is only 40% of the correct value. On the other hand, as Fig. 1 shows, the energy distribution between the two photons is given rather accurately by the extremely simple momentum-translation spectrum, Eq. (3.11). The correct spectrum, Eq. (3.12), is very much more complicated. It is very difficult to obtain by perturbative methods.

It would appear that the momentum-translation method retains a usefulness even outside its domain of applicability for giving quick simple analytical results that can provide a useful guide to qualitative behavior.

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First-Order Stark Shifts for Low Electric Fields

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First-order Stark shifts and level-crossing fields have been calculated for states $n=2$, 3, 4 and $Z=1$, 2, 3, 4, for applied electric fields from 0 up to a few kV/cm, using the solutions of the Dirac–Coulomb Hamiltonian. Comparison with the earlier work of Lüders and the experiments of Steubing, Junge, and Gunther has been made.

I. INTRODUCTION

There has been a good deal of interest in the experimental study of the Stark effect in recent years.[1] The use of Stark shifts to measure electric fields has been a standard technique in plasma physics. The effect of electric fields on the electron distributions in atoms has been a matter of interest. Methods of detecting small splittings of atomic levels, of the order of 10^{-4} cm^{-1} in the optical range and 10^{-7} cm^{-1} in the radio-frequency range, have recently been developed. The methods of atomic beams propagated perpendicular to the direction of observation of emission and absorption, instead of the observation of vapors,[2] have increased the sensitivity by a factor of 1000, and the Stark shifts can now be observed for as small a field as 10^3 to 10^5 V/cm. The novel radiospectroscopic techniques which have a resolution of 10^{-7} cm^{-1} are used to measure shifts between the sublevels of a given spectroscopic term. Furthermore, the phenomenon of double radio-optical resonance has made it possible to use the high resolving power of radiospectroscopic methods to study the Stark effect in excited states of atoms.[3] Some difficulties encountered in this radio-optical-resonance method have been eliminated in the method of level crossing[4] and in the beat method[5] where one observes the anomalous increase in the depth of modulation of the exciting term which is split in the electric field. Only the natural width

TABLE I. Stark-shift calculations for $n=2$, $Z=4$.

j	μ	n_F	F MV cm^{-1}	Stark shift using Dirac wave functions (cm^{-1})	Stark-shift Luders's calculations (cm^{-1})
$\frac{3}{2}$	$\frac{1}{2}$	+1	0.2	0.294 231	0.294 461
			0.4	1.171 366	1.172 346
			0.6	2.615 130	2.617 216
			0.8	4.599 243	4.602 874
			1.0	7.089 028	7.094 558
			1.2	10.043 625	10.051 319
			1.4	13.418 507	13.428 542
$\frac{1}{2}$	$\frac{1}{2}$	0	0.2	−89.796 186	−89.745 283
			0.4	−86.546 617	−86.494 786
			0.6	−83.612 549	−83.560 100
			0.8	−80.992 480	−80.939 678
			1.0	−78.676 516	−78.623 625
			1.2	−76.647 472	−76.594 715
			1.4	−74.882 425	−74.829 977
$\frac{1}{2}$	$\frac{1}{2}$	−1	0.2	−97.206 534	−97.158 236
			0.4	−101.333 210	−101.286 590
			0.6	−105.711 072	−105.666 219
			0.8	−110.315 251	−110.272 252
			1.0	−115.120 94	−115.079 953
			1.2	−120.104 668	−120.065 689

TABLE II. Stark-shift calculations for $n=3$, $Z=1$ and $Z=3$.

