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Stark Effect in Hydrogenic Atoms: Comparison of Fourth-Order Perturbation Theory with WKB Approximation

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The Schrödinger equation for a hydrogenic atom in a uniform electric field is separated in parabolic coordinates, and WKB quantization rules are obtained for two of the separated equations. In the weak-field limit, the quantization rules are expanded in powers of the field and evaluated analytically. From the results, a power series for the energy eigenvalues is obtained which agrees with all known results of perturbation theory to fourth order. For strong fields, the quantization rules are evaluated numerically for states for which the perturbation series is expected to be least accurate. It is found that the perturbation results to fourth order agree with the numerical results for the energy eigenvalues to one part in a thousand for the highest fields possible, and that the addition of the fourth order in perturbation theory improves the accuracy of the perturbation series, contrary to the conclusions of an earlier work. Finally, the accuracy for the measurement of fields from observed Stark shifts by using the perturbation theory is estimated.

I. INTRODUCTION

The Stark effect in hydrogen has often been studied by perturbation theory. The first-order effect was derived by Schrödinger,[1] the second-order by Epstein,[2] the third-order by Doi,[3] and the fourth-order by Basu.[4] In practice, particularly in the measurement of electric fields from the observed Stark shifts, the energy eigenvalues must be known for high fields for which the application of perturbation theory is not *a priori* justified. Instead we apply the WKB method, which does not assume weak fields as perturbation theory does, to the Stark effect in hydrogenic atoms.

The most systematic derivation of the WKB quantization rule has been given by Dunham.[5] In his treatment, the eigenfunction of the one-dimensional Schrödinger equation,

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}\right) + V(x)\psi = E\psi, \tag{1}$$

is written

$$\psi(x) = \exp\left(\frac{i}{\hbar}\int^x y(x')dx'\right) . \tag{2}$$

The equation determining $y(x)$ is

$$\frac{\hbar}{i}\left(\frac{dy}{dx}\right) + y^2 = 2m(E - V), \tag{3}$$

which is solved by the WKB (asymptotic) expansion

$$y = \sum_{n=0}\left(\frac{\hbar}{i}\right)^n y_n(x) . \tag{4}$$

The substitution of Eq. (4) into Eq. (3) allows the determination of the y_n. Dunham showed that ψ expressed in terms of the y_n will be bounded and single valued only if the y in Eq. (4) satisfies the condition

$$\oint y(x)\,dx = N2\pi\hbar, \qquad N = 0, 1, 2, \ldots, \tag{5}$$

where the contour is to enclose the classically allowed region of the potential in the complex plane of x. By substituting Eq. (4) into Eq. (5), Dunham reduced the quantization rule to the compact form:

$$\oint (E-V)^{1/2}dx - \frac{\hbar^2}{64m}\oint\left(\frac{d}{dx}(E-V)\right)^2 (E-V)^{-5/2}dx$$
$$-\frac{\hbar^4}{8192m^2}\oint\left[49\left(\frac{d}{dx}(E-V)\right)^4(E-V)^{-11/2}\right.$$
$$\left.-16\left(\frac{d}{dx}(E-V)\right)\left(\frac{d^3}{dx^3}(E-V)\right)(E-V)^{-7/2}\right]dx$$
$$+\ O(\hbar^6) = \frac{(N+\frac{1}{2})\,2\pi\hbar}{(2m)^{1/2}}\ . \tag{6}$$

In deriving Eq. (6), Dunham implicitly assumed that $V(x)$ has no singularities along the real x axis, and that $\psi \to 0$ as $x \to \pm\infty$. When these conditions are not satisfied in a given problem, it becomes necessary to change variables in such a way that the new problem does satisfy Dunham's conditions. Such a procedure was originally suggested by Langer[6] for the case where Eq. (1) is the radial equation for the central potential problem. By employing the Langer transformation, it is possible to show that not only does the first-order WKB quantization integral lead to the exact eigenvalue spectrum for the Coulomb potential and the three-dimensional harmonic oscillator, but also that the second- and third-order integrals are identically zero for these cases.[7]

The earliest application of the WKB method to the Stark-effect problem in hydrogen was made by Wentzel.[8] He applied the quantization rule given by Eq. (5) to equations of the form

$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2\psi}{dx^2}+\frac{1}{x}\ \frac{d\psi}{dx}\right)$$
$$-\left(\pm eFx + E + \frac{e^2\pm\beta}{2x} - \frac{m^2}{4x^2}\ \frac{\hbar^2}{2\mu}\right)\psi = 0, \tag{7}$$

(symbols will be explained below) in which ψ satisfies the boundary conditions $\psi \to 0$ at $x = 0$ and $x = \infty$, which are not those of a problem to which Dunham's rule is applicable. Moreover, Eq. (7) is singular at $x = 0$. Thus, Eq. (5) is not directly applicable in this case. In the past, indiscriminate application of the quantization rule to problems which do not satisfy Dunham's conditions, such as the radial equations for the Coulomb potential and harmonic-oscillator problems, has led to incorrect results.[9] Thus, it is necessary to treat the Stark effect by WKB methods with proper regard to the conditions of applicability of the quantization rule.

