[70] A. A. Tkachenko, Vestn. Leningr. Univ. Ser. Fiz. i Khim. No. 22, 167 (1958).

[71] O. G. Ludwig, private communication.

[72] R. J. Drachman, Phys. Rev. 150, 10 (1966).

[73] S. Kahana, Phys. Rev. 129, 1622 (1963).

[74] J. P. Carbotte and S. Kahana, Phys. Rev. 139, A213 (1965).

[75] J. P. Carbotte, Phys. Rev. 144, 309 (1966).

[76] K. L. Rose and S. DeBenedetti, Phys. Rev. 138, A927 (1965).

[77] E. J. Woll, Phys. Rev. 145, 268 (1966); and in Positron Annihilation, edited by A. T. Stewart and L. O. Roellig (Academic Press, Inc., New York, 1967), p. 329.

[78] R. K. Nesbet, Advan. Chem. Phys. 9, 321 (1965).

[79] E. Hylleraas, Advan. Quantum Chem. 1, 1 (1964).

[80] P.-O. Löwdin, Advan. Chem. Phys. 2, 207 (1959).

[81] R. G. Parr, Quantum Theory of Molecular Electronic Structure (W. A. Benjamin, Inc., New York, 1963).

[82] V. I. Goldanskii, private communication.

[83] C. C. J. Roothaan, J. Chem. Phys. 19, 1445 (1951).

[84] F. E. Harris, J. Chem. Phys. 32, 3 (1960); H. S. Taylor and F. E. Harris, Mol. Phys. 6, 183 (1963).

[85] C. F. Lebeda, Ph.D. thesis, University of Iowa, 1968 (unpublished).

[86] R. A. Bonham, J. Mol. Spectry. 15, 112 (1965).

[87] M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. London 243, 221 (1951).

[88] G. Hultgren, private communication.

PHYSICAL REVIEW VOLUME 178, NUMBER 1 5 FEBRUARY 1969

Exact Treatment of the Stark Effect in Atomic Hydrogen*

Millard H. Alexander
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

(Received 25 July 1968)

A boundary-condition method is used to investigate the energy levels of atomic hydrogen in a uniform electric field. At low fields the misbehavior of trial eigensolutions in the nonclassical region enables one to obtain high-accuracy upper and lower bounds to the Stark shift. At higher fields the energy levels are treated as resonant states imbedded in a continuum. A modified WKB approach is used to obtain both the position and width of these resonances. Comparison is made with the usual perturbation-theory results.

I. INTRODUCTION

An adequate explanation of the Stark effect in atomic hydrogen was one of the first tests applied to the old[1] and new[2,3] quantum theories. The application of perturbation theory was successful in confirming both the linear and quadratic Stark effects.[2,4] Recently these results have been extended to higher order.[5] Several authors have also treated the Stark effect using the WKB technique.[6,7] As yet, however, no exact solution of the appropriate Schrödinger equation has been undertaken. This is perhaps due to the well-known fact that at large distances from the proton the potential energy becomes infinitely negative.[3,8,9] Thus the electric field, however weak, eventually strips off the atomic electron. The problem then becomes more complicated than a simple determination of bound-state energy levels.

In this paper we use a modification of the boundary-condition method, recently used by Rosenthal and Wilson,[10,11] to investigate the energy levels of atomic hydrogen in a uniform electric field. We obtain series solutions to the appropriate Schrödinger equation for various trial eigenvalues. At low fields the nature of the misbehavior of these solutions in the nonclassical regions changes as the sequence of trial eigenvalues crosses the true eigenvalue. This enables us to obtain high-accuracy upper and lower bounds to the Stark Shift. The uncertainty in the energy caused by the unbounded character of the state is less than the difference between these bounds.

At higher fields it becomes necessary to consider explicitly the unbound character of the initially bound states, which now appear as resonant (metastable) states imbedded in a continuum. We use the boundary-condition method together with a modification of the WKB technique to obtain the phase shift of the asymptotic (unbound) eigenfunction. In exact analogy with elementary scattering theory, analysis of the energy dependence of this phase shift yields both the position and width of the metastable levels.

II. GENERAL REMARKS

The Schrödinger equation for atomic hydrogen in a uniform electric field of strength F directed along the z axis is separable in parabolic coordinates, ξ, η, ϕ, yielding the three ordinary differential equations[9,12]

$$\left(\frac{d^2}{d\phi^2}+m^2\right)\Phi(\phi)=0\;, \tag{1}$$

$$\left[\frac{d}{d\xi}\left(\xi\frac{d}{d\xi}\right)-\frac{F\xi^2}{4}+\frac{E\xi}{2}-\frac{m^2}{4\xi}+Z_1\right]M(\xi)=0\;, \tag{2}$$

and

$$\left[\frac{d}{d\eta}\left(\eta\frac{d}{d\eta}\right)+\frac{F\eta^2}{4}+\frac{E\eta}{2}-\frac{m^2}{4\eta}+Z_2\right]L(\eta)=0\ . \tag{3}$$

