Theory of Hyperfine Structure*

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Numerical values for the one-electron integrals of interest in the analysis of atomic hyperfine structure have been calculated by using screened relativistic wave functions. Ratios of these integrals, representing the relativistic correction factors of Casimir, are given to replace the older values which neglected shielding effects. The most marked changes occur in the studies of the octopole interaction and hfs anomalies in p-states. The calculated one-electron magnetic dipole integral, when compared with the experimental ratio, dipole hfs/nuclear moment, makes it possible to deduce the magnitude of atomic polarization (Sternheimer) effects. In the doublet p-states that were studied, the polarization terms seem to be almost entirely of the sort discussed in an earlier paper: excitation of s-electrons. In a general discussion of polarization calculations we give some explanation of the large correction factors for the fine structure, dipole and quadrupole hyperfine structure that were calculated by Sternheimer (the radial redistribution of charge terms). It is also suggested that large polarization corrections may be needed for the octopole interaction.

INTRODUCTION

MEASUREMENTS of atomic hyperfine structure to determine nuclear magnetic dipole moments have to a large extent been supplanted by the more direct measurements of nuclear resonances in externally applied magnetic fields. However, for the determination of all other nuclear moments—electric quadrupole, magnetic octopole, and so forth—it is felt that we shall have to rely on observing the interactions with the electronic structure surrounding the nucleus. Of the three structures used in experimental work: atoms, molecules, and bulk matter (usually crystals) we emphasize the first, solely because of its relative simplicity.

In an earlier paper[1] the general analysis of hyperfine structure in atoms was set up and a number of detailed aspects were worked out. This is the second report in a continuing program of analysis for determining the values of nuclear moments to an accuracy of a few percent.

First-order atomic hyperfine structure is described generally by some relation like the following:

Measured hfs = nuclear moment
$\qquad\qquad$ × electronic matrix element.

Our goal is a reliable evaluation of the electronic matrix element. The operators involved are presumed to be well known (I), and it is the wave function of the electronic system that is being studied. In the first approximation of the "closed inner shell" model of atomic structure only the one (or few) valence electron(s) contribute to this matrix element and it is these one-electron integrals that we attempt to evaluate in this work. The contribution of all other electrons (polarization corrections) has been the subject of much work by Sternheimer,[2] some of whose results are rather unsatisfactory in comparison with experimental data. We shall speak here only qualitatively of the polarization effects and leave their actual calculation for future work.[3]

The results of the present work include a revised evaluation of the relativistic correction factors used in I, revised values for the nuclear octopole moments, corrections to the analysis of hfs anomalies, some remarks on the polarization corrections of Sternheimer, and—in the appendix—a completion of the earlier analysis of second-order corrections to the octopole interaction.

EVALUATION OF ONE-ELECTRON INTEGRALS IN HFS

Evaluation of the one-electron matrix elements in hfs reduces (see I) to the problem of working out a characteristic radial integral for each multipole. The expectation value of r^{-3} for the dipole interactions was first estimated by Goudsmit and by Fermi and Segrè by comparison with the hydrogenic wave functions,

$$\langle r^{-3}\rangle_{\text{hydrogen}} = \frac{Z^3}{n^3 a_0^3 l(l+\frac{1}{2})(l+1)},$$

except that for n and Z they used effective quantum numbers n^*, derived from the term values, and shielded nuclear charges Z_0, Z_i. The determination of Z_i has always been something of a sport; in fact, the general success of this formula in correctly determining nuclear dipole moments is somewhat surprising.

Later work made great use of the similar dependence of magnetic dipole and electric quadrupole hfs as well as fine structure on $\langle r^{-3}\rangle$ to derive the lesser known of

[1] C. Schwartz, Phys. Rev. 97, 380 (1955). This work will be referred to as I; numbering of equations will follow consecutively from the last (63) of I, and notation in this work will conform to usages in I.

[2] R. Sternheimer, Phys. Rev. 80, 102 (1950); 84, 244 (1951); 86, 316 (1952); 95, 736 (1954).

