PHYSICAL REVIEW A VOLUME 18, NUMBER 5 NOVEMBER 1978

Perturbation theory of the Stark effect in hydrogen to arbitrarily high order

Harris J. Silverstone
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

(Received 5 December 1977)

The solution of the Stark effect in hydrogen to arbitrarily high orders of perturbation theory is made feasible by the explicit formula for the Nth-order energy in terms of the separation constants through Nth order, derived here. The Nth-order separation constant $\beta_i^{(N)}$ is shown to be a polynomial of total degree $N+1$ in the parabolic quantum number n_i and the magnetic quantum number m. The polynomial coefficients have been tabulated through seventeenth order and are listed here through tenth order. Similarly, the Nth-order energy is a polynomial in the quantum numbers n_1, n_2, and m. The polynomial coefficients (which are more numerous than for $\beta_i^{(N)}$) have been tabulated through seventeenth order and are listed here through seventh order. Seventeenth order is high enough to permit a clear numerical demonstration of the asymptotic character of the perturbation series, and a "maximum useful field strength" is defined and illustrated. Energies calculated by perturbation theory for specific states are shown to be in excellent agreement with energies calculated nonperturbatively.

I. INTRODUCTION

The Stark effect in hydrogen was the first quantum-mechanical problem to be treated by Rayleigh-Schrödinger perturbation theory.[1] The perturbed energy is easy to obtain in first and second order. Third order[2] requires some effort, but fourth order[3,4] is already so tedious that the correct formula was finally obtained only in 1973.[5] Higher orders have not been published, except for the ground state,[6,7] although there have been a number of nonperturbative calculations.[8–16]

Recently there has been experimental interest in high Rydberg states of atoms.[17] Since detection techniques for these hydrogenic states have involved ionization of the atoms by an external electric field, it is of some interest to have accurate formulas for the Stark shifts and for the ionization lifetimes. The asymptotic formula[18,19] for the lifetimes depends sensitively on the accuracy of the computed perturbed energy and separation constant.

The purpose of this paper is to discuss the solution of the Stark effect in hydrogen to arbitrarily high orders of perturbation theory.

In each order of perturbation theory, the separation constant and energy are polynomials in the parabolic and magnetic quantum numbers. We show that the total degree of the polynomials is only about half of that expected. We give the polynomial coefficients for the separation constant to tenth order and the energy coefficients to seventh order. Tables of both through seventeenth order are available from the Physics Auxiliary Publication Service (PAPS).[20]

Although the relation between the values of the separation constants and the energy is very simple, the relation between the two perturbation series is not, because the expansion parameter for the separation constant series explicitly involves the energy. In the past it was unnecessary to go beyond fourth order, and a successive substitution method sufficed. Here the order may be arbitrarily high, so that we must derive the explicit relationship between the two series.

The Stark-effect perturbation series do not converge: they are asymptotic.[21] For a given number of terms, it is possible to find a heuristic maximum useful field strength, which we illustrate through some simple numerical calculations.

II. PERTURBATION THEORY EQUATIONS FOR THE SEPARATION CONSTANTS

In this section the perturbation-theory equations for the separation constants are restated so that all the relevant quantities are polynomials in the quantum numbers.

The Schrödinger equation for hydrogen in a uniform electrostatic field,

$$(-\tfrac{1}{2}\nabla^2 - 1/r + Fz - E)\Psi = 0 \tag{1}$$

separates in scaled parabolic coordinates,[1,22,23]

$$x=(-2E)^{-1/2}(\sigma\rho)^{1/2}\cos\phi\,, \tag{2}$$

$$y=(-2E)^{-1/2}(\sigma\rho)^{1/2}\sin\phi\,, \tag{3}$$

$$z=\tfrac{1}{2}(-2E)^{-1/2}(\sigma-\rho)\,, \tag{4}$$

$$\Psi=(\sigma\rho)^{-1/2}\Phi_1(\sigma)\Phi_2(\rho)e^{im\phi}\,, \tag{5}$$

$$\left[-\sigma\left(\frac{d}{d\sigma}\right)^2+\frac{(m^2-1)}{(4\sigma)}+\tfrac{1}{4}\sigma+f\sigma^2-\beta_1\right]\Phi_1(\sigma)=0\,, \tag{6}$$

$$\left[-\rho\left(\frac{d}{d\rho}\right)^2+\frac{(m^2-1)}{(4\rho)}+\tfrac{1}{4}\rho-f\rho^2-\beta_2\right]\Phi_2(\rho)=0\,, \tag{7}$$

$$f=\tfrac{1}{4}(-2E)^{-3/2}F\,. \tag{8}$$

The energy is determined from the separation constants by

$$E=-\tfrac{1}{2}(\beta_1+\beta_2)^{-2}\,. \qquad (9)$$

Since the quantum number m appears only in the form $\frac{1}{4}(m^2-1)$, we denote the combination by M for convenience[24]

$$M=\tfrac{1}{4}(m^2-1)\,. \qquad (10)$$

We also introduce the symbol k_i for the unperturbed separation constants,[5] which play a major role in subsequent formulas

$$k_i=\beta_i^{(0)} \qquad (11)$$

$$=n_i+\tfrac{1}{2}|m|+\tfrac{1}{2}\quad (n_i=0,1,2,\ldots)\,. \qquad (12)$$

k_i is a more convenient label than the parabolic quantum numbers n_1 and n_2.

Since the essential difference between Eqs. (6) and (7) for β_1 and β_2 is the sign of f, it is sufficient to consider only one, say Eq. (6), and we write

$$\beta_1=\beta(k_1,M,f)\,, \qquad (13)$$

$$\beta_2=\beta(k_2,M,-f)\,, \qquad (14)$$

$$\beta(k,M,f)=\sum_{n=0}^{\infty}\beta^{(N)}(k,M)f^N\,. \qquad (15)$$

When there is no danger of confusion, subscripts will be omitted. Subscripts will be indicated for the parabolic quantum numbers n_1 and n_2, however, because we wish to reserve n (without a subscript) to represent the "principal quantum number."