Here E is the total energy of the system whose eigenfunction may be written as

$$\psi(\xi,\eta,\phi)=L(\eta)M(\xi)\Phi(\phi)\ . \tag{4}$$

The two separation constants Z_1 and Z_2 obey the relation

$$Z_1+Z_2=1 \tag{5}$$

and in the zero-field case have the values

$$Z_1=(2n_1+m+1)/2N \tag{6a}$$

and $$Z_2=(2n_2+m+1)/2N\ , \tag{6b}$$

N being the principal quantum number of the parent hydrogen orbital. The two parabolic quantum numbers n_1 and n_2 are related to N by

$$N=n_1+n_2+m+1\ . \tag{7}$$

The integration of Eq. (1) is trivial, yielding the usual azimuthal functions. The quantum number m is, of course, just the angular momentum about the imposed field direction. Equations (2) and (3) are both boundary-value equations with singularities at 0 and ∞. Consequently they possess properly behaved solutions only for certain related values of the energy E and the two separation constants Z_1 and Z_2. This fact, together with Eq. (5), results in constraints on the allowed values of the energy.

III. SOLUTION OF THE ξ EQUATION

Equation (2) has singularities at $\xi=0$ and $\xi=\infty$. The substitution $M'(\xi)=\sqrt{\xi}\,M(\xi)$ transforms Eq. (2) into the Schrödinger form

$$\left(-\frac{1}{2}\frac{d^2}{d\xi^2}+V(\xi)-\epsilon\right)M'(\xi)=0\ , \tag{8}$$

where

$$V(\xi)=\tfrac{1}{8}\left[F\xi-4Z_1/\xi+(m^2-1)/\xi^2\right]\ , \tag{9}$$

and $\epsilon=\frac{1}{4}E$. The potential function V increases to $+\infty$ with increasing ξ. Thus the solutions of Eq. (2) are related to the bound eigenfunctions of Eq. (8). For each value of the energy E there exists only a discrete set of allowable values of Z_1 for which M behaves correctly at the two singularities.

We assume a series solution to Eq. (2) of the form

$$M=e^{-\xi/2N}\sum_{n=0}^{\infty}a_n\xi^n\ , \tag{10}$$

and further write the energy E and the separation constant Z_1 as

$$E=\Delta E-1/2N^2\ , \tag{11a}$$

and $$Z_1=\Delta Z_1+(2n_1+m+1)/2N\ . \tag{11b}$$

Here ΔE and ΔZ_1 represent the shifts in the energy and in the separation constant from their zero-field values. Following the well-known technique of power series solutions to ordinary differential equations,[13] we substitute the expansion (10) into Eq. (2) and equate coefficients of powers of ξ to zero to obtain the following four-term recursion relation for the coefficients a_n:

$$N(4n^2-m^2)a_n+4(N\Delta Z_1+n_1+\tfrac{1}{2}m+1-n)a_{n-1}+2N\Delta E a_{n-2}-NFa_{n-3}=0\ . \tag{12}$$

Inserting trial values of ΔE and ΔZ_1 and setting $a_0=1$, we can compute as many of the a_n as desired from Eq. (12). One way to examine the solution that these coefficients represent is to compare them with the expansion coefficients of $\exp(+\xi/2N)$, namely $b_n=1/(2N)^n n!$.[11] If for all n greater than some value n_0, $|a_n|>|b_n|$, then M will tend to $+\infty$ if the a_n are all positive or to $-\infty$ if the a_n are all negative. This is indeed what happens; after a certain point the computed coefficients become either all positive or all negative. In Appendix A we show how it is possible to prove from this that the computed function diverges to $+\infty$ or to $-\infty$. The transition from positive to negative divergence indicates that two successive trial values of ΔZ_1 straddle the true value. By repeatedly subdividing the grid of trial values, one can obtain extremely precise upper and lower bounds to the exact ΔZ_1 for a given ΔE. Since the use of parabolic coordinates correctly lifts the degeneracy of the zero-field hydrogen orbitals,[9] once one specifies the initial quantum numbers n_1, n_2, and m in Eqs. (9), (11a), and (11b), there will exist only one allowable value of ΔZ_1 for each ΔE. This series of allowable values defines a continuous curve in the $(\Delta E, \Delta Z_1)$ plane along which the function $M(\xi)$ is well behaved.

IV. SOLUTION OF THE η EQUATION: LOW-FIELD CASE

The substitution $L'(\eta)=\sqrt{\eta}\,L(\eta)$ converts Eq. (3) into an equation similar to Eq. (8), namely

$$\left(-\frac{1}{2}\frac{d^2}{d\eta^2}+V(\eta)-\epsilon\right)L'(\eta)=0\ , \tag{13}$$

where

$$V(\eta)=\tfrac{1}{8}\left[-F\eta-4Z_2/\eta+(m^2-1)/\eta^2\right]\ , \tag{14}$$

and, as before, $\epsilon=\frac{1}{4}E$. Since $V(\eta)$ tends to $-\infty$ for large η, the solution $L'(\eta)$ becomes oscillatory in the asymptotic region. Herein lies the unbounded character of the Stark levels. In contrast with Eq.

