

## Stark Effect in Hydrogen: Dispersion Relation, Asymptotic Formulas, and Calculation of the Ionization Rate via High-Order Perturbation Theory

Harris J. Silverstone

*Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21238*

and

Barry G. Adams, Jiri Cizek, and Peter Otto<sup>(a)</sup>

*Quantum Theory Group, Department of Applied Mathematics, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

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By a generalization of the Herbst-Simon dispersion relation for hydrogen in an electric field, an expansion asymptotic in  $N$  for the perturbed energy coefficient  $E_{n_1 n_2 m}^{(N)}$  is obtained from the formal asymptotic expansion (in the field strength  $F$ ) for the ionization rate. Perturbation-theory calculations of  $E_{n_1 n_2 m}^{(N)}$  to  $N \sim 150$  confirm the formula. Via reverse use of the dispersion relation, perturbation-theory values of  $E_{n_1 n_2 m}^{(N)}$  yield numerical values for constants in the ionization-rate expansion that are tedious to obtain directly. Ionization rates so calculated compare favorably with values obtained by others.

One of the oldest quantum mechanical problems is the calculation of the perturbed energy and ionization rate for hydrogen in the Stark effect.<sup>1-3</sup> Renewed interest in the Stark effect has been stimulated in part by recent experiments, such as by Koch,<sup>4</sup> by Stebbings,<sup>5</sup> and by Littman, Zimmerman, and Keppner<sup>6</sup> on highly excited states of hydrogen and other atoms, and also in part by the discovery of Herbst and Simon<sup>7</sup> of a dispersion relation between the ground-state energy shift and ionization rate, which implied a formula asymptotic in  $N$  for the Rayleigh-Schrödinger perturbed energy  $E^{(N)}$ .

This Letter's purpose is to discuss several aspects of the dispersion relation for excited states. (i) We generalize<sup>8</sup> the dispersion relation for any parabolic and magnetic quantum numbers  $n_1, n_2$ , and  $m$ . (ii) With use of the formal asymptotic expansion in the field strength  $F$  for the ionization rate  $\Gamma_{n_1 n_2 m}$ , we integrate the dispersion relation to get a formula for the energy, which when expanded in a power series in  $F$  gives (iii) a formula<sup>8</sup> for the Rayleigh-Schrödinger energies  $E_{n_1 n_2 m}^{(N)}$  asymptotic in  $N$ . Certain constants  $a_k^{n_1 n_2 m}$  in the  $\Gamma_{n_1 n_2 m}$  expansion are tedious to obtain analytically and carry over into the formulas for  $E_{n_1 n_2 m}^{(N)}$ . (iv) We get the  $a_k^{n_1 n_2 m}$  numerically by matching the asymptotic formula to values of  $E_{n_1 n_2 m}^{(N)}$  obtained directly from high-order perturbation theory ( $N \sim 150$ ), and (v) we then use the numerical  $a_k^{n_1 n_2 m}$  to calculate the ionization rate. Thus we calculate  $\Gamma_{n_1 n_2 m}$  (indirectly) via ordinary perturbation theory.

The generalized dispersion relation is

$$\hat{E}(n_1, n_2, m, F) = \frac{1}{\pi} \int_0^\infty dx \left[ \frac{\text{Im} \hat{E}(n_1, n_2, m, x)}{x - F - i\epsilon} + (-1)^{N_0} \frac{\text{Im} \hat{E}(n_2, n_1, m, x)}{x + F} \right], \quad (1)$$

where

$$\hat{E}(n_1, n_2, m, F) = F^{-N_0} \left[ E(n_1, n_2, m, F) - \sum_{N_0}^{N_0-1} E_{n_1 n_2 m}^{(N)} F^N \right],$$

and  $E(n_1, n_2, m, F)$  is the outgoing-wave complex energy eigenvalue. Equation (1) may be "derived" from Cauchy's formula, under the "assumptions" that there is an  $N_0$  such that  $|z^{-N_0} E(n_1, n_2, m, z)| \rightarrow 0$  as  $|z| \rightarrow \infty$ , that  $E(n_1, n_2, m, z)$  has one branch cut running from  $+0$  to  $+\infty$  and a second running from  $-\infty$  to  $-\infty$ , and that  $E(n_1, n_2, m, -z) = E(n_2, n_1, m, z)$ . (More rigorous discussions appear in Ref. 8.)