In a more recent application of WKB methods to the Stark effect in hydrogen, Rice and Good[10] have used connection eigenfunctions to derive a quantization rule for the problem separated in parabolic coordinates. In the weak-field limit, this rule leads to the perturbation series for the energy eigenvalues correct to first order only. Since it is not clear why the quantization rule should be more accurate for high fields than for low fields, it appears that it will be substantially inaccurate for all fields.

In the present work, the Schrödinger equation for the problem is separated in parabolic coordinates, and WKB quantization rules are derived for two of the separated equations. In the weak-field limit the quantization rules are expanded in powers of the field and evaluated analytically. From the results, a power series in the electric field for the energy eigenvalues is obtained which agrees with all known results of perturbation theory to fourth order. In the strong-field limit, the quantization rules are evaluated numerically for selected states. Comparison of the numerical eigenvalues so obtained with those predicted by the perturbation series suggests that the latter are accurate to one part in a thousand for the highest fields possible when the fourth-order term is included, contrary to the conclusions reached by Basu.[4, 11]

II. QUANTIZATION RULE

The complete Schrödinger equation for a hydrogenic atom with a nucleus of charge Ze and mass M, and an electron of charge $-e$ and mass m, bound by a Coulomb potential and placed in a uniform electric field $\mathcal{E}'$ in the $-z$ direction, with relativistic and spin-orbit effects neglected, leads to the following equation in the relative coordinates:

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + \left(-\frac{Ze^2}{r} - eFz\right)\psi = E\psi\ . \tag{8}$$

Here, r is the relative distance between nucleus and electron, z is the projection of r in the direction of the field, μ is the reduced mass, $F = \mathcal{E}'\{1 + [m/(M+m)](Z-1)\}$, and E is the energy of relative motion.

In parabolic coordinates

$$\xi = r + z, \qquad \eta = r - z\ , \quad \varphi = \varphi \tag{9}$$

where $\xi \geqslant 0$ and $\eta \geqslant 0$,

the equation reduces to

$$-\frac{\hbar^2}{2\mu}\left\{\frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right)\right]+\frac{1}{\xi\eta}\frac{\partial^2\psi}{\partial\varphi^2}\right\}$$

$$-\frac{2Ze^2}{\xi+\eta}\psi-\tfrac{1}{2}eF(\xi-\eta)\psi=E\psi\ , \qquad (10)$$

which may be separated by taking

$$\psi(\xi,\eta,\varphi)=\frac{f(\xi)}{\sqrt{\xi}}\,\frac{g(\eta)}{\sqrt{\eta}}\,e^{im\varphi}, \quad m=0,\ \pm1,\ \ldots\ . \qquad (11)$$

The resulting equations are

$$-\frac{\hbar^2}{2\mu}\frac{d^2f}{d\xi^2}-\left(\tfrac{1}{8}eF\xi+\frac{Ze^2-\beta}{4\xi}-\frac{m^2-1}{4\xi^2}\frac{\hbar^2}{2\mu}\right)f=\tfrac{1}{4}Ef\ , \qquad (12a)$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2g}{d\eta^2}-\left(-\tfrac{1}{8}eF\eta+\frac{Ze^2-\beta}{4\eta}-\frac{m^2-1}{4\eta^2}\frac{\hbar^2}{2\mu}\right)g=\tfrac{1}{4}Eg, \qquad (12b)$$

where β is a separation constant.

The quantization rule is not directly applicable to these equations, because the equivalent potentials are singular at $\xi=0$ and $\eta=0$, and the requirement that ψ be bounded imposes the boundary conditions $f\to0$ as $\xi\to0$ and $g\to0$ as $\eta\to0$. Thus, the conditions for the applicability of Dunham's quantization rule are not satisfied. This difficulty is similar to that occurring in the radial problem for a central potential. To resolve the situation we adapt the procedure introduced by Langer[6] for the radial problem. Letting

$$\xi=e^{2\delta x},\quad \delta>o;\quad f(\xi)=e^{\delta x}X(x)\ ,\quad -\infty<x>\infty \qquad (13)$$

we obtain as the equation for X

$$-\frac{\hbar^2}{2\mu}\frac{d^2X}{dx^2}-\delta^2\left(\tfrac{1}{8}eFe^{3\delta x}+\tfrac{1}{4}(Ze^2+\beta)e^{\delta x}\right.$$

$$\left.+\tfrac{1}{4}Ee^{2\delta x}-\tfrac{1}{4}m^2\frac{\hbar^2}{2\mu}\right)X=0. \qquad (14)$$

The equivalent potential of Eq. (14) has no singularities in the finite plane, and as $x\to\infty$ it can easily be shown that X vanishes exponentially. As $x\to-\infty$, an asymptotic solution is $X=e^{\delta|m|x/2}$, which vanishes as $x\to-\infty$ for $m\neq0$. For $m=0$, we may consider the limit $\delta\to\infty$, $m\to0$, and $\delta|m|\to c>0$. Then X will vanish as $x\to-\infty$. The above procedure is proper since, as will be seen presently, δ can be chosen quite arbitrarily. In this manner, we have satisfied the conditions for the applicability of the quantization rule to Eq. (14).