(8), Eq. (13) is a one-point boundary-value equation,[12] possessing well-behaved solutions for each ΔE, ΔZ_1 pair arising from the previous solution of the ξ equation.

The presence of the electric field transforms the bound zero-field states into slowly decaying, metastable states, which are initially concentrated in the atomic region ($\eta \simeq a_0$).[6,9,14] Such a metastable state may be represented by a wave packet with η component[15]

$$\chi(\eta) = \eta^{-1/2} \int L'(\eta, Z_2, \epsilon) f(\epsilon)\, d\epsilon\ , \tag{15}$$

$f(\epsilon)$ being an unspecified weight factor. In order that the wave packet be initially concentrated in the atomic region, the only important contributions to the integral in Eq. (15) must come from energies for which

$$|L'(\eta)|_{\eta \simeq 1} \gg |L'(\eta)|_{\eta\ \text{large}}\ . \tag{16}$$

The range of energies over which this inequality holds is a measure of the width of the metastable level.

Now, examination of $V(\eta)$ shows that at low fields there exists a large nonclassical region, defined by $V - \epsilon > 0$, inside of which

$$(1/L')\, d^2L'/d\eta^2 > 0\ . \tag{17}$$

In order for the inequality (16) to hold, L' must not diverge with increasing η inside the nonclassical region. If it then were possible to choose two trial energies such that inside the nonclassical region one eigenfunction L' was diverging positively while the other was diverging negatively, one could thereby bracket the range of energies implied by (16). By subsequently tightening the grid of trial eigenvalues, one could obtain upper and lower bounds to the Stark shift.

To do so we proceed as in the solution of the ξ equation. Assuming a series solution of the form

$$L = e^{-\eta/2N} \sum_{n=0}^{\infty} a_n \eta^n\ , \tag{18}$$

and writing

$$\Delta Z_2 = -\Delta Z_1\ , \tag{19}$$

we substitute (18) into Eq. (3) to obtain the recursion relation

$$N(4n^2 - m^2) a_n + 4(-N\Delta Z_1 + n_2 + \tfrac{1}{2} m + 1 - n) a_{n-1} + 2N\Delta E a_{n-2} + NF a_{n-3} = 0\ . \tag{20}$$

Inserting various ΔE, ΔZ_1 pairs obtained from the previous solution of the ξ equation[16] and setting $a_0 = 1$, we can compute as many coefficients as desired. As before, it is instructive to compare these coefficients with the expansion coefficients of $\exp(+\eta/2N)$, namely $b_n = 1/(2N)^n n!$. If we find $|a_n| > |b_n|$ for all n with $N_0 \le n \le N_1$, then $L(\eta)$ will diverge positively in this range if all the a_n are positive, or diverge negatively if the a_n are negative. Eventually, as n becomes greater than N_1, the a_n will no longer be of the same sign. This sign alternation at large n will reflect the oscillatory behavior of $L(\eta)$ in the asymptotic region. If, however, N_1 is sufficiently greater than N_0, a simple inspection of the expansion coefficients will suffice to determine the behavior of L' in the nonclassical region. In Appendix B we show how one can obtain the upper limit N_1, once N_0 is known.

In practice, at low to medium fields, $N_1 \gg N_0$ and the above criterion may be used. The complete procedure is simple. For a given ΔE one computes ΔZ_1 by solving the ξ equation (Sec. III).[16] One then proceeds as outlined in this Section to determine whether the corresponding function $L'(\eta)$ is diverging positively or negatively in the nonclassical region. Repetition of this procedure yields upper and lower bounds to the Stark shift. We have computed these bounds for the lowest (1s) state of atomic hydrogen ($n_1 = n_2 = m = 0$) at a number of low and medium field strengths.[17] The results are shown in Table I. Obviously, very precise bounds can be obtained.

The standard treatment of the Stark effect by perturbation theory leads to an expression for the Stark shift as a power series in the field strength of the form[3–5,9]

$$\Delta E_{\text{pert}} = -\sum_{n=1}^{\infty} \frac{\alpha_n F^n}{n!}\ . \tag{21}$$

For the lowest state only the coefficients of even powers are nonvanishing. By convention the first-two coefficients, α_2 and α_4, are called, respectively, the polarizability and hyperpolarizability.[18] For the hydrogen 1s level one finds, to fourth order,[19]

$$\Delta E(1s) \simeq -\tfrac{9}{4} F^2 - \tfrac{3555}{64} F^4. \tag{22}$$

Table I also contains a comparison of our results with those obtained using Eq. (22). Clearly, at low to medium fields the fourth-order perturbation theory results represent an upper bound to the exact Stark shifts. From the difference between our results and the fourth-order perturbation theory values one can obtain a crude estimate to the sixth-order term in atomic hydrogen. We find $\alpha_6(1s) = (3.530 \pm 0.015) \times 10^6$ a.u.