To make all the important quantities in the calculation polynomials, we introduce an *un-normalized* basis. Let $|j\rangle$ denote the function,

$$|j\rangle=N_j[(n_1+j)!/(n_1+j+|m|)!^3]^{1/2}$$

$$\times\,\sigma^{(|m|+1)/2}e^{-\sigma/2}L_{n_1+j+|m|}^{|m|}(\sigma)\,, \qquad (16)$$

where $L_{n_1+j+|m|}^{|m|}$ denotes the usual generalized Laguerre polynomial,[25] and N_j is a constant that spoils the normalization, given by

$$N_j=\prod_{i=0}^{j-1}[(k+i)(k+i+1)-M]^{1/2}\quad (j\geq 1)$$

$$=1\quad (j=0) \qquad (17)$$

$$=\prod_{i=1}^{|j|}[(k-i)(k-i+1)-M]^{-1/2}\quad (-1\geq j\geq -n_1)\,. \qquad (18)$$

[Here k means $n_1+\frac{1}{2}|m|+\frac{1}{2}$, as in Eq. (12).] The $|j\rangle$ are eigenfunctions of the unperturbed Hamiltonian $h^{(0)}$,

$$h^{(0)}|j\rangle=\left[-\sigma\left(\frac{d}{d\sigma}\right)^2+\frac{M}{\sigma}+\tfrac{1}{4}\sigma\right]|j\rangle \qquad (19)$$

$$=(k+j)\,|j\rangle\,. \qquad (20)$$

Note that the difference of any two unperturbed eigenvalues is an integer. The function $|0\rangle$, which is normalized to unity (with volume element $\sigma^{-1}d\sigma$), is the unperturbed eigenfunction belonging to the unperturbed separation constant k.

The matrix of the perturbation, which is defined by

$$\sigma^2|j\rangle=\sum_i v_{ij}(k,M)\,|i\rangle\,, \qquad (21)$$

is straightforward to evaluate from the well-known properties of the generalized Laguerre polynomials.[26] One finds that the nonzero v_{ij} are polynomials in k and M:

$$v_{ij}(k,M)=1\quad (i=j+2) \qquad (22)$$

$$=-4(k+j+\tfrac{1}{2})\quad (i=j+1) \qquad (23)$$

$$=6(k+j)^2-2M\quad (i=j) \qquad (24)$$

$$=-4(k+j-\tfrac{1}{2})[(k+j-1)(k+j)-M]\quad (i=j-1) \qquad (25)$$

$$=[(k+j-2)(k+j-1)-M]\times[(k+j-1)(k+j)-M]\quad (i=j-2) \qquad (26)$$

$$=0\quad (|i-j|>2)\,. \qquad (27)$$

In the usual manner, with "intermediate normalization," we expand the perturbed eigenfunctions $\Phi^{(N)}$ on the basis $\{|j\rangle\}$ and obtain recursive relations for the expansion coefficients and for the separation constant:

$$\Phi=\sum_N \Phi^{(N)}f^N\,, \qquad (28)$$

$$\Phi^{(0)}=|0\rangle\,, \qquad (29)$$

$$\Phi^{(N)}=\sum_{j\neq 0}c_j^{(N)}(k,M)\,|j\rangle\quad (N\geq 1)\,, \qquad (30)$$

$$c_j^{(0)}=\delta_{j0}\,, \qquad (31)$$

$$c_l^{(N)}=-\frac{1}{l}\left(\sum_{j\neq 0}v_{lj}c_j^{(N-1)}-\sum_{\nu=1}^{N-1}\beta^{(N-\nu)}c_j^{(\nu)}\right)\quad (l\neq 0)\,, \qquad (32)$$

$$\beta^{(N)}(k,M)=\sum_{j\neq 0}v_{0j}c_j^{(N-1)}\,. \qquad (33)$$

Because each nonzero v_{ij} is a polynomial in k and M of total degree $2-i+j$ (where $|i-j|\leq 2$) in k and $M^{1/2}$, it is apparent from Eqs. (31)–(33) that the wave function coefficients $c_l^{(N)}$ are also polynomials in k and M of total degree $2N-l$ in k and $M^{1/2}$. (Note that l must satisfy $-2N\leq l\leq 2N$ for $c_l^{(N)}$ to be nonzero.) Similarly, the separation constants $\beta^{(N)}(k,M)$ are polynomials in k and M of maximum total degree $2N$ in k and $M^{1/2}$. Actually, we prove in Sec. III that the degree of

$\beta^{(N)}$ is only $N+1$. Since $\beta^{(N)}$ is known[5] to have parity $(-1)^{N+1}$ with respect to k, we can write for $c_j^{(N)}$ and for $\beta^{(N)}$,

$$c_j^{(N)}(k,M) = \sum_{s=0}^{2N-j} \sum_{r=0}^{[(2N-j-s)/2]} c_{jrs}^{(N)} M^r k^s , \qquad (34)$$

$$\beta^{(N)} = \sum_{r=0}^{[(N+1)/2]} \sum_{t=0}^{[(N+1)/2]-r} \beta_{r,N+1-2r-2t}^{(N)} \times M^r k^{N+1-2r-2t} , \qquad (35)$$

where $c_{jrs}^{(N)}$ and $\beta_{rs}^{(N)}$ are constant coefficients, and where $[i]$ denotes the greatest integer $\leqslant i$.

By programming the recursion formulas (31)–(33) with the polynomial formulas (34), (35), and (22)–(27), one can generate with a computer the numerical values for the polynomial coefficients to as high an order as is desired. In Table I we have listed $\beta_{rs}^{(N)}$ for $N \leqslant 10$. Orders 1–4 agree with Alliluev and Malkin.[5] The coefficients appear to be even integers for $N \leqslant 10$. Since the calculation has been carried out in double precision on a Digital Equipment Corp. System-10 computer, it is not possible to tell if the coefficients are integers beyond tenth order, as the numbers of significant digits in the $\beta_{rs}^{(N)}$ are too large. The number of nonzero $\beta_{rs}^{(2N)}$ in $2N$th order is $\frac{1}{2}(N+1)(N+2)$, and the number in $(2N+1)$st order is $\frac{1}{2}(N+1)(N+4)$. Tables of $\beta_{rs}^{(N)}$ for $N \leqslant 17$ are available from PAPS.[20]

TABLE I. Separation constant, orders 1–10. $\beta^{(N)} = \sum \beta_{rs}^{(N)} M^r k^s$.