Replacing $E-V$ in Eq. (6) by

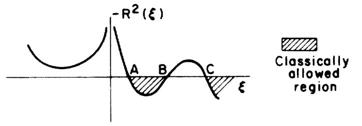

FIG. 1. Behavior of $-R^2(\xi)$ on the real axis.

$$\delta^2\left[\tfrac{1}{8}eF\,e^{3\delta x}+\tfrac{1}{4}(Ze^2+\beta)\,e^{\delta x}\right.$$

$$\left.+\tfrac{1}{4}E\,e^{2\delta x}-\tfrac{1}{4}m^2(\hbar^2/2\mu)\right]\ ,$$

and changing the integration variable from x back to ξ according to Eq. (13), we obtain

$$\oint R\,d\xi-\frac{\hbar^2}{64\mu}\oint\left(\frac{d}{d\xi}(\xi^2R^2)\right)R^{-5}\frac{d\xi}{\xi^4}-\frac{\hbar^4}{8192\mu^2}$$

$$\times\oint\left\{49\left(\frac{d}{d\xi}(\xi^2R^2)\right)^4R^{-11}-16\xi\left(\frac{d}{d\xi}(\xi^2R^2)\right)\right.$$

$$\left.\times\left[\left(\xi\frac{d}{d\xi}\right)^3(\xi^2R^2)\right]R^{-7}\right\}\frac{d\xi}{\xi 8}+O(\hbar^6)=(n_1+\tfrac{1}{2})\frac{2\pi\hbar}{(2\mu)^{1/2}};$$

$$n_1=0,\ 1,\ 2,\ \ldots, \qquad (15)$$

where $\quad R^2=\tfrac{1}{8}eF\xi+\tfrac{1}{4}E+\dfrac{Ze^2+\beta}{4\xi}-\dfrac{m^2}{4\xi^2}\dfrac{\hbar^2}{2\mu}\ .$

A similar rule holds for the η variable except that F is replaced by $-F$, β by $-\beta$, and n_1 by n_2.

According to Dunham's method, the contour is to enclose a branch cut in the complex plane, made along the classically allowed region of the potential. Figure 1 shows the behavior of $-R^2$ for real ξ, and Fig. 2 shows the behavior of $-R^2$ for real η. For the η variable the contour is to enclose region $B'C'$, as shown in Fig. 4. For the ξ variable there are two classically allowed regions as shown in Fig. 1; however, that for $\xi>C$ corresponds to the possibility of ionization which is related to the fact that the Stark-effect problem has no discrete spectrum. Ignoring this difficulty, as is customarily done, we draw the contour as in Fig. 3, thus neglecting the possibility of tunneling.

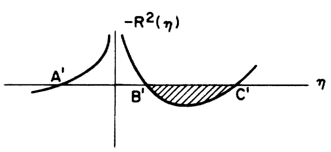

FIG. 2. Behavior of $-R^2(\eta)$ on the real axis.

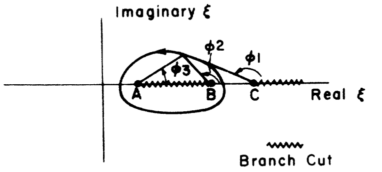

FIG. 3. Contour of integration for the quantization rule for the ξ variable. The phase angles ϕ_1, ϕ_2, and ϕ_3 serve to define $R(\xi)$ and range from 0 to 2π.

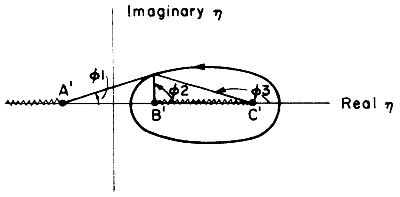

FIG. 4. Contour of integration for the quantization rule for the η variable. The phase angles ϕ_1, ϕ_2 and ϕ_3 serve to define $R(\eta)$ and range from $-\pi$ to π.