V. SOLUTION OF THE η EQUATION: HIGH-FIELD CASE

As the field strength increases, the nonclassical region decreases markedly in width. It is no longer possible to extract any information about the level positions from a simple inspection of the expansion coefficients. Another approach is needed. Asymptotically Eq. (13) admits the usual WKB solution[20]

$$L' \simeq CA^{-1/4} \cos\left(\int_a^\eta \sqrt{A}\, d\eta' - \tfrac{1}{4}\pi + \delta\right), \tag{23}$$

TABLE I. Upper and lower bounds to the Stark shift for the 1*s* state of atomic hydrogen: low-field case.

Field strength[a]	Stark shift[a] Upper bound	Lower bound	Perturbation theory[b]
0.02	$-9.092\,242\,56\times10^{-4}$	$-9.092\,242\,59\times10^{-4}$	$-9.088\,875\,00\times10^{-4}$
0.01	$-2.255\,604\,56\times10^{-4}$	$-2.255\,604\,61\times10^{-4}$	$-2.255\,546\,87\times10^{-4}$
0.009	$-1.826\,170\,85\times10^{-4}$	$-1.826\,170\,90\times10^{-4}$	$-1.826\,144\,43\times10^{-4}$
0.008	$-1.442\,288\,19\times10^{-4}$	$-1.442\,288\,23\times10^{-4}$	$-1.442\,275\,20\times10^{-4}$
0.007	$-1.103\,839\,50\times10^{-4}$	$-1.103\,839\,66\times10^{-4}$	$-1.103\,833\,68\times10^{-4}$
0.006	$-8.107\,221\,93\times10^{-5}$	$-8.107\,221\,95\times10^{-5}$	$-8.107\,198\,88\times10^{-5}$
0.005	$-5.628\,479\,36\times10^{-5}$	$-5.628\,479\,37\times10^{-5}$	$-5.628\,471\,68\times10^{-5}$
0.004	$-3.601\,423\,99\times10^{-5}$	$-3.601\,424\,01\times10^{-5}$	$-3.601\,422\,00\times10^{-5}$
0.001	$-2.250\,055\,54\times10^{-6}$	$-2.250\,055\,58\times10^{-6}$	$-2.250\,055\,47\times10^{-6}$

[a] All quantities are in atomic units. To extend the above results to the case of an arbitrary hydrogen-like ion with nuclear charge Z, one must multiply the field strength by Z^3 and the Stark shift by Z^2 (see Ref. 12).

[b] Fourth-order perturbation theory results, see Eq. (22) of text.

where $A=2(\epsilon-V)$. C is an arbitrary constant, δ is the phase shift, and a is the outer classical turning point, defined by $V(a)-\epsilon=0$.

It is still possible, of course, to expand L' as a power series about the origin and solve for the expansion coefficients. One may then evaluate the asymptotic phase shift δ by matching up the logarithmic derivative of the series solution with the logarithmic derivative of (23) at some point η_0, with $\eta_0>a$. We obtain

$$\delta(\Delta E,\eta_0)=\tfrac{1}{4}\pi-\int_a^{\eta_0}\sqrt{A}\,d\eta+\tan^{-1}\left[-\frac{1}{4}A^{-3/2}\left(\frac{dA}{d\eta}+4A\,d\ln\right)\right]_{\eta=\eta_0}, \tag{24}$$

where $d\ln$ denotes the logarithmic derivative of the series solution and where the argument of the arctangent is evaluated at $\eta=\eta_0$.

The function L' of Eq. (23) is only an asymptotically correct solution to Eq. (13). Thus the value of δ obtained from Eq. (24) should converge to some limiting value $\delta(\Delta E,\infty)$ as the matching point η_0 goes to ∞. A somewhat faster convergence is obtained by using[21]

$$L'\simeq CA^{-1/4}\cos\left(\int_a^{\eta}\sqrt{A}\,d\eta'-\tfrac{1}{4}\pi+\delta-\tfrac{5}{48}A^{-3/2}dA/d\eta\right), \tag{25}$$

which leads to a new expression for the phase shift

$$\delta(\Delta E,\eta_0)=\tfrac{1}{4}\pi-\int_a^{\eta_0}\sqrt{A}\,d\eta+\tfrac{5}{48}A^{-3/2}dA/d\eta+\tan^{-1}B, \tag{26}$$

where

$$B=-\frac{1}{4}A^{-3/2}\left(\frac{dA}{d\eta}+4A\,d\ln\right)\times\left[1+\frac{5}{32}A^{-3}\left(\frac{dA}{d\eta}\right)^2-\frac{5}{48}A^{-2}\left(\frac{d^2A}{d\eta^2}\right)\right]^{-1}. \tag{27}$$

In order to obtain the phase shift δ as a function of ΔE for a given external field, we first fix the energy and solve the ξ equation for ΔZ_1 using the technique of Sec. III. Then using Eq. (5) and the modified WKB technique of this section, we find $\delta(\Delta E)$ from Eq. (26).