		$n=3$					
		$Z=1$				$Z=3$	
F V/cm	Exact Dirac (cm^{-1})	Lüders's work (cm^{-1})	Symmetric Hamiltonian (cm^{-1})	F kV/cm	Exact Dirac (cm^{-1})	Lüders's work (cm^{-1})	Symmetric Hamiltonian (cm^{-1})
			$j=\frac{5}{2}$, $\mu=\frac{1}{2}$, $n_F=2$				
100.4	0.010 613 8	0.010 613 8	0.033 873	10	0.164 407	0.164 430	0.166 932 34
200.8	0.033 672 0	0.033 672 0	0.066 774 6	20	0.606 753	0.606 834	0.333 864
300.2	0.062 320 9	0.062 322 5	0.100 162 0	30	1.238 854	1.239 033	0.500 797
401.6	0.094 200 6	0.094 202 3	0.133 549 3	40	1.998 812	1.999 106	0.667 729 3
502.0	0.128 098	0.128 101 32	0.166 936	50	2.851 092	2.851 529	0.834 661
			$j=\frac{5}{2}$, $\mu=\frac{3}{2}$, $n_F=1$				
100.4	0.071 751 7	0.071 756 15	0.017 638	10	0.012 698 4	0.012 698 0	0.088 190 2
200.8	0.022 344 3	0.022 344 8	0.035 276 1	20	0.048 550 2	0.048 549 9	0.176 380
301.2	0.039 903 3	0.039 903 7	0.052 914 2	30	0.102 377	0.102 381	0.264 570
401.6	0.058 279 3	0.053 279 7	0.070 552 3	40	0.168 795	0.168 805	0.352 760
502.0	0.077 009 8	0.077 011 5	0.088 190 4	50	0.243 659	0.243 668	0.440 951

of terms sets a limit to the sensitivity of these methods.[6]

While quite a few theoretical papers have appeared on the Stark effect due to high fields and high-frequency alternating fields,[7] a relativistic study of Stark shifts for small uniform electric fields has not been made. After the classical estimates of Kramers,[8] Schlapp and Rojansky[9] examined the effect of spin-orbit coupling in atoms subjected to Stark fields, using the Darwin approximation to the Dirac equation as a basis for theoretical calculations.[10] Lüders[11] calculated first-order Stark effects and intensities of the hydrogen lines making use of the Pauli approximation to the Dirac equation and Pauli spinors as basis sets in the perturbation calculation. In the present work we have examined the effects on Lüders's results of using the solutions of the exact Dirac–Coulomb Hamiltonian as basis sets.

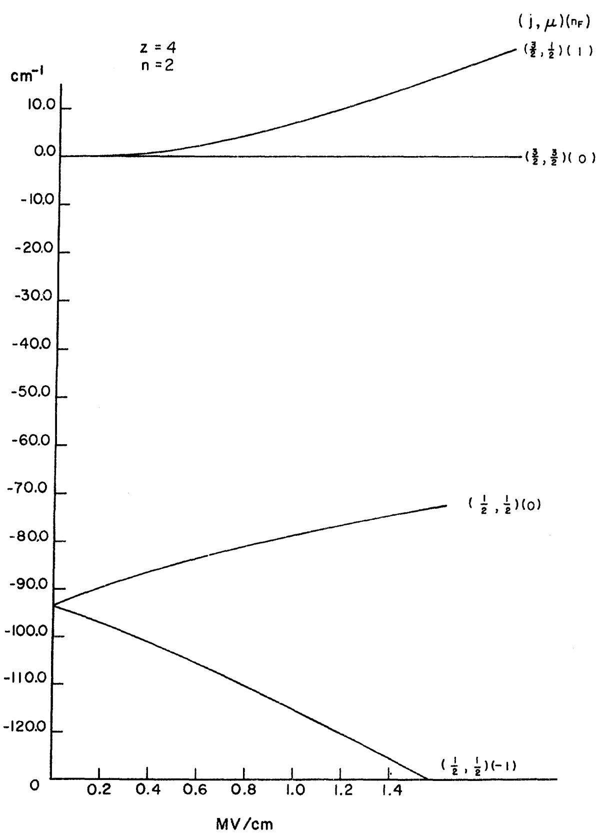

FIG. 1. First-order Stark shifts for $n=2$, $Z=4$.

II. RESULTS AND DISCUSSION

The Stark shifts have been calculated using well-known degenerate perturbation theory. Unlike the approach of Schrödinger and Epstein which was suited to the nonrelativistic case and in the absence of parabolic solutions to the Dirac–Coulomb problem, the basis set chosen here is the solution in spherical polar coordinates. Essential details of the theory are given in Lüders's work, and we give in the Appendix the typical matrix element that is involved in the secular determinant. The first-order Stark shifts presented here are for levels with principal quantum numbers $n=2, 3, 4, 5,$

TABLE III. Level-crossing field for $n=3$, $Z=1$ and $Z=3$.