III. WEAK-FIELD LIMIT

The quantization rule (15) cannot be integrated by the method of residues, because (as Figs.3 and 4 show) a branch point is always outside the contour so that it cannot be deformed to a circle at infinity. However, we can evaluate the rule in the weak-field limit by expanding it in powers of F about $F = 0$. The resulting integrals are easily evaluated by the method of residues because when F is set equal to zero, the troublesome branch point disappears. An example of the method of integration is given in the Appendix. It can be shown [12] by considering the general form of the y_n in Eq. (4) and by introducing dimensional arguments that the WKB integrals of $O(\hbar^6)$ or higher in Eq. (15) do not contribute through $O(F^4)$. As a result, we may expect to obtain the correct contributions through $O(F^4)$ by using only the integrals given in Eq. (15). The above, however, is not a rigorous argument in view of the asymptotic nature of the WKB expansion. [13]

The evaluated quantization rule to $O(F^4)$ becomes

$$A(Ze^2+\beta) + (eF/E^2)[B(Ze^2+\beta)^2 + CE] + (eF/E^2)^2[D(Ze^2+\beta)^3 + G(Ze^2+\beta)E]$$

$$+ (eF/E^2)^3[H(Ze^2+\beta)^4 + I(Ze^2+\beta)^2E + JE^2] + (eF/E^2)^4[K(Ze^2+\beta)^5$$

$$+ L(Ze^2+\beta)^3E + M(Ze^2+\beta)E^2] = (n_1+\tfrac{1}{2}|m|+\tfrac{1}{2})[2\pi\hbar/(2\mu)^{1/2}](-2E)^{1/2}, \tag{16}$$

where

$$A = \pi/2, \quad B = \tfrac{3}{32}\pi\sqrt{2}, \quad C = \tfrac{1}{16}(m^2-1)\pi\sqrt{2}(\hbar^2/\mu), \quad D = \tfrac{35}{512}\pi\sqrt{2}, \quad G = \tfrac{15}{256}(m^2-\tfrac{5}{3})\pi\sqrt{2}(\hbar^2/\mu),$$

$$H = 1155\pi\sqrt{2}/2^{14}, \quad I = 315(m^2-7/3)\pi\sqrt{2}/2^{12}(\hbar^2/\mu), \quad J = [35(m^2-6)m^2+175]\pi\sqrt{2}/2^{12}(\hbar^4/\mu^2),$$

$$K = 45045\pi\sqrt{2}/2^{19}, \quad L = 15015(m^2-3)\pi\sqrt{2}/2^{17}(\hbar^2/\mu), \quad M = [3465(m^2-\tfrac{22}{3})m^2 + 31185]\pi\sqrt{2}/2^{17}(\hbar^4/\mu^2),$$

with the equivalent result for the η variable in terms of the integer n_2.

Assuming solutions of the form

$$E = \sum_{i=o}^{4} E^{(i)}F^i, \quad \beta = \sum_{i=o}^{4} \beta^{(i)}F^i .$$

Substituting these in Eq. (16) and separating different orders in F, we are able to determine the $E^{(i)}$ and $\beta^{(i)}$ recursively from the simultaneous quantization rules. We thus obtain in terms of $n = n_1+n_2+|m|+1$, $\epsilon_0 = e^4\mu/\hbar^2$ (the atomic unit of energy), and $\mathcal{E} = F(e^5\mu^2/\hbar^4)^{-1}$ (the field in a.u.)

$$E = Z^2\epsilon_0\{-1/2n^2 - \tfrac{3}{2}n(n_1-n_2)(\mathcal{E}/Z^3) - (\tfrac{1}{16}n^4)[17n^2 - 3(n_1-n_2)^2 - 9m^2 + 19](\mathcal{E}/Z^3)^2 - \tfrac{3}{32}n^7(n_1-n_2)$$

$$\times [23n^2-(n_1-n_2)^2+11m^2+39](\mathcal{E}/Z^3)^3-(\tfrac{1}{1024}n^{10})[5487n^4+35\,182n^2-1134m^2(n_1-n_2)^2$$

$$+1806n^2(n_1-n_2)^2-3402n^2m^2-3093(n_1-n_2)^4-549m^4+5754(n_1-n_2)^2$$

$$-8622m^2+16\,211](\mathcal{E}/Z^3)^4+O(\mathcal{E}^5)\}. \qquad (17)$$

To $O(\mathcal{E}^3)$, Eq. (17) agrees with the perturbation series terms.[1-3] The fourth-order term for the ground state, $-Z^2\epsilon_0\frac{3555}{64}(\mathcal{E}/Z^3)^4$, agrees with that given by Sewell[14] and Mendelsohn.[15] The fourth-order term for the states, $n=5$, $|m|=4$, $n_1=n_2=0$, $-Z^2\epsilon_0$ 1404, 764, 160 $(\mathcal{E}/Z^3)^4$, agrees with unpublished results of Mendelsohn's method.[16] The above comparisons check the correctness of six of the ten terms in the bracket multiplying the fourth-order term in Eq. (17). The authors have not been able to see Basu's paper[4] because of its inaccessibility, and thus have not been able to check the correctness of the entire $O(F^4)$ term. But it appears that the quantization rule leads to the correct results in the weak-field limit.