If one plots $\delta(\Delta E)$ as a function of energy, one finds that the asymptotic phase shift is quasiconstant over most of the energy range, while undergoing a rapid change of magnitude π over a narrow energy spread, as shown in Fig. 1 for a particular case. This behavior is remarkably similar to that encountered in the elementary treatment of scattering by a central potential where a rapid change in the phase shift indicates the existence of a metastable state.[22] By analogy, then, we identify the resonances found here with the initially bound electronic energy levels. This hypothesis is further confirmed by the fact that the asymptotic amplitude C of $L'(\eta)$ goes through a sharp minimum at resonance.

Making the usual separation of the total phase shift into resonant and nonresonant contributions

$$\delta(\Delta E)=\delta_{NR}(\Delta E)+\delta_R(\Delta E), \tag{28}$$

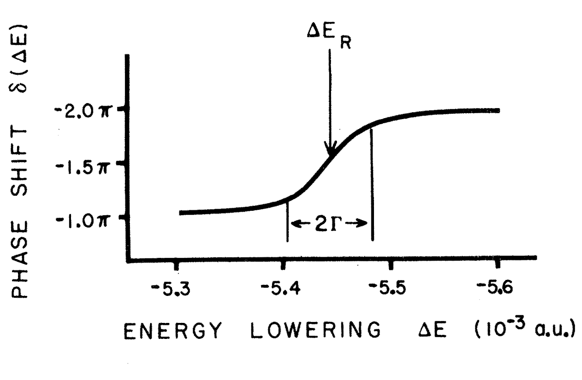

FIG. 1. Energy dependence of the asymptotic phase shift for the 1*s* state of atomic hydrogen in an electric field of 2.440×10^8 V/cm. The resonance parameters are $\Delta E_R=-5.4425\times10^{-3}$ a.u. and $\Gamma=4.10\times10^{-5}$ a.u.

TABLE II. Stark shift and width of the 1*s* state of atomic hydrogen: high-field case. All quantities are in a.u. (see Ref. 12).

Field strength	Stark shift Present work	 Perturbation theory[a]	Level width
0.12	-3.6×10^{-2}	-4.39×10^{-2}	3.1×10^{-2}
0.11	-3.1×10^{-2}	-3.53×10^{-2}	2.2×10^{-2}
0.10	-2.7×10^{-2}	-2.80×10^{-2}	1.5×10^{-2}
0.09	-2.22×10^{-2}	-2.19×10^{-2}	8.8×10^{-3}
0.08	-1.75×10^{-2}	-1.67×10^{-2}	4.6×10^{-3}
0.07	-1.30×10^{-2}	-1.24×10^{-2}	1.9×10^{-3}
0.06	-9.20×10^{-3}	-8.82×10^{-3}	5.2×10^{-4}
0.05	-6.105×10^{-3}	-5.972×10^{-3}	7.8×10^{-5}
0.04	-3.7715×10^{-3}	-3.7422×10^{-3}	4.0×10^{-6}
0.03	-2.074273×10^{-3}	-2.06999×10^{-3}	2.3×10^{-8}

[a] Fourth-order perturbation theory results, see Eq. (22) of text.

we identify the Stark energy shift ΔE_R as that value for which $\delta_R(\Delta E_R)=\frac{1}{2}\pi$. Using the Breit-Wigner parameterization of the resonant phase shift

$$\delta_R(\Delta E)\simeq\tan^{-1}[\Gamma/2(\Delta E_R-\Delta E)]\,, \qquad (29)$$

for ΔE near ΔE_R, one finds the width of the resonance to be given by

$$\Gamma^{-1}=\frac{1}{2}\frac{d}{d\Delta E}\,\delta_R(\Delta E)\bigg|_{\Delta E=\Delta E_R}\,. \qquad (30)$$

In Table II are listed the values of ΔE_R and Γ obtained for various values of the field strength in the case of the 1*s* state of atomic hydrogen. These results are shown graphically in Fig. 2. As the field strength increases, the resonance becomes less sharp.[23] Since the nonclassical barrier through which the electron must tunnel decreases rapidly with increasing field strength, the lifetime of the metastable state should also decrease. The resonance width Γ is equal to the ionization probability of the metastable state.[22] Table III lists the ionization probability of the 1*s* state at various field strengths. Also shown are results obtained by the methods of Lanczos[6] and of Rice and Good.[7] The Lanczos method involves a standard WKB solution of Eq. (13); that of Rice and Good, a standard WKB solution of both Eqs. (8) and (13). The Rice and Good results are seen to be somewhat too large; those of Lanczos, considerably too small.