[3] A calculation of the hfs of lithium, with polarization (configuration interaction) effects included, has been started by R. K. Nesbet of M.I.T.

these quantities from the better known. The corrections to these ratios, which arise mainly from relativistic effects, were given by Casimir (reference 3 of I) and others who used the analytical eigenfunction for a Dirac electron in a pure Coulomb field with zero binding energy. The same procedure was used in I to calculate the octopole integral relative to the fine structure or to the dipole integral, and also for our analysis of s-electron configuration interaction.

The starting point of the present work was the desire to have more reliable values for the relativistic correction factors F, R, T, G, S, H, C''/C' (see I), as well as Z_i which is defined by the fine structure. Reasons for doubting the Casimir values are as follows: some of these factors can be easily calculated by using Dirac hydrogen wave functions for $n=1$, 2; then it is seen that they differ significantly from the Casimir values at $n=\infty$. In a many-electron atom, the first correction to the purely Coulomb potential Ze^2/r at small values of r is the constant shielding potential of all the other electrons that can be estimated from the Thomas-Fermi statistical model to be approximately $-1.9Z^{4/3}e^2/a_0$. Thus, in the region near the nucleus that is important for hfs integrals, the electronic wave functions behave as hydrogen wave functions characterized by a principal quantum number $n_{\rm eff}\sim\frac{1}{2}Z^{1/3}$ that barely exceeds 2 in the heaviest atom.

We decided to undertake a program of numerical integration of the Dirac radial equations for some reasonable atomic potential in order to calculate all the hfs integrals without appealing to mathematical approximations. The facilities of the M.I.T. electronic digital computer, Whirlwind I, were used for this work.

CALCULATIONS

The Dirac radial equations for an electron in a central field are (see I):

$$\left(\frac{d}{dx}-\frac{\kappa}{x}\right)f(x)=\frac{2}{\alpha}\left[1-\frac{\alpha^2}{4}[\epsilon-2\phi(x)]\right]g(x),$$

$$\left(\frac{d}{dx}+\frac{\kappa}{x}\right)g(x)=\frac{\alpha}{2}[\epsilon-2\phi(x)]f(x),$$

(64)

where $x=r/a_0$, $a_0=\hbar^2/me^2$, ϵ is the binding energy in Rydbergs$=e^2/2a_0$, $\alpha=e^2/\hbar c=1/137$, $\kappa=(j-l)(j+l+\frac{1}{2})$. $V(r)$, the potential seen by the electron, $=(e/a_0)\phi(x)$; the normalization integral is

$$\int_0^\infty dx(f^2+g^2)=N.$$

(65)

The only problem is to define the screened field $\phi(x)$. Ideally, $\phi(x)$ should be that field which gives the eigenfunctions f, g that are just the Hartree-Fock functions for the particular atom. It is, of course, impossible to make this comparison; therefore, we shall use a reason-

able potential, ϕ, and compare some of the results— term values, fine structure—with experimental values, as a test.

We have actually used the convenient form suggested by Tietz.[4]

$$\phi(x)=\frac{1}{x}\left[1+\frac{Z-1}{(1+\beta x)^2}\right].$$

(66)

In Fig. 1 we have plotted, for the purpose of comparison, the exact Thomas-Fermi shielding function, Tietz's approximation $(1+0.643Z^{1/3}x)^{-2}$, and the Hartree equivalent $Z_p(x)$ for neutral gallium $(Z=31)$. In our work, β in formula (66) will be treated as a parameter to be varied so that good values for the term energies and fine-structure splittings are obtained. We actually end by taking ratios between calculated fine-structure and hfs integrals, and the exact value of β will have negligible effect on these comparisons.