We integrate Eq. (1) after using  $\Gamma_{n_1 n_2 m}(F) = -2F^{N_0} \text{Im} \hat{E}(n_1, n_2, m, F)$ , the formal asymptotic expansion<sup>9-11</sup>

$$\Gamma_{n_1 n_2 m}(F) \sim [n_2^3 n_2! (n_2 + m)!]^{-1} \exp[3(n_1 - n_2)] \left(\frac{1}{4} n^3 F\right)^{-2n_2 - m - 1} \exp[-2/(3n^3 F)] \sum_k a_k^{n_1 n_2 m} (3n^3 F/2)^k, \quad (2)$$

and the exponential-type integral<sup>12</sup>  $E_n(z) = \int_1^\infty t^{-n} e^{-zt} dt$  to obtain

$$\begin{aligned} \hat{E}(n_1, n_2, m, F) \sim & (2\pi n^3)^{-1} (\frac{3}{2} n^3)^{N_0} (\frac{3}{2} n^3 F)^{-1} \\ & \times \{ -[n_2!(n_2+m)!]^{-1} \exp[3(n_1-n_2)] 6^{2n_2+m+1} \\ & \times \sum_k a_k^{n_1 n_2 m} (2n_2+m+N_0-k)! \exp(-2/3n^3 F) E_{2n_2+m+N_0-k+1}(e^{-\pi i} 2/3n^3 F) \\ & + [n_1!(n_1+m)!]^{-1} \exp[3(n_2-n_1)] 6^{2n_1+m+1} (-1)^{N_0} \\ & \times \sum_k a_k^{n_2 n_1 m} (2n_1+m+N_0-k)! \exp(2/3n^3 F) E_{2n_1+m+N_0-k+1}(2/3n^3 F) \}. \end{aligned} \quad (3)$$

From the well-known asymptotic expansion<sup>12</sup> for  $E_n(z)$  [or by expanding the denominators of Eq. (1) in  $F/x$ ] one obtains the power series

$$E(n_1, n_2, m, F) \sim \sum E_{n_1 n_2 m}^{(N)} F^N, \quad E_{n_1 n_2 m}^{(N)} \sim A_{n_1 n_2 m}^{(N)} + (-1)^N A_{n_2 n_1 m}^{(N)}, \quad (4)$$

$$A_{n_i n_j m}^{(N)} = -[2\pi n^3 n_j! (n_j+m)!]^{-1} \exp[3(n_i-n_j)] 6^{2n_j+m+1} (3n^3/2)^N \sum_k a_k^{n_i n_j m} (2n_j+m+N-k)!. \quad (5)$$

In Eqs. (1)–(5),  $m \geq 0$ ; for  $m < 0$ , one can use  $E(n_1, n_2, -m, F) = E(n_1, m_2, m, F)$ . When  $n_1 = n_2$ , only even-order  $E^{(N)}$  are nonzero; when  $n_1 \neq n_2$ , the larger  $(2n_i+m+N)!$  eventually dominates. The  $N!$  behavior is related to Borel summability.<sup>13</sup> The leading term of Eqs. (4) and (5) for the ground state (note that  $a_0^{n_1 n_2 m} \equiv 1$ ) was derived by Benassi, Grecchi, Harrell, and Simon.<sup>14</sup> The leading term of Eq. (2) has been discovered or rediscovered at least three times.<sup>9–11</sup> Damburg and Kolosov<sup>11</sup> have given formulas from which  $a_1^{n_1 n_2 m}$  and  $a_2^{n_1 0 0}$  can be inferred:

$$a_1^{n_1 n_2 m} = \frac{1}{3} n_2 (n_2 + m - 5) - \frac{8}{3} (n_1^2 + n_2^2) - \frac{19}{3} n_1 n_2 - \frac{35}{6} (n_1 + n_2)(m + 1) - \frac{11}{8} m^2 - \frac{20}{3} m - \frac{107}{18}; \quad (6)$$

$$a_2^{n_1 0 0} = \frac{32}{9} n_1^4 + \frac{325}{18} n_1^3 + \frac{7567}{216} n_1^2 + \frac{11019}{324} n_1 + \frac{7363}{648}. \quad (7)$$

