Stark effect and perturbation approximations in hydrogenlike atoms

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Two different perturbation series, the weak- and strong-field expansions, for approximating any resonances of the Stark effect in the hydrogen atom, are given. Together they cover the entire regime of field values up to the points when the resonances disappear.

I. INTRODUCTION

While most quantum-mechanics textbooks present the Stark effect in the hydrogen atom as an important application of the time-independent perturbation method,[1] it was pointed out long ago by Titchmarsh[2] that a hydrogen atom in the presence of an electric field, no matter how small, has no discrete energy eigenvalues, but that its spectrum extends continuously over $(-\infty, \infty)$. Nevertheless Titchmarsh pointed out that a meaning can be assigned to the perturbation expansion

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{1.1}$$

in such cases; one way in which this can be done is to consider the right-hand side as an approximation not to a perturbed eigenvalue but to a pole of the perturbed Green's function. If the perturbed spectrum is continuous, the perturbed Green's function has no poles on or above the real axis. But Titchmarsh showed that it has poles just below the real axis and that there is a pole E_n' in the neighborhood of $E_n^{(0)}$ such that

$$E_n' = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots . \tag{1.2}$$

Even though E_n' is not real, its imaginary part (which is negative) is an exponentially small function of λ as $\lambda \to 0$. The spectrum of the perturbed equation is highly concentrated in the neighborhood of the real numbers E_n given approximately by Eq. (1.1). The sense in which this is true may be understood if we consider the probability that the particle is in a state for which E is in the interval (α, β). This probability tends to zero as $\lambda \to 0$ if the interval (α, β) does not contain any of the numbers

$$E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots .$$

The poles of the perturbed Green's function in such cases are referred to as resonances. The Borel summability of the usual perturbation series for the resonances of the Stark effect in the hydrogen atom was shown by Graffi and Grecchi[3] and by Herbst and Simon,[4] and the convergence of the diagonal Padé approximants sequence was shown by Graffi, Grecchi, Levoni, and Maioli.[5]

Thus, although many quantum-mechanics texts probably gave a wrong interpretation of formula (1.1), the expansion on the right-hand side of (1.1) is meaningful when it is correctly interpreted and "suitably" summed.

In this paper we derive two different perturbation expansions for representing the resonances of the Stark effect in the hydrogen atom depending on the strength of the applied electric field *and* the quantum numbers. The results which we present are analogous to those of the anharmonic oscillator problem with the Hamiltonian given by

$$H = \tfrac{1}{2}(-d^2/dx^2 + x^2) + \lambda x^4 , \tag{1.3}$$

for which the nth energy level E_n has been shown[6-8] to be well approximated by one of the two following expansions:

$$E_n = n + \tfrac{1}{2} + \tfrac{3}{4}\lambda[1 + 2n(n+1)] - \lambda^2\left(\frac{(n+1)(n+\frac{3}{2})^2(n+2)}{2+3\lambda(2n+3)} - \frac{n(n-\frac{1}{2})^2(n-1)}{2+3\lambda(2n-1)} + \frac{(n+1)(n+2)(n+3)(n+4)}{16[4+6\lambda(2n+5)]} - \frac{n(n-1)(n-2)(n-3)}{16[4+6\lambda(2n-3)]}\right) + \cdots , \tag{1.4}$$

$$E_n = \lambda^{1/3}\left(\epsilon_n + \alpha_n \lambda^{-2/3} + \beta_n \lambda^{-4/3} + \cdots\right), \tag{1.5}$$

depending on whether the quantity

$$\Lambda_n \equiv \lambda(n + \tfrac{1}{2}) \tag{1.6}$$

is respectively smaller or greater than a particular constant c (which is of the order of $\frac{1}{16}$). Note that, no matter how small λ is, there will always be a quantum number above which the second expansion (1.5) is more appropriate. This is not to say that the right-hand side of (1.4), which is a Padé-approximant-type sequence, would not converge in theory if Λ_n were greater than c. It is just that the convergence would probably be so slow in that case that its use would become impractical. On the other hand, the use of (1.5) for the case $\Lambda_n > c$ showed rapid convergence. For any given resonance of the Stark effect we also determine the value of the electric field above which the resonance disappears.

Indeed, that the Stark problem can be reduced to an analogous quartic-anharmonic-oscillator problem if one uses the parabolic coordinates was known to Sommerfeld[9] in 1929. In this formulation the Stark problem reduces to a problem of two different quartic anharmonic oscillators with centrifugal terms the eigenvalues of which, when equated, yield the resonances of the Stark effect. We use Titchmarsh's version of the WKB formula[10] (which is *more* than a zeroth-order WKB) and its corresponding expansions given in an earlier paper[11] to obtain the energy eigenvalues of the quartic anharmonic oscillators with centrifugal terms. The Titchmarsh's formula we used has been extensively tested in earlier papers[8,12] and shown to be remarkably accurate. More important, our work showed that the formula gives the correct behavior of, for example, the dependence of the energy eigenvalues on λ and n in (1.4) and (1.5), even when it does not give the coefficients of the expansions exactly. The remarkable fact is that even for the ground state the error involved is already very small.

With Titchmarsh's formula expanded appropriately, equating the eigenvalues of the two quartic anharmonic oscillators gives the resonances μ ($\equiv 2mE/\hbar^2$) of the Stark effect implicitly in the two formulas (3.20) and (4.19), which we present in Secs. III and IV, depending on the values of the external electric field b *and* the quantum numbers n,p,m. The use of a beautiful inversion formula developed by Lagrange[13] then yields two explicit formulas for μ, Eqs. (3.29) and (4.26). The former is closely related to the usual perturbation expansion; the latter is new. For convenience, we call these two expansions the weak- and strong-field expansions, respectively, even though the names are strictly incorrect (or even misleading) for the same reason stated following Eq. (1.6), namely, that no matter how small the external field b is, there will always be resonances above certain values of quantum numbers for which the second "strong"-field expansion should be used.

The use of the WKB method for the Stark problem was first employed by Wentzel,[14] one of the originators of the method. He used what is now called the higher-order WKB approximations[15-18] to obtain the usual perturbation expansion up to second order in the electric field strength. He did not derive the strong-field expansion. Landau and Lifshitz[1] mentioned the use of the zero-order WKB method for the Stark problem but did not pursue it, since they saw it as expressing E implicitly in terms of elliptic integrals and solving it numerically, a solution which did not appear to be illuminating to them. Our use of Titchmarsh's WKB formula involves the elliptic integrals only formally, because we were able to expand them in simple power series, to obtain the general terms, and to invert them. The final formulas which we give, Eqs. (3.20), (3.29), (4.19), and (4.26), are simple and explicit, which together with the tabulated values of the coefficients given in Tables I and III can be used to approximate any resonance of the Stark effect in the hydrogen atom to very high degrees of accuracy (within, of course, the Titchmarsh WKB approximation).