j	μ	n_F	j'	μ'	n_F'	$Z=1$	$Z=3$
$\frac{3}{2}$	$\frac{1}{2}$	1	$\frac{3}{2}$	$\frac{3}{2}$	0	100.0 V/cm	2.7×10^4 V/cm
$\frac{3}{2}$	$\frac{1}{2}$	1	$\frac{5}{2}$	$\frac{5}{2}$	0	350.0 V/cm	7.75×10^4 V/cm

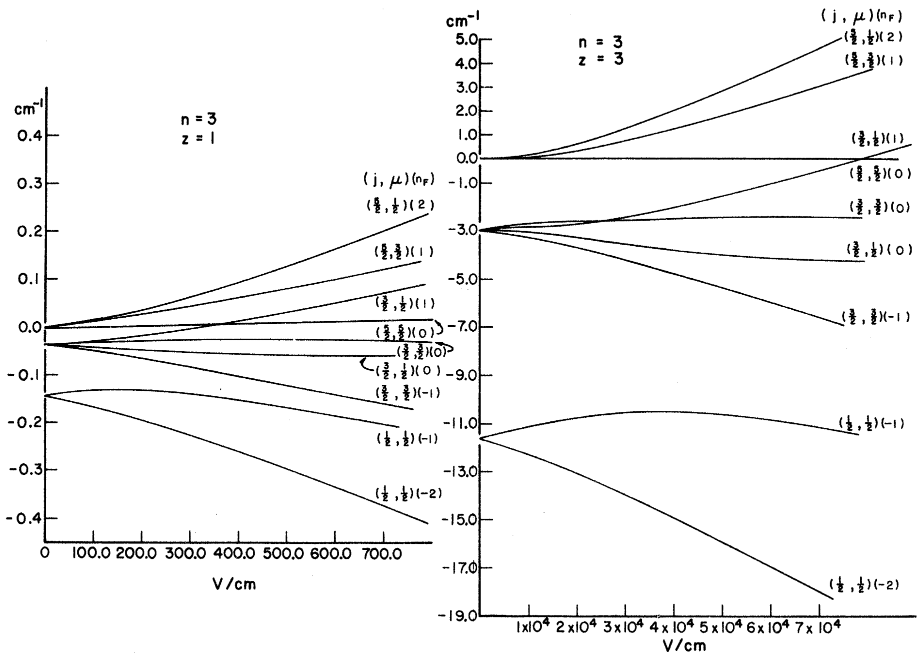

FIG. 2. First-order Stark shifts for $n=3$, $Z=1$ and $Z=3$.

6 for atomic numbers $Z=1, 2, 3, 4$. The results for several other Z values are stored on tape. The values of the electric fields used in the calculations are dependent on the Z values such that the fine-structure splitting and Stark shifts are comparable but yet the Lamb shift is negligible. The energy level with $\kappa=-n$ and $\mu=(n-\frac{1}{2})$ is not affected by the electric field, and this is, therefore, taken as the reference level for computing the energy shifts of other sublevels within a given n value. In Fig. 1 are shown the Stark splittings of the $n=2$ term in the atom with $Z=4$ for electric fields ranging from 0 to 351.4 kV/cm. The fine-structure splitting in this case is of the order of 93.4 cm^{-1}. The degeneracy is lifted and the $2S_{1/2}^{1/2}$ and $2P_{1/2}^{1/2}$ states separate. No level crossing is observed here. Since only the Stark field has been treated as a perturbation, the spin-orbit interaction being included in the unperturbed Hamiltonian, one might

TABLE IV. Level-crossing fields for $n=4$, $Z=2$.

j	μ	n_F	j'	μ'	n_F'	Level-crossing fields
$\frac{5}{2}$	$\frac{1}{2}$	1	$\frac{5}{2}$	$\frac{5}{2}$	0	1120 V/cm
$\frac{5}{2}$	$\frac{1}{2}$	2	$\frac{7}{2}$	$\frac{7}{2}$	0	1130 V/cm
$\frac{5}{2}$	$\frac{3}{2}$	1	$\frac{7}{2}$	$\frac{7}{2}$	0	1500 V/cm
$\frac{5}{2}$	$\frac{1}{2}$	2	$\frac{7}{2}$	$\frac{5}{2}$	1	2425 V/cm
$\frac{5}{2}$	$\frac{1}{2}$	1	$\frac{7}{2}$	$\frac{7}{2}$	0	2650 V/cm
$\frac{5}{2}$	$\frac{5}{2}$	-1	$\frac{3}{2}$	$\frac{3}{2}$	-1	2520 V/cm
$\frac{3}{2}$	$\frac{1}{2}$	0	$\frac{3}{2}$	$\frac{3}{2}$	-1	1200 V/cm