IV. STRONG-FIELD LIMIT

We now proceed to find the range of "weak" fields for which Eq. (17) is an accurate representation of the energy eigenvalues. It is useful to rewrite the latter in the form

$$E=-\frac{\epsilon_0}{2n^2}\{1+3[(n_1-n_2)/n]R_n+(1/8n^2)[17n^2-3(n_1-n_2)^2-9m^2+19]R_n{}^2+\frac{3}{16}[(n_1-n_2)/n^3][23n^2-(n_1-n_2)^2$$

$$+11m^2+39]R_n{}^3+(1/512n^4[5487n^4+35\,182-1134m^2(n_1-n_2)^2+1806n^2(n_1-n_2)^2-3402n^2m^2-3093(n_1-n_2)^4$$

$$-549m^4+5754(n_1-n_2)^2-8622m^2+16\,211]R_n{}^4\}, \qquad (18)$$

where $R_n=(\mathcal{E}/Z^3)n^4$. R_n is the ratio of F to the electric field due to the nucleus at a distance of the nth Bohr radius of the given atom. It can be seen that the coefficients of powers of R_n are bounded for all n. Thus, the relative magnitude of successive terms in the series for high fields depends almost solely on the possible values of R_n. Table I gives the largest possible values of R_n, $R_{n\,\max}$, for several states with extreme values of n_1 and n_2 calculated from the observed ionization fields of those states.[17] For states with intermediate values of the quantum numbers, $R_{n\,\max}$ will have values intermediate to those shown above.

The rate of decrease of successive terms of Eq. (18) at high fields will be poorest when n_2 is near its maximum value. Thus, it is important to determine unambiguously the accuracy of the perturbation series given by Eq. (18) for these states at high fields. To do this, we integrated the quantization rule represented by Eq. (15) numerically.

The use of one, two, or all three of the integrals in (15) gives numerical eigenvalues correct to $O(\hbar)$, $O(\hbar^2)$, and $O(\hbar^4)$, respectively. The first integral was evaluated numerically along the ξ axis of Fig. 3 from A to B, since its integrand has no singularities. This procedure is not applicable to the other integrals since their integrands have nonintegrable singularities at A and B. Thus, the integration was carried out about a circular contour enclosing A and B. The phases were defined as in Fig. 3 in order to ensure the single-valued nature of all integrands. All integrals were evalu-

TABLE I. Values of $R_{n\,\max}$ for hydrogen.

n	n_1	n_2	$\lvert m\rvert$	$R_{n\,\max}$	n	n_1	n_2	$\lvert m\rvert$	$R_{n\,\max}$
5	0	4	0	0.122	7	0	6	0	0.154
5	4	0	0	0.088	7	6	0	0	0.093
6	0	5	0	0.144	8	0	7	0	0.144
6	5	0	0	0.093	8	7	0	0	0.096

ated by using an IBM 360-50 computer and it was ensured that numerical errors appeared only in the sixth significant figure of the final results. An analogous procedure with reference to Fig. 4 was used for the η variable.

In carrying out the integration, trial values were chosen for E and β. If we denote by $I(F, E, \beta)$ the value of the integral on the left-hand side of Eq. (15) to a given order in $\hbar$, then the corrections for the trial values ΔE and $\Delta\beta$ are determined by the simultaneous equations

$$I(F,E,\beta)+\frac{\partial I\,(F,E,\beta)}{\partial E}\,\Delta E+\frac{\partial I\,(F,E,\beta(\Delta\beta}{\partial\beta}$$

$$=(n_1+\tfrac{1}{2})\,2\pi\hbar/(2\mu)^{1/2}\quad ,$$

$$I(-F,E,-\beta)+\frac{\partial I(-F,E,-\beta)}{\partial E}-\frac{\partial I(-F,E,-\beta)\,\Delta\beta}{\partial\beta}$$

$$=(n_2+\tfrac{1}{2})\,2\pi\hbar/(2\mu)^{1/2}.$$

The partial derivatives above are determined by the method of finite differences. By replacing E by $E+\Delta E$, and β by $\beta+\Delta\beta$, and iterating the above procedure, we obtain the numerical approximation for E to a given order in $\hbar$.

Table II shows the values of the Stark shift obtained in this manner for the ground state of hydrogen at high fields. These results are compared with those predicted by the perturbation series of Mendelsohn[15] up to the tenth order in the field, and with the results obtained by Alexander[18] who has recently given a detailed numerical analysis of the Stark effect in the ground state of hydrogen. For fields for which $\mathcal{E} < 0.03$, Alexander finds reasonable agreement between his results and those of fourth-order perturbation theory. For fields for which $0.03 \leq \mathcal{E} \leq 0.06$ he uses a modified WKB approach to find the eigenvalues. We find that our WKB eigenvalues fall almost exactly between his results and those of fourth-order perturbation theory in this range. Alexander also calculates the Stark shift for $0.07 \leq \mathcal{E} \leq 0.12$ but we can make no comparison with these results, since, for $\mathcal{E} > 0.065$, the potential barrier in the direction opposite the field, which is responsible for binding, is already lower than the binding energy.[15] In these situations one cannot speak of bound states in any sense (even if tunneling is neglected), although metastable states arising from resonant scattering can exist.[18]

The comparison of Table II is, however, of academic importance only. The ionization fields of the $n = 2$ states in hydrogen are estimated by Mendelsohn's method to be of the order of 0.004 a.u., other states having even lower ionization fields. Thus, no spectral lines are possible for fields larger than approximately 0.004 a.u. But even at this field the Stark shift for the ground

TABLE II. Stark shift for the ground state of hydrogen at high fields.