N	r	s	$\beta_{rs}^{(N)}$	N	r	s	$\beta_{rs}^{(N)}$	N	r	s	$\beta_{rs}^{(N)}$
1	0	2	6	7	0	2	484 419 360		1	6	−18 689 372 876 160
	1	0	−2		0	4	3 997 074 984		1	8	−4 741 154 003 520
					0	6	6 142 374 000		2	0	104 008 003 840
2	0	1	−10		0	8	1 905 807 816		2	2	2 121 721 190 976
	0	3	−68		1	0	−60 441 600		2	4	4 891 069 777 440
	1	1	36		1	2	−1 663 495 776		2	6	2 112 491 924 256
					1	4	−4 778 464 320		3	0	−25 354 142 720
3	0	2	660		1	6	−2 379 352 416		3	2	−313 679 336 640
	0	4	1 500		2	0	46 142 240		3	4	−313 746 377 280
	1	0	−120		2	2	657 768 432		4	0	2 306 958 208
	1	2	−1 032		2	4	728 298 480		4	2	12 987 661 680
	2	0	44		3	0	−8 886 688		5	0	−66 513 664
					3	2	−53 877 984				
4	0	1	−2 210		4	0	450 696	10	0	1	−6 733 922 487 500
	0	3	−37 900						0	3	−255 756 162 331 848
	0	5	−42 756	8	0	1	−2 564 063 050		0	5	−1 272 588 709 670 760
	1	1	12 960		0	3	−83 943 936 120		0	7	−1 872 704 078 101 248
	1	3	35 640		0	5	−331 953 386 940		0	9	−947 164 090 664 440
	2	1	−3 636		0	7	−330 097 271 640		0	11	−131 843 747 886 864
					0	9	−75 783 847 700		1	1	59 428 632 961 080
5	0	2	381 264		1	1	20 998 605 600		1	3	640 629 497 858 400
	0	4	2 093 280		1	3	182 925 628 704		1	5	1 534 645 588 890 960
	0	6	1 400 784		1	5	302 909 140 800		1	7	1 130 767 102 209 600
	1	0	−54 240		1	7	104 928 884 208		1	9	218 322 729 416 880
	1	2	−1 029 600		2	1	−12 837 436 200		2	1	−40 501 147 719 024
	1	4	−1 364 160		2	3	−60 110 940 120		2	3	−271 104 353 086 320
	2	0	33 712		2	5	−39 436 837 272		2	5	−369 115 567 782 192
	2	2	229 200		3	1	2 155 524 912		2	7	−112 468 417 051 680
	3	0	−3 680		3	3	4 336 206 000		3	1	8 691 108 323 328
					4	1	−98 489 844		3	3	35 612 199 123 840
6	0	1	−1 656 500						3	5	21 237 767 907 552
	0	3	−43 002 592	9	0	2	1 078 065 703 680		4	1	−717 606 581 400
	0	5	−113 822 520		0	4	11 206 248 868 800		4	3	−1 343 525 553 360
	0	7	−50 118 384		0	6	25 598 194 895 280		5	1	19 093 706 352
	1	1	12 051 720		0	8	17 695 955 613 600				
	1	3	72 439 200		0	10	3 118 465 869 552				
	1	5	55 719 216		1	0	−123 998 092 800				
	2	1	−5 881 416		1	2	−4 217 580 898 560				
	2	3	−13 182 480		1	4	−17 545 111 106 880				
	3	1	552 912								

III. THEOREM ON TOTAL DEGREE OF $\beta^{(N)}$

In this section we prove that the total degree of $\beta^{(N)}$ with respect to k and $M^{1/2}$ is $N+1$.

Alliluev and Malkin[5] observed extensive cancellation in calculating $\beta^{(2)}$, $\beta^{(3)}$, and $\beta^{(4)}$ that reduced the total degrees in k and $M^{1/2}$ to 3, 4, and 5 from 4, 6, and 8, respectively. To prove the cancellation for arbitrary order, the author finds it necessary first to convert to an orthonormal basis, and then to introduce a new coordinate representation not directly connected to the σ representation, but which has the same matrix representation. The new coordinate representation yields a tractable equation for the logarithm of the eigenfunction, which in turn gives the polynomial degree of $\beta^{(N)}$ directly, without the necessity of cancelling higher terms.

The orthonormal basis is obtained by removing the N_j from the definition of the functions $|j\rangle$:

$$|j\rangle' = N_j^{-1}|j\rangle .$$

In the $|j\rangle'$ basis, the matrix of the perturbation becomes[27]

$$v'_{ij}(k,M) = [(k+j+1)(k+j+2)-M]^{1/2} \times [(k+j)(k+j+1)-M]^{1/2} \quad (i=j+2), \tag{36}$$

$$= -4(k+j+\tfrac{1}{2})\,[(k+j)(k+j+1)-M]^{1/2} \quad (i=j+1), \tag{37}$$

$$= 6(k+j)^2 - 2M \quad (i=j), \tag{38}$$

$$= -4(k+j-\tfrac{1}{2})[(k+j)(k+j-1)-M]^{1/2} \quad (i=j-1), \tag{39}$$

$$= [(k+j-2)(k+j-1)-M]^{1/2} \times [(k+j-1)(k+j)-M^{1/2} \quad (i=j-2), \tag{40}$$

$$= 0 \quad (|i-j|>2). \tag{41}$$

The new coordinate representation is obtained by the correspondence,

$$|\mu\rangle' = (2\pi)^{-1/2} e^{i\mu\phi} . \tag{42}$$

In the ϕ representation the unperturbed Hamiltonian is essentially the angular momentum operator $\hat{l}_z$, while v becomes a function of both ϕ and $\hat{l}_z$

$$h^{(0)} = \hat{l}_z + k \tag{43}$$

$$= -i\,\frac{d}{d\phi} + k , \tag{44}$$

$$\begin{aligned}\hat{v} = {}& e^{2i\phi}[(k+\hat{l}_z)(k+\hat{l}_z+1)-M]^{1/2}[(k+\hat{l}_z+1)(k+\hat{l}_z+2)-M]^{1/2} - 4e^{i\phi}(k+\hat{l}_z+\tfrac{1}{2})[(k+\hat{l}_z)(k+\hat{l}_z+1)-M]^{1/2} \\ &+ 6(k+\hat{l}_z)^2 - 2M - 4e^{-i\phi}(k+\hat{l}_z-\tfrac{1}{2})[(k+\hat{l}_z)(k+\hat{l}_z-1)-M]^{1/2} + e^{-2i\phi}[(k+\hat{l}_z-2)(k+\hat{l}_z-1)-M]^{1/2} \\ &\times [(k+\hat{l}_z-1)(k+\hat{l}_z)-M]^{1/2} .\end{aligned} \tag{45}$$

The unperturbed eigenfunction $\Phi^{(0)}$ is just the constant $(2\pi)^{-1/2}$.

We introduce what is essentially the logarithmic derivative of Φ by

$$\Phi(\phi) = (2\pi)^{-1/2} \exp\left[i\int^{\phi} \chi(\phi')\,d\phi'\right], \tag{46}$$

where $\chi \to 0$ when $f \to 0$. Since $\Phi(\phi)$ is single valued, we must have

$$\int_0^{2\pi} \chi(\phi)\,d\phi = 0 . \tag{47}$$

The eigenvalue equation for Φ then yields the equation satisfied by χ,

$$\chi(\phi) + k - \beta = -\exp\left[-i\int^{\phi} \chi(\phi')\,d\phi'\right] f\hat{v} \exp\left[i\int^{\phi} \chi(\phi')\,d\phi'\right] . \tag{48}$$

For the purpose of obtaining the behavior of χ and β for large k and M, we expand $\hat{v}$ in a power series in $\hat{l}_z$,

$$\hat{v} = v_0(\phi) + v_1(\phi)\hat{l}_z + v_2(\phi)\hat{l}_z^2 + \cdots , \tag{49}$$

and χ in a power series in f,

$$\chi = f\chi^{(1)} + f^2\chi^{(2)} + \cdots . \tag{50}$$

The v_μ depend on ϕ; for instance,

$$v_0(\phi)=e^{2i\phi}[k(k+1)-M]^{1/2}[(k+1)(k+2)-M]^{1/2}-4e^{i\phi}(k+\tfrac{1}{2})[k(k+1)-M]^{1/2}+6k^2-2M$$
$$-4e^{-i\phi}(k-\tfrac{1}{2})[k(k-1)-M]^{1/2}+e^{-2i\phi}[(k-1)(k-2)-M]^{1/2}[(k-1)k-M]^{1/2}. \qquad (51)$$

From Eqs. (45) and (49) we can characterize the behavior of v_μ for large k and M, or more precisely, for fixed but arbitrary k^2/M,

$$v_\mu(\phi)=O[(ak+bM^{1/2})^{2-\mu}], \qquad (52)$$

where the constants a and b depend on the ratio k^2/M.