The range of x was limited to $0.0001\leqslant x\leqslant 12$ for most of the atoms studied, and this total region was broken up into 484 intervals with spacings varying from 0.000005 to 0.1. Numerical integration was carried out by the computer, using a fourth-order Kutta-Gill method at a rate of approximately two intervals per second. With some particular values of the parameters κ, Z, and some guessed values of ϵ and β,
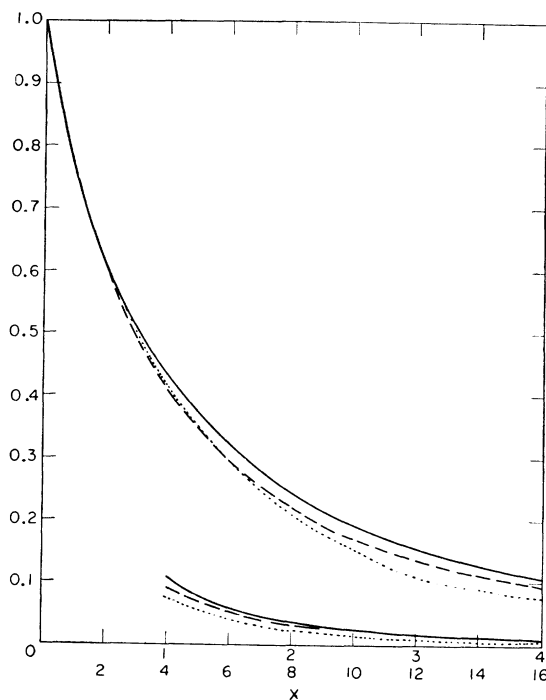

FIG. 1. Screening functions for atomic potential in neutral gallium; note doubled abscissa. Thomas-Fermi function, solid curve; Tietz's approximation, dashed curve; Hartree, Z_p/Z [from A. J. Freeman, Phys. Rev. **91**, 1410 (1953)], dotted curve.

[4] T. Tietz, J. Chem. Phys. **22**, 2094 (1954); **23**, 1167 (1955).

the ratio f/g at $x=0.0001$ is determined by a simple power series expansion, and Eqs. (64) are integrated to $x=12$. For $x>12$, ϕ is put$=0$, and $f(12)$, $g(12)$ are joined to the appropriate spherical Hankel functions for this outer region. The eigenvalue criterion is that the coefficient of the exponentially increasing Hankel function determined by this matching should go to zero. With a fixed value of β, ϵ would be varied to make this coefficient go to zero by a simple linear interpolation-searching procedure which improved the value of ϵ by approximately a factor of 10 for each complete iteration when we were fairly near the correct value. Alternatively, we could specify the energy eigenvalue ϵ and vary the potential parameter β. Thus, for each atomic state, an energy eigenvalue accurate to within one part in 10^5 could be obtained after about 20 minutes of machine computation time.

If this procedure is repeated with one value of β for $\kappa=+2$ and -1 ($p_{3/2}$ and $p_{1/2}$), we have immediately the doublet fine-structure splitting $\delta=\epsilon_{1/2}-\epsilon_{3/2}$ (measured in Rydberg units). Another program took the calculated eigenvalues and used a fourth-order numerical integration formula to calculate the normalization integral (65) and the quantities of interest for hfs:

$$\int_0^\infty fgx^{-2}dx \qquad (p_{\frac{1}{2}} \text{ and } p_{\frac{3}{2}})$$

$$\int_0^\infty (f^2+g^2)x^{-3}dx \qquad (p_{\frac{3}{2}})$$

$$\int_0^\infty fgx^{-4}dx \qquad (p_{\frac{3}{2}}).$$

This was all worked out for two different values of the potential parameter β for each of the following atomic doublet states: B $2p$, Al $3p$, Ga $4p$, In $5p$, Tl $6p$, Cl $3p^5$, Br $4p^5$, I $5p^5$. We intended to use these two sets of data for interpolating or extrapolating to that value of β that best reproduced the experimental values of ϵ, δ. The actual use of the calculated numbers is displayed in the following sections; the raw numerical results have been given in a previous report.[5]