Field strength (a.u.)	Stark shift ($\times 10^{-3}$ a.u.)								
	This work			Alexander[a]	Mendelsohn[b]				
	$O(\hbar)$	$O(\hbar^2)$	$O(\hbar^4)$		$O(F^2)$	$O(F^4)$	$O(F^6)$	$O(F^8)$	$O(F^{10})$
0.03	−0.961	−2.046	−2.072	−2.074273	−2.0250	−2.0700	−2.0736	−2.0741	−2.0742
0.04	−1.713	−3.669	−3.757	−3.7715	−3.6000	−3.7422	−3.7623	−3.7675	−3.7695
0.05	−2.691	−5.794	−6.029	−6.105	−5.6250	−5.9722	−6.0488	−6.0799	−6.0989
0.06	−3.898	−8.449	−8.995	−9.20	−8.1000	−8.8199	−9.0489	−9.1823	−9.2999

[a] See Ref. 18.

[b] See Ref. 15.

state given by Alexander agrees with that of fourth-order perturbation theory to better than one part in 10^6. There is at present no spectroscopic technique able to measure a shift so accurately. Furthermore, it is easy to show that the ionization field is given by[15] $\mathcal{E} = (1/4Z)\,E^2$, where E is the energy in a.u. Since the ground-state energy is such a slowly varying function of the field, we find that $\mathcal{E}$ = 0.065 a.u. (3.3×10^8 V/cm) whether we use E calculated using second-order or higher-order perturbation theory. The latter result is identical to that obtained using a two-parameter variational calculation[19] and is in good agreement with the experimental value[20] of about 3×10^8 V/cm determined from a field-emission experiment. Thus, fourth-order perturbation theory is perfectly adequate for the ground state.

Table III gives a comparison of the WKB eigenvalues obtained by numerically integrating the quantization rule, and the eigenvalues predicted by the perturbation series [Eq. (18)] for several excited states, for values of R_n near $R_{n\,\max}$ (fields near the ionization field). The eigenvalues in all cases have been divided by the respective energies at zero field in order to make comparisons between different states meaningful. Only states with n_2 attaining its maximum value are shown. It is for these kinds of states that the perturbation series will "converge" most slowly at fields near the ionization field.

It may be seen that for the states shown, the WKB series of eigenvalues converges much more rapidly than does the perturbation series. Previous work[13] on the numerical evaluation of the WKB quantization rule [Eq. (6)] has found that for excited states, the difference between the $O(\hbar^4)$ WKB eigenvalue and the eigenvalue obtained by a numerical integration of Schrödinger's equation is generally smaller than the difference between the $O(\hbar^4)$ and $O(\hbar^2)$ WKB eigenvalues. Thus, we will take the $O(\hbar^4)$ results in Table III as the "exact" eigenvalues, and the difference between $O(\hbar^4)$ and $O(\hbar^2)$ as their uncertainty. We see that this uncertainty is only 0.01% of the energy. The perturbation eigenvalue to $O(F^3)$ is seen to be correct to 0.5% while the addition of the $O(F^4)$ term improves the accuracy to 0.1% or better for the states shown. For other states (with n_2 not its maximum value), or for lower fields, we know that the perturbation series converges more rapidly than for the case already considered because of lower values of R_n. Thus, we expect the series to be even more accurate than the above estimates suggest. We may conclude that for all excited states and all possible fields below ionization the addition of the $O(F^4)$ term will improve the accuracy of the perturbation series.

This conclusion does not agree with that reached by Basu[4, 11] who appears to have derived the fourth-order term by perturbation theory. He concluded

TABLE III. Energy eigenvalues of excited states of hydrogen at their respective ionization fields.[a]

n[c]	$Rn \cong R_{n\max}$	WKB Shifts $O(\hbar)$	$O(\hbar^2)$	$O(\hbar^4)$	Perturbation Shifts[b] $O(F)$	$O(F^2)$	$O(F^3)$	$O(F^4)$
4	0.100	−0.79225	−0.79374	−0.79377	−0.77535	−0.79590	−0.79244	−0.79399
5	0.195	−0.72514	−0.72670	−0.72675	−0.70000	−0.73094	−0.72393	−0.72724
6	0.143	−0.67596	−0.67655	−0.67660	−0.64358	−0.68288	−0.67230	−0.67740
7	0.143	−0.66367	−0.66472	−0.66475	−0.63264	−0.67138	−0.66057	−0.66541

[a] The eigenvalues are given in units of the zero-field eigenvalue of that state.