The system of equations obtained by substituting Eqs. (15), (49), and (50) for β, $\hat{v}$, and χ into Eq. (48) and collecting froms of the same order in f,

$$k-\beta^{(0)}=0, \qquad (53)$$

$$\chi^{(1)}-\beta^{(1)}=-v_0(\phi), \qquad (54)$$

$$\chi^{(2)}-\beta^{(2)}=-\sum_{\mu=1}^{\infty}v_\mu(\phi)\left(-i\frac{d}{d\phi}\right)^{\mu-1}\chi^{(1)}, \qquad (55)$$

$$\chi^{(3)}-\beta^{(3)}=-\sum_{\mu=1}^{\infty}v_\mu(\phi)\left(-i\frac{d}{d\phi}\right)^{\mu-1}\chi^{(2)}-\sum_{\mu=0}^{\infty}v_\mu(\phi)(-i)^{\mu-2}\sum_{\nu=1}^{\mu-1}\binom{\mu-1}{\nu}\left[\left(\frac{d}{d\phi}\right)^{\mu-1-\nu}\chi^{(1)}\right]\left[\left(\frac{d}{d\phi}\right)^{\nu-1}\chi^{(1)}\right], \qquad (56)$$

and so forth, can be solved recursively. The $\beta^{(N)}$ are obtained via the single-valuedness condition (47)

$$\beta^{(1)}=(2\pi)^{-1}\int_0^{2\pi}v_0(\phi)\,d\phi, \qquad (57)$$

$$\beta^{(2)}=(2\pi)^{-1}\int_0^{2\pi}\sum_{\mu=1}^{\infty}v_\mu(\phi)\left(-i\frac{d}{d\phi}\right)^{\mu-1}\chi^{(1)}\,d\phi, \qquad (58)$$

and so forth. It is not our purpose to solve Eqs. (53)–(56) for $\chi^{(N)}$ and $\beta^{(N)}$, but only to determine their behavior for large k and M. From Eqs. (51), (52), and (57), we see that $\chi^{(1)}$ and $\beta^{(1)}$ are $O[(ak+bM^{1/2})^2]$. From Eqs. (52) and (55), we see that $\chi^{(2)}$ and $\beta^{(2)}$ are $O[(ak+bM^{1/2})^3]$. It follows inductively from Eqs. (52) and (47) and from the system of equations whose first four members are Eqs. (53)–(56), that $\chi^{(N)}$ and $\beta^{(N)}$ are $O[(ak+bM^{1/2})^{N+1}]$. But since $\beta^{(N)}$ is a polynomial in k and M, to know its behavior for large k and $M^{1/2}$ is to know its total degree.

IV. PERTURBATION SERIES FOR E FROM THE SERIES FOR β_1 AND β_2

The usual procedure to obtain the series in F for E,

$$E=E^{(0)}+E^{(1)}F+E^{(2)}F^2+\cdots, \qquad (59)$$

from the series in f for $\beta_1+\beta_2$—expansion of $-\frac{1}{2}(\beta_1+\beta_2)^{-2}$ in a series in f and successive approximation to eliminate E from $f=F(-2E)^{-3/2}$—is unwieldy after the first few terms, and also unnecessary: the "formula of Lagrange"[28] performs both steps at once.

Let us denote by γ the sum of the separation constants,

$$\gamma=\beta_1+\beta_2 \qquad (60)$$

$$=\gamma^{(0)}+\gamma^{(1)}f+\gamma^{(2)}f^2+\cdots, \qquad (61)$$

$$\gamma^{(N)}=\beta_1^{(N)}+\beta_2^{(N)} \qquad (62)$$

$$=\beta^{(N)}(k_1,M)+(-1)^N\beta^{(N)}(k_2,M). \qquad (63)$$

γ may be regarded as the "perturbed principal quantum number," since $\gamma^{(0)}$ is the usual unperturbed principal quantum number n

$$\gamma^{(0)}=k_1+k_2 \qquad (64)$$

$$=n_1+n_2+|m|+1 \qquad (65)$$

$$=n. \qquad (66)$$

The explicit formula that we derive for $E^{(N)}$ in terms of the sums of the separation constants $\gamma^{(N)}$ is

$$E^{(N)}=4^{-N}\sum_{\substack{i_1\geq 0,\, i_2\geq 0,\,\cdots,\, i_n\geq 0\\ (i_1+2i_2+3i_3+\cdots+Ni_N=N)}}\frac{(3N-3)!}{(3N-2-\sum_j i_j)!\,i_1!\,i_2!\cdots i_N!}\gamma^{(0)3N-2-\Sigma_j i_j}\,\gamma^{(1)i_1}\,\gamma^{(2)i_2}\cdots\gamma^{(N)i_N}. \tag{67}$$

For example,

$$E^{(1)}=\tfrac{1}{4}\gamma^{(1)}, \tag{68}$$

$$E^{(2)}=4^{-2}(\gamma^{(0)3}\gamma^{(2)}+\tfrac{3}{2}\gamma^{(0)2}\gamma^{(1)2}), \tag{69}$$

$$E^{(3)}=4^{-3}(\gamma^{(0)6}\gamma^{(3)}+6\gamma^{(0)5}\gamma^{(1)}\gamma^{(2)}+5\gamma^{(0)4}\gamma^{(1)3}). \tag{70}$$

The summation in Eq. (67), although complex in appearance, is just over the distinct partitions of N into sums of positive integers.[29]

The derivation takes only a few lines. The relations (8), (9), (60), and (61) among E, $\beta_1+\beta_2$, f, F, and γ translate into an implicit equation for γ:

$$\gamma=\gamma^{(0)}+\gamma^{(1)}(\tfrac{1}{4}\gamma^3F)+\gamma^{(2)}(\tfrac{1}{4}\gamma^3F)^2+\cdots. \tag{71}$$

Langrange's formula gives any desired function of the solution of the above implicit equation, in particular, $-\frac{1}{2}\gamma^{-2}$:

$$E=-\tfrac{1}{2}\gamma^{-2}, \tag{72}$$

$$=-\frac{1}{2}\gamma^{(0)-2}+\sum_{\mu=1}^{\infty}\frac{1}{\mu!}\left(\frac{d}{d\gamma^{(0)}}\right)^{\mu-1}\times\left\{\left[\frac{d}{d\gamma^{(0)}}\left(-\frac{1}{2}\gamma^{(0)-2}\right)\right]\times\left[\sum_{\nu=1}^{\infty}\gamma^{(\nu)}\left(\frac{1}{4}\gamma^{(0)3}F\right)^{\nu}\right]^{\mu}\right\}. \tag{73}$$

Collecting all terms multiplying F^N and evaluating the derivatives, one obtains Eq. (67).