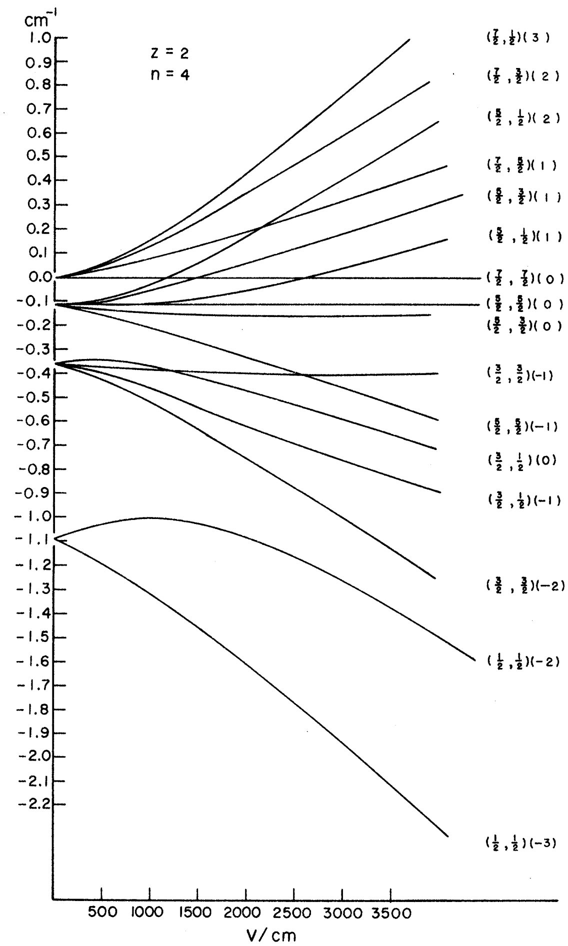

FIG. 3. First-order Stark shifts for $n=4$, $Z=2$.

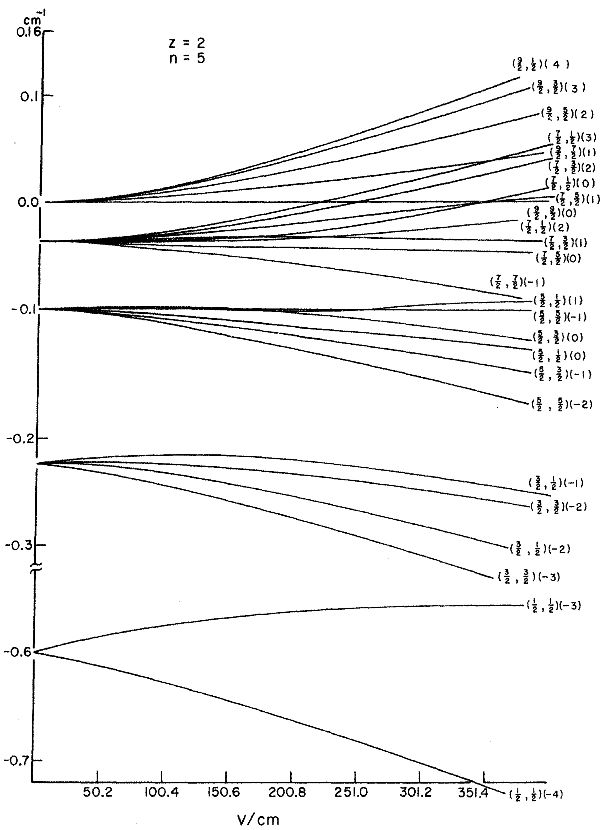

FIG. 4. First-order Stark shifts for $n=5$, $Z=2$.