[b] See Eq. (18).

[c] For all cases shown $n_1 = 0$, $m = 0$, $n_2 = n - 1$.

that at higher fields the best accuracy could be obtained by neglecting the $O(F^4)$ term. He arrived at this result by comparing the predictions of the series with the results of an experiment.[17] In this experiment the electric fields were measured from the Stark shift of some spectral lines and then used to predict shifts of other lines. However, the fields calculated by Gebauer *et al.* appear to be in error, possibly as a result of inaccurate values of e, $\hbar$, and μ used in the calculations. Since the fourth-order Stark effect is minute even at high fields, these errors could well account for Basu's conclusions.

Considering now the measurement of fields from the observed Stark shifts, we see in Table III that the Stark shifts are as large as one-half of the total energy for the states shown at very high fields. The shift of a spectral line is due mostly to the shift in energy of the upper of the two states in question. Thus, an optimum measurement is accomplished when the upper state is near ionization, and thus has the largest shift possible. In that case the conditions studied here will be satisfied. For states with n_2 maximum we expect accuracies of 0.2% for the Stark shift of the line when calculated from the perturbation series to $O(F^4)$. For such states most of the shift (90%) is of first order, so that the electric fields can be calculated to 0.2% accuracy from the measured shifts. For other kinds of states the accuracy might be larger because the perturbation series is expected to be more accurate, though this gain might be partially canceled by the fact that for other states the Stark shift is a smaller fraction of the total energy.

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APPENDIX

We give an example of the evaluation of the quantization rule. The first integral in Eq. (15) is to $O(F)$

$$\oint\left(\tfrac{1}{4}E+\frac{Ze^2+\beta}{4\xi}-\frac{m^2}{4\xi^2}\frac{\hbar^2}{2\mu}\right)^{1/2}d\xi+\tfrac{1}{16}eF\oint\xi d\xi\Big/\left(\tfrac{1}{4}E+\frac{Ze^2+\beta}{4\xi}-\frac{m^2}{4\xi^2}\frac{\hbar^2}{2\mu}\right)^{1/2} \circ$$

The integrand has only two branch points. Thus, we may use the method of residues to evaluate it. The residue of the integrand of the first integral above at $\xi = 0$ is (see Fig. 3 for sign) $-i\frac{1}{2}\,|m|\,\hbar/(2\mu)^{1/2}$, while the integrand of the second has no residue there. Changing variables to $z = 1/\xi$ we have

$$-\oint\left[\tfrac{1}{4}E+\tfrac{1}{4}(Ze^2+\beta)z-\tfrac{1}{4}m^2(\hbar^2/2\mu)z^2\right]^{1/2}\frac{dz}{z^2}-\tfrac{1}{16}eF\oint\left[\tfrac{1}{4}E+\tfrac{1}{4}(Ze^2+\beta)z-\tfrac{1}{4}m^2(\hbar^2/2\mu)z^2\right]^{-1/2}\frac{dz}{z^3}\ .$$

The residues at $z = 0(\xi = \infty)$ are

$$-\frac{1}{4i}\frac{Ze^2+\beta}{(-E)^{1/2}}\,,\qquad -\tfrac{1}{16}eF\left(-\tfrac{1}{2}m^2\frac{1}{i(-E)^{3/2}}\frac{\hbar^2}{\mu}+\tfrac{3}{4}\frac{(Ze^2+\beta)^2}{i(-E)^{5/2}}\right)\ .$$

The second integral in Eq. (15) is to $O(F)$

$$-\frac{\hbar^2}{64\mu}\oint\left\{\left[\tfrac{1}{2}E\xi+\tfrac{1}{4}(Ze^2+\beta)\right]^2/\left[\tfrac{1}{4}E+(Ze^2+\beta)/4\xi-(m^2/4\xi^2)\hbar^2/2\mu\right]^{5/2}\right\}\frac{d\xi}{\xi^4}$$

$$-\frac{\hbar^2}{64\mu}\tfrac{3}{4}eF\oint\left\{\left[\tfrac{1}{2}E\xi+\tfrac{1}{4}(Ze^2+\beta)\right]/\left[\tfrac{1}{4}E+(Ze^2+\beta)/4\xi-(m^2/4\xi^2)\hbar^2/2\mu\right]^{5/2}\right\}\frac{d\xi}{\xi^2}$$

$$+(\hbar^2/64\mu)\tfrac{5}{16}eF\oint\left\{\tfrac{1}{2}E\xi+\tfrac{1}{4}(Ze^2+\beta)\right]^2/\left[\tfrac{1}{4}E+(Ze^2+\beta)/4\xi-(m^2/4\xi^2)\hbar^2/2\mu\right]^{7/2}\right\}\frac{d\xi}{\xi^3}\ .$$