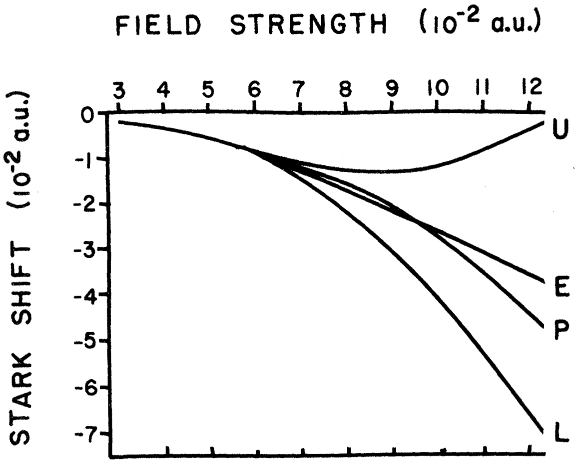

FIG. 2. High-field values of the Stark shift for the 1*s* state of atomic hydrogen. Curve E is the exact result (ΔE_R), while curve *P* is the fourth-order perturbation theory result [Eq. (22) of text]. Curves U and L are upper and lower bounds to the Stark shift, defined by $\Delta E_R\pm\Gamma$.

We notice from Tables I and II and Fig. 2 that the fourth-order perturbation theory results, although representing an upper bound to the exact Stark shift at low to medium fields, become too large at high fields. This might suggest that the perturbation expansion of Eq. (21) is only an asymptotic series, which, if carried far enough, would diverge even at extremely small field strengths. Although less accurate than the boundary-condition method and eventually divergent if carried to high order, perturbation theory does have the advantage of providing general formulas for the Stark shift of type (21) which contain the field strength as an explicit parameter.

ACKNOWLEDGMENTS

The author would like to thank Carey Rosenthal and Professor E. Bright Wilson, Jr., for much helpful discussion.

TABLE III. Ionization probability of the 1*s* state of atomic hydrogen in a strong electric field.

Field strength (V/cm)	Ionization probability (sec^{-1}) Lanczos[a]	 Rice/Good[a]	 this work
2.857×10^{8}	3.16×10^{12}	1.45×10^{13}	1.10×10^{13}
2.440×10^{8}	5.23×10^{11}	2.35×10^{12}	1.69×10^{12}
2.027×10^{8}	3.94×10^{10}	1.73×10^{11}	1.29×10^{11}
1.617×10^{8}	7.40×10^{8}	3.19×10^{9}	2.41×10^{9}

[a] Ionization probabilities calculated by D.S. Bailey, J. R. Hiskes, and A.C. Riviere [Nucl. Fusion 5, 41 (1965)] using the WKB methods of Lanczos (Ref. 6) and of Rice and Good (Ref. 7).

APPENDIX A: DIVERGENCE THEOREM FOR THE ξ EQUATION

We present this theorem for the case of zero angular momentum about the field axis ($m = 0$). An analogous theorem is possible for $m \neq 0$. We define $c_n = a_n/(2N)^n n!$ and $b_n = c_n/c_{n-1}$. Then, if the energy is *lowered* by the application of the electric field ($\Delta E < 0$), the divergence theorem is:

> If for $\Delta E < 0$, there is an n such that $b_{n-2} > 0$, $b_{n-1} > 0$, and $n > 2(N\Delta Z_1 + n_1 + 1)$, then $b_{n'} > 1$, for all $n' \geqslant n$. (A1)

Proof. Using the above definitions of c_n and b_n and the basic recursion scheme [Eq. (12)], we obtain

$$2nb_n = 4n - \alpha + 2\beta \frac{n-1}{b_{n-1}} + 4\gamma \frac{(n-1)(n-2)}{b_{n-1}b_{n-2}}, \tag{A2}$$

where $\alpha = 4(N\Delta Z_1 + n_1 + 1)$,

$\beta = -2\Delta E N^2$, and $\gamma = FN^3$.

Now, if $\Delta E < 0$, then $\beta, \gamma > 0$. If, furthermore, $b_{n-1} > 0$, $b_{n-2} > 0$, and $n > \frac{1}{2}\alpha$, we find $b_n > 1$ and the theorem (A1) is established.

In other words, if n, b_{n-1}, and b_{n-2} satisfy the conditions of (A1), then all the succeeding comparison coefficients $c_{n'}$ will remain of same sign and continuously increase in magnitude. Thus the series component of $M(\xi)$ [Eq. (10)] will eventually diverge faster than $\exp(+\xi/2N)$ and $M(\xi)$ will itself diverge to $+\infty$ or to $-\infty$ depending on the sign of the expansion coefficients.

