numbers l_2 and m_2: on the other hand, HM calculate for $l_2=0$ only. When the target consists of ground-state H atoms, the difference between the two calculations is known[3,9]: At high incident proton energies ($p\gg 1$) only the $l_2=0$ term contributes significantly to the sum, and both calculations give the same result; in the neighborhood of the resonance for forming highly excited final states ($p\sim 1$) the $l_2=0$ term contributes only 28% of the cross section. When the target atoms have $n_1\neq 1$, we expect a similar result to hold: Comparison between the present results and those of HM for Li bears out this expectation. At incident proton energies of 25 keV, the cross section for forming final states with $n_2=10$ contains 80% $l_2=0$ contributions; at $6\frac{1}{4}$ keV (in the neighborhood of the maximum) it contains 35% $l_2=0$ terms.

Finally, we emphasize again that the cross section for forming highly excited states by charge-exchange reactions of the general type (1) is only one ingredient in a calculation of the equilibrium fraction of excited neutrals in the outgoing beam. It is also necessary to know the cross sections for all processes which disrupt the atoms, and these are not all available. (In particular, the total cross section for ionization of H atoms by collision with alkali atoms is necessary: this quantity does not seem to be known, nor is it easy to calculate.)

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Stark Effect of the Hyperfine Structure of Cesium-133†

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The change $\Delta(\mathcal{E})$ in transition frequency of the $(F=4, M_F=0)\leftrightarrow(F=3, M_F=0)$ transition of the ground state of Cs^{133} as a result of the application of an external electric field $\mathcal{E}$ has been calculated theoretically. The effects of differences in the ground-state wave functions due to the hyperfine interaction have been included, as well as differences in energy denominators due to hyperfine structure. The calculation gives $\Delta(\mathcal{E})=-1.9\times10^{-6}(1\pm0.1)\mathcal{E}^2$ cps, which is to be compared with the experimental value of $-2.29\times10^{-6}(1\pm0.03)\mathcal{E}^2$ cps, where $\mathcal{E}$ is in V/cm.

I. INTRODUCTION

In 1957, Haun and Zacharias[1] measured the change $\Delta(\mathcal{E})$ of the transition frequency of the $(F=4, M_F=0)\leftrightarrow(F=3, M_F=0)$ transition in the ground state of Cs^{133} in an electric field $\mathcal{E}$. They found $\Delta(\mathcal{E})=-2.29\times10^{-6}\ (1\pm0.03)\mathcal{E}^2$ cps, where $\mathcal{E}$ is the electric field in V/cm. These authors made an order-of-magnitude calculation of this effect, using perturbation theory and assuming that only the $6p$ levels were mixed with the ground state. As a further approximation, they neglected the hyperfine structure of the $6p$ levels and found theoretically $\Delta(\mathcal{E})\approx-0.82\times10^{-6}\mathcal{E}^2$ cps. Schwartz[2] attempted a complete calculation of this Stark effect including the wave function differences between $F=4$ and $F=3$ states, but the attempt was unsuccessful owing to lack of values for some of the matrix elements. Recently Anderson[3] completed a more accurate calculation, omitting the difference in wave functions and assuming an average value for the energy of the fine structure terms. Anderson's result, $\Delta(\mathcal{E})=-2.67\times10^{-6}\times\mathcal{E}^2$ cps,[4] is much closer to the experimental result.

Recently, some theoretical calculations of cesium wave functions have been published[5-7] as have revised experimental values for the polarizability of the cesium atom.[8,9] In the following calculation of the Stark shift, we use the new wave functions and polarizability values, and in addition we take into account the mixing of the ground state $F=4$ and $F=3$ wave functions with the

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hyperfine states of higher levels through the hyperfine interaction.

II. EQUATIONS

The magnetic dipole hyperfine interaction Hamiltonian is, in mks units,

$$\mathcal{H}_{\mathrm{hfs}}=-(\mu_0/4\pi)(e^2g_I/2mM)\mathbf{P}\cdot\mathbf{I}, \tag{1}$$

where

$$\mathbf{P}\equiv[(8\pi/3)\mathbf{s}\delta(r)+(((\mathbf{l}-\mathbf{s})/r^3)+(3(\mathbf{s}\cdot\mathbf{r})\mathbf{r}/r^5))] \tag{2}$$

and μ_0 is the magnetic permeability of the vacuum, g_I the nuclear g factor, I the nuclear spin operator, and m, M the rest masses of the electron and proton respectively.[10]

In computing matrix elements of the operator $\mathbf{P}$, we use the following prescription.[11] In the expression $\mathbf{P}$, for values of the radius r less than ϵ, replace $1/r^3$ by zero, evaluate all integrals, then take the limit of ϵ tending to zero. As indicated in Ref. 11 this prescription results in the fact that for expectation values of $\mathbf{P}$ for S states, the contribution from the term in large parentheses in Eq. (2) vanishes identically, and the only contribution is from the well-known Fermi-Segre term $(8\pi/3)\delta(r)\mathbf{s}$.