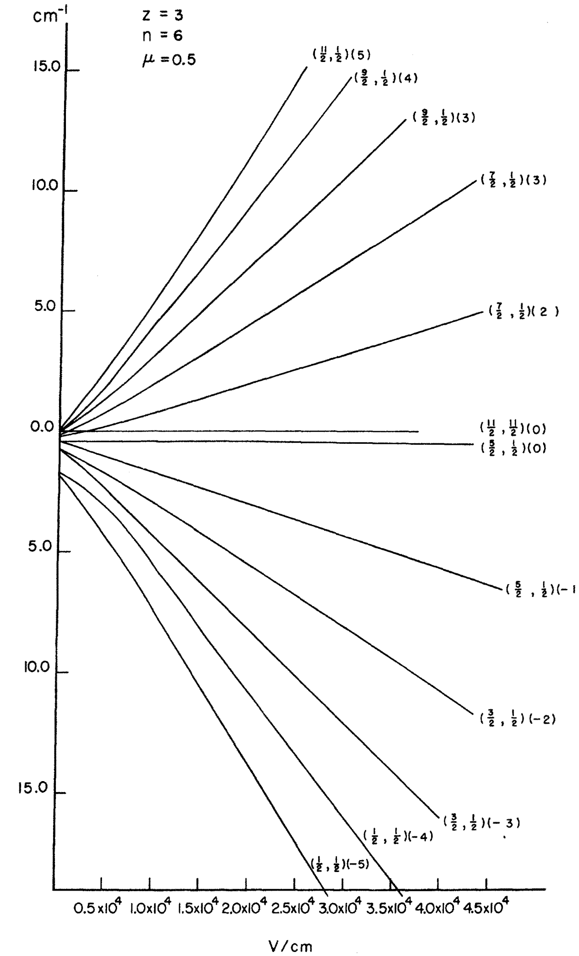

FIG. 5. First-order Stark shifts for $n=6$, $Z=3$.

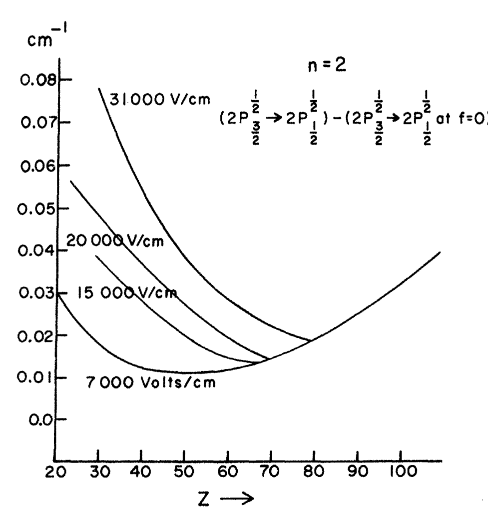

FIG. 6. Effect of electric field on the transition $2P_{3/2}^{1/2} \to 2P_{1/2}^{1/2}$ as a function of Z.

expect the level shift to be linearly dependent on the field. However, it is easily seen that this is not so if we bear in mind the near degeneracy of the zero-order levels. In Fig. 2 are shown the shifts of the levels with $n=3$, $Z=1$, and $Z=3$ for field strengths from 0 to 700 V/cm as well as 70 000 V/cm. In Tables I and II a comparison is made of the shifts calculated on the basis of the Dirac Hamiltonian, Lüders's estimates, and also calculations made using the solutions of the symmetric Hamiltonian.[12] The approximately relativistic symmetric Hamiltonian has been used in other experimental situations[13] because of the simplicity of its radial solutions, and we are interested to know its range of validity for this problem. In Table III we show the field strengths at which various levels cross. Similarly, Fig. 3 shows the shifts for $n=4$, $Z=2$ for field strengths 0 to 3500 V/cm, and Table IV shows the field strengths at which different levels cross. Figure 4 shows the splittings for $n=5$, $Z=2$ and Fig. 5 for $n=6$, $Z=3$. In Fig. 6 we show the effect of electric field on the transition $2P_{3/2}^{1/2} \to 2P_{1/2}^{1/2}$ as a function of Z. In Figs. 1 through 5 we see that the term $J=n-\frac{1}{2}$, $\mu=n-\frac{1}{2}$ does not have first-order Stark effects. To study the effect of an electric field on