RESULTS 1: USE OF TIETZ'S POTENTIAL FOR ATOMIC WAVE FUNCTIONS

The one-parameter Tietz formula (66) was found to be a very simple and, we believe, accurate form for constructing shielded atomic wave functions. It is suggested that an extended form

$$(1+\beta x+\gamma x^2)^{-2},$$

with β, γ as suitably parameterized functions of atomic

[5] Quarterly Progress Report, Research Laboratory of Electronics, Massachusetts Institute of Technology (January 15, 1956), p. 70.
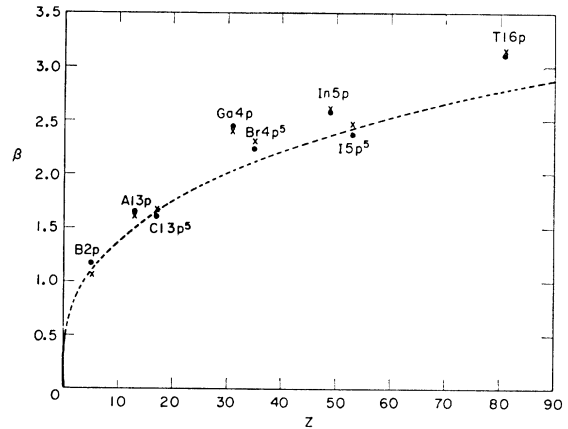

FIG. 2. Values of the potential parameter β calculated to give experimental values of term energies (crosses) and fine-structure splittings (circles), with Tietz's value $\beta=0.643Z^{1/3}$.

number, could give an excellent representation of shielded atomic potentials. In this extended form, β controls the initial slope of the function and γ controls the rate of decrease for large x.

In Fig. 2 we plot the values of β that give the experimental values of $\epsilon_{1/2}$ (crosses) and δ (circles) for the several atoms mentioned, together with Tietz's value $\beta=0.643Z^{1/3}$ (dotted curve).

In some additional calculations, it was found that one value of β gave the term values of the $6s$, $6p$, and $7p$ levels of Cs, each of which is within one percent of the experimental value. Also, the matrix elements $\langle s|x|p\rangle$ between these states were calculated and found to be in good agreement with the measured transition rates.

RESULTS 2: RELATIVISTIC CORRECTION FACTORS

The ratios between any two hfs integrals or between the fine-structure and any hfs integral calculated at one particular value of the potential (β), are very insensitive to moderate changes in β; hence they can be reliably obtained directly from our calculated values. By factoring out the theoretical values of the ratios in the limit of no shielding and $\alpha Z \rightarrow 0$ we have determined the ratios of the relativistic correction factors. For the p-doublets, we have

$$\frac{R}{F_{\frac{3}{2}}}=\frac{1}{274}\frac{\int_0^\infty (f^2+g^2)x^{-3}dx(p_{\frac{3}{2}})}{\int_0^\infty fgx^{-2}dx(p_{\frac{3}{2}})}; \qquad (67a)$$

$$\theta=\frac{F_{\frac{1}{2}}}{F_{\frac{3}{2}}}\left|\frac{C_{\frac{1}{2}}}{C_{\frac{3}{2}}}\right|^2=-\frac{N_{\frac{3}{2}}}{N_{\frac{1}{2}}}\frac{\int_0^\infty fgx^{-2}dx(p_{\frac{1}{2}})}{2\int_0^\infty fgx^{-2}dx(p_{\frac{3}{2}})}; \qquad (67b)$$
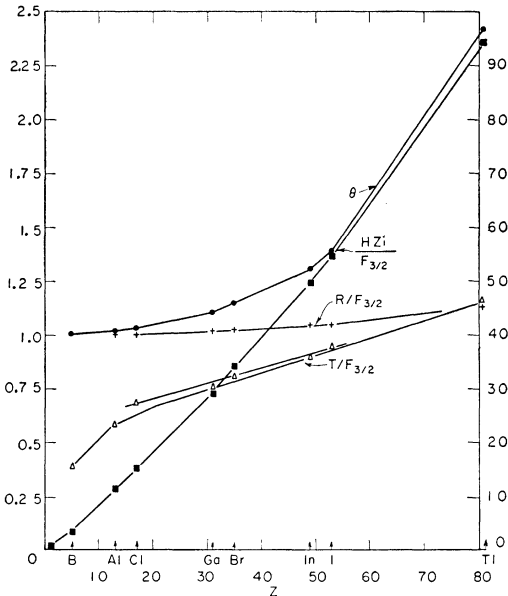
FIG. 3. Calculated relativistic correction factors for p electrons. $HZ_i/F_{3/2}$ is measured on the right-hand ordinate, all others on the left. The values for θ and $R/F_{3/2}$ are very well represented by Casimir's formulas. The strong depression of $T/F_{3/2}$ results from screening of the electronic wave function. $HZ_i/F_{3/2}$ represents only the one-electron fine structure and neglects the exchange effect.