We assume that the atomic states may be characterized by state vectors $|nLSJIFM_F\rangle$. To find out which states are connected by the hyperfine interaction and also to determine the zero-field hyperfine splitting, we calculate

$$\langle nLSJIFM_F|\mathcal{H}_{\mathrm{hfs}}|n'L'S'J'I'F'M_F'\rangle =\frac{-\mu_0e^2g_I}{4\pi 2mM}\langle aJIFM_F|\mathbf{P}\cdot\mathbf{I}|a'J'IF'M_F'\rangle, \tag{3}$$

where a designates the set of quantum numbers (n,L,S), and I is the same for all states. Recognizing $\mathbf{P}\cdot\mathbf{I}$ as a scalar product of tensor operators of order 1, we use the powerful methods of Racah[12] to reduce the matrix elements of $\mathbf{P}\cdot\mathbf{I}$

$$\langle aJIFM_F|\mathbf{P}\cdot\mathbf{I}|a'J'IF'M_F'\rangle =(-1)^{J'+I+F'}\begin{Bmatrix}F & I & J\\ 1 & J' & I\end{Bmatrix}\langle aJ\|\mathbf{P}\|a'J'\rangle\langle I\|\mathbf{I}\|I\rangle \times\delta_{FF'}\delta_{M_FM_F'}, \tag{4}$$

where the factor in curly brackets is the 6-j symbol[12–14] and the "double-bar" matrix element

$$\langle I\|I\|I\rangle=\hbar[I(I+1)(2I+1)]^{1/2}.$$

For the first-order perturbations due to the hyperfine interaction, we shall need only the matrix elements diagonal in J; the 6-j symbol in Eq. (4) then is

$$\begin{Bmatrix}F & I & J\\ 1 & J & I\end{Bmatrix}=(-1)^{F+I+J+1} \times\frac{2[I(I+1)+J(J+1)-F(F+1)]}{[2I(2I+1)(2I+2)2J(2J+1)(2J+2)]^{1/2}}. \tag{5}$$

For the S states, i.e., $a=(n,0,S)$ and $a'=(n',0,S)$, our "prescription" for the matrix elements of $\mathbf{P}$ results in

$$\langle aJ\|\mathbf{P}\|a'J\rangle=\langle aJ\|(8\pi/3)\delta(r)\mathbf{s}\|a'J\rangle. \tag{6}$$

Again using the methods of Racah, we find for (6)

$$\left\langle n0SJ\left\|\frac{8\pi}{3}\delta(r)\mathbf{s}\right\|n'0SJ\right\rangle =\frac{8\pi}{3}(-1)^{S+J+1}(2J+1)\begin{Bmatrix}S & J & L\\ J & S & 1\end{Bmatrix} \times\hbar[S(S+1)(2S+1)]^{1/2}\langle n\|\delta(r)\|n'\rangle. \tag{7}$$

Combining Eqs. (4), (5), and (7) we obtain the matrix elements of $\mathcal{H}_{\mathrm{hfs}}$ between S states of cesium ($S_{1/2}$; $L=0$, $J=S=\frac{1}{2}$; $I=\frac{7}{2}$) with different n

$$W(F)=\mu_0\beta\mu_{nm}g_I\tfrac{2}{3}[66/4-F(F+1)]\langle n\|\delta(r)\|n'\rangle, \tag{8}$$

where β is the Bohr magneton and μ_{nm} the nuclear magneton. The matrix element $\langle n\|\delta(r)\|n'\rangle$ is just the product of the values of the S-state functions $|n\rangle$ and $|n'\rangle$ at $r=0$

$$\langle n\|\delta(r)\|n'\rangle=\underset{n;\,L=0}{\psi_{n\;L=0}}{}^{*}(0)\underset{n';\,L=0}{\psi_{n'\;L=0}}(0)\equiv\underset{nS}{\psi_{nS}}{}^{*}(0)\underset{n'S}{\psi_{n'S}}(0).$$

For future reference, we calculate here, from (8) with $n'=n=6$, the zero-field hyperfine splitting for the Cs^{133} ground state[15]

$$\Delta W\equiv W(n=6,F=4)-W(n=6,F=3) =-\mu_0\beta\mu_{nm}g_I(16/3)|\psi_{6S}(0)|^2. \tag{9}$$

For non-S states, Eq. (6) becomes

$$\langle aJ\|\mathbf{P}\|a'J'\rangle=\left\langle nLSJ\left\|\left(\frac{\mathbf{l}-\mathbf{s}}{r^3}+\frac{3(\mathbf{s}\cdot\mathbf{r})\mathbf{r}}{r^5}\right)\right\|n'L'S'J\right\rangle, \tag{10}$$

the evaluation of which is quite complicated for the general case. One can show, however, that the matrix elements of (10) diagonal except in n, in the one electron

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[10] This calculation is done without relativistic corrections. For cesium ($Z=55$), relativistic corrections to the matrix elements calculated here are estimated to be of the order of 10%.

[11] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 22.

[12] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1960), 2nd ed.

[13] See, for example, B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1963).