V. POLYNOMIAL FORMS FOR $E^{(N)}$

$E^{(N)}$ can be evaluated as a polynomial in k_1, k_2, and M via Eq. (67), which expresses $E^{(N)}$ in terms of the $\gamma^{(N)}$, which in turn are expressed as polynomials via Eq. (35). The resulting formula is slightly simplified, however, by first factoring $\gamma^{(0)}=k_1+k_2=n$ out of each $\gamma^{(N)}$

For even N, we find from Eqs. (63) and (35) that

$$\gamma^{(N)}=\sum_{r=0}^{N/2}\sum_{\mu=0}^{N/2-r}\beta^{(N)}_{r,2\mu+1}M^r(k_1^{2\mu+1}+k_2^{2\mu+1})\quad (N\text{ even}), \tag{74}$$

$$=(k_1+k_2)\sum_{r=0}^{N/2}\sum_{\mu=0}^{N/2-r}\beta^{(N)}_{r,2\mu+1}M^r\times(k_1^{2\mu}-k_1^{2\mu-1}k_2+k_1^{2\mu-2}k_2^2-\cdots+k_2^{2\mu})\quad (N\text{ even}), \tag{75}$$

while for odd N,

$$\gamma^{(N)}=\sum_{r=0}^{(N+1)/2}\sum_{\mu=0}^{(N+1)/2-r}\beta^{(N)}_{r,2\mu}M^r(k_1^{2\mu}-k_2^{2\mu})\quad (N\text{ odd}), \tag{76}$$

$$=(k_1+k_2)\sum_{r=0}^{(N+1)/2}\sum_{\mu=0}^{(N+1)/2-r}\beta^{(N)}_{r,2\mu}M^r(k_1^{2\mu-1}-k_1^{2\mu-2}k_2+\cdots-k_2^{2\mu-1})\quad (N\text{ odd}). \tag{77}$$

Thus the product of γ's in Eq. (67) has the natural factorization,

$$\gamma^{(0)3N-2-\Sigma_j i_j}\gamma^{(1)i_1}\gamma^{(2)i_2}\cdots\gamma^{(N)i_N}=n^{3N-2}\left(\frac{\gamma^{(1)}}{\gamma^{(0)}}\right)^{i_1}\left(\frac{\gamma^{(2)}}{\gamma^{(0)}}\right)^{i_2}\cdots\left(\frac{\gamma^{(N)}}{\gamma^{(0)}}\right)^{i_N}. \tag{78}$$

Taking this factorization into account, we infer from Eq. (67) the formula for $E^{(N)}$:

$$E^{(N)}=4^{-N}n^{3N-2}\sum_{r\geq 0}\sum_{i\geq 0}\sum_{\substack{j\geq 0\\ (i+j+N\text{ even},\\ i+j+2r\leq N)}}E^{(N)}_{rij}M^r k_1^i k_2^j. \tag{79}$$

When N is odd, it is clear from Eq. (76) that $\gamma^{(N)}$ is divisible by k_1-k_2. Consequently $E^{(N)}$ [each term of which in Eq. (67) must contain at least one γ factor of odd order] is also divisible by k_1-k_2, implying an alternative polynomial decom-

TABLE II. Perturbed energy, orders 1–7. $E^{(N)}=4^{-N}n^{3N-2}\sum E^{(N)}_{rij}M^r k_1^i k_2^j$.

N	r	i	j	$E^{(N)}_{rij}$	N	r	i	j	$E^{(N)}_{rij}$	N	r	i	j	$E^{(N)}_{rij}$	N	r	i	j	$E^{(N)}_{rij}$
1	0	1	0	6	5	0	5	0	31 920		0	1	3	−18 397 680		0	2	3	−387 343 440
	0	0	1	−6		0	4	1	95 088		0	0	4	−8 482 320		0	1	4	−647 145 360
						0	3	2	62 160		0	2	0	−12 409 432		0	0	5	−259 786 800
2	0	2	0	−14		0	2	3	−62 160		0	1	1	−10 958 528		0	3	0	692 482 344
	0	1	1	−40		0	1	4	−95 088		0	0	2	−12 409 432		0	2	1	537 695 544
	0	0	2	−14		0	0	5	−31 920		0	0	0	−1 360 000		0	1	2	−537 695 544
	0	0	0	−10		0	3	0	277 440		1	4	0	909 216		0	0	3	−692 482 344
	1	0	0	36		0	2	1	265 440		1	3	1	3 445 344		0	1	0	256 412 640
						0	1	2	−265 440		1	2	2	5 047 776		0	0	1	−256 412 640
3	0	3	0	132		0	0	3	−277 440		1	1	3	3 445 344		1	5	0	−9 092 832
	0	2	1	156		0	1	0	182 544		1	0	4	909 216		1	4	1	−27 488 928
	0	1	2	−156		0	0	1	−182 544		1	2	0	9 907 200		1	3	2	−19 002 912
	0	0	3	−132		1	3	0	11 904		1	1	1	18 734 400		1	2	3	19 002 912
	0	1	0	300		1	2	1	1 344		1	0	2	9 907 200		1	1	4	27 488 928
	0	0	1	−300		1	1	2	−1 344		1	0	0	9 292 320		1	0	5	9 092 832
	1	1	0	264		1	0	3	−11 904		2	2	0	421 200		1	3	0	−133 799 040
	1	0	1	−264		1	1	0	27 360		2	1	1	−324 000		1	2	1	−138 516 480
						1	0	1	−27 360		2	0	2	421 200		1	1	2	138 516 480
4	0	4	0	−1 860		2	1	0	34 800		2	0	0	301 584		1	0	3	133 799 040
	0	3	1	−5 340		2	0	1	−34 800		3	0	0	222 432		1	1	0	−154 141 344
	0	2	2	−7 548												1	0	1	154 141 344
	0	1	3	−5 340						7	0	7	0	12 865 608		2	3	0	3 864 720
	0	0	4	−1 860	6	0	6	0	−616 216		0	6	1	55 273 752		2	2	1	−2 482 320
	0	2	0	−9 100		0	5	1	−2 327 664		0	5	2	88 743 240		2	1	2	2 482 320
	0	1	1	−13 580		0	4	2	−3 758 904		0	4	3	46 243 224		2	0	3	−3 864 720
	0	0	2	−9 100		0	3	3	−4 106 816		0	3	4	−46 243 224		2	1	0	7 757 904
	0	0	0	−1 760		0	2	4	−3 758 904		0	2	5	−88 743 240		2	0	1	−7 757 904
	1	2	0	4 536		0	1	5	−2 327 664		0	1	6	−55 273 752		3	1	0	5 369 952
	1	1	1	4 536		0	0	6	−616 216		0	0	7	−12 865 608		3	0	1	−5 369 952
	1	0	2	4 536		0	4	0	−8 482 320		0	5	0	259 786 800					
	1	0	0	9 720		0	3	1	−18 397 680		0	4	1	647 145 360					
	2	0	0	2 196		0	2	2	−19 846 320		0	3	2	387 343 440					