TABLE I. The expansion coefficients  $a_k^{n_1 n_2 m}$  for both  $E_{n_1 n_2 m}^{(N)}$  and  $\Gamma_{n_1 n_2 m}(F)$ , obtained from Eqs. (6) and (7) and by fitting Eqs. (4) and (5) with perturbation-theory  $E_{n_1 n_2 m}^{(N)}$ .

$n_1$	$n_2$	$m$	$k$	$a_k^{n_1 n_2 m}$	± Estimated error <sup>a</sup>
0	0	0	0	1.	
			1 <sup>b</sup>	-107/18	
			2 <sup>c</sup>	7363/648	
			3	-47.0360	± 0.0002
			4	92.65	± 0.2
1	0	0	0	1.	
			1 <sup>b</sup>	-130/9	
			2 <sup>c</sup>	33053/324	
			3	-663.45	± 0.1
			4	4450.	± 20.
0	1	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
0	0	0	0	1.	
			1 <sup>b</sup>	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0

<sup>a</sup>The errors given are a subjective estimate of the authors based on the behavior of the extrapolation procedure.

<sup>b</sup>Value is from Eq. (6).

<sup>c</sup>Value is from Eq. (7).

But even to obtain  $a_2^{n_1 0 0}$  involved “rather cumbersome” calculations,<sup>11</sup> and higher-order exact  $a_k^{n_1 n_2 m}$  are not currently available. We obtain them numerically by extracting them from perturbation-theory values of  $E_{n_1 n_2 m}^{(N)}$ .

We calculated perturbation theoretic  $E_{n_1 n_2 m}^{(N)}$  for  $N \lesssim 150$  by a modification of a method<sup>5</sup> previously applied to  $N \leq 25$ , based on separation in parabolic coordinates. We also calculated perturbation-theoretic  $E_{000}^{(N)}$  for  $N \leq 82$  via the formalism of the  $SO(4, 2)$  Lie algebra.<sup>16–18</sup> The use of two independent methods on different computers permitted us to be rather certain of the accuracy of the  $E_{000}^{(N)}$ : We found agreement to thirteen significant figures for all orders  $\leq 82$ .

From numerical values of  $E_{n_1 n_2 m}^{(N)}$  calculated by perturbation theory, the  $a_k^{n_1 n_2 m}$  can be obtained by numerically fitting Eqs. (4) and (5) (cf. Bender and Wu<sup>19</sup>). The number of significant figures obtainable, however, falls rapidly as  $k$  increases. For illustration, the values of  $a_k^{000}$  (the ground state),  $a_k^{100}$ , and  $a_k^{010}$ , for  $k \leq 5$ , are listed in Table I. It is harder to extract  $a_k^{100}$  than  $a_k^{010}$  from  $E_{100}^{(N)}$ , because the terms in which  $a_k^{010}$  appears are roughly  $N^2 e^{-6}$  larger than those in which  $a_k^{100}$  appears. ( $a_k^{100}$  could also be found from a corresponding asymptotic formula for the perturbed separation coefficient  $\beta_{n_2 m}^{(N)}$ .)

In Table II, we have listed perturbation-theo-

TABLE II. Comparison of  $E_{n_1 n_2 m}^{(N)}$  calculated by Rayleigh-Schrödinger perturbation theory and by the asymptotic formula [Eqs. (4) and (5)] with use of the  $a_k^{n_1 n_2 m}$  given in Table I.