The behavior of some selected resonances as functions of the external electric field are presented in Fig. 2. The necessity of using our weak and strong-field expansions as well as the determination of the values of the field above which the resonances disappear is explained in the following sections.

II. STARK EFFECT IN THE HYDROGEN ATOM

In this section we follow Titchmarsh's presentation[2] in reducing the Stark problem in the hydrogen atom to the problem of two quartic anharmonic oscillators.

The Schrödinger equation for the hydrogen atom in an electric field directed along the z axis is

$$\nabla^2\psi + (2M/\hbar^2)(E + e^2/r - e\mathcal{E}z)\psi = 0\,, \qquad (2.1)$$

where E denotes total energy, $\mathcal{E}$ electric field strength, and e, M, and $\hbar$ have their usual meanings. If we set

$$\mu \equiv 2ME/\hbar^2, \quad a \equiv 2Me^2/\hbar^2, \quad b \equiv Me\mathcal{E}/\hbar^2\,, \qquad (2.2)$$

Eq. (2.1) can be written more simply as

$$\nabla^2\psi + (\mu + a/r - 2bz)\psi = 0\,. \qquad (2.3)$$

If we use the cylindrical coordinates (ρ, z, ϕ), we let

$$x = \rho\cos\varphi, \quad y = \rho\sin\varphi, \quad z = z\,, \qquad (2.4)$$

and if we use the polar spherical coordinates (r, θ, ϕ), we further substitute

$$\rho = r\sin\theta, \quad z = r\cos\theta\,. \qquad (2.5)$$

The parabolic coordinates which we use are related to the cylindrical coordinates by

$$\rho = uv, \quad z = \tfrac{1}{2}(u^2 - v^2)\,, \qquad (2.6)$$

where u and v vary over $(0,\infty)$. On substituting

$$\psi = \rho^{-1/2}\sigma\begin{cases}\cos m\varphi\\ \sin m\varphi\end{cases} \qquad (2.7)$$

into Eq. (2.3), we obtain the following equation for σ in the parabolic coordinates:

$$\frac{\partial^2\sigma}{\partial u^2}+\frac{\partial^2\sigma}{\partial v^2}+[\mu(u^2+v^2)+2a-b(u^4-v^4)-(m^2-\tfrac{1}{4})(1/u^2+1/v^2)]\sigma=0\,, \tag{2.8}$$

which is separable with

$$\sigma=\chi(u)\omega(v)\,, \tag{2.9}$$

where

$$-\frac{d^2\chi}{du^2}+[-\mu u^2+bu^4+(m^2-\tfrac{1}{4})u^{-2}]\chi=\kappa\chi \tag{2.10}$$

and

$$-\frac{d^2\omega}{dv^2}+[-\mu v^2-bv^4+(m^2-\tfrac{1}{4})v^{-2}]\omega=(\kappa'+2a)\omega \tag{2.11}$$

and

$$\kappa=-\kappa'\,. \tag{2.12}$$

The new eigenvalue parameters κ and κ', or more precisely κ_{nm} and κ'_{pm}, with their corresponding eigenfunctions $\chi_{nm}(u)$ and $\omega_{pm}(v)$, are those corresponding to the quantum anharmonic oscillators in the potentials

$$U(u)=-\mu u^2+bu^4+(m^2-\tfrac{1}{4})u^{-2} \tag{2.13}$$

and

$$V(v)=-\mu v^2-bv^4+(m^2-\tfrac{1}{4})v^{-2}\,, \tag{2.14}$$

respectively. These potentials are sketched in Fig. 1 (remembering that μ is negative) for the case $b>0$ and $m\geq 1$. For $m=0$, the values of U and V tend to $-\infty$ as $u\to 0$ and $v\to 0$. The equation for determining the resonances μ_{npm} corresponding to the quantum numbers n,p,m of the Stark effect is given by

$$\kappa_{nm}=-\kappa'_{pm}\,. \tag{2.15}$$

It is easy to see that when $b=0$, Eq. (2.15) gives the energy levels of the hydrogen atom

$$\mu_{npm}=-\tfrac{1}{4}a^2(n+p+m+1)^{-2} \tag{2.16}$$

for $n,p,m=0,1,2,\ldots$. The number $n+p+m+1$ is the total quantum number. To treat the case $b>0$, we begin by using Titchmarsh's WKB formula,[10] which gives κ_{nm} and κ'_{pm} implicitly as follows[19]:

$$\pi^{-1}\int_0^{u_0}(\kappa_{nm}+\mu u^2-bu^4)^{1/2}du=n+\tfrac{1}{2}m+\tfrac{1}{2} \tag{2.17}$$

and

$$\pi^{-1}\int_0^{v_0}(\kappa'_{pm}+2a+\mu v^2+bv^4)^{1/2}dv=p+\tfrac{1}{2}m+\tfrac{1}{2}\,, \tag{2.18}$$

where u_0 and v_0 are the smallest positive roots of

$$\kappa_{nm}+\mu u^2-bu^4=0 \tag{2.19}$$

and

$$\kappa'_{pm}+2a+\mu v^2+bv^4=0\,, \tag{2.20}$$

respectively. The left-hand sides of Eqs. (2.17) and (2.18) can be expressed in terms of the elliptic integrals of the first and second kinds, and we obtain

$$(6\pi b)^{-1}\{[(\mu^2+4b\kappa_{nm})^{3/4}-\mu(\mu^2+4b\kappa_{nm})^{1/4}]\,K(k_1)+2\mu(\mu^2+4b\kappa_{nm})^{1/4}E(k_1)\}=n+\tfrac{1}{2}m+\tfrac{1}{2}\,, \tag{2.21}$$

where

$$k_1^2=\tfrac{1}{2}[1+\mu(\mu^2+4b\kappa_{nm})^{-1/2}]\,, \tag{2.22}$$

and

$$-(\sqrt{2}/6\pi b)\{-\mu+[\mu^2-4b(\kappa'_{pm}+2a)]^{1/2}\}^{1/2}\times\{[\mu^2-4b(\kappa'_{pm}+2a)]^{1/2}K(k_2)+\mu E(k_2)\}=p+\tfrac{1}{2}m+\tfrac{1}{2}\,, \tag{2.23}$$

where

$$k_2^2=\frac{-\mu-[\mu^2-4b(\kappa'_{pm}+2a)]^{1/2}}{-\mu+[\mu^2-4b(\kappa'_{pm}+2a)]^{1/2}}\,. \tag{2.24}$$