TABLE III. Odd-order energies with k_1-k_2 factored out, orders 1–7.

$$E^{(N)}=4^{-N}(k_1-k_2)n^{3N-2}\sum E^{(N)\prime}_{rij}M^r k_1^i k_2^j.$$

N	r	i	j	$E^{(N)\prime}_{rij}$	N	r	i	j	$E^{(N)\prime}_{rij}$	N	r	i	j	$E^{(N)\prime}_{rij}$
1	0	0	0	6		1	1	1	13 248		0	1	1	1 230 177 888
						1	0	2	11 904		0	0	2	692 482 344
3	0	2	0	132		1	0	0	27 360		0	0	0	256 412 640
	0	1	1	288		2	0	0	34 800		1	4	0	−9 092 832
	0	0	2	132							1	3	1	−36 581 760
	0	0	0	300	7	0	6	0	12 865 608		1	2	2	−55 584 672
	1	0	0	264		0	5	1	68 139 360		1	1	3	−36 581 760
						0	4	2	156 882 600		1	0	4	−9 092 832
5	0	4	0	31 920		0	3	3	203 125 824		1	2	0	−133 799 040
	0	3	1	127 008		0	2	4	156 882 600		1	1	1	−272 315 520
	0	2	2	189 168		0	1	5	68 139 360		1	0	2	−133 799 040
	0	1	3	127 008		0	0	6	12 865 608		1	0	0	−154 141 344
	0	0	4	31 920		0	4	0	259 786 800		2	2	0	3 864 720
	0	2	0	277 440		0	3	1	906 932 160		2	1	1	1 382 400
	0	1	1	542 880		0	2	2	1 294 275 600		2	0	2	3 864 720
	0	0	2	277 440		0	1	3	906 932 160		2	0	0	7 757 904
	0	0	0	182 544		0	0	4	259 786 800		3	0	0	5 369 952
	1	2	0	11 904		0	2	0	692 482 344					

position,

$$E^{(N)} = 4^{-N}(k_1 - k_2)n^{3N-2} \times \sum_{\substack{r\le 0 \; i\le 0 \; j\le 0 \\ (i+j \text{ even}, \\ i+j+2r\le 2N-1)}} E_{rij}^{(N)\prime} M^r k_1^i k_2^j \quad (N \text{ odd}) . \qquad (80)$$

To find the numerical values of the polynomial coefficients $E_{rij}^{(N)}$, one must substitute Eqs. (75) and (77) for $\gamma^{(N)}/\gamma^{(0)}$ into Eq. (67) and collect terms proportional to $M^r k_1^i k_2^j$. To evaluate the $E_{rij}^{(N)\prime}$, it is necessary to divide the polynomials $E^{(N)}$ by $k_1 - k_2$. It is straightforward to carry out these calculations on a computer, and we have listed the values of the $E_{rij}^{(N)}$ and the $E_{rij}^{(N)\prime}$ for orders 1–7 in Tables II and III.

The number of nonzero $E^{(2N)}$ is $\frac{1}{3}(N+1)(N+\frac{3}{2})(N+2)$, which is also the number of nonzero $E_{rij}^{(2N+1)\prime}$. The number of nonzero $E_{rij}^{(2N+1)}$ is $\frac{1}{3}(N+1)(N+2)(N+3)$. As these numbers increase rapidly as N increases, we have not included tables for orders higher than $N=7$. Tables of $E_{rij}^{(N)}$ and $E_{rij}^{(N)\prime}$ for $N \leq 17$ are available from PAPS.[20]

VI. CALCULATION OF PERTURBED ENERGIES FOR SPECIFIC STATES

The perturbed energy of a specific state can be calculated by putting the appropriate values of k_1, k_2, and M into Eq. (79) to get $E^{(N)}$, and then the desired value of F into Eq. (59) to get E. Given the asymptotic nature of the perturbation series, the question naturally arises how large a field strength can be used. For example, we list in Table IV the termwise contributions to the ground-state energy for fields of 0.02 and 0.10 a.u. At the lower field, the terms decrease in magnitude monotonically, the last term being 10^{-11} a.u. At the higher field, the terms decrease in magnitude until the sixth order, then *increase* monotonically so that the sixteenth-order term is almost 3.5 times the zeroth-order term. The behavior exhibited at the higher field is characteristic of an asymptotic series.

The terms of an asymptotic power series typically tend to decrease in magnitude until some critical term is reached, after which they tend to increase without limit.[30] In favorable cases the value of the $(N+1)$st term is a measure of the error in the Nth partial sum. In the higher-field example of Table IV, we would accordingly regard the fourth partial sum, −0.5281 a.u., as optimum, with an error of the order of 0.0049 a.u. The accurate value of the perturbed energy is reported[10] to be −0.5275 a.u.

The important question from a practical point of view is how accurately the energy can be computed. That is, given a maximum error ϵ and a maximum number of terms available, what is the maximum value of F that can be used in the series, and how many terms should be included. Towards answering these questions, we fix ϵ and consider the sequence of numbers, $F_N(\epsilon)$:

$$F_N(\epsilon) = |\epsilon/E^{(N)}|^{1/N} \quad (\text{for } E^{(N)} \neq 0) . \qquad (81)$$

$F_N(\epsilon)$ is the value of F for which the Nth term has magnitude ϵ. Intuitively, we expect $F_n(\epsilon)$ to tend first to increase, then decrease as N increases. The maximum value of $F_N(\epsilon)$ can be taken as a "maximum useful field for error ϵ," and the corresponding order of N (which also depends on ϵ) indicates how many terms should be included, since at this value of F, the magnitudes of the terms preceding and following the Nth are larger than the Nth, which has the magnitude ϵ. If $F_N(\epsilon)$ is still increasing at the last term available, then $F_N(\epsilon)$ may still be regarded as the "maximum useful field for error ϵ," but with the qualification, "with terms of orders $\leq N$," since if more terms were available, it might be possible to go to higher fields without increasing the error.