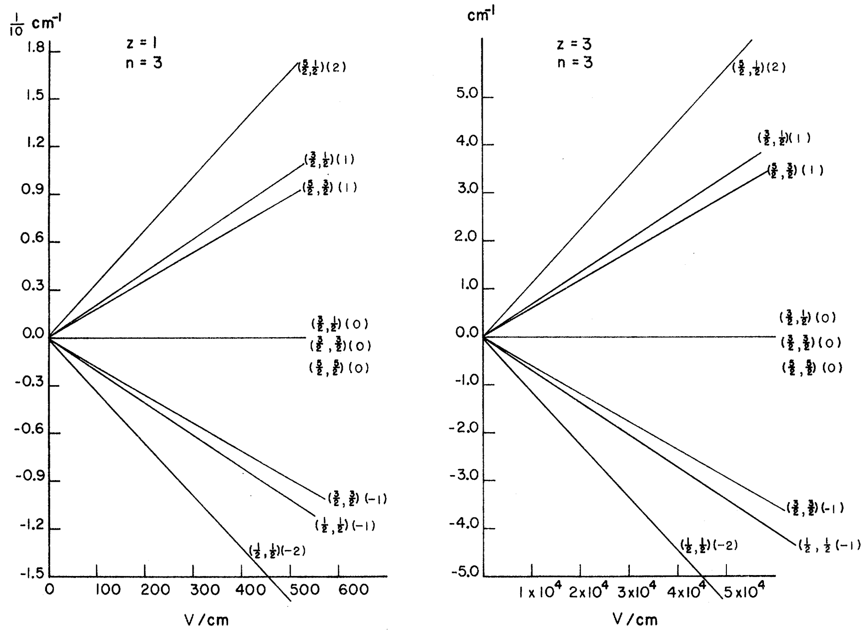

FIG. 7. First-order Stark shifts for $n=3$, $Z=1$ and $Z=3$ using symmetric Hamiltonian.

terms like $2P^{3/2}_{3/2}$, $3D^{5/2}_{5/2}$, $4F^{7/2}_{7/2}$, $5G^{9/2}_{9/2}$, and $6H^{11/2}_{11/2}$ second-order perturbation theory is needed.

Figure 7 shows the energy-level shifts calculated on the basis of the symmetric Hamiltonian. Because of the $O(4)$ symmetry of this Hamiltonian the

TABLE V. Parameter for the first-order Stark effect in hydrogen.

			First-order Stark constant in $cm^{-1}/kV\ cm^{-1}$		
n	n_f	nn_f	Dirac	Symmetric	Experimental
2	1	2	0.056 31	0.052 788	
3	2	6	0.063 17	0.055 645	
			0.064 97	0.055 445	
	1	3	0.065 45	0.067 181	
			0.062 4		
			0.064 50	0.058 55	
4	3	12	0.064 21	0.057 06	
	2	8	0.064 21	0.066 59	0.064 49
			0.065 11	0.059 45	
	1	4	0.064 39	0.066 82	0.064 28
			0.064 23	0.060 82	
			0.064 02	0.057 39	
5	4	20	0.063 95	0.058 15	
	3	15	0.063 95	0.066 19	0.064 02
			0.063 85	0.059 81	
				0.066 62	
	2	10	0.064 53	0.061 11	
				0.05849	
	1	5	0.064 21	0.066 05	
				0.066 29	
				0.059 88	
				0.061 85	