Equations (2.21) and (2.23), though in closed forms, are not useful as they stand, because we need κ_{nm} and κ'_{pm} in explicit form to use Eq. (2.15) to determine μ. The inversion, namely, the expression of κ_{nm} and κ'_{pm} explicitly in terms of μ,

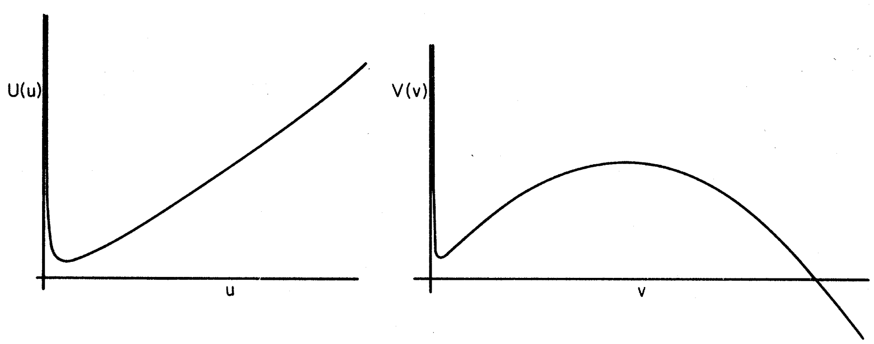

FIG. 1. Potentials $U(u)$ and $V(v)$ for $b>0$ and $m\geq 1$.

b, n, p, and m can be carried out in an elegant manner with the aid of a beautiful formula developed by Lagrange,[13] as we explain below.

III. WEAK-FIELD EXPANSION

Consider Eq. (2.21) and let us write

$$\zeta \equiv 4b\kappa_{nm}(-\mu)^{-2}\,. \tag{3.1}$$

Then Eq. (2.21) can be writen as

$$(8/3\pi)\{[(1+\zeta)^{3/4}+(1+\zeta)^{1/4}]K(k_1) - 2(1+\zeta)^{1/4}E(k_1)\} = 8b(2n+m+1)(-\mu)^{-3/2}\,, \tag{3.2}$$

where

$$k_1^2 = \tfrac{1}{2}[1-(1+\zeta)^{-1/2}]\,. \tag{3.3}$$

If we now write

$$\tau_{nm} \equiv 8b(2n+m+1)(-\mu)^{-3/2} \tag{3.4}$$

and

$$\phi_1(\zeta) \equiv \tfrac{3}{8}\pi\zeta\{[(1+\zeta)^{3/4}+(1+\zeta)^{1/4}]K(k_1) - 2(1+\zeta)^{1/4}E(k_1)\}^{-1}\,, \tag{3.5}$$

then Eq. (2.21) can be writen as

$$\zeta = \tau_{nm}\phi_1(\zeta) \tag{3.6}$$

and Lagrange's formula[13] can be immediately applied to give

$$\zeta = \sum_{j=1}^{\infty} \frac{\tau_{nm}^j}{j!}\left(\frac{d}{d\zeta}\right)^{j-1}\phi_1(\zeta)^j\bigg|_{\zeta=0}\,, \tag{3.7}$$

or, using the definitions of ζ and τ_{nm} in Eqs. (3.1) and (3.4), we have

$$\kappa_{nm} = 2(2n+m+1)(-\mu)^{1/2}\left(1+\sum_{j=1}^{\infty} A_j\tau_{nm}^j\right), \tag{3.8}$$

where

$$A_j = \frac{1}{(j+1)!}\left(\frac{d}{d\zeta}\right)^j \phi_1(\zeta)^{j+1}\bigg|_{\zeta=0}\,. \tag{3.9}$$

The series expansion in powers of ζ of the function $\phi_1(\zeta)$ when $\zeta<1$ has been given previously in Ref. 11:

$$\phi_1(\zeta) = \left(1+\sum_{j=1}^{\infty} a_j\zeta^j\right)^{-1}\,, \tag{3.10}$$

where

$$a_j = \frac{(-1)^j\Gamma(2j+\frac{1}{2})}{2^{2j}\pi^{1/2}j!\,\Gamma(j+2)} = \frac{(-1)^j(4j-1)!!}{2^{4j}j!\,(j+1)!}\,. \tag{3.11}$$

Writing

$$\phi_1(\zeta) \equiv 1+\sum_{j=1}^{\infty} f_j^{(1)}\zeta^j\,, \tag{3.12}$$

we have computed the values of A_j using Eqs. (3.9)–(3.12) for $j=1$–30, and they are tabulated in Table I. In Eq. (3.12), $f_j^{(1)}$ can be expressed explicitly in terms of the a_j by the formula

$$f_0^{(1)} = 1/a_0\,, \tag{3.12$'$}$$

where $a_0=1$ in this case and

$$f_n^{(1)} = \frac{(-1)^n}{n!\,a_0^{n+1}}\begin{vmatrix} 2a_1 & a_0 & 0 & & & \\ 4a_2 & 3a_1 & 2a_0 & \cdot & & \\ 6a_3 & 5a_2 & 4a_1 & \cdot & \cdot\ \ 0 & \\ & \vdots & & \cdot & \cdot\ \ \cdot & \\ (2n-4)a_{n-2} & (2n-5)a_{n-3} & (2n-6)a_{n-4} & \cdot & (n-2)a_0 & 0 \\ (2n-2)a_{n-1} & (2n-3)a_{n-2} & (2n-4)a_{n-3} & & \cdot & (n-1)a_0 \\ na_n & (n-1)a_{n-1} & (n-2)a_{n-2} & \cdot & \cdot\ \ \cdot & a_1 \end{vmatrix}\,. \tag{3.12$''$}$$

The actual computations of $f_j^{(1)}$ and A_j were carried out, however, by recursions.

It follows from Lagrange's theorem that the series on the right-hand side of Eq. (3.8) converges if

$$\tau_{nm} < \phi_1(1)^{-1} = 0.928 \equiv R_1\,, \tag{3.13}$$

where the value of $\phi_1(1)$ was obtained by making use of the closed-form expression for $\phi_1(\zeta)$ in Eq. (3.5).