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[15] E. Fermi, Z. Physik **60**, 320 (1930).

case are[12,16]

$$\left\langle nL\tfrac{1}{2}J\left\|\left(\frac{\mathbf{l}-\mathbf{s}}{r^3}+\frac{3(\mathbf{s}\cdot\mathbf{r})\mathbf{r}}{r^5}\right)\right\|n'L\tfrac{1}{2}J\right\rangle$$

$$=\left[\frac{(2J+1)}{J(J+1)}\right]^{1/2}L(L+1)\hbar\left\langle nL\left|\frac{1}{r^3}\right|n'L'\right\rangle;$$

thus for the matrix elements of $\mathcal{H}_{\rm hfs}$ between these states we have

$$W=\frac{\mu_0}{2\pi}\beta\mu_{nm}g_I\frac{[I(I+1)-J(J+1)-F(F+1)]}{2J(J+1)}$$

$$\times L(L+1)\left\langle nL\left|\frac{1}{r^3}\right|n'L\right\rangle. \qquad (11)$$

For hydrogenic wave functions, which we assume apply here,

$$\left\langle nL\left|\frac{1}{r^3}\right|n'L\right\rangle=\frac{2a_0^{-3}Z^{3/2}Z'^{3/2}}{L(L+1)(2L+1)n^{3/2}n'^{3/2}}, \qquad (12)$$

where a_0 is the Bohr radius.[17] In terms of the value of the hydrogenic wave function at $r=0$, which for S states is[18,19]

$$\psi_{nS}(0)=(1/\pi^{1/2})(Z/na_0)^{3/2}, \qquad (13)$$

Eq. (11) becomes, for the states with $L\neq 0$,

$$\langle nL\tfrac{1}{2}JIF|\mathcal{H}_{\rm hfs}|n'L\tfrac{1}{2}JIF\rangle=\frac{3}{32}\frac{\psi_{nS}(0)\psi_{n'S}(0)}{[\psi_{6S}(0)]^2}$$

$$\times\Delta W\frac{[F(F+1)-I(I+1)-J(J+1)]}{J(J+1)(2L+1)}, \qquad (14)$$

where ΔW is given by Eq. (9), and the wave functions $\psi_{nS}(0)$ at the origin are all assumed to be real.

III. PERTURBED WAVE FUNCTIONS

Assuming that the external electric field $\mathcal{E}$ is applied along the z axis, we have for the external perturbation, which we will later consider as a perturbation on the hyperfine states,

$$\mathcal{H}_{\rm ext}=ez\mathcal{E};$$

z is the direction of the quantization axis. The operator z has nonzero matrix elements between the ground $(6S_{1/2})$ state and any P state; thus it is important to know the exact wave functions for the ground state and higher P states in the absence of the electric field. These exact wave functions which we require are the ground state and P-state wave functions as they are perturbed by the effect of their hyperfine interaction with other states of the same F, M_F [see Eq. (4)].

A. Perturbed Ground-State Wave Functions

For the first-order perturbed ground-state wave functions, the perturbation theory and Eqs. (8) and (9) yield,

$$\langle 6S_{1/2}'F|=\langle 6S_{1/2}F|-\sum_{n=7}^{\infty}\frac{\langle 6S_{1/2}F|\mathcal{H}_{\rm hfs}|nS_{1/2}F\rangle}{(W_{nS_{1/2}}-W_{6S_{1/2}})}\langle nS_{1/2}F|$$

$$=\langle 6S_{1/2}F|+\sum_{n=7}^{\infty}\left\{\frac{1}{8}\frac{\psi_{nS}(0)[16.5-F(F+1)]}{\psi_{6S}(0)(W_{nS_{1/2}}-W_{6S_{1/2}})}\right\}$$

$$\times\Delta W\langle nS_{1/2}F|$$

$$\equiv\langle 6S_{1/2}F|+\sum_{n=7}^{\infty}\mathcal{A}_{n\frac{1}{2}F}\langle nS_{1/2}F|. \qquad (15)$$

The prime in $\langle 6S_{1/2}'F|$ indicates the perturbed wave function.

B. Perturbed *P*-State Wave Functions

For the perturbed $6p$ wave functions we find

$$\langle 6P_J'F|$$

$$=\langle 6P_JF|-\sum_{n=7}^{\infty}\frac{\langle 6P_JF|\mathcal{H}_{\rm hfs}|nP_JF\rangle}{(W_{nP_J}-W_{6P_J})}\langle nP_JF|. \qquad (16)$$

With Eq. (14), this becomes

$$\langle 6P_J'F|=\langle 6P_JF|-\sum_{n=7}^{\infty}\left\{\frac{1}{32}\frac{\psi_{nS}(0)}{\psi_{6S}(0)}\right.$$

$$\times\frac{[F(F+1)-J(J+1)-63/4]}{J(J+1)}$$

$$\left.\times\left[\frac{\Delta W}{(W_{nP_J}-W_{6P_J})}\right]\right\}\langle nP_JF|$$

$$\equiv\langle 6P_JF|+\sum_{n=7}^{\infty}\mathcal{B}_{nJF}\langle nP_JF|. \qquad (17)$$

Similarly, we find for the $7p$ wave functions

$$\langle 7P_J'F|=\langle 7P_JF|-\sum_{n=6}^{\infty}\frac{1}{32}\frac{\psi_{7S}(0)\psi_{nS}(0)}{[\psi_{6S}(0)]^2}$$

$$\times\frac{[F(F+1)-J(J+1)-63/4]}{J(J+1)}$$

$$\times\left[\frac{\Delta W}{(W_{nP_J}-W_{7P_J})}\right]\langle nP_JF|$$

$$\equiv\langle 7P_JF|+\sum_{n=6}^{\infty}{}'\,\mathcal{C}_{nJF}\langle nP_JF|. \qquad (18)$$

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[16] M. Mizushima, lecture notes, University of Colorado, 1962 (unpublished).