Order	$E_{n_1 n_2 m}^{(N)}$ by asymptotic expansion to term k			$E_{n_1 n_2 m}^{(N)}$ by perturbation theory
	k=0	3	5	
ground state $n_1=0, n_2=0, m=0$				
10	$-3.996474085 \times 10^8$	$-1.864273203 \times 10^8$	$-1.759326110 \times 10^8$	$-1.945319605 \times 10^8$
30	$-9.714025167 \times 10^{37}$	$-7.897322788 \times 10^{37}$	$-7.897924293 \times 10^{37}$	$-7.897811108 \times 10^{37}$
50	$-3.703729008 \times 10^{73}$	$-3.279092637 \times 10^{73}$	$-3.279135055 \times 10^{73}$	$-3.279134470 \times 10^{73}$
70	$-4.850589779 \times 10^{112}$	$-4.449391052 \times 10^{112}$	$-4.449406966 \times 10^{112}$	$-4.449406910 \times 10^{112}$
90	$-2.000554940 \times 10^{154}$	$-1.871123931 \times 10^{154}$	$-1.871126441 \times 10^{154}$	$-1.871126438 \times 10^{154}$
110	$-7.111439484 \times 10^{197}$	$-6.733615461 \times 10^{197}$	$-6.733619562 \times 10^{197}$	$-6.733619559 \times 10^{197}$
130	$-9.628490607 \times 10^{242}$	$-9.194526355 \times 10^{242}$	$-9.194529249 \times 10^{242}$	$-9.194529248 \times 10^{242}$
150	$-2.828678874 \times 10^{289}$	$-2.717977245 \times 10^{289}$	$-2.717977730 \times 10^{289}$	$-2.717977730 \times 10^{289}$
excited state $n_1=1, n_2=0, m=0$				
10	$-6.883958372 \times 10^{18}$	$-2.931449795 \times 10^{17}$	$-1.594716773 \times 10^{17}$	$-1.247119323 \times 10^{18}$
25	$2.186883327 \times 10^{54}$	$1.136023758 \times 10^{54}$	$1.140689592 \times 10^{54}$	$1.139904838 \times 10^{54}$
40	$-4.446779891 \times 10^{93}$	$-2.980690620 \times 10^{93}$	$-2.982624298 \times 10^{93}$	$-2.982601906 \times 10^{93}$
55	$1.956524041 \times 10^{135}$	$1.464777114 \times 10^{135}$	$1.465029693 \times 10^{135}$	$1.465028976 \times 10^{135}$
70	$-4.580728565 \times 10^{178}$	$-3.651445906 \times 10^{178}$	$-3.651685321 \times 10^{178}$	$-3.651685117 \times 10^{178}$
85	$2.420337907 \times 10^{223}$	$2.008508550 \times 10^{223}$	$2.008567904 \times 10^{223}$	$2.008567875 \times 10^{223}$
100	$-1.705384915 \times 10^{269}$	$-1.455619003 \times 10^{269}$	$-1.455641404 \times 10^{269}$	$-1.455641398 \times 10^{269}$
115	$1.082850832 \times 10^{316}$	$9.436075774 \times 10^{315}$	$9.436157909 \times 10^{315}$	$9.436157893 \times 10^{315}$
130	$-4.706327872 \times 10^{363}$	$-4.167086682 \times 10^{363}$	$-4.167108856 \times 10^{363}$	$-4.167108853 \times 10^{363}$
145	$1.118686686 \times 10^{412}$	$1.003083772 \times 10^{412}$	$1.003087198 \times 10^{412}$	$1.003087198 \times 10^{412}$

TABLE III. Asymptotic expansion for the ionization rate compared with accurate numerical values, in atomic units.

