elliptic coordinates $\xi = (r_1 + r_2)/R$ and $\eta = (r_1 - r_2)/R$ for the problem of two Coulomb centers.

It is seen from (28) that $a(R) > 0$ if $\widetilde{R} > R_*$. This agrees fully with the numerical calculation[30] of higher orders of the $1/n$ expansion, according to which the coefficients $\varepsilon^{(k)} < 0$ for $\widetilde{R} > R_*$, and the series (1) ceases to be alternating.

7. Let us list in conclusion the main results of the present paper. They are Eqs. (11) and (16) for the asymptotes of higher orders of the $1/n$ expansion, and also the character of the power singularity (12) near the collision point $\nu = \nu_*$ of classical solutions. These results are valid for an arbitrary potential $V(r)$ and agree with numerical calculations of the coefficients $\varepsilon^{(k)}$.

Problems without spherical symmetry, i.e., the Stark effect in hydrogen and the problem of two Coulomb centers, have also been considered. For a certain value of the parameter $F = n^4\mathscr{E} = F_*$ or $R = n^2 R_*$ a collision (coalescence) of the classical orbits, stable and unstable, occurs. In the first case two orbits merge, while in the second case three. Correspondingly, the exponents of the power-law singularity of the parameter a are different, either $-5/4$ or $-3/2$ [see Eqs. (12) and (27) and Appendix C]. Explicit analytic expressions for the asymptote parameter a have been obtained both for the V-funnel potential (3a) with $N = 1$ and 2 and for the problem of two Coulomb centers.

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APPENDIX A

For the Yukawa and Hulthén potentials the asymptote of higher orders of the $1/n$ expansion has a more complicated form than (2):

$$\begin{aligned} \varepsilon^{(k)}(\nu) &\approx k!\{a^k k^\beta c_0[1 + O(1/k)] \\ &+ \operatorname{Re}(A^k k^{\beta_1} C)[1 + O(1/k)]\} = k!\{a^k k^\beta c_0 \\ &+ a_1^k k^{\beta_1} c_1 \cos(k\theta + \varphi) + \ldots\}, \quad k \to \infty, \end{aligned} \tag{A1}$$

where $a(\nu) > 0$ for $\nu_{cr} < \nu < \nu_*$, and the parameters A and C are complex: $A = a_1 \exp(i\theta)$ and $C = c_1 \exp(i\varphi)$.

Numerical calculation of these parameters with the help of known coefficients $\varepsilon^{(k)}$ can be performed using the Borel transformation

$$B(z) = \sum_{k=0}^{\infty}{}' \frac{\varepsilon^{(k)}}{k!} z^k. \tag{A2}$$

The Borel transformant $B(z)$ has at $z = z_0 = a^{-1}$ the near-

est-to-zero singularity whose character is determined by the parameter β in (A1):

$$B(z) \propto (z-z_0)^{-(\beta+1)} \tag{A3}$$

[the second term of the asymptote (A1) corresponds to complex conjugate singularities of the Borel transformant at the points $z = 1/A$ and $1/A^*$]. To find the parameters α and β, we have used integral approximants[32] found from the equation [cf. (20)]

$$P_L(z)+Q_L(z)f(z)+R_L(z)\frac{df}{dz}=0, \tag{A4}$$

whence

$$f(z)=\exp\left(-\int_0^z \frac{Q_L(t)}{R_L(t)}\,dt\right) \times\left\{f(0)-\int_0^z dt\,\frac{P_L(t)}{R_L(t)}\exp\left(\int_0^t \frac{Q_L(t')}{R_L(t')}\,dt'\right)\right\}, \tag{A5}$$

where P_L, Q_L, and R_L are polynomials of degree L. It follows from (A5) that if $Q_L(z)/R_L(z) = \rho(z-z_0)^{-1}+\ldots$ at $z\to z_0$, the function $f(z)$ has a power-law singularity: $f(z) \propto (z^0 - z_0)^{-\rho}$. Accordingly, $z_0 = 1/a$ is defined as the smallest, in absolute value, zero of the polynomial $R_L(z)$ with the exponent $\beta = \rho - 1$, where $\rho = \operatorname{Res} Q_L(z)/R_L(z)|_{z=z_0}$. Using this method for the Yukawa potential, we have found that $\beta = -1.50 \pm 0.01$ (for $\nu > \nu_{cr}$), which agrees with Eq. (11).

Owing to the second term of the asymptote (A1), the coefficients $\varepsilon^{(k)}$ may start to oscillate with increase of k, i.e., the series (1) is not constant-sign.[6)] For $\nu > \nu_{cr}$ the first term begins to dominate in (A1), and the coefficients $\varepsilon^{(k)}(\nu)$ with $k \gg 1$ become positive. A function with such coefficients has a finite imaginary part, as is readily seen by considering the simplest example (the Euler series[33])

$$F(z)=\sum_{k=0}^{\infty} k!\quad z^k=-z^{-1}e^{-1/z}\Gamma(0,-1/z), \tag{A6}$$

$$\operatorname{Im} F(x)=\pi x^{-1}e^{-1/x},\quad 0<x<\infty, \tag{A7}$$

where $\Gamma(0,t)$ is the incomplete gamma function.