[17] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1959).

[18] N. F. Ramsey, *Nuclear Moments* (John Wiley & Sons, Inc., New York, 1953).

[19] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

The prime on the sum in (18) indicates $n\neq 7$. In the final calculation of the Stark shift we shall see that the terms involving the $\mathcal{A}_{nJF}$ make the largest contribution, the $\mathcal{B}_{nJF}$ and $\mathcal{C}_{nJF}$ involving essentially higher order corrections. The values of $\mathcal{A}_{nJF}$, $\mathcal{B}_{nJF}$, and $\mathcal{C}_{nJF}$ are given in Tables I, II, and III. The ratios of wave functions used were[5]:

$$\psi_{7S}(0)/\psi_{6S}(0)=0.466\,,$$
$$\psi_{8S}(0)/\psi_{6S}(0)=0.294\,,$$
$$\psi_{9S}(0)/\psi_{6S}(0)=0.209\,.$$

The required energy denominators were obtained from the well-known tables of Moore.[20]

TABLE I. Coefficients $\mathcal{A}_{nJF}$ for hfs-perturbed cesium $6S$ wave functions.

$$\mathcal{A}_{nJF}\equiv\left(\frac{\psi_{nS}(0)}{\psi_{6S}(0)}\right)\left[\frac{[16.5-F(F+1)]}{8}\right]\left[\frac{\Delta W}{(W_{nS_{1/2}}-W_{6S_{1/2}})}\right]$$

(Multiply entries by 10^{-6}.)

n	$j\diagdown F$	4	3
7	$\frac{1}{2}$	-3.37	$+4.33$
8	$\frac{1}{2}$	-1.63	$+2.08$
9	$\frac{1}{2}$	-1.04	$+1.34$

TABLE II. Coefficients $\mathcal{B}_{nJF}$ for hfs-perturbed cesium $6P$ wave functions.

$$\mathcal{B}_{nJF}\equiv\left(\frac{\psi_{nS}(0)}{\psi_{6S}(0)}\right)\frac{[F(F+1)-J(J+1)-63/4]}{32J(J+1)}\left(\frac{\Delta W}{W_{nP_J}-W_{6P_J}}\right)$$

(Multiply entries by 10^{-6}.)

n	$j\diagdown F$	5	4	3	2
7	$\frac{1}{2}$		-1.966	$+2.529$	
8	$\frac{1}{2}$		-0.904	$+1.16$	
9	$\frac{1}{2}$		-0.567	$+0.729$	
7	$\frac{3}{2}$	-1.223	-0.0583	$+0.874$	$+1.573$
8	$\frac{3}{2}$	-0.560	-0.026	$+0.400$	$+0.721$
9	$\frac{3}{2}$	-0.351	-0.017	$+0.250$	$+0.452$

TABLE III. Coefficients $\mathcal{C}_{nJF}$ for hfs-perturbed cesium $7P$ wave functions.

$$\mathcal{C}_{nJF}\equiv\frac{\psi_{7S}(0)\psi_{nS}(0)}{[\psi_{6S}(0)]^2}\,\frac{[F(F+1)-J(J+1)-63/4]}{32J(J+1)}\left(\frac{\Delta W}{W_{nP_J}-W_{7P_J}}\right)$$

(Multiply entries by 10^{-6}.)

n	$j\diagdown F$	5	4	3	2
6	$\frac{1}{2}$		$+1.966$	-2.529	
8	$\frac{1}{2}$		-1.539	$+1.980$	
9	$\frac{1}{2}$		-0.741	$+0.953$	
6	$\frac{3}{2}$	$+1.223$	$+0.0583$	-0.874	-1.573
8	$\frac{3}{2}$	-0.957	-0.0455	$+0.684$	$+1.230$
9	$\frac{3}{2}$	-0.455	-0.0217	$+0.325$	$+0.585$

IV. MATRIX ELEMENTS OF z

As indicated in Sec. III, we need the matrix elements of the operator z, $\langle nLSJIFM_F|z|n'L'S'J'I'F'M_F'\rangle$, with $S=S'=\frac{1}{2}$, $I=I'=\frac{7}{2}$, and $M_F=0$. Calculations similar to those of Sec. II yield[12]

$$\langle nLSJ\tfrac{7}{2}F0|z|n'L'S'J'\tfrac{7}{2}F'M_F'\rangle$$
$$=(-1)^{J+I+F+F'+9/2}\begin{pmatrix}F & 1 & F'\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}J & F & \frac{7}{2}\\ F' & J' & 1\end{Bmatrix}$$
$$\times[(2F+1)(2F'+1)]^{1/2}\langle nLSJ\|r\|n'L'SJ'\rangle$$
$$\equiv Q_{JF0,J'F'0}\langle nLSJ\|r\|n'L'SJ'\rangle\,, \tag{19}$$

where the factor in large parenthesis is the 3-j symbol.[12]