$$\frac{T}{F_{\frac{3}{2}}} = \frac{3}{2Z^2} \frac{\int_0^\infty fgx^{-4}dx(p_{\frac{3}{2}})}{\int_0^\infty fgx^{-2}dx(p_{\frac{3}{2}})};$$ (67c)

$$\frac{HZ_i}{F_{\frac{3}{2}}} = -\frac{45.68\delta N_{\frac{3}{2}}}{\int_0^\infty fgx^{-2}dx(p_{\frac{3}{2}})}.$$ (67d)

The calculated values of these ratios are shown in Fig. 3 as heavy marks, and smooth curves have been drawn to facilitate interpolation. Effects of shell structure, i.e., different behavior for p versus p^5 configurations, are most apparent in the values of $T/F_{3/2}$ and somewhat apparent in θ. We want to compare these results with those gained by using Casimir's approach, which neglects shielding.

Shielding corrections, as we would expect, are most pronounced for the lighter elements, although they are not negligible even for the heaviest. Values of $R/F_{3/2}$ are essentially identical to Casimir's, any shielding effects canceling out the ratio, since both these integrals are $\langle r^{-3} \rangle$ in the region removed from the nucleus. The calculated values of θ are also in excellent agreement with those given by Casimir's formulas (see I); this is thought to be somewhat fortuitous, but nevertheless serves to recommend Casimir's admittedly approximate

formula for future use.[6] In Casimir's theory, $H/F_{3/2}$ is very close to unity for all Z and so our ratio (67d) should give very nearly just Z_i defined by

$$\delta = (l+\tfrac{1}{2})\alpha^2 \left\langle \frac{1}{r}\frac{\partial V}{\partial r}\right\rangle \equiv (l+\tfrac{1}{2})\alpha^2 HZ_i\langle r^{-3}\rangle,$$ (68)

where we neglect the two-electron exchange contributions to fine structure which will be discussed later. Our values of Z_i are larger than we expected, thus indicating that Casimir's work overestimates $F_{3/2}$ and underestimates H.[6] These criticisms are supported by the comparison of results for pure hydrogenic wave functions for principal quantum numbers $n=1$ and $n=\infty$.

The most outstanding new result is in $T/F_{3/2}$, the ratio of octopole to dipole integrals. The chief assumption in the Casimir approach is that the hfs integrals have almost all their contribution in the region very close to the nucleus. Actually, the dipole integral $\sim\langle r^{-3}\rangle$ in a p-state extends for a considerable distance into the total electron cloud of the atom, more so in the lighter elements. Consequently, the rapidly oscillating Casimir wave functions give too small a value for all $\langle r^{-3}\rangle$-dependent quantities. This large error, as we have stated before, cancels out almost completely in comparisons involving dipole, quadrupole, and fine structure; however it does show up in the ratio with the octopole integral, which depends essentially on the electron density at $r=0$.

We also calculated the off-diagonal $p_{1/2}-p_{3/2}$ matrix elements of the dipole and quadrupole operators for indium and thallium and found values for the relativistic correction factors ξ, η that were essentially equal to the values given by Casimir's formulas (see I).

The chief results of this analysis of ratios is a rather large correction to the octopole integrals, which will be applied in a later section, and another similar revision, which will now be discussed.

RESULTS 3: CORRECTIONS TO hfs ANOMALIES IN $p_{\frac{1}{2}}$-STATES

The theoretical analysis of the aspects of hfs anomalies (i.e., isotope effects in hfs), which are ascribed to either the Bohr-Weisskopf (B-W, nuclear magnetization distribution) or Breit-Rosenthal (B-R, nuclear charge distribution) effects, depends on the ratio of the valence electron's charge density at $r=0$ to the entire dipole integral. These ratios (b coefficients) were previously worked out, using the unshielded Casimir wave functions. The analysis of our calculations described above gives shielding corrections for these b-coefficients for $p_{1/2}$-states. We find that the theoretical strength of B-W or B-R effects for $p_{1/2}$-states should be reduced from their earlier given values by dividing by the

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[6] Closer study reveals that the factors $F_{1/2}$, $F_{3/2}$ in (67b) are overestimated by Casimir and the factor $|C_{1/2}/C_{3/2}|^2$ is underestimated, although the errors accidentally compensate.