The corresponding explicit expansions for κ'_{pm} can be obtained similarly from Eq. (2.23). However, this is not necessary, as we note from Eqs. (2.17) and (2.18) that all we need do is to change κ_{nm} to $\kappa'_{pm}+2a$, n to p, and b to $-b$. Thus we deduce immediately that, if we define

$$\tau'_{pm} \equiv 8b(2p+m+1)(-\mu)^{-3/2}\,, \tag{3.14}$$

then we have, from Eq. (3.8),

TABLE I. Values of A_j and c_j for $j=1$–30.

j	A_j	c_j
1	0.937 500 000 0$E-01$	0.281 250 000 0$E+00$
2	−0.166 015 625 0$E-01$	0.556 640 625 0$E-01$
3	0.572 204 589 8$E-02$	0.111 236 572 3$E-01$
4	−0.254 845 619 2$E-02$	0.192 761 421 2$E-02$
5	0.130 458 176 1$E-02$	0.381 074 845 8$E-03$
6	−0.729 318 475 4$E-03$	0.563 671 346 7$E-04$
7	0.433 330 527 8$E-03$	0.135 944 155 8$E-04$
8	−0.269 238 312 4$E-03$	0.102 940 414 6$E-05$
9	0.173 109 630 5$E-03$	0.665 455 390 8$E-06$
10	−0.114 356 222 3$E-03$	−0.707 605 628 0$E-07$
11	0.772 195 708 5$E-04$	0.594 455 195 5$E-07$
12	−0.530 978 968 9$E-04$	−0.181 136 272 8$E-07$
13	0.370 728 957 0$E-04$	0.824 098 388 8$E-08$
14	−0.262 234 019 4$E-04$	−0.320 298 370 0$E-08$
15	0.187 585 770 2$E-04$	0.134 923 910 8$E-08$
16	−0.135 507 500 0$E-04$	−0.557 632 421 4$E-09$
17	0.987 340 150 2$E-05$	0.235 162 240 3$E-09$
18	−0.724 911 764 2$E-05$	−0.994 638 220 2$E-10$
19	0.535 872 955 9$E-05$	0.424 349 448 2$E-10$
20	−0.398 561 105 8$E-05$	−0.182 024 173 9$E-10$
21	0.298 075 576 0$E-05$	0.785 346 960 9$E-11$
22	−0.224 044 412 8$E-05$	−0.340 523 551 2$E-11$
23	0.169 170 809 6$E-05$	0.148 328 205 3$E-11$
24	−0.128 272 082 0$E-05$	−0.648 915 439 6$E-12$
25	0.976 352 394 3$E-06$	0.284 892 399 3$E-12$
26	−0.745 793 191 0$E-06$	−0.125 652 951 6$E-12$
27	0.571 546 976 3$E-06$	0.554 231 419 4$E-13$
28	−0.439 343 344 1$E-06$	−0.248 068 532 7$E-13$
29	0.338 674 493 3$E-06$	0.106 772 243 1$E-13$
30	−0.261 760 622 6$E-06$	−0.527 235 531 9$E-14$

$$\kappa'_{pm}+2a=2(2p+m+1)(-\mu)^{1/2}\left(1+\sum_{j=1}^{\infty}(-1)^j A_j\tau'^{j}_{pm}\right), \tag{3.15}$$

where the A_j are defined as before by Eq. (3.9). The series on the right-hand side of Eq. (3.15) converges if

$$\tau'_{pm}<\phi_2(1)^{-1}=1.200\equiv R_2\,, \tag{3.15$'$}$$

which follows from the fact that

$$\phi_2(\zeta)=(3\pi\zeta/8\sqrt{2})[1+(1-\zeta)^{1/2}]^{-1/2}\times[-(1-\zeta)^{1/2}K(k_2)+E(k_2)]^{-1}\,, \tag{3.16}$$

where

$$k_2^2=[1-(1-\zeta)^{1/2}]/[1+(1-\zeta)^{1/2}]\,, \tag{3.17}$$

as one can readily deduce from Eqs. (2.23) and (2.24), with the definition of ζ now being

$$\zeta\equiv 4b(\kappa'_{pm}+2a)(-\mu)^{-2} \tag{3.18}$$

and the analog of Eq. (3.6) being

$$\zeta=\tau'_{pm}\phi_2(\zeta)\,.$$

An alternative expansion for κ'_{pm} is given in Appendix A.

From Eqs. (3.8), (3.15), and (2.15), the equation for determining the resonances μ of the Stark effect in the case

$$\tau_{nm}<R_1 \tag{3.19a}$$

and

$$\tau'_{pm}<R_2 \tag{3.19b}$$

is given by

$$(-\mu)^{1/2}\left(1+\sum_{j=1}^{\infty}A_j(\tau^j_{nm}+(-1)^j\tau'^{j}_{pm})\right)=\tfrac{1}{2}a(n+p+m+1)^{-1}\,. \tag{3.20}$$

Equation (3.20) is our weak-field formula in which the μ appears implicitly. With the values of A_j presented in Table I a simple iteration procedure, which consists of truncating successively the series on the left-hand side of Eq. (3.20), enables one to compute μ_{npm} to very high degree of accuracy. Table II shows the convergence of μ_{000} from this truncation procedure for some selected values of b, where N is the number of terms used on the left-hand side of Eq. (3.20). Note that for these values of b, conditions (3.19) are satisfied.

We can express μ explicitly in terms of b, n, p, and m from Eq. (3.20) by again making use of Lagrange's formula. Let

$$\zeta\equiv 8b(-\mu)^{-3/2} \tag{3.21}$$

or

$$(-\mu)^{1/2}=(8b/\zeta)^{1/3}\,; \tag{3.22}$$

then Eq. (3.20) can be written as

$$\left(\frac{\zeta}{8b}\right)^{1/3}=\frac{2(n+p+m+1)}{a}\left(1+\sum_{j=1}^{\infty}A'_j\zeta^j\right), \tag{3.23}$$

where

$$A'_j=[(2n+m+1)^j+(-1)^j(2p+m+1)^j]A_j\,. \tag{3.24}$$

From Eq. (3.23) we get

$$\zeta=s\phi_3(\zeta)\,, \tag{3.25}$$

where

$$s\equiv 64b(n+p+m+1)^3/a^3 \tag{3.26}$$

and

$$\phi_3(\zeta)\equiv\left(1+\sum_{j=1}^{\infty}A'_j\zeta^j\right)^3. \tag{3.27}$$

Applying Lagrange's theorem to Eq. (3.25) then gives

$$\zeta=\sum_{j=1}^{\infty}\frac{s^j}{j\,!}\left(\frac{d}{d\zeta}\right)^{j-1}\phi_3(\zeta)^j\bigg|_{\zeta=0}\,, \tag{3.28}$$

TABLE II. Convergence of μ_{000}/a^2 obtained from the weak-field formula (3.20) for some selected values of b/a^3.