The "double-bar" matrix element of r in Eq. (19) is related to the total intensity $S(A,A')\equiv S(nLJ,n'L'J')$ of the line summed over the magnetic quantum numbers and polarizations, by[12,17]

$$S(A,A')=|\langle nLSJ\|e\mathbf{r}\|n'L'SJ'\rangle|^2\,, \tag{20}$$

which is related to the radial integrals of Stone by the equation[6,7]

$$S(A,A')=e^2\sigma^2(A,A')K(A,A')\,, \tag{21}$$

where $K(A,A')$ is the summation and integration over the spin and angular parts. The absolute value of the matrix element in Eq. (19) is thus

$$|\langle nLSJ\|\mathbf{r}\|n'L'SJ'\rangle|=\sigma(A,A')K^{1/2}(A,A')\,. \tag{22}$$

As we shall see in the next section, our calculation requires only the products of matrix elements having the same $Q_{JF0,J'F'0}$ and $K^{1/2}(A,A')$; thus we need only calculate $Q^2{}_{JF0,J'F'0}K(A,A')$ for the transitions involved. These values are given in Table IV.

TABLE IV. $Q^2{}_{JF0,J'F'0}K(LJ,L'J')$ for transitions involved in cesium stark effect.

$LJF \leftrightarrow$	$L'J'F'$	$Q^2{}_{JF0,J'F'0}K(LJ,L'J')$
0 $\frac{1}{2}$ 4	1 $\frac{1}{2}$ 3	1/9
0 $\frac{1}{2}$ 4	1 $\frac{3}{2}$ 5	5/27
0 $\frac{1}{2}$ 4	1 $\frac{3}{2}$ 3	1/27
0 $\frac{1}{2}$ 3	1 $\frac{1}{2}$ 4	1/9
0 $\frac{1}{2}$ 3	1 $\frac{3}{2}$ 2	1/7
0 $\frac{1}{2}$ 3	1 $\frac{3}{2}$ 4	5/63

The values of the radial integrals $\sigma(A,A')$ of Eq. (22) we calculate from the oscillator strengths of Stone, which agree well with one set of experimental values for the Principal Series but are some 20% higher than another.[6] The values of σ are given in Table V. The sign of each $\sigma(A,A')$ was determined by visual inspection of the plots of the wave functions of Stone.[5]

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[20] C. E. Moore, Natl. Bur. Std. Circ. No. 467 (1949).

TABLE V. Radial integrals $\sigma(A,A')$ as used in this calculation (in units of 10^{-10} m).

Levels A	A'	$\sigma(A,A')$	Levels A	A'	$\sigma(A,A')$
$6S_{1/2}$	$6P_{1/2}$	-3.12	$7S_{1/2}$	$8P_{3/2}$	$+0.698$
$6S_{1/2}$	$6P_{3/2}$	-3.10	$7P_{1/2}$	$8S_{1/2}$	$+5.67$
$6S_{1/2}$	$7P_{1/2}$	$+0.190$	$7P_{3/2}$	$8S_{1/2}$	$+6.23$
$6S_{1/2}$	$7P_{3/2}$	$+0.331$	$6P_{1/2}$	$9S_{1/2}$	$+0.351$
$6P_{1/2}$	$7S_{1/2}$	$+2.54$	$6P_{3/2}$	$9S_{1/2}$	$+0.353$
$6P_{3/2}$	$7S_{1/2}$	$+2.91$	$7P_{1/2}$	$9S_{1/2}$	-1.28
$7S_{1/2}$	$7P_{1/2}$	-6.90	$7P_{3/2}$	$9S_{1/2}$	-1.19
$7S_{1/2}$	$7P_{3/2}$	-6.72	$8S_{1/2}$	$9P_{3/2}$	$+1.24$
$6P_{1/2}$	$8S_{1/2}$	-0.651	$7S_{1/2}$	$9P_{1/2}$	-0.137
$6P_{3/2}$	$8S_{1/2}$	-0.669	$7S_{1/2}$	$9P_{3/2}$	-0.275
$6S_{1/2}$	$8P_{1/2}$	-0.0584	$6S_{1/2}$	$9P_{1/2}$	-0.0269
$6S_{1/2}$	$8P_{3/2}$	-0.137	$6S_{1/2}$	$9P_{3/2}$	-0.0790
$7S_{1/2}$	$8P_{1/2}$	$+0.448$			

V. POLARIZABILITY OF CESIUM; ENERGY PERTURBATION

Figure 1 illustrates the hyperfine structure of the ground and first excited levels of the cesium atom. States connected by the external perturbation $\mathcal{H}_{\text{ext}}=ez\mathcal{E}$, as determined by selection rules [i.e., the 3-j and 6-j symbols in Eq. (19)], are joined by arrows. Similar transitions can take place between the ground-state and $7P$ levels, etc.