Table I. Calculated values of hfs integrals. For use of these numbers, see the text.

	B $2p$	Al $3p$	Ga $4p$	In $5p$	Tl $6p$	Cl $3p^5$	Br $4p^5$	I $5p^5$
δ (exp)	0.000139	0.001021	0.007528	0.02016	0.071013	0.008028	0.033580	0.069281
$\epsilon_{1/2}$	0.4796 (0.367)	0.3885 (0.573)	0.4150 (0.588)	0.4185 (0.644)	0.4770 (0.701)	1.0348 (0.828)	0.9846 (0.832)	0.9202 (0.843)
β	1.2836 (-0.223)	1.7190 (-0.233)	2.4521 (-0.193)	2.5937 (-0.164)	3.1231 (-0.159)	1.6390 (-0.255)	2.2353 (-0.210)	2.3632 (-0.209)
$a_0^2 \int_0^\infty fgr^{-2}dr\,(p_{1/2})$	0.0037380 (0.835)	0.0086317 (0.932)	0.025982 (0.980)	0.048380 (0.998)	0.16635 (1.020)	0.049119 (0.953)	0.10297 (0.980)	0.15937 (0.988)
$a_0^2 \int_0^\infty fgr^{-2}dr\,(p_{3/2})$	-0.0018655 (0.833)	-0.0042518 (0.927)	-0.011783 (0.969)	-0.018571 (0.980)	-0.034432 (0.975)	-0.023857 (0.952)	-0.045056 (0.983)	-0.057652 (0.993)
$a_0^3 \int_0^\infty (f^2+g^2)r^{-3}dr\,(p_{1/2})$	0.51122 (0.834)	1.1669 (0.929)	3.2701 (0.971)	5.2864 (0.982)	10.619 (0.978)	6.5595 (0.952)	12.570 (0.985)	16.558 (0.996)
$a_0^4 \int_0^\infty fgr^{-4}dr\,(p_{3/2})$	-0.011940 (1.185)	-0.27831 (1.113)	-5.6309 (1.046)	-26.460 (1.026)	-173.98 (1.003)	-3.1222 (1.061)	-29.704 (1.037)	-101.506 (1.024)

factors 1.68 for Al; 1.49 for Cl; 1.38 for Ga; 1.30 for Br; 1.22 for In; 1.19 for I; 1.10 for Tl. For other elements we can easily interpolate. It should also be pointed out that, in view of recent experiments, we should use a nuclear charge radius of approximately $1.2A^{1/3}\times10^{-13}$ cm in these theories instead of the larger values used earlier.

RESULTS 4: FIXING THE POTENTIAL; COMPARISON WITH EXPERIMENTAL DATA

The absolute magnitudes, not just ratios, of all the hfs integrals depend strongly on the value of the potential parameter β. Our plan is to interpolate these integrals—calculated for two different potentials—as linear functions of the calculated fine structure δ and take their final value at that point which corresponds to the experimentally measured fine structure. These interpolated points do not generally give the correct term value but we console ourselves with the observation that the separation of the pairs of points in Fig. 2 is not very great. We are falling back on the old feeling that fine structure and hfs are closely akin, and the energy is only a secondary criterion.