N	$b/a^3=2\times10^{-3}$	$b/a^3=4\times10^{-3}$	$b/a^3=6\times10^{-3}$
6	−0.250 272 018 7	−0.251 088 315 6	−0.252 449 687 4
8	−0.250 272 018 7	−0.251 088 320 3	−0.252 449 799 0
10	−0.250 272 018 7	−0.251 088 320 4	−0.252 449 805 8
12	−0.250 272 018 7	−0.251 088 320 4	−0.252 449 806 2
14	−0.250 272 018 7	−0.251 088 320 4	−0.252 449 806 2

or since $\mu=-4b^{2/3}\zeta^{-2/3}$ from Eq. (3.21), we get

$$\mu=-\tfrac{1}{4}a^2(n+p+m+1)^{-2}\left(1+\sum_{j=1}^{\infty}C_js^j\right)^{-2/3}, \quad (3.29)$$

where

$$C_j=\frac{1}{(j+1)!}\left(\frac{d}{d\zeta}\right)^j\phi_3(\zeta)^{j+1}\bigg|_{\zeta=0}. \quad (3.30)$$

We see that the appropriate expansion parameter here is s, which is the *product* of b/a^3 and $(n+p+m+1)^3$ (to within a constant multiplier). It is clear that no matter how small b is, there will always be quantum numbers above which the above perturbation expansion is not valid.

It is instructive to compare the first few terms on the right-hand side of Eq. (3.29) with the usual exact perturbation series. From Eq. (3.29) and using Eq. (3.30), we get

$$\mu=-\tfrac{1}{4}a^2(n+p+m+1)^{-2}+6(n-p)(n+p+m+1)a^{-1}b - 4(n+p+m+1)^4[17(n+p+m+1)^2-10(n-p)^2] \times a^{-4}b^2+\cdots, \quad (3.31)$$

while the usual exact perturbation series up to the terms in b^2 is

$$\mu=-\tfrac{1}{4}a^2(n+p+m+1)^{-2}+6(n-p)(n+p+m+1)a^{-1}b - 2(n+p+m+1)^4[17(n+p+m+1)^2-3(n-p)^2 - 9m^2+19]a^{-4}b^2+\cdots. \quad (3.32)$$

The difference between the two equations begins appearing only in the coefficient of b^2. For the ground state $n=p=m=0$, the coefficients of b^2/a^4 in (3.31) and (3.32) are −68 and −72, respectively. In the case $n\gg p$ and $n\gg m$, the coefficients of b^2/a^4 in (3.31) and (3.32) approach the same value. This is true also for all the coefficients in the higher-order terms. The usual exact perturbation series (3.32) includes the increasingly higher-order WKB approximations, and a straightforward summation of this series gives divergent results.[16–18] Our series (3.31), on the other hand, is a convergent series, provided that

$$s\equiv 64b(n+p+m+1)^3/a^3<R_{npm}, \quad (3.33)$$

where the radius of convergence R_{npm} is positive and finite for any finite values of n, p, and m. The relation between the usual exact Rayleigh-Schrödinger perturbation series and the perturbation series obtained from a WKB approximation has been pointed out in an earlier paper.[20]

We see that the coefficients C_j in (3.29) are, in general, rather complicated functions of the quantum numbers n, p, and m. It can now be appreciated that for numerical purposes our earlier implicit formula (3.20) is clearly more convenient to use, since the A_j are independent of n, p, and m. In some special cases, however, the dependence on n, p, and m in C_j can be factored out, leaving only pure numbers which are independent of n, p, and m and which can then be tabulated. Let us write

$$\phi_4(\zeta)\equiv\left(1+\sum_{j=1}^{\infty}A_j\zeta^j\right)^3\equiv 1+\sum_{j=1}^{\infty}f_j^{(4)}\zeta^j, \quad (3.34)$$

where the A_j are the same A_j defined previously and tabulated in Table I; let us also define

$$c_j\equiv\frac{1}{(j+1)!}\left(\frac{d}{d\zeta}\right)^j\phi_4(\zeta)^{j+1}\bigg|_{\zeta=0}. \quad (3.35)$$

It can be readily shown that for the following special cases,

$$C_j=\begin{cases}(2n+m+1)^jc_j, & n\gg p,\ n\gg m, \quad (3.36)\\ (-1)^j(2p+m+1)^jc_j, & n\ll p,\ m\ll p, \quad (3.37)\\ [1+(-1)^j](2n+m+1)^jc_j, & n=p. \quad (3.38)\end{cases}$$

The above results follow from Eqs. (3.30) and (3.27), because in those cases the n, p, and m dependence in (3.24) becomes a factor with a simple power which can be absorbed in ζ in (3.27), thereby enabling us simply to redefine another variable. The values of c_j calculated from (3.35) are given in Table I for $j=1$–30. The values of μ for these special cases can thus be readily calculated from our explicit formula (3.29) to very high accuracy.

IV. STRONG-FIELD EXPANSION

For the weak-field expansions given in Sec. III to be valid, we stated the conditions (3.19). We first note that the condition $\tau'_{pm}<R_2$ cannot be violated. The equation

$$\tau'_{pm}=R_2 \quad (4.1)$$

gives the eigenvalue of the anharmonic oscillator with the potential $V(v)$ in Fig. 1 at the top of the well. In this case, k_2 in Eq. (2.24) approaches unity and

$$\mu^2=4b(\kappa'_{pm}+2a). \quad (4.2)$$

Substituting (4.2) into (2.23) gives (4.1). Thus Eq. (4.1) determines the value of b (which depends on n, p, and m) above which the resonance μ_{npm} disappears.