A. Polarizability of the $F=4$, $M_F=0$ Substate of Cs^{133}

We first neglect the hyperfine perturbation of the wave functions, i.e., use the uncorrected $\langle nP_JF|$ functions, and calculate the energy perturbations on the $6S_{1/2}$, $F=4$, $M_F=0$ ground state due to the applied electric field. This allows us to evaluate the importance of each term in the calculation, and also to calculate the atomic polarizability. The first-order perturbation energy vanishes; the second-order term is

$$\Delta^{(2)}E\quad(\mathcal{E})_{F=4,M_F=0}=\frac{-e^2\mathcal{E}^2}{4\pi\epsilon_0}\sum_{n=6}^{\infty}\left[\frac{|\langle 6S_{1/2}4|z|nP_{1/2}3\rangle|^2}{(W_{nP_{1/2}}-W_{6S_{1/2}})}+\frac{|\langle 6S_{1/2}4|z|nP_{3/2}5\rangle|^2}{(W_{nP_{3/2}}-W_{6S_{1/2}})}+\frac{|\langle 6S_{1/2}4|z|nP_{3/2}3\rangle|^2}{(W_{nP_{3/2}}-W_{6S_{1/2}})}\right].\tag{23}$$

A similar expression is obtained for $\Delta^{(2)}E(\mathcal{E})_{F=3,M_F=0}$. It turns out that with the above uncorrected wave functions, these two energy changes are the same, so that there is no Stark effect of the hyperfine structure in the approximation in which $\mathcal{A}_{nJF}=\mathcal{B}_{nJF}=\mathcal{C}_{nJF}=0$ in Eqs. (15) through (18).

The polarizability α of the ground state is defined by

$$\Delta E=-\tfrac{1}{2}\alpha\mathcal{E}^2,\tag{24}$$

where ΔE is the energy change in the ground state due to an applied electric field $\mathcal{E}$; thus we can equate (23) and (24):

$$\alpha=\frac{2e^2}{4\pi\epsilon_0}\sum_{n=6}\left[\frac{|\langle 6S_{1/2}4|z|nP_{1/2}3\rangle|^2}{(W_{nP_{1/2}}-W_{6S_{1/2}})}+\frac{|\langle 6S_{1/2}4|z|nP_{3/2}5\rangle|^2}{(W_{nP_{3/2}}-W_{6S_{1/2}})}+\frac{|\langle 6S_{1/2}4|z|nP_{3/2}3\rangle|^2}{(W_{nP_{3/2}}-W_{6S_{1/2}})}\right].\tag{25}$$

With the values of Q^2K and σ given in Tables IV and V, we find for α,

$$\alpha=[64.73+0.301+0.041]\times10^{-24}\ \text{cm}^3=65.07\ \text{Å}^3,\tag{26}$$

where the three terms in the above are the contributions of the $n=6$, 7, and 8 terms, respectively. Stone and Reitz[21] find $\alpha=66.5$ Å^3, which agrees with the independent theoretical calculation of Sternheimer[22] of $\alpha=67.7$ Å^3, but disagrees with that obtained by Dalgarno and Kingston[23] ($\alpha=53.8$ Å^3). The reason for the discrepancy will be discussed in more detail in Sec. VI.

B. Perturbation on hfs States Due to Electric Field

To find the Stark effect of the ground-state hyperfine splitting, we now calculate the difference of two terms similar to Eq. (23), one with $F=4$, the other with $F=3$, but using the perturbed wave functions and exact energy denominators

$$\Delta(\mathcal{E})\equiv\Delta^{(2)}E_{F=4}(\mathcal{E}')-\Delta^{(2)}E_{F=3}(\mathcal{E}').\tag{27}$$

The prime on $\mathcal{E}$ in (27) indicates the use of the hyperfine-perturbed wave functions of Eqs. (15) through (18), and exact energy denominators;

$$\begin{aligned}\langle nS_JF| &\to \langle nS_J'F|,\\ \langle nP_JF| &\to \langle nP_J'F|,\\ (W_{nP_J}-W_{6S_{1/2}}) &\to (W_{nP_{J,F'}}-W_{6S_{1/2},F}).\end{aligned}\tag{28}$$

Thus we have theoretically for $\Delta(\mathcal{E})$, with $M_F=0$,

$$\frac{\Delta(\mathcal{E})}{\mathcal{E}^2}=\frac{-e^2}{4\pi\epsilon_0}\left\{\sum_{n=6}^{\infty}\left[\frac{|\langle 6S_{1/2}'4|z|nP_{1/2}'3\rangle|^2}{(W_{nP_{1/2}3}-W_{6S_{1/2}4})}+\frac{|\langle 6S_{1/2}'4|z|nP_{3/2}'5\rangle|^2}{(W_{nP_{3/2}5}-W_{6S_{1/2}4})}+\frac{|\langle 6S_{1/2}'4|z|nP_{3/2}'3\rangle|^2}{(W_{nP_{3/2}3}-W_{6S_{1/2}4})}\right.\right.$$
$$\left.\left.-\frac{|\langle 6S_{1/2}'3|z|nP_{1/2}'4\rangle|^2}{(W_{nP_{1/2}4}-W_{6S_{1/2}3})}-\frac{|\langle 6S_{1/2}'3|z|nP_{3/2}'2\rangle|^2}{(W_{nP_{3/2}2}-W_{6S_{1/2}3})}-\frac{|\langle 6S_{1/2}'3|z|nP_{3/2}'4\rangle|^2}{(W_{nP_{3/2}4}-W_{6S_{1/2}3})}\right]\right\}.\tag{29}$$