None of the above integrands has a nonzero residue at $\xi = 0$. By changing variables to $z = 1/\xi$ it can be shown, as we did above, that the residues at $z = 0$ are, respectively,

$$0, \quad + \tfrac{3}{16}\, eF\, (\hbar^2/\mu)\, i\, (-E)^{-3/2}\ , \quad \text{and } -\tfrac{5}{32} eF\, (\hbar^2/\mu)\, i (-E)^{-3/2}\ .$$

The third integral in Eq. (15) can be shown not to contribute in $O(F)$ so that the quantization rule to $O(F)$ is obtained by multiplying $-2\pi i$ by the sum of residues that we have obtained. We obtain

$$\frac{\pi}{\sqrt{2}}\, \frac{Ze^2+\beta}{(-E)^{1/2}} - \pi\, |m|\, \frac{\hbar}{(2\mu)^{1/2}} - \tfrac{1}{16} eF\, \pi\, \frac{\hbar^2}{\mu}\, \frac{m^2-1}{(-E)^{3/2}} + \tfrac{3}{32}\, \pi\, eF\, \frac{(Ze^2+\beta)^2}{(-E)^{5/2}}$$

as the left-hand side of Eq. (15) to $O(F)$. Multiplying the quantization rule by $(-2E)^{1/2}$, and transferring the term proportional to $|m|$ to the right-hand side of the equation, we reduce the quantization rule to

$$\frac{\pi}{\sqrt{2}} (Ze^2+\beta) + \frac{eF}{E^2} \left[\tfrac{3}{32}\pi\sqrt{2}\, (Ze^2+\beta)^2 + (m^2-1)\, \tfrac{1}{16}\, \pi\sqrt{2}\, (\hbar^2/\mu) E\right] = (n_1 + \tfrac{1}{2} + \tfrac{1}{2}\, |m|)\, 2\pi\, \frac{\hbar}{(2\mu)^{1/2}} (-2E)^{1/2}\ , \tag{A1}$$

which contains the first terms of Eq. (16). The quantization rule for the η equation is

$$\frac{\pi}{\sqrt{2}} (Ze^2-\beta) - \frac{eF}{E^2} \left[\tfrac{3}{32}\, \pi\sqrt{2}\, (Ze^2-\beta)^2 + (m^2-1)\, \tfrac{1}{16}\, \pi\sqrt{2}\, \frac{\hbar^2}{\mu} E\right] = (n_2 + \tfrac{1}{2} + \tfrac{1}{2}\, |m|)\, 2\pi\, \frac{\hbar}{(2\mu)^{1/2}} (-2E)^{1/2}\ . \tag{A2}$$

Letting $E = E^{(0)} + E^{(1)}F$, and $\beta = \beta^{(0)} + \beta^{(1)}F$, adding (A1) and (A2) and keeping terms through $O(F)$ we obtain

$$\frac{2\pi}{\sqrt{2}} Ze^2 + \frac{2eF}{[E^0]^2} \left[\tfrac{3}{32}\, \pi\sqrt{2}\ 4\beta^{(0)}\, Ze^2\right] = n\, 2\pi\, \frac{\hbar}{2\mu} \left((-2E^{(0)})^{1/2} - \frac{E^{(1)}F}{(-2E^{(0)})^{1/2}}\right)\ , \tag{A3}$$

with $n = n_1 + n_2 + |m| + 1$.

From the zeroth-order terms it follows that

$$E^{(0)} = -\frac{Z^2 e^4 \mu}{2\hbar^2 n^2} = -\frac{Z^2 \epsilon_0}{2n^2}\ . \tag{A4}$$

Subtracting (A2) from (A1) and keeping only zeroth-order terms we obtain

$$(2\pi/\sqrt{2})\, \beta^{(0)} = (n_1 - n_2)\, 2\pi\, [\hbar/(2\mu)^{1/2}] (-2E^{(0)})^{1/2},$$

from which

$$\beta^{(0)} = Ze^2(n_1 - n_2)/n. \tag{A5}$$

From the first-order term in (A3) and the use of (A4) and (A5), we obtain

$$E^{(1)}F = -\tfrac{3}{2} (\hbar^2/Ze\mu)\, n(n_1 - n_2) = -Z^2\epsilon_0\, \tfrac{3}{2}\, n(n_1 - n_2)\, \mathcal{E}/Z^3\ . \tag{A6}$$

Equations (A4) and (A6) are the first terms of Eq. (17). The rest may be obtained in an analogous way.

It is important to point out that the direct application of the quantization rule [Eq. (6)] to the singular equations (12a) and (12b) will not lead to the above results. For example, the factor of $m^2 - 1$ in these equations will lead, in analogy with the development of this Appendix, to the expression $n = n_1 + n_2 + (m^2-1)^{1/2} + 1$, rather than $n = n_1 + n_2 + |m| + 1$ in the zero-field energy (A4).

Note that for $m = 0$ the eigenvalues would be complex. The fact that more accurate results are obtained by replacing $M^2 - 1$ by m^2, when the WKB quantization condition is applied to Eqs. (12a) and (12b), has been previously noted.[21]

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