On the other hand, there will always be values of n such that

$$\tau_{nm} > R_1 . \tag{4.3}$$

In this case, let us write

$$\eta \equiv -\mu/(4b\kappa_{nm})^{1/2} \tag{4.4}$$

and write Eq. (2.21) as

$$(8/3\pi\eta^{3/2})\{(1+\eta^2)^{3/4}+\eta(1+\eta^2)^{1/4}]\, K(k) - 2\eta(1+\eta^2)^{1/4}E(k)\} = 8b(2n+m+1)(-\mu)^{-3/2} , \tag{4.5}$$

where

$$k^2 = \tfrac{1}{2}[1-\eta(1+\eta^2)^{-1/2}] . \tag{4.6}$$

Defining τ_{nm} as in Eq. (3.4), we can write Eq. (4.5) as

$$\eta = \tau_{nm}^{-2/3}\psi_1(\eta) , \tag{4.7}$$

where

$$\psi_1(\eta) \equiv (8/3\pi)^{2/3}\{[(1+\eta^2)^{3/4}+\eta(1+\eta^2)^{1/4}]\, K(k) - 2\eta(1+\eta^2)^{1/4}E(k)\}^{2/3} . \tag{4.8}$$

The use of Lagrange's theorem gives

$$\eta = \sum_{j=1}^{\infty} \frac{\tau_{nm}^{-2j/3}}{j\,!}\left(\frac{d}{d\eta}\right)^{j-1}\psi_1(\eta)^j\bigg|_{\eta=0} \tag{4.9}$$

or

$$\kappa_{nm}^{-1/2} = [2b^{1/6}(2n+m+1)^{2/3}]^{-1}\sum_{j=0}^{\infty} h_j\tau_{nm}^{-2j/3} , \tag{4.10}$$

where

$$h_j \equiv \frac{1}{(j+1)!}\left(\frac{d}{d\eta}\right)^{j}\psi_1(\eta)^{j+1}\bigg|_{\eta=0} . \tag{4.11}$$

Thus we obtain

$$\kappa_{nm} = 4b^{1/3}(2n+m+1)^{4/3}\left(\sum_{j=0}^{\infty} h_j\tau_{nm}^{-2j/3}\right)^{-2} \tag{4.12}$$

or

$$\kappa_{nm} = 4b^{1/3}(2n+m+1)^{4/3}\sum_{j=0}^{\infty} B_j\tau_{nm}^{-2j/3} , \tag{4.13}$$

where the coefficients B_j are defined by

$$\sum_{j=0}^{\infty} B_j x^j = \left(\sum_{j=0}^{\infty} h_j x^j\right)^{-2} . \tag{4.14}$$

The series expansion in powers of η of the function $\psi_1(\eta)$ when $\eta < 1$ has been given previously in Ref. 11:

$$\psi_1(\eta) = \left(\sum_{j=0}^{\infty} b_j\eta^j\right)^{2/3} , \tag{4.15}$$

where

$$b_j = [(-1)^j 2^j\Gamma(\tfrac{1}{4}(2j+1))]/[(2\pi)^{1/2}j\,!\,\Gamma(\tfrac{1}{4}(2j+7)-j)] . \tag{4.16}$$

Writing

$$\psi_1(\eta) \equiv \sum_{j=0}^{\infty} g_j^{(1)}\eta^j , \tag{4.17}$$

we have computed the values of B_j from Eqs. (4.11) and (4.14)–(4.17) for $j = 0$–30 and tabulated them in Table III. The series on the right-hand side of (4.13) is convergent if $\tau_{nm} > R_1$.

Thus from Eqs. (3.15), (4.13), and (2.15), the equation for determining the resonances μ of the Stark effect in the case

$$\tau_{nm} > R_1 \tag{4.18a}$$

and

$$\tau'_{pm} < R_2 \tag{4.18b}$$

is given by

TABLE III. Values of B_j and D_j for $j = 0$–30.

j	B_j	D_j
0	0.546 267 325 1 $E+00$	
1	0.675 457 518 1 $E+00$	0.409 430 481 0 $E+00$
2	−0.186 799 733 1 $E+00$	0.195 636 775 1 $E+00$
3	0.430 301 073 8 $E-01$	−0.859 491 802 7 $E-01$
4	0.298 240 895 0 $E-01$	0.108 664 947 5 $E-01$
5	−0.565 884 242 1 $E-01$	−0.222 723 370 2 $E-01$
6	0.517 622 551 7 $E-01$	0.970 420 114 3 $E-01$
7	−0.339 083 590 9 $E-01$	−0.160 008 077 5 $E+00$
8	0.203 480 156 8 $E-01$	0.176 362 861 2 $E+00$
9	−0.197 285 281 6 $E-01$	−0.210 106 489 2 $E+00$
10	0.297 402 266 7 $E-01$	0.360 625 868 6 $E+00$
11	−0.417 430 794 9 $E-01$	−0.643 952 270 3 $E+00$
12	0.487 093 735 4 $E-01$	0.996 886 186 0 $E+00$
13	−0.505 748 009 5 $E-01$	−0.145 212 564 9 $E+01$
14	0.533 828 978 4 $E-01$	0.227 121 930 8 $E+01$
15	−0.636 468 264 7 $E-01$	−0.382 088 267 2 $E+01$
16	0.830 697 176 8 $E-01$	0.637 011 748 2 $E+01$
17	−0.108 131 755 1 $E+00$	−0.102 680 683 6 $E+02$
18	0.134 651 316 1 $E+00$	0.165 675 660 4 $E+02$
19	−0.163 063 215 1 $E+00$	−0.274 810 598 3 $E+02$
20	0.199 648 876 2 $E+00$	0.462 777 286 6 $E+02$
21	−0.252 766 202 0 $E+00$	−0.775 278 166 3 $E+02$
22	0.327 841 764 5 $E+00$	0.129 221 141 9 $E+03$
23	−0.426 168 218 3 $E+00$	−0.216 707 300 5 $E+03$
24	0.549 102 769 5 $E+00$	0.367 000 107 1 $E+03$
25	−0.704 197 892 9 $E+00$	−0.623 764 783 7 $E+03$
26	0.907 915 602 4 $E+00$	0.105 957 462 1 $E+04$
27	−0.118 288 831 7 $E+01$	−0.180 256 680 6 $E+04$
28	0.155 329 570 2 $E+01$	0.307 826 340 4 $E+04$
29	−0.204 448 559 6 $E+01$	−0.525 006 240 9 $E+04$
30	0.268 952 902 9 $E+01$	0.918 178 325 8 $E+04$

$$a-(2p+m+1)(-\mu)^{1/2}\left(1+\sum_{j=1}^{\infty}(-1)^j A_j \tau'^{\,j}_{pm}\right)$$
$$=2b^{1/3}(2n+m+1)^{4/3}\sum_{j=0}^{\infty}B_j\tau_{nm}^{-2j/3}. \qquad (4.19)$$

Equation (4.19) is our strong-field formula, in which the μ appears implicitly. With the values of A_j and B_j presented in Tables I and III, a simple iteration procedure which consists of truncating successively the series on the left- and right-hand sides enables one to compute μ_{npm} to very high degrees of accuracy. Table IV shows the convergence of $\mu_{10,0,0}$ from this truncation procedure for some selected values of b, where N_A and N_B are the number of terms used on the left- and right-hand sides of Eq. (4.19). Note that for these values of b, conditions (4.18) are satisfied.