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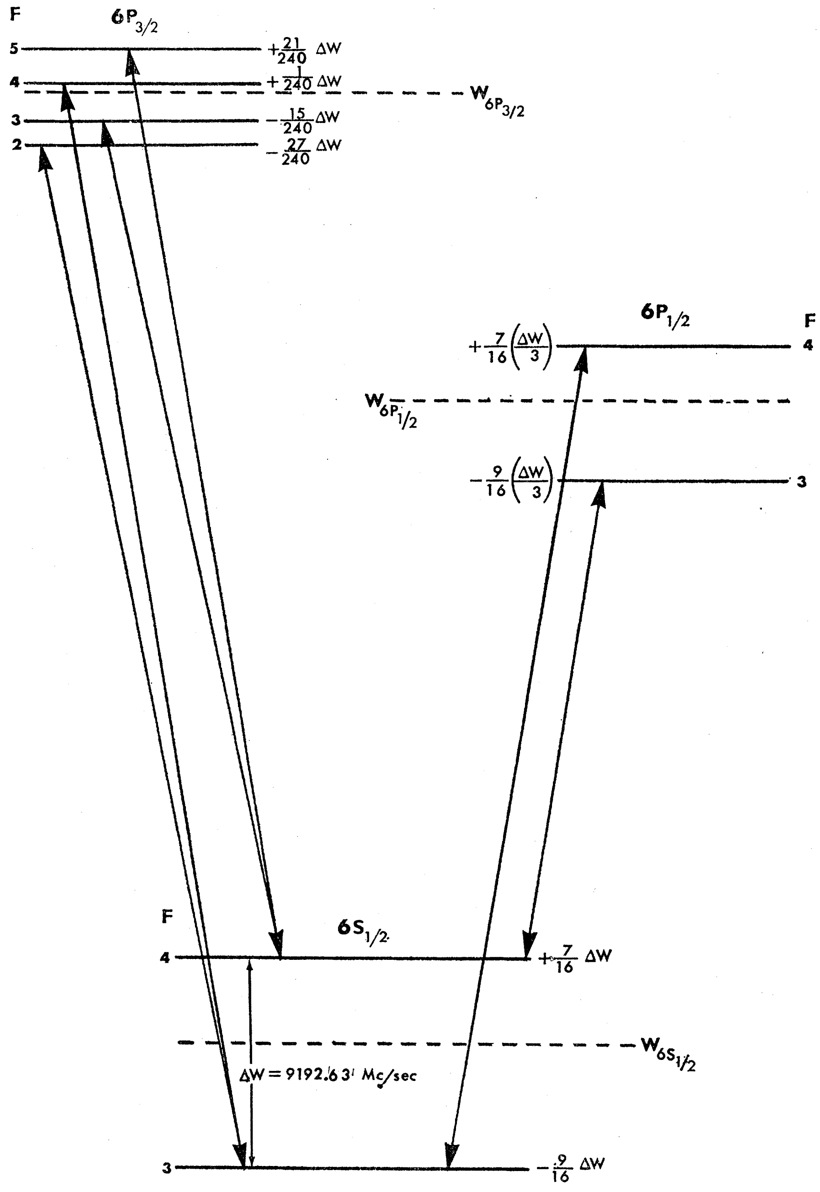

FIG. 1. Hyperfine structure of ground and first excited levels of Cs^{133} (dotted lines denote the center of gravity of a level). Note: Energies and splittings not drawn to scale.

By inspection of the energy-level diagram (Fig. 1), we find that the energy denominators for the $n=6$ term in Eq. (29) are, to order ΔW,

$$
\begin{aligned}
&(W_{6P_{1/2}3}-W_{6S_{1/2}4})^{-1}\cong(W_{6P_{1/2}}-W_{6S_{1/2}})^{-1}[1+5\Delta W/8(W_{6P_{1/2}}-W_{6S_{1/2}})]=(W_{6P_{1/2}}-W_{6S_{1/2}})^{-1}(1+17.14\times10^{-6}),\\
&(W_{6P_{1/2}4}-W_{6S_{1/2}3})^{-1}\cong(W_{6P_{1/2}}-W_{6S_{1/2}})^{-1}[1-17\Delta W/24(W_{6P_{1/2}}-W_{6S_{1/2}})]=(W_{6P_{1/2}}-W_{6S_{1/2}})^{-1}(1-19.43\times10^{-6}),\\
&(W_{6P_{3/2}5}-W_{6S_{1/2}4})^{-1}\cong(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}[1+7\Delta W/20(W_{6P_{3/2}}-W_{6S_{1/2}})]=(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}(1+9.149\times10^{-6}),\\
&(W_{6P_{3/2}2}-W_{6S_{1/2}3})^{-1}\cong(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}[1-9\Delta W/20(W_{6P_{3/2}}-W_{6S_{1/2}})]=(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}(1-11.76\times10^{-6}),\\
&(W_{6P_{3/2}3}-W_{6S_{1/2}4})^{-1}\cong(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}[1+\Delta W/2(W_{6P_{3/2}}-W_{6S_{1/2}})]=(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}(1+13.07\times10^{-6}),\\
&(W_{6P_{3/2}4}-W_{6S_{1/2}3})^{-1}\cong(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}[1-17\Delta W/30(W_{6P_{3/2}}-W_{6S_{1/2}})]=(W_{6P_{3/2}}-W_{6S_{1/2}})^{-1}(1-14.81\times10^{-6}).
\end{aligned}
\tag{30}
$$

