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

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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 $E_{n_1n_2m}^{(N)}$ is obtained from the formal asymptotic expansion (in the field strength F) for the ionization rate. Perturbation-theory calculations of $E_{n_1n_2m}^{(N)}$ to $N\sim 150$ confirm the formula. Via reverse use of the dispersion relation, perturbation-theory values of $E_{n_1n_2m}^{(N)}$ yield numerical values for constants in the ionization-rate expansion that are tediuous 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.[1-3] Renewed interest in the Stark effect has been stimulated in part by recent experiments, such as by Koch,[4] by Stebbings,[5] and by Littman, Zimmerman, and Keppner[6] on highly excited states of hydrogen and other atoms, and also in part by the discovery of Herbst and Simon[7] 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[8] 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 $\Gamma_{n_1n_2m}$, 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[8] for the Rayleigh-Schrödinger energies $E_{n_1n_2m}^{(N)}$ asymptotic in N. Certain constants $a_k^{n_1n_2m}$ in the $\Gamma_{n_1n_2m}$ expansion are tedious to obtain analytically and carry over into the formulas for $E_{n_1n_2m}^{(N)}$. (iv) We get the $a_k^{n_1n_2m}$ numerically by matching the asymptotic formula to values of $E_{n_1n_2m}^{(N)}$ obtained directly from high-order perturbation theory ($N\sim 150$), and (v) we then use the numerical $a_k^{n_1n_2m}$ to calculate the ionization rate. Thus we calculate $\Gamma_{n_1n_2m}$ (indirectly) via ordinary perturbation theory.

The generalized dispersion relation is

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

where

$$\hat{E}(n_1,n_2,m,F)=F^{-N_0}[E(n_1,n_2,m,F)-\sum_{N_0}^{N_0-1}E_{n_1n_2m}{}^{(N)}F^N],$$

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 $|z^{-N_0}E(n_1,n_2,m,z)|\to 0$ as $|z|\to\infty$, that $E(n_1,n_2,m,z)$ has one branch cut running from $+0$ to $+\infty$ and a second running from -0 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 $\Gamma_{n_1n_2m}(F)=-2F^{N_0}\mathrm{Im}\hat{E}(n_1,n_2,m,F)$, the formal asymptotic expansion[9-11]

$$\Gamma_{n_1n_2m}(F)\sim[n^3n_2!\,(n_2+m)!\,]^{-1}\exp[3(n_1-n_2)](\tfrac{1}{4}n^3F)^{-2n_2-m-1}\exp[-2/(3n^3F)]\sum_k a_k^{n_1n_2m}(3n^3F/2)^k, \tag{2}$$

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

$$\hat{E}(n_1,n_2,m,F)\sim-(2\pi n^3)^{-1}(\tfrac{3}{2}n^3)^{N_0}(\tfrac{3}{2}n^3F)^{-1}$$
$$\times\{-[n_2!(n_2+m)!]^{-1}\exp[3(n_1-n_2)]6^{2n_2+m+1}$$
$$\times\sum_k a_k^{n_1n_2m}(2n_2+m+N_0-k)!\exp(-2/3n^3F)E_{2n_2+m+N_0-k+1}(e^{-\pi i}2/3n^3F)$$
$$+[n_1!(n_1+m)!]^{-1}\exp[3(n_2-n_1)]6^{2n_1+m+1}(-1)^{N_0}$$
$$\times\sum_k a_k^{n_2n_1m}(2n_1+m+N_0-k)!\exp(2/3n^3F)E_{2n_1+m+N_0-k+1}(2/3n^3F)\}. \quad (3)$$

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

$$E(n_1,n_2,m,F)\sim\sum E_{n_1n_2m}{}^{(N)}F^N,\quad E_{n_1n_2m}{}^{(N)}\sim A_{n_1n_2m}{}^{(N)}+(-1)^N A_{n_2n_1m}{}^{(N)}, \quad (4)$$

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

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.[13] The leading term of Eqs. (4) and (5) for the ground state (note that $a_0^{n_1n_2m}\equiv 1$) was derived by Benassi, Grecchi, Harrell, and Simon.[14] The leading term of Eq. (2) has been discovered or rediscovered at least three times.[9-11] Damburg and Kolosov[11] have given formulas from which $a_1^{n_1n_2m}$ and $a_2^{n_100}$ can be inferred:

$$a_1^{n_1n_2m}=\tfrac{1}{3}n_2(n_2+m-5)-\tfrac{8}{3}(n_1^2+n_2^2)-\tfrac{19}{3}n_1n_2-\tfrac{35}{6}(n_1+n_2)(m+1)-\tfrac{11}{6}m^2-\tfrac{20}{3}m-\tfrac{107}{18}; \quad (6)$$

$$a_2^{n_100}=\tfrac{32}{9}n_1^4+\tfrac{325}{18}n_1^3+\tfrac{7567}{216}n_1^2+\tfrac{11019}{324}n_1+\tfrac{7363}{648}. \quad (7)$$