It may be mentioned that steps (4.11)–(4.14) leading to the determination of the coefficients B_j (or A_j) can be varied, although the final results for these coefficients must, of course, be the same. An alternative procedure for the determination of B_j from the function $\psi_1(\eta)$ is given in Appendix B.

We can express μ explicitly in terms of b, n, p, and m from Eq. (4.19) by directly applying Lagrange's theorem to Eq. (4.19). However, Eq. (4.19), as it will be noted, is a Laurent-type series rather than a simple Taylor series. This means that we would have a formula of the form $(d/d\eta)^j\psi(\eta)^{j+1}$, with the value of η evaluated at points other than zero—a somewhat inconvenient procedure. The following procedure is more convenient:

We assume that the left-hand side of (4.19) has a known value, by first assuming the unperturbed value of μ_0 of μ, where

$$\mu_0=-\tfrac{1}{4}a^2(n+p+m+1)^{-2}, \qquad (4.20)$$

where the subscripts n, p, and m on the μ's have been dropped for convenience. If we write

$$t_N\equiv\frac{a-(2p+m+1)(-\mu_N)^{1/2}\left(1+\sum_{j=1}^{\infty}(-1)^jA_j\tau'^{\,j}_{pm}\right)}{2b^{1/3}(2n+m+1)^{4/3}}-B_0, \qquad (4.21)$$

where $N=0$ in the beginning but is increased in steps of 1 in the following iterations and where the μ in τ'_{pm} has been assumed to have the value μ_N, then Eq. (4.19) can be written as

$$\eta=t_N\psi_2(\eta), \qquad (4.22)$$

where

$$\eta\equiv\tau_{nm}^{-2/3} \qquad (4.23)$$

and

$$\psi_2(\eta)\equiv\left(\sum_{j=1}^{\infty}B_j\eta^{j-1}\right)^{-1}\equiv\sum_{j=0}^{\infty}g_j^{(2)}\eta^j. \qquad (4.24)$$

Application of Lagrange's theorem to (4.22) gives

$$\eta=\sum_{j=1}^{\infty}\frac{t_N^j}{j!}\left(\frac{d}{d\eta}\right)^{j-1}\psi_2(\eta)^j\Big|_{\eta=0}, \qquad (4.25)$$

or, writing the μ thus obtained in (4.25) as μ_{N+1}, where N denotes the order of iteration as explained earlier, we get

$$\mu_{N+1}=-4b^{2/3}(2n+m+1)^{2/3}B_1^{-1}t_N\left(1+\sum_{j=1}^{\infty}D_jt_N^j\right), \qquad (4.26)$$

where

$$D_j\equiv\frac{B_1}{(j+1)!}\left(\frac{d}{d\eta}\right)^j\psi_2(\eta)^{j+1}\Big|_{\eta=0}. \qquad (4.27)$$

The values of D_j calculated from Eqs. (4.27) and (4.24) for $j=1$–30 are given in Table III. Thus beginning with μ_0 given by (4.20) and t_0 given by (4.21) and using the values of B_1 and D_j given in Table III, we get μ_1 from Eq. (4.26). We then use μ_1 to obtain t_1 from (4.21) and substitute this into (4.26) to obtain μ_2. The process is repeated until μ_{N+1} converge to the accuracy desired. Equation (4.26) is our explicit strong-field formula for the resonances μ of the Stark effect in the hydrogen atom.

We have used Eqs. (3.20) and (4.19) to obtain μ_{npm}/a^2 for $p=m=0$, $n=0,1,\ldots,10$ for a wide range of values of b/a^3, which are plotted in Fig. 2. The solid lines correspond to those values obtained by using Eq. (3.20), namely, when conditions (3.19) are satisfied, and the dotted lines corre-

TABLE IV. Convergence of $\mu_{10,0,0}/a^2$ obtained from the strong-field formula (4.19) for some selected values of b/a^3.

N_A, N_B	$b/a^3=8\times10^{-7}$	$b/a^3=10^{-6}$	$b/a^3=2\times10^{-6}$
6, 6	−0.001 562 907 1	−0.001 447 939 5	−0.000 898 825 2
7, 7	−0.001 567 354 7	−0.001 448 943 6	−0.000 898 828 7
8, 8	−0.001 565 741 3	−0.001 448 655 9	−0.000 898 829 1
9, 9	−0.001 566 672 0	−0.001 448 788 5	−0.000 898 829 4
10, 10	−0.001 565 834 2	−0.001 448 693 3	−0.000 898 829 5

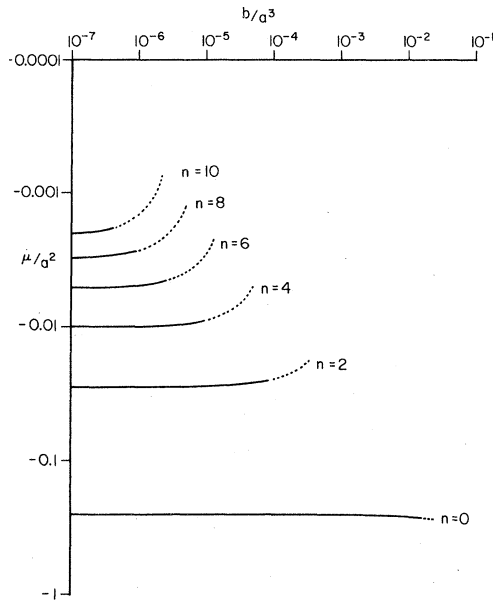

FIG. 2. $\mu_{n\,00}/a^2$ vs b/a^3 for various values of n (note the logarithmic scales).

spond to those obtained by using Eq. (4.19), namely, when conditions (4.18) are satisfied. For every given resonance the line terminates at a certain value of b/a^3 which is determined by Eq. (4.1). It will be noted that if $p>n$, only the weak-field formula (3.20) need be used for determining μ up to the value of b above which the resonance disappears. However, if $n>p$, there will always be a region for which the strong-field formula (4.19) must be used. Note that the values of b/a^3 for which the strong-field formula was used are very small and decrease rapidly as the value of n increases.