As shown in Sec. 5, summing the $1/n$ expansion allows us to restore the imaginary part Γ of the level energy, beginning already with $\nu = \nu_{cr}$, though in the interval $\nu_{cr} < \nu < \nu_*$ all coefficients of the expansion (1) are real. On the other hand, for $\nu > \nu_*$ the coefficients $\varepsilon^{(k)}(\nu)$ become complex. In this case, to find the width Γ, it is sufficient to use the simplest method of summation, e.g., partial sums of the $1/n$ expansion (23).

APPENDIX B

Consider the potential (3a) for $g < 0$, when it contains a barrier ($N > 0$). In this case $\mu = (-g)^{1/(N+1)}$, $f(x) = 1 + N^{-1}x^{N+1}$,

$$\nu = x_0 - x_0^{N+2}, \tag{B1}$$

$$\varepsilon^{(0)} = -(1-\xi)\left(1+\frac{N+2}{N}\xi\right),\quad \omega=\left[\frac{1-(N+2)\xi}{1-\xi}\right]^{-1/2}, \tag{B2}$$

where $\xi = x_0^{N+1}$. Hence

$$x_*=(N+2)^{-1/(N+1)},\quad \nu_*=(N+1)(N+2)^{-(N+2)/(N+1)},$$
$$C=[2(N+2)]^{1/4},\quad A=5/3\cdot 2^{-17/4}(N+2)^{1/4}. \tag{B3}$$

The energy $\varepsilon^{(0)}(\nu)$ decreases monotonically with $\nu = n^2\mu$ and at the collision point $\nu = \nu_*$ reaches the value $\varepsilon_* = -[1 + (N^2 + 2N)^{-1}]$. Equation (B2) yields

$$\varepsilon^{(0)}=\varepsilon_*\left(1-\frac{2}{N+2}\omega^2\right)\left(1-\frac{\omega^2}{N+2}\right)^{-2}. \tag{B4}$$

The case $N = 1$ corresponds to the "spherical model" for the Stark effect in hydrogen. Note that the constants C and A in this case have the same values as in the case of the exponential potential (but different values of ν_*, see Table II).

The function φ in (16) is given by

$$\varphi(y,\nu)=y^{-2}-2y^{-1}-2N^{-1}\nu^{N+1}y^N-\varepsilon^{(0)}(\nu). \tag{B5}$$

Since the classical energy $\varepsilon^{(0)}$ corresponds to the minimum of effective potential, $\varphi(y,\nu)$ has a multiple root $y = y_0$ ($y_0 < y < y_2$ is the below-barrier region, in which $\varphi > 0$, see Fig. 3). The integral in (16), which is, generally speaking, elliptic for $N = 1$ and 2, can therefore be expressed through elementary functions. Omitting the details of the calculations, we can write the final formulas. For $N = 1$ (spherical model) we have

$$a^{-1}=4\left[z+\frac{z^3}{3(1-z^2)}-\operatorname{arth} z\right] =\begin{cases} {}^8/_{15}z^5(1+{}^{10}/_7z^2+\ldots), & z\to 0,\\ \dfrac{2}{3(1-z)}+2\ln(1-z)+\left(\dfrac{7}{3}-2\ln 2\right)+\ldots, & z\to 1,\end{cases} \tag{B6}$$

where $z = [(1-3x_0^2)/(1-x_0^2)]^{1/2} \equiv \omega$. To derive this expression, we have used the relation

$$\varepsilon^{(0)}=-{}^4/_3(1-{}^2/_3z^2)(1-{}^1/_3z^2)^{-2}$$

[see (B4) for $N = 1$]. The ν-dependence of z can be found directly from the equation

$$(1-z^2)(1-{}^1/_3z^2)^{-3}=(\nu/\nu_*)^2, \tag{B7}$$

which yields

$$z(\nu)=\begin{cases} 1-\nu^2-{}^7/_2\nu^4+\ldots, & \nu\to 0,\\ [6(1-\nu/\nu_*)]^{1/4}, & \nu\to\nu_*=2\cdot 3^{-3/4}.\end{cases}$$

Hence

$$a={}^3/_2\nu^2[1-3\nu^2\ln(\nu^2/2)+O(\nu^4\ln\nu)],\quad \nu\to 0, \tag{B8}$$

and as $\nu\to\nu_*$ we arrive at the formula (12) with the coefficient $A = 5\cdot 3^{-1/4}\cdot 2^{-17/4} = 0.19967$. For $N = 2$ we get

$$a^{-1}=2\left[3^{1/2}(1-{}^1/_2z^2)(1-z^2)^{-1/2}\operatorname{arctg}\frac{3^{1/2}z}{2(1-z^2)^{1/2}}-\operatorname{arth}\frac{3z}{z^2+2}\right], \tag{B9}$$

where $z = [(1-4x_0^3)/(1-x_0^3)]^{1/2}$ and $x_0(\nu)$ is found from (B1). Note that the variable z again coincides with the frequency ω of classical oscillations. Furthermore,