TABLE I. The expansion coefficients $a_k^{n_1n_2m}$ for both $E_{n_1n_2m}{}^{(N)}$ and $\Gamma_{n_1n_2m}(F)$, obtained from Eqs. (6) and (7) and by fitting Eqs. (4) and (5) with perturbation-theory $E_{n_1n_2m}{}^{(N)}$.

n_1	n_2	m	k	$a_k^{n_1n_2m}$	± Estimated error[a]
0	0	0	0	1.	
			1[b]	-107/18	
			2[c]	7363/648	
			3	-47.0360	± 0.0002
			4	92.65	± 0.2
			5	-1350.	± 20.
1	0	0	0	1.	
			1[b]	-130/9	
			2[c]	33053/324	
			3	-663.45	± 0.1
			4	4450.	± 20.
			5	-34000.	± 3000.
0	1	0	0	1.	
			1[b]	-142/9	
			2	28655/324	± 0.00005
			3	-381.832	± 0.01
			4	1455.7	± 1.0
			5	-11700.	± 200.

[a]The errors given are a subjective estimate of the authors based on the behavior of the extrapolation procedure.

[b]Value is from Eq. (6).

[c]Value is from Eq. (7).

But even to obtain $a_2^{n_100}$ involved "rather cumbersome" calculations,[11] and higher-order exact $a_k^{n_1n_2m}$ are not currently available. We obtain them numerically by extracting them from perturbation-theory values of $E_{n_1n_2m}{}^{(N)}$.

We calculated perturbation theoretic $E_{n_1n_2m}{}^{(N)}$ for $N\leq 150$ by a modification of a method[5] 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.[16-18] 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 ≤ 82.

From numerical values of $E_{n_1n_2m}{}^{(N)}$ calculated by perturbation theory, the $a_k^{n_1n_2m}$ can be obtained by numerically fitting Eqs. (4) and (5) (cf. Bender and Wu[19]). 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^2e^{-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 $\beta_{n_2m}{}^{(N)}$.)

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	$E_{n_1n_2m}^{(N)}$ by asymptotic expansion to term k: k=0	3	5	$E_{n_1n_2m}^{(N)}$ by perturbation theory
	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[a]: $\Gamma^{(0)}$	$\Gamma^{(5)}$	$\Gamma^{(num)}$	Ref.
1	0	0	0	0.02351	8.234×10^{-11}	6.608×10^{-11}	6.616×10^{-11}	11
				0.03145	7.194×10^{-8}	5.857×10^{-8}	5.839×10^{-8}	11
				0.03942	4.588×10^{-6}	3.114×10^{-6}	3.110×10^{-6}	11
				0.04745	6.669×10^{-5}	4.117×10^{-5}	4.106×10^{-5}	11
				0.05556	4.428×10^{-4}	2.459×10^{-4}	2.442×10^{-4}	11
				0.04	5.78×10^{-6}	3.90×10^{-6}	3.89×10^{-6}	20
				0.06	9.96×10^{-4}	5.19×10^{-4}	5.15×10^{-4}	20
				0.08	1.20×10^{-2}	4.67×10^{-3} [b]	4.51×10^{-3}	21
				0.10	5.09×10^{-2}	1.28×10^{-2} [b]	1.45×10^{-2}	20
2	1	0	0	0.003	3.61×10^{-10}	2.12×10^{-10}	2.12×10^{-10}	11
				0.004	2.81×10^{-7}	1.36×10^{-7}	1.36×10^{-7}	11
				0.005	1.45×10^{-5}	5.64×10^{-6}	5.73×10^{-6}	11
				0.006	1.94×10^{-4}	5.74×10^{-5}	6.09×10^{-5}	11
2	0	1	0	0.0025	1.66×10^{-10}	9.92×10^{-11}	9.92×10^{-11}	11
				0.0030	2.49×10^{-8}	1.32×10^{-8}	1.32×10^{-8}	11
				0.0035	8.29×10^{-7}	3.88×10^{-7}	3.86×10^{-7}	11
				0.0040	1.09×10^{-5}	4.45×10^{-6}	4.44×10^{-6}	11

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

[b] Equation (2) with $k \leq 4$. The $k = 5$ term is no longer useful.

retic values for $E_{n_1n_2m}^{(N)}$ 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" $a_k^{n_1n_2m}$ for calculating ionization rates, we list in Table III values of Γ_{000}, Γ_{100}, and Γ_{010} obtained from Eq. (2). The agreement with accurate values obtained from numerical solutions[11,20,21] is excellent. For the $n=2$ states, the six-term results are significantly better than the two-term results of Damburg and Kolosov.[11]

Thus we have demonstrated the agreement of perturbation-theory $E_{n_1n_2m}^{(N)}$ with the asymptotic formula [Eqs. (4) and (5)] obtained from the dispersion relation, and the practicality of extracting the $a_k^{n_1n_2m}$ from the perturbation-theory energies for subsequent calculation of ionization rates.

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