TABLE IV. Termwise contributions to the ground-state energy at low and high fields, in a.u.

Order	$F=0.02$ a.u.		$F=0.10$ a.u.	
N	$F^N E^{(N)} \times 10^{12}$	Partial sum	$F^N E^{(N)} \times 10^4$	Partial sum
0	−500 000 000 000	−0.500 000 000 000	−5000	−0.5000
2	−900 000 000	−0.500 900 000 000	−225	−0.5225
4	−8 887 500	−0.500 908 887 500	−56	−0.5281
6	−314 097	−0.500 909 201 597	−49	−0.5330
8	−20 332	−0.500 909 221 930	−79	−0.5409
10	−1 992	−0.500 909 223 922	−195	−0.5604
12	−271	−0.500 909 224 193	−663	−0.6266
14	−49	−0.500 909 224 242	−2992	−0.9259
16	−11	−0.500 909 224 254	−17347	−2.6606

TABLE V. Perturbed coefficients $E^{(N)}$ and maximum field parameters for the ground state for various error limits, in a.u.

		$F_N(E)=\lvert\epsilon/E^{(N)}\rvert^{1/N}$ $\epsilon=0.5\times$			
N	$E^{(N)}$	10^{-2}	10^{-4}	10^{-6}	10^{-8}
0	−0.5				
2	−2.25	0.0471	0.00471	0.000471	0.0000471
4	−55.546 875	0.0974	0.0308	0.00974	0.00308
6	−4 907.771 484 375	0.100	0.0466	0.0216	0.0100
8	−794 236.926 452 636 718	0.0944	0.0531	0.0298	0.0168
10	−194 531 960.466 499 329	0.0873	0.0551	0.0348	0.0219
12	−66 263 036 523.689 170 9	0.0806	0.0549	0.0374	0.0255
14	−29 924 943 988 411.939 5	0.0747	0.0537	0.0387	0.0278
16	−17 346 970 495 631 198.5	0.0694	0.0520	0.0390	0.0293

To illustrate the calculation of the maximum useful field, we list in Table V the values of $E^{(N)}$ and $F_N^{(N)}(\epsilon)$ for $|\epsilon/E^{(0)}|=10^{-2}$, 10^{-4}, 10^{-6}, and 10^{-8} for the ground state. Note that the ground state $E^{(N)}$ for orders 2–10, when truncated to ten significant figures, agree exactly with Mendelsohn's.[7] For an error of 10^{-2} relative to $E^{(0)}$, the maximum $F_N(\epsilon)$ occurs at $N=6$. Accordingly we would take E only through fourth order, and F not greater than 0.1 a.u. For a relative error of 10^{-4}, the maximum $F_N(\epsilon)$ occurs at $N=12$. Accordingly we would use the tenth-order partial sum with F not greater than 0.0551 a.u. For relative errors of 10^{-6} or 10^{-8}, we would use all terms available, and we would limit F by 0.0390 a.u. and by 0.0293 a.u., respectively.

In Table VI, we list $F_{17}(10^{-6}E^{(0)})$ or, in the cases for which $n_1=n_2$, $F_{16}(10^{-6}E^{(0)})$ for a number of states. As with the ground state, $F_N(\epsilon)$ is still increasing at $N=17$ for relative error 10^{-6} (and 10^{-8}). For values of F less than those in Table VI, the energy through seventeenth order has a relative accuracy of 10^{-6}.

In Table VII, we compare some typical perturbation-theory energies with energies computed nonperturbatively. Not only is the agreement excellent, but we observe that for the ground state the error turns out to be less in magnitude than the imaginary part of the energy corresponding to purely-outgoing-wave boundary conditions,[10,18,31] while for the excited state listed, the error is approximately one order of magnitude larger than

TABLE VI. Maximum useful field for accuracy 10^{-6} relative to $E^{(0)}$, for E calculated to 17th order for various states.

n	m	n_1	n_2	F(a.u.)	n	m	n_1	n_2	F(a.u.)	n	m	n_1	n_2	F(a.u.)
1	0	0	0	3.90×10^{-2}		0	3	0	3.06×10^{-4}		1	3	0	1.38×10^{-4}
						1	0	2	3.21×10^{-4}		2	0	2	1.45×10^{-4}
2	0	0	1	3.76×10^{-3}		1	1	1	3.40×10^{-4}		2	1	1	1.51×10^{-4}
	0	1	0	3.76×10^{-3}		1	2	0	3.21×10^{-4}		2	2	0	1.45×10^{-4}
	1	0	0	3.95×10^{-3}		2	0	1	3.44×10^{-4}		3	0	1	1.55×10^{-4}
						2	1	0	3.44×10^{-4}		3	1	0	1.55×10^{-4}
3	0	0	2	8.80×10^{-4}		3	0	0	3.55×10^{-4}		4	0	0	1.59×10^{-4}
	0	1	1	9.52×10^{-4}										
	0	2	0	8.80×10^{-4}	5	0	0	4	1.33×10^{-4}	10	0	9	0	9.29×10^{-6}
	1	0	1	9.43×10^{-4}		0	1	3	1.44×10^{-4}					
	1	1	0	9.43×10^{-4}		0	2	2	1.49×10^{-4}	14	2	0	11	2.56×10^{-6}
	2	0	0	9.80×10^{-4}		0	3	1	1.44×10^{-4}					
						0	4	0	1.33×10^{-4}	15	0	14	0	1.89×10^{-6}
4	0	0	3	3.06×10^{-4}		1	0	3	1.38×10^{-4}					
	0	1	2	3.40×10^{-4}		1	1	2	1.52×10^{-4}	20	0	19	0	6.07×10^{-7}
	0	2	1	3.40×10^{-4}		1	2	1	1.52×10^{-4}	25	0	24	0	2.50×10^{-7}

TABLE VII. Energies calculated perturbatively compared with energies calculated nonperturbatively.