In practice these conditions are met rather easily. In the case of the 1s state of hydrogen in a field of strength 0.009 a.u., for $\Delta E = -1.826\,170\,85 \cdot 10^{-4}$ a.u. (see Table I), and for an upper bound to ΔZ_1 which differs by not more than 1 part in 10^{-10} from its true value, the requisite value of n in (A1) is only 18.

An entirely similar divergence theorem is possible in the case of a positive Stark shift ($\Delta E > 0$). We simply state the theorem without proof:

> If for $\Delta E > 0$, there is an n such that $b_{n-2} > 0$, $b_{n-1} > 1$, and $n > 2(N\Delta Z_1 + n_1 + 1)/(1 - 2\Delta E N^2)$, then $b_{n'} > 1$, for all $n' \geqslant n$. (A3)

APPENDIX B: PARTIAL DIVERGENCE THEOREM FOR THE η EQUATION

Here, as in the previous Appendix, we consider explicitly only the $m = 0$ case with $\Delta E < 0$. We define $c_n = a_n/(2N)^n n!$ and $b_n = c_n/c_{n-1}$, where the coefficients now refer to the η expansion of Eq. (18). Retaining the parameters β and γ of Appendix A and redefining α as $\alpha = 4(-n\Delta Z_1 + n_2 + 1)$, we write the partial divergence theorem as follows: divergence theorem (B1) is established for $n \leqslant n_+$.

In practice at low to medium fields one finds $n_+ \gg n_-$, so that the function $L(\eta)$ exhibits divergent behavior over a large range of n. With the same example used in Appendix A, we find $n_- = 2$, $n = 19$, and $n_+ = 56$. In fact the upper limit n_+ given in (B1) is somewhat restrictive; actual computation of the high-order coefficients shows that $b_n > 1$ for $17 \leqslant n \leqslant 76$.

> If, for $\Delta E < 0$, $\gamma(\gamma + 3 - \alpha) > -\frac{1}{4}$, and if there is an n such that $n > n_-$, $b_{n-1} > 1$, and $b_{n-2} > 1$, then $b_{n'} > 1$, for all n' with $n \leqslant n' \leqslant n_+$, where n_- and n_+ are given by
>
> $$n_\pm = \tfrac{1}{4}\gamma^{-1}\{1 + 6\gamma \pm [4\gamma^2 + 4\gamma(3 - \alpha) + 1]^{1/2}\}. \tag{B1}$$

Proof. As in Appendix *A* we use the recursion relation (20) and the above definitions of α, β, and γ to write

$$2nb_n = 4n - \alpha + 2\beta \frac{n-1}{b_{n-1}} - 4\gamma \frac{(n-1)(n-2)}{b_{n-1}b_{n-2}}. \tag{B2}$$

Now, if $\Delta E < 0$, then, as before, $\beta, \gamma > 0$. If furthermore $b_{n-1} > 1$ and $b_{n-2} > 1$, we have

$$b_n > 1 + [2n - \alpha - 4\gamma(n-1)(n-2)]/2n. \tag{B3}$$

The coefficient b_n will be greater than unity provided the quantity in brackets in (B3) is greater than zero. This quantity is a quadratic function of n whose two roots are given by n_- and n_+ with $n_+ \geqslant n_-$. Since the term in n^2 enters in with a minus sign, b_n will be greater than unity for all values of n lying between n_- and n_+.[24] Thus the

---

*Research supported in part by a Grant extended Harvard University by the National Science Foundation, GP-6413.

[1] P. S. Epstein, Ann. Physik 50, 489 (1916); K. Schwarzchild; Sitzber. Berliner Akad. (1916) p. 548.

[2] E. Schrödinger, Ann. Physik 80, 457 (1926); P.S. Epstein, Phys. Rev. 28, 695 (1926); G. Wentzel, Z. Physik 38, 518 (1926); I. Waller, *ibid.* 38, 635 (1926).

[3] E.U. Condon and G.H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, England, 1963) p. 397.

[4] Y. Ishida and S. Hiyama, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 9, 1 (1928).

[5] N.-Hoe, E. Bannerjea, H.-W. Drawin, and L. Herman, J. Quant. Spectry. Radiative Transfer 5, 835 (1965).

[6] C. Lanczos, Z. Physik 62, 518 (1930); 65, 431 (1930); 68, 204 (1931).

[7] M. H. Rice and R. H. Good, Jr., J. Opt. Soc. Am. 52, 239 (1962).

[8] J. R. Oppenheimer, Phys. Rev. 31, 66 (1928).

[9] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Springer-Verlag, Berlin, 1957) p. 228.

[10] C. M. Rosenthal and E. B. Wilson, Jr., Phys. Rev. Letters 19, 143 (1967).

[11] C. M. Rosenthal and E. B. Wilson, Jr., to be published.