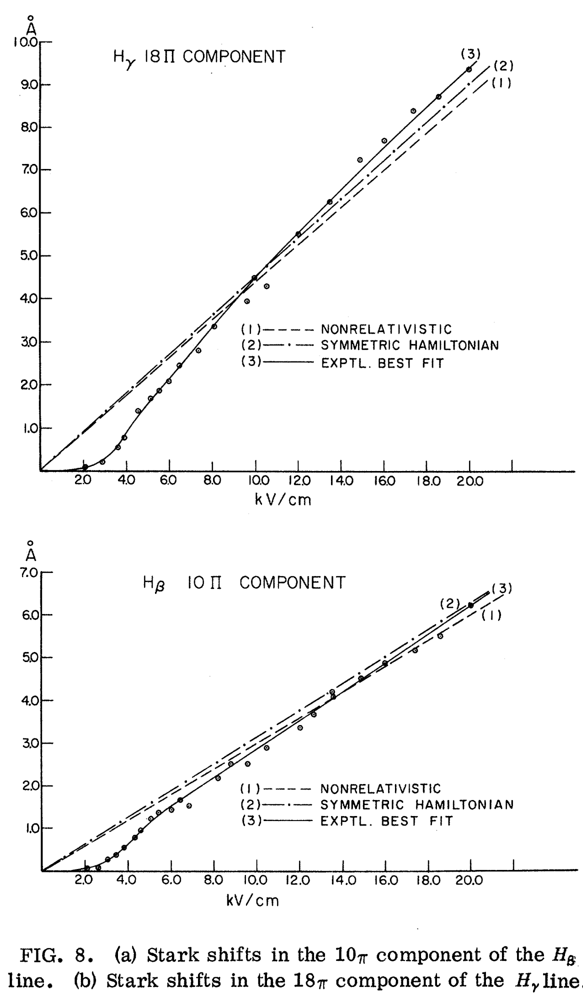

FIG. 8. (a) Stark shifts in the 10π component of the H_β line. (b) Stark shifts in the 18π component of the H_γ line.

states with different j within a given n are degenerate and the shifts are linear just as in the nonrelativistic case. Steubing and Junge[14] measured the Stark shifts in the 10π component of the H_β line and the 18π component of the H_γ line. Figures 8(a) and 8(b) show the calculated shifts, and Table V gives a comparison of the experimental and theoretical values of the proportionality constant. The experimental shift is quadratic for fields below 5000 V/cm. A discussion of these features as well as the explanation for the discrepancy between theory and experiment concerning the absence of experimental Stark shift for fields less than 200 V/cm has already been given by Lüders.[11] Steubing and Gunther[15] made measurements of the Stark shifts of the 4686-Å line of ionized helium. Figure 9 shows the comparison of experimental and theoretical results, and is essentially Fig. 7 of the paper of Steubing and Gunther, since in these cases the symmetric Hamiltonian and the exact Dirac–Coulomb Hamiltonian give more or less indistinguishable predictions. The proportionality constant turns out to be 6.402 $cm^{-1}/MV\ cm^{-1}$.

The calculations of Lüders using the Pauli approximation differ but little from those based on the exact Dirac solutions for low-Z values, the difference being of the order 10^{-3} to 10^{-8} cm^{-1}. Hence Lüders's curves could not be shown on the same graph for comparison with ours. While only the Darwin term was ignored by Lüders as far as the unperturbed Hamiltonian was concerned, his approximation really consisted in using Pauli spinors for the basis set in the perturbation calculation. The negligible difference between our two results shows then that the most important relativistic effect is spin-orbit coupling which Lüders had included. To this extent our work only confirms Lüders's calculations. In addition, however, the level-crossing fields are also given here. For cases other than hydrogen and ionized helium the basis set should perhaps be derived from a relativistic Hartree–Fock solution of a many-particle Hamiltonian. As far as the symmetric Hamiltonian is concerned, as is to be expected, it gives close results to the exact Dirac results when Z/k is small and the applied electric field relatively high.

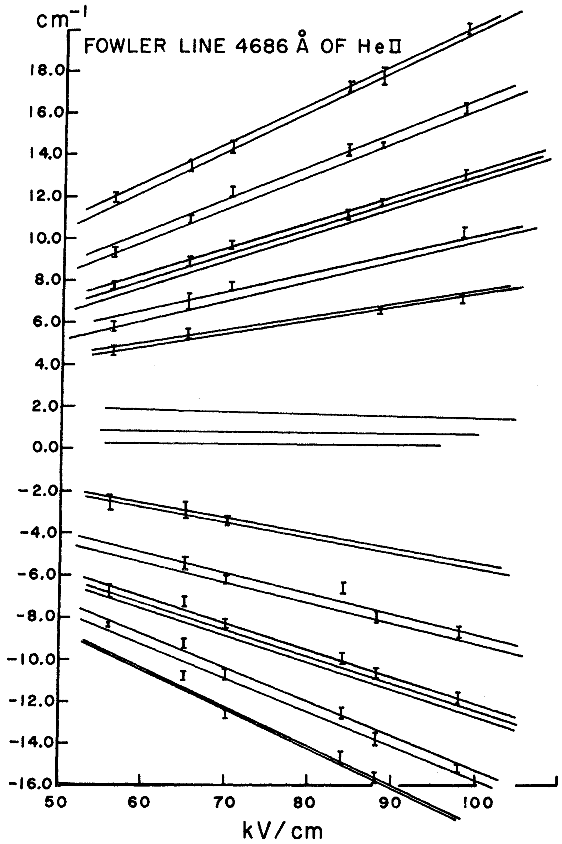

FIG. 9. Experimental and theoretical Stark shifts of 4686-Å line of He II.