F(a.u.)	E(a.u.) calculated by perturbation theory	Order N	Next term[a] $\lvert F^{N+1}E^{(N+1)}\rvert$	E(a.u.) calculated nonperturbatively
		Ground state		
0.001	−0.500 002 250 055 55	16	$<10^{-15}$	−0.500 002 250 055 56[b]
0.004	−0.500 036 014 240 15	16	$<10^{-15}$	−0.500 036 014 240 0[b]
0.005	−0.500 056 284 793 79	16	$<10^{-15}$	−0.500 056 284 793 7[b]
0.006	−0.500 081 072 219 07	16	$<10^{-15}$	−0.500 081 072 219 4[b]
0.007	−0.500 110 383 950 08	16	$<10^{-15}$	−0.500 110 383 958[b]
0.008	−0.500 144 228 820 08	16	$<10^{-15}$	−0.500 144 228 821[b]
0.009	−0.500 182 617 086 12	16	$<10^{-15}$	−0.500 182 617 088[b]
0.01	−0.500 225 560 457 96	16	$<10^{-15}$	−0.500 225 560 459[b]
0.02	−0.500 909 224 254	16	$<10^{-11}$	−0.500 909 224 258[b]
0.03	−0.502 074 263 6	16	$<74\times10^{-10}$	−0.502 074 273[b]
0.04	−0.503 771 46	14	75×10^{-8}	−0.503 771 5[b]
0.05	−0.506 099	10	16×10^{-6}	−0.506 105 4[c]
0.06	−0.509 18	8	12×10^{-5}	−0.509 204[c]
0.07	−0.512 94	6	46×10^{-5}	−0.513 08[c]
0.08	−0.516 7	4	13×10^{-4}	−0.517 56[c]
0.09	−0.521 9	4	26×10^{-4}	−0.522 4[c]
0.10	−0.528 1	4	49×10^{-4}	−0.527 5[c]
0.11	−0.527 2	2	81×10^{-4}	−0.532 5[c]
0.12	−0.532	2	12×10^{-3}	−0.537 4[c]
	Excited state with $n=5$, $m=1$, $n_1=3$, $n_2=0$			
1.556×10^{-4}	−0.016 855 16	17	$\sim15\times10^{-8}$	−0.016 855 237 2[d]
1.9448×10^{-4}	−0.016 182 1	12	57×10^{-7}	−0.016 179 388 5[d]
2.1393×10^{-4}	−0.015 868	10	18×10^{-6}	−0.015 860 468[d]
2.5282×10^{-4}	−0.015 294	6	79×10^{-6}	−0.015 269 204[d]
2.9172×10^{-4}	−0.014 78	4	20×10^{-5}	−0.014 740 243[d]
3.3061×10^{-4}	−0.014 30	2	49×10^{-5}	−0.014 242 49[d]

[a] For the ground state, the next term is $F^{N+2}E^{(N+2)}$.

[b] Reference 8. We have taken the average of Alexander's upper and lower bounds.

[c] Reference 10.

[d] Reference 15.

the imaginary part of the energy.

Finally, in Table VIII we give the perturbed energy for a particular state of the $n=14$ level to illustrate the accuracy obtainable (absolute, ~6 $\times 10^{-9}$ a.u.; relative, $\sim 2\times 10^{-6}$) for a state experimentally observed in sodium, at field strengths at which ionization rates have been measured.[17]

TABLE VIII. Energy through 17th order for $n=14$, $m=2$, $n_1=0$, $n_2=11$.

F (a.u.)	E (a.u.)	$F^{17}E^{(17)}$
2.4×10^{-6}	−0.003 157 057 8	9×10^{-10}
2.5×10^{-6}	−0.003 185 402 6	17×10^{-10}
2.6×10^{-6}	−0.003 214 132 7	33×10^{-10}
2.7×10^{-6}	−0.003 243 283 3	63×10^{-10}

VII. CONCLUDING REMARKS

It has been shown how to generate the explicit formulas for the perturbed separation constant and energy in the Stark effect in hydrogen as polynomials in the quantum numbers, for arbitrarily high orders, and the usefulness of these formulas has been demonstrated by numerical examples. We conclude with some practical observations.

The number of nonzero polynomial coefficients in $\beta^{(N)}$ and $E^{(N)}$increases as $\frac{1}{2}N^2$ and $\frac{1}{3}N^3$, respectively. The total number of $c_{irs}^{(N)}$ for orders up to and including N is roughly of order N^4. As N increases, the large number of quantities becomes troublesome. The maximum value of $N=17$ that appears in this paper represents the largest calculation that fit in a computer memory of 256k words without extensive effort to conserve storage, without explicit overlaying, and without using disk files for intermediate results.

If one is interested in only a few states, to generate the $\beta^{(N)}$and $E^{(N)}$ as polynomials for very high N would not appear to be as efficient as to generate the numerical values directly from Eqs. (32), (33), (63), and (67). Compared to the effort required to program the polynomial solution, it is rather easy to program Eqs. (32) and (33) to get numerical values of the $\beta^{(N)}$ for specific states. The general formula (67) then produces the $E^{(N)}$ from the $\beta^{(N)}$ with an even more modest effort. Such a computer program has been written to give $\beta^{(N)}$ and $E^{(N)}$ through $N=25$.

For some practical purposes, the energies computed by perturbation theory are probably of sufficiently high accuracy, since in some cases the errors inherent in the use of the asymptotic series comparable with the widths of the levels, which are nonzero because of field ionization. One is not normally interested in the energy of a state to an accuracy too much finer than its width.

Finally, we note that the perturbation series is much easier to use than any of the nonperturbative schemes.

Note added in proof. Precise measurements of intense-field Stark shifts in highly excited states of hydrogen have now been reported by Peter M. Koch [Phys. Rev. Lett. (to be published)]. In the two cases analyzed in detail, the discrepancy between perturbation theory and experiment is less than the experimental uncertainty for a large $n_2 - n_1$ state ($n=30$, $n_1=0$, $n_2=29$, $m=0$), but more than an order of magnitude larger than the uncertainty for a large $n_1 - n_2$ state ($n=25$, $n_1=21$, $n_2=2$, $|m|=1$). In the latter case, successive partial sums alternately bracket the experimental value from above and below. The author is grateful to Professor Koch for a preprint of his paper and for helpful discussions.

ACKNOWLEDGMENT

The author would like to thank the Johns Hopkins University for supporting the computer calculations, and Dennis P. Carroll for helpful discussions.

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[21] E. C. Titchmarsh, *Eigenfunction Expansions Associated with Second-Order Differential Equations*, 2nd ed. (Oxford U.P., London, 1958), Chap. 20.

[22] See, for instance, L. D. Landau and E.M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1958).

[23] The notation is that of Ref. 18.

[24] The quantity $\frac{1}{4}(1-m^2)$ is the eigenvalue of the Casimir operator for the group $O(2,1)$, whose relevance to the Stark effect in hydrogen was exploited by Alliluev and Malkin (Ref. 5).

[25] There are unfortunately several different notations in use. We follow Ref. 21. The equation $L_n^m(x) = (d/dx)^m L_n(x)$ may aid in identifying the notation. In terms of the usage in Abramowitz and Stegun (Ref. 26) $L_{n+m}^m(x)$ (here) $= (-1)^n (n+m)!\, L_n^{(m)}(x)$ (Abramowitz and Stegun).

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[27] Cf. Eqs. (26) of Ref. 5.

[28] See, for instance, Eq. (3.6.7) of Ref. 26.

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