[12] We shall use atomic units throughout. The atomic unit of electric field intensity is 1 a.u. $= 1.71 \times 10^7$ esu $= 5.142 \times 10^9$ V/cm. (Ref. 9). The present results may be extended to the case of an arbitrary hydrogen-

like ion of nuclear charge Z by converting to the $1/Z$ system of units. The new unit of length is $1/Z$ a.u.; the new unit of energy, $1/Z^2$ a.u.; and the unit of field intensity, $1/Z^3$ a.u.

[13] E. L. Ince, Ordinary Differential Equations (Dover Publications, Inc., New York, 1926).

[14] L. B. Redei, Phys. Letters **1**, 191 (1962).

[15] Here we have surpressed the time dependence.

[16] Our method of solution to the ξ equation yields both upper and lower bounds to ΔZ_1 for a given ΔE. After obtaining these bounds to high precision (10 significant figures), we then average them for use in solving the η equation.

[17] All calculations were carried out with double-precision arithmetic. The determination of upper and lower bounds to ΔE, differing by less than 1 part in 10^8 and involving the determination of ΔZ_1 to within 1 part in 10^{10}, takes less than 20 sec on an IBM 7094.

[18] C. A. Coulson, A. Maccoll, and L. E. Sutton, Trans. Faraday Soc. **81**, 106 (1952); P. W. Langhoff, J. D. Lyons, and R. P. Hurst, Phys. Rev. **148**, 18 (1966).

[19] For the determination of the 2nd order term, see Ref. 9. The exact 4th order term is due to A. Dalgarno, Quantum Theory, edited by Bates, (Academic Press, Inc., New York, 1961) Vol. 1, p. 187.

[20] A. Messiah, Mécanique Quantique (Dunod, Paris, 1965) Vol. I, pp. 194–202.

[21] This form includes the first element of the correction term given by Messiah; Eq. (45), p. 196 of Ref. 20. For the 1s state of hydrogen at a field strength of 0.05 a.u., the phase shift obtained from Eq. (26) has converged to within 1 part in 10^4 at $\eta_0 = 40$ a.u. Using Eq. (24), one obtains the same degree of convergence only for $\eta_0 > 80$ a.u.

[22] Reference 20, pp. 336–342.

[23] Indeed, for fields greater than 0.12 a.u. the slope of $\delta(\Delta E)$ becomes very nearly constant. It is then impossible to distinguish any resonant behavior at all.

[24] We assume that there exist two real roots. If the roots are imaginary, then b_n is always less than unity and it becomes impossible to establish a partial divergence theorem. We have not encountered this situation.

PHYSICAL REVIEW VOLUME 178, NUMBER 1 5 FEBRUARY 1969

Measurement of an Emission Cross Section for the Collision Reaction $H^+ + N_2(X^1\Sigma_g{}^+, v=0) \rightarrow H(3p,3d) + N_2{}^+(B^2\Sigma_u{}^+, v=0)$ Using Photon-Coincidence Techniques*

S. J. Young, J. S. Murray, and J. R. Sheridan†

Physics Department and Geophysical Institute, University of Alaska, College, Alaska

(Received 24 June 1968)

The measurement of the cross section for the emission of a Balmer-α and a $N_2{}^+(0,0)$ first-negative-band photon from a hydrogen atom and a $N_2{}^+$ molecule excited simultaneously in the same $H^+ + N_2$ electron-capture collision has been performed in the proton velocity range from 0.54×10^8 cm/sec to 2.40×10^8 cm/sec. The measurement has been accomplished using the technique of single photon-coincidence detection. To within the random error of the experiment, the cross section has only a single-peak structure with a maximum value of 1.2×10^{-18} cm^2 at a velocity of 1.15×10^8 cm/sec. The magnitude and shape of the measured cross section is found to be in good agreement with a cross section calculated by assuming that final-state excitations of the two product systems are uncorrelated.

I. INTRODUCTION

The specification of a particular collision reaction between two systems, both of which have internal structure, must necessarily include a statement of the structural state of both product systems. If the systems are prepared in given initial states and total rather than differential reaction cross sections are desired, the specification of the final internal states of both systems defines a unique collision reaction. However, in previous cross-section measurements for such systems the final states of both colliding partners have not been specified.

An experiment in which the initial and final states of both reacting systems are specified has been carried out at our laboratory for the specific case of simultaneous excitation of the 3p or 3d state of hydrogen and the 0 vibrational level of the $B^2\Sigma_u{}^+$ state of $N_2{}^+$ (hereafter referred to as the "B state") in electron-capture collisions of protons with nitrogen molecules. Specifically, we have measured the cross section for production of Balmer-α radiation from the 3p or 3d states of hydrogen and 3914 Å $N_2{}^+$ band emission in a single-proton–nitrogen collision. This measurement has been accomplished by counting single photons in coincidence.

This method for measuring collision-reaction cross sections consists, in brief, in the detection of the two photons resulting from the excitation of