Similar approximations hold for the energy denominators for higher n values, except that there, the hyperfine splittings of the upper levels are proportional to $[\psi_{nS}(0)]^2/[\psi_{6S}(0)]^2$ and the corrections are correspondingly smaller. Since the $n=8$ and $n=9$ terms in (29) contribute less than 0.2 and 0.01%, respectively to the Stark shift $\Delta(\mathcal{E})$, we neglect completely the $n=9$ and higher terms in the sum, and approximate the $n=8$ energy denominators by neglecting the hyperfine structure of the $8p$ levels [note that $\psi_{8S}(0)^2/\psi_{6S}(0)^2 \cong 0.09$].

The experimental values for the hyperfine splittings of some of the excited states are known,[24] and they turn out to be roughly one-third of the theoretical values used here. This calculation could thus be improved slightly by using those observed values.

We summarize, in Table VI, the calculated Stark shift for Cs^{133} in various approximations, giving the contributions from $N=6$, 7, and 8 terms, and analyzing these further into contributions from the perturbed wave functions and from the hyperfine splittings of the levels.

TABLE VI. Contributions to Stark shift of Cs^{133}, in units of $10^{-6}\ \mathcal{E}^2$ cps, $\mathcal{E}$ in V/cm.

Nonzero coefficients in hfs perturbed wave functions	Source of contribution \ n	6	7	8
$\mathcal{A}_{7JF}$	Wave function	-0.750	-0.088	-0.003
	hfs shifts	-1.493	-0.0035	-0.000
	Total $\Delta(\mathcal{E})=-2.337$			
$\mathcal{A}_{7JF}$, $\mathcal{B}_{7JF}$	Wave function	-0.754	-0.088	-0.003
	hfs shifts	-1.493	-0.0035	-0.000
	Total $\Delta(\mathcal{E})=-2.341$			
$\mathcal{A}_{7JF}$, $\mathcal{B}_{7JF}$, $\mathcal{C}_{6JF}$	Wave function	-0.754	-0.088	-0.003
	hfs shifts	-1.493	-0.0035	-0.000
	Total $\Delta(\mathcal{E})=-2.338$			
$\mathcal{A}_{7JF}$, $\mathcal{A}_{8JF}$, $\mathcal{B}_{7JF}$, $\mathcal{C}_{6JF}$	Wave function	-0.667	-0.0478	-0.003
	hfs shifts	-1.493	-0.0035	-0.000
	Total $\Delta(\mathcal{E})=-2.214$			
$\mathcal{A}_{7JF}$, $\mathcal{A}_{8JF}$, $\mathcal{A}_{9JF}$, $\mathcal{B}_{7JF}$, $\mathcal{C}_{6JF}$	Wave function	-0.696	-0.0521	-0.003
	hfs shifts	-1.493	-0.0035	-0.000
	Total $\Delta(\mathcal{E})=-2.248$			

VI. COMMENTS AND CONCLUSIONS

Although the direct use of the wave functions of Ref. 5 yields a theoretical Stark effect very close to the experimental value, it should be noted that the polarizability calculated from these wave functions is considerably higher than presently accepted experimental values.[8,9] These wave functions also correspond to experimental oscillator strength values for cesium[25] which, though measured by the hook method to a high degree of accuracy (±1%), are 20% higher than earlier measurements done by the magnetic rotation method, and which also seem to be inconsistent with the results for alkali atoms in general. We believe that the values for the polarizability of cesium most appropriate for this calculation are the empirical value $53.8(1\pm0.1)\times10^{-24}$ cm^3 derived by Dalgarno and Kingston[23] from the oscillator strength data of Minkowski and Mühlenbruch,[26] the atomic-beam experimental value of $(52.5\pm6.5)\times10^{-24}$ cm^3 obtained by Salop *et al.*,[9] and the atomic-beam experimental value $(48\pm6)\times10^{-24}$ cm^3 of Ref. 8.

Since the Stark effect is proportional to the polarizability, the use of $\alpha_{\mathrm{Cs}}=53.8(1\pm0.1)\times10^{-24}$ cm^3 reduces our calculated Stark effect by the factor 53.8/65.07, and we find

$$\begin{aligned}\Delta(\mathcal{E}) &= (53.8/65.07)(-2.25\times10^{-6}\ \mathcal{E}^2\ \text{cps})\\ \Delta(\mathcal{E}) &= -1.9\times10^{-6}(1\pm0.1)\mathcal{E}^2\ \text{cps},\end{aligned} \tag{31}$$

where the error is taken to be due entirely to the uncertainty in α_{Cs}.

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[26] R. Minkowski and W. Mühlenbruch, Z. Physik **63**, 198 (1930).