APPENDIX

In the notation now familiar[16] and using Racah algebra, a typical matrix element of the secular determinant is calculated to be

$$\langle \psi_{n\kappa\mu} | F e r \cos\theta | \psi_{n\kappa'\mu'} \rangle = Fe\, \delta_{\mu\mu'}\, C(j'\mu' 1 0 | j\mu) \langle j' \| Y_1 \| j \rangle \sum_{\tau} C(l\ \mu-\tau\ 1 0 | l'\ \mu-\tau) f f'$$
$$\times \left(\{1 + [(1-\epsilon)(1-\epsilon')/(1+\epsilon)(1+\epsilon')]^{1/2}\} [(n-k)(n-k') I_{11} + (N-k)(N'-k') I_{22}] \right.$$
$$\left. - \{1 - [(1-\epsilon)(1-\epsilon')/(1+\epsilon)(1+\epsilon')]^{1/2}\} [(n-k)(N'-k') I_{12} + (n-k')(N-k) I_{21}] \right), \quad (1)$$

where we have used the abbreviations

κ = Dirac quantum number,

$j \equiv j(\kappa)$,

$j' \equiv j(\kappa')$,

$l \equiv l(\kappa)$,

$l' \equiv l(\kappa')$,

$$k = |\kappa| = j + \tfrac{1}{2}\ ,$$
$$\gamma = [k^2 - (\alpha z)^2]^{1/2} = \gamma(k), \quad \gamma' \equiv \gamma(k')\ ,$$
$$N \equiv [n^2 - 2(n-k)(k-\gamma)]^{1/2} = N(k,\gamma), \quad N \equiv N(k',\gamma')\ ,$$
$$f \equiv \left(\frac{1}{\Gamma(2\gamma+1)}\right)\left(\frac{\Gamma(2\gamma+n-k+1)(1+\epsilon)}{\Gamma(n-k+1)\,4N(N-k)}\right)^{1/2}$$
$$= f(n,\gamma,k,N)\ ,$$
$$f' \equiv f(n,\gamma',k',N')\ ,$$
$$\epsilon \equiv \{1 + [\alpha z/(n+\gamma-k)]^2\}^{1/2} = \epsilon(n,k)\ ,$$
$$\epsilon' \equiv \epsilon(n,k')\ . \tag{2}$$

The radial integrals I_{ij} are

$$I_{ij} = \int_0^\infty \varphi_i(k)\, r^3 \varphi_j(k')\, dr, \quad i,j = 1,2 \tag{3}$$

where

$$\begin{aligned}\varphi_1(k) &= e^{-\lambda r}(2\lambda r)^{\gamma-1}\, {}_1F_1(-n+k+1,\ 2\gamma+1;\ 2\lambda r)\ ,\\ \varphi_2(k) &= e^{-\lambda r}(2\lambda r)^{\gamma-1}\, {}_1F_1(-n+k,\ 2\gamma+1;\ 2\lambda r)\ ,\end{aligned} \tag{4}$$

and $\lambda = Z/Na_0$, a_0 being the radius of the first Bohr orbit. These convergent integrals are easily evaluated following standard techniques.[17] I_{11}, for instance, turns out to be

$$I_{11} = \left(\frac{2}{Na_0}\right)^{\gamma-1}\left(\frac{2}{N'a_0}\right)^{\gamma'-1}$$
$$\times\left[\sum_{S=0}^{\infty}\sum_{q=0}^{S} \frac{(-n+k+1)_{S-q}}{(2\gamma+1)_{S-q}(S-q)!}\right.$$
$$\times\left(\frac{2}{Na_0}\right)^{S-q}\frac{(-n+k'+1)_q}{(2\gamma'+1)_q\, q!}\left(\frac{2}{N'a_0}\right)^q$$
$$\left.\times\left(\frac{1}{N}+\frac{1}{N'}\right)^{\gamma+\gamma'+2+S}\Gamma(\gamma+\gamma'+S+2)\right]\ . \tag{5}$$

We have used Kummer's notation

$$(a)_b \equiv a(a+1)\cdots(a+b-1)\ , \tag{6}$$

with $(a)_0 = 1$ for all a.

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