$$a(\nu)=\frac{2}{\pi}\left(\nu^{1/2}-\frac{6}{\pi}\nu^3\ln\nu+\ldots\right),\quad \nu\to 0 \tag{B10}$$

and $|a(\infty)| = \frac{1}{2}\pi$; for $\nu \to \nu_* = 0.4725$ the formula (12) with $A = 0.2476$ is valid. The formulas for the V-funnel potential are obtained from the foregoing by the change $g \to -g$. We have

$$\nu = x_0 + x_0^3, \quad \omega = [(1+3x_0^2)/(1+x_0^2)]^{1/2}. \tag{B11}$$

Therefore $z > 1$ and $\tanh^{-1} z = \tanh^{-1}(1/z) \pm i\pi/2$, due to which the parameter a becomes complex (as mentioned above, this corresponds to oscillations of the $1/n$-expansion coefficients). In particular, as $g \to \infty$ we have $z \to 3^{1/2}$ and

$$a = {}^1/_2[3^{1/2} - \ln(2+3^{1/2}) \pm i\pi]^{-1}, \tag{B12}$$

$|a(\infty)| = 0.1578$.

For the spherical model we find the same limiting value $a(\infty)$, as is easily verified with the help of (B6).

APPENDIX C

To verify numerically the expression (12), we consider the Stark effect. The asymptote parameter a can be represented in the form

$$a(F) = (F_* - F)^{-\beta}[b_0 + b_1(F_* - F)^{\beta'} + \ldots] \tag{C1}$$

$(\beta, \beta' > 0)$. It is convenient to introduce the variables ξ and τ:

$$\xi = -\frac{\ln|a(F)|}{\ln|F - F_*|}, \quad \tau = -\frac{1}{\ln|F - F_*|}, \tag{C2}$$

we have then as $F \to F_*$

$$\xi(\tau) = \beta + (\ln|b_0|)\tau + O(\tau \exp(-\beta'/\tau)). \tag{C3}$$

Therefore the exponent β is determined by extrapolating $\xi(\tau)$ to the point $\tau = 0$. The behavior of $\xi(\tau)$ is shown in Fig. 4 up to $\tau = 0.2$ (or $|F - F_*| \approx 0.01$). It is seen that it agrees with the value $\beta = 1.25$ which follows from (12). Thus, we have shown that the $a(F)$ singularity in the case of the Stark effect is the same as in the case of spherically symmetric potentials.

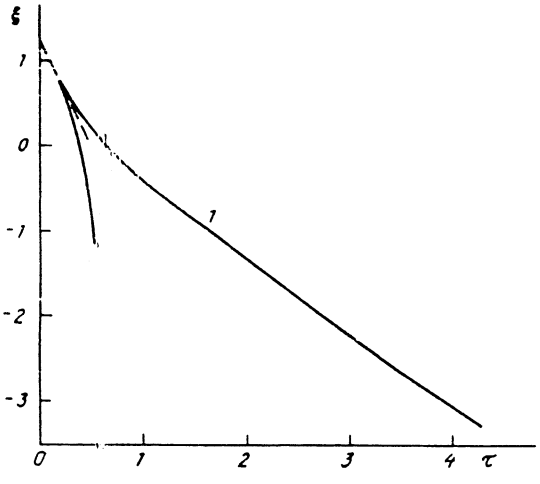

FIG. 4. Numerical calculation of the singularity exponent β in the case of the Stark effect: $1 - F < F_*$; $2 - F > F_*$; the dashed line is the extrapolation to $\tau = 0$.

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[1)] Only the first digits of the $1/n$ expansion coefficients are given, which is enough to draw a conclusion about their behavior with increasing k. The calculation of $\varepsilon^{(k)}$ has been performed with a "fourfold" accuracy, as needed for the summation of the series (1) (see Sec. 5).

[2)] In Ref. 26 this formula has been derived using expansion of the reduced energy ε in powers of ν. Recurrence relations have been found[24] for the coefficients of this expansion, which can be explicitly solved for $\nu \to 0$. Note that (8) corresponds to knotless $(n = l + 1)$ states.

[3)] The variable ξ, unlike r and x, remains of order unity as $n \to \infty$.

[4)] Here we assume that the potential has the form (4). This form is suitable for any spherically symmetric potential if no restrictions are imposed on the screening function $f(x)$ at zero and at infinity.

[5)] Owing to this, the series (1) diverge, and to calculate the energy ε with high accuracy it is necessary to use the methods of summation of divergent series, such as the method of the Padé approximants (PA), etc. It is important that in many cases (e.g., for the V funnel potential[4,12]) the first two or three terms of the $1/n$ expansion give the energy and wave functions to an accuracy acceptable in physics.

[6)] Thus, for $\nu \approx 0.532 < \nu_{cr}$ (the Yukawa potential) we have $\theta = \pi/2$ and $|a| \ll a_1$, therefore the period of sign alternation in the sequence $\varepsilon^{(k)}$ equals two (which is confirmed by numerical calculations).

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