V. SUMMARY

We have presented two different types of perturbation formulas for approximating the resonances of the Stark effect in the hydrogen atom. The formulas (3.20) and (4.19), and (3.29) and (4.26) are simple and together cover the entire regime. We have used them to calculate several selected resonances as functions of the applied electric field. Some interesting features are clearly exhibited in Fig. 2. The extensive table of coefficients presented in Tables I and III enables one to compute readily any resonances of the Stark effect to high degrees of accuracy (within the approximation of Titchmarsh's formula).

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APPENDIX A

The eigenvalues κ'_{pm} of Eq. (2.18) were approximated by the expansions (3.15) in this paper, i.e., expansions about $\tau'_{pm}=0$. For those eigenvalues near the top of the potential well $V(v)$, i.e., when $\tau'_{pm}\simeq R_2$, κ'_{pm} should be more appropriately approximated by an expansion about $\tau'_{pm}=R_2$. Though we did not use it, we shall write out this expansion in this appendix.

In Eq. (3.16), instead of expanding $\phi_2(\zeta)$ about $\zeta=0$, we define a new variable

$$\theta \equiv (1-\zeta)^{1/2} \tag{A1}$$

and expand about $\theta=0$. Let us write

$$\phi_2(\theta)\equiv \theta\{1-(1+\theta)^{1/2}[-\theta K(k_2)+E(k_2)]\}^{-1}, \tag{A2}$$

where

$$k_2^2=(1-\theta)/(1+\theta),\quad k_2'^2=1-k_2^2=2\theta/(1+\theta). \tag{A3}$$

The elliptic integrals $K(k_2)$ and $E(k_2)$ can be expanded inpower series in θ by the formulas[21]

$$K(k_2)=\sum_{m=0}^{\infty}\frac{(1/2)_m(1/2)_m}{m!m!}\times[\ln(1/k_2')-\psi(m+\tfrac{1}{2})+\psi(m+1)]k_2'^{2m}, \tag{A4}$$

where ψ is the digamma function and

$$E(k_2)=1+\tfrac{1}{4}\sum_{m=0}^{\infty}\frac{(1/2)_m(3/2)_m}{m!(m+1)!}[2\ln(1/k_2')+\psi(m+2)-\psi(m+\tfrac{3}{2})]k_2'^{2m+2}. \tag{A5}$$

By defining the expansion parameter t'_{pm} by

$$t'_{pm}\equiv 1-(3\pi b/\sqrt{2})(2p+m+1)(-\mu)^{-3/2} \tag{A6}$$

$$=1-\tau'_{pm}/R_2, \tag{A7}$$

the expansion about $t'_{pm}=0$ for κ'_{pm} is

$$\kappa'_{pm}+2a=\frac{(-\mu)^2}{4b}\left[1-t'^2_{pm}\left(\sum_{j=0}^{\infty}e_j t'^j_{pm}\right)^2\right], \tag{A8}$$

where

$$e_j\equiv\frac{1}{(j+1)!}\left(\frac{d}{d\theta}\right)^j\phi_2(\theta)^{j+1}\bigg|_{\theta=0} \tag{A9}$$

and where $\phi_2(\theta)$ is given by (A2).

Using the expansion (A8) for κ'_{pm}, we determine the resonances μ of the Stark effect as before by equating

$$-\kappa'_{pm}=\kappa_{nm}, \tag{A10}$$

where κ_{nm} is given by Eq. (3.8) or (4.12), depending on whether $\tau_{nm}<R_1$ or $\tau_{nm}>R_1$, τ'_{pm} being always less than R_2.

APPENDIX B

In this appendix we give an alternative method of determining B_j of Eq. (4.19) from $\psi_1(\eta)$ of Eq. (4.8) or (4.17) to show the variety of steps which can be taken.

From Eq. (4.7), if we consider a function

$$f(\eta)=\eta^2\,, \tag{B1}$$

then Lagrange's theorem gives

$$\eta^2=\sum_{j=1}^{\infty}\frac{\tau_{nm}^{-2j/3}}{j!}\left(\frac{d}{d\eta}\right)^{j-1}[2\eta\psi_1(\eta)^j]\Big|_{\eta=0} \tag{B2}$$

$$\equiv \tau_{nm}^{-4/3}\sum_{j=0}^{\infty}h'_j\tau_{nm}^{-2j/3}\,, \tag{B3}$$

or using the definition of η given by Eq. (4.4), we get

$$\kappa_{nm}=4b^{1/3}(2n+m+1)^{4/3}\left(\sum_{j=0}^{\infty}h'_j\tau_{nm}^{-2j/3}\right)^{-1} \tag{B4}$$

$$=4b^{1/3}(2n+m+1)^{4/3}\sum_{j=0}^{\infty}B_j\tau_{nm}^{-2j/3}\,. \tag{B5}$$

In this method we obtain the coefficients B_j from the coefficients h'_j given by

$$h'_j=\frac{1}{(j+2)!}\left(\frac{d}{d\eta}\right)^{j+1}[2\eta\psi_1(\eta)^{j+2}]\Big|_{\eta=0} \tag{B6}$$

by the relation

$$\sum_{j=0}^{\infty}B_jx^j=\left(\sum_{j=0}^{\infty}h'_jx^j\right)^{-1}. \tag{B7}$$

Using the formula we employed in Eqs. (3.12′) and (3.12″), we can represent B_j explicitly in terms of h'_j. The representations are the same as Eqs. (3.12′) and (3.12″) with $f_j^{(1)}$ replaced by B_j and a_j replaced by h'_j. For numerical purposes, it is easier to use recursion relations for the determination of B_j.

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$$\psi''(x)+[\lambda-q(x)-l(l+1)x^{-2}]\psi(x)=0$$

is

$$\frac{1}{\pi}\int_{x'_n}^{x_n}[\lambda_{nl}-q(x)-l(l+1)x^{-2}]^{1/2}dx=n+\tfrac{3}{4}.$$

The Titchmarsh formula, on the other hand, is

$$\frac{1}{\pi}\int_0^{x_n}[\lambda_{nl}-q(x)]^{1/2}dx=n+\tfrac{1}{2}l+\tfrac{3}{4}.$$

This was proved under the condition $q(x)\to+\infty$ when $x\to\infty$. The potential $V(v)$ does not strictly satisfy this condition. But if the value of b is very small compared to $-\mu$, and if the value of $\kappa'_{pm}+2a$ is well below the top of the well, we may expect a situation resembling that condition. That the values of b are very small, even in cases when the "strong-field" expansion need be used, will be seen in the following sections.

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