n	$n_1$	$n_2$	m	Field strength	Ionization rate <sup>a</sup>			Ref.
					$\Gamma^{(0)}$	$\Gamma^{(5)}$	$\Gamma^{(num)}$	
1	0	0	0	0.02351	$8.234 \times 10^{-11}$	$6.608 \times 10^{-11}$	$6.616 \times 10^{-11}$	11
				0.03145	$7.194 \times 10^{-8}$	$5.857 \times 10^{-8}$	$5.839 \times 10^{-8}$	11
				0.03942	$4.588 \times 10^{-6}$	$3.114 \times 10^{-6}$	$3.110 \times 10^{-6}$	11
				0.04745	$6.669 \times 10^{-5}$	$4.117 \times 10^{-5}$	$4.106 \times 10^{-5}$	11
				0.05556	$4.428 \times 10^{-4}$	$2.459 \times 10^{-4}$	$2.442 \times 10^{-4}$	11
				0.04	$5.78 \times 10^{-6}$	$3.90 \times 10^{-6}$	$3.89 \times 10^{-6}$	20
				0.06	$9.96 \times 10^{-4}$	$5.19 \times 10^{-4}$	$5.15 \times 10^{-4}$	20
				0.08	$1.20 \times 10^{-2}$	$4.67 \times 10^{-3}$ b	$4.51 \times 10^{-3}$	21
2	1	0	0	0.10	$5.09 \times 10^{-2}$	$1.28 \times 10^{-2}$ b	$1.45 \times 10^{-2}$	20
				0.003	$3.61 \times 10^{-10}$	$2.12 \times 10^{-10}$	$2.12 \times 10^{-10}$	11
				0.004	$2.81 \times 10^{-7}$	$1.36 \times 10^{-7}$	$1.36 \times 10^{-7}$	11
				0.005	$1.45 \times 10^{-5}$	$5.64 \times 10^{-6}$	$5.73 \times 10^{-6}$	11
2	0	1	0	0.006	$1.94 \times 10^{-4}$	$5.74 \times 10^{-5}$	$6.09 \times 10^{-5}$	11
				0.0025	$1.66 \times 10^{-10}$	$9.92 \times 10^{-11}$	$9.92 \times 10^{-11}$	11
				0.0030	$2.49 \times 10^{-8}$	$1.32 \times 10^{-8}$	$1.32 \times 10^{-8}$	11
				0.0035	$8.29 \times 10^{-7}$	$3.88 \times 10^{-7}$	$3.86 \times 10^{-7}$	11
				0.0040	$1.09 \times 10^{-5}$	$4.45 \times 10^{-6}$	$4.44 \times 10^{-6}$	11

<sup>a</sup> $\Gamma^{(N)}$  = Eq. (2), with  $k \leq N$ ;  $\Gamma^{(num)}$  is obtained from the references in last column.

<sup>b</sup>Equation (2) with  $k \leq 4$ . The  $k = 5$  term is no longer useful.

retic values for  $E_{n_1 n_2 m}^{(N)}$  along with asymptotic-formula values with use of one, four, and six terms in Eq. (5). The agreement is remarkable.

To show the utility of "perturbation-theory-extracted"  $a_k^{n_1 n_2 m}$  for calculating ionization rates, we list in Table III values of  $\Gamma_{000}$ ,  $\Gamma_{100}$ , and  $\Gamma_{010}$  obtained from Eq. (2). The agreement with accurate values obtained from numerical solutions<sup>11,20,21</sup> is excellent. For the  $n=2$  states, the six-term results are significantly better than the two-term results of Damburg and Kolosov.<sup>11</sup>

Thus we have demonstrated the agreement of perturbation-theory  $E_{n_1 n_2 m}^{(N)}$  with the asymptotic formula [Eqs. (4) and (5)] obtained from the dispersion relation, and the practicality of extracting the  $a_k^{n_1 n_2 m}$  from the perturbation-theory energies for subsequent calculation of ionization rates.

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<sup>(a)</sup>Permanent address: Institute for Theoretical Chemistry, University of Nuremberg, Erlangen, Germany.

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<sup>8</sup>Since the submission of this manuscript, the authors

have received communications from E. Harrell and B. Simon, "The Mathematical Theory of Resonances Whose Widths are Exponentially Small" (to be published), and from L. Benassi and V. Grecchi, "Resonances in the Stark Effect and Strongly Asymptotic Approximants" (to be published), which contain similar formulas.

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