There is one more correction to be made, however, before we can take this final step. The fine structure in a many-electron atom is not solely the result of the motion of the valence electron in the fixed Hartree-Fock central field of the nucleus and all other electrons; but this one-electron problem is all that we have calculated. There are exchange matrix elements of the mutual spin-orbit interaction between electrons (Breit interaction) which are not included in the formula (68) even when V includes the exchange electrostatic potential. We have estimated the magnitude of this correction to our calculated one-electron fine structure, using simple analytical forms for the wave functions involved, and we find a correction to δ of $-11a_0^3\langle r^{-3}\rangle$ cm^{-1} for all the atoms studied here,[7] with an estimated uncertainty of approximately $\pm20\%$. This exchange correction, which amounts to a fraction $-1/Z$ of the total fine structure, comes chiefly from interaction of the valence p electron

[7] In boron this effect is very important and a more detailed study will be necessary.

with the K-shell and a smaller contribution from the L-shell; the uncertainty in the exact magnitude of this correction will limit the accuracy of our final numbers.

In Table I we give values of the calculated hfs integrals chosen by interpolating against the calculated values of δ at that value of δ which equals the experimental doublet fine structure[8] (i.e., neglecting the exchange correction). In Table I, δ and $\epsilon_{1/2}$ are in Rydberg units, while all other quantities are dimensionless. The numbers in parentheses are the fractional increases in the particular quantities for a unit fractional increase in δ. That is, we actually calculated for each quantity x the values (x_1,δ_1) and (x_2,δ_2). The table gives

$$x_0 = \frac{x_2(\delta_0-\delta_1)-x_1(\delta_0-\delta_2)}{(\delta_2-\delta_1)},$$

where δ_0 is the measured value of the fine structure and the quantity in parentheses is

$$\frac{(x_2-x_1)\delta_0}{(\delta_2-\delta_1)x_0}.$$

Thus, for chlorine with the fine-structure exchange correction of $-11\times6.56/109\,737\pm20\%=-0.00066\pm0.00013$, we would want to take our calculated hfs integrals at a value of δ that is increased by $(66\pm1.3)/803=(8.2\pm1.6)\%$. This yields

$$a_0^2 \int_0^\infty fgr^{-2}dr\,(p_{\frac12})=0.049119$$
$$\times[1+(0.953)(0.082\pm0.016)]=0.0530\pm0.0008,$$

$$a_0^2 \int_0^\infty fgr^{-2}dr\,(p_{\frac32})=-0.023857$$
$$\times[1+(0.952)(0.082\pm0.016)]=-0.0257\pm0.0004,$$

and so forth.

[8] The experimental value for the $2p$ fine-structure splitting of boron, 0.000139 Ry$=15.3\pm0.2$ cm^{-1}, comes from Dr. S. P. Davis (private communication), Spectroscopy Laboratory, MIT. Other data came from Landolt-Bornstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, und Technik* (Springer-Verlag, Berlin, 1950), Vol. 1, Part 6.

We would like to check this determination of the hfs integrals by comparing them with the measured dipole interactions for which the nuclear magnetic moment is known by independent measurements. However, it is not surprising that there are a number of discrepancies in these comparisons; this is attributable to the effects of electronic configuration interactions (core polarization). We shall, therefore, use our calculated values of the one-electron dipole hfs in order to deduce the magnitude of these polarization corrections that are defined according to the formula:

$$\frac{\text{(measured hfs)}}{\text{(measured nuclear moment)}}$$

$$= \text{(calculated one-electron matrix element)}$$
$$\times (1+R); \quad (69)$$

and we compare these apparent values of R_m (for magnetic dipole hfs) with the numbers calculated by Sternheimer for a few atoms.

These polarization effects can be described as follows, using the language of perturbation theory. The zeroth-order atomic wave function describes a series of closed shells and one (or a few) valence electrons; and with this wave function only the valence electrons contribute to the hfs matrix element. The first-order correction to this wave function contains states in which some electron from the core is moved into all of the many unoccupied energy levels outside the core. This "virtual

excitation" of a core electron comes about through the electrostatic interaction of this core electron with the valence electron(s). The polarization contribution to hfs is mainly the cross matrix element of the hfs interaction between the zeroth-order wave function and these first-order, polarized-core, wave functions.

For a doublet p valence state there are several modes of excitation of core electrons; we shall limit our attention to the two modes which appear from Sternheimer's work to be the most important ones. These two are the excitation of a core electron in an s-orbit into a higher unoccupied s-orbit ($s{\rightarrow}s'$ mode), and the spherical symmetric part of the excitation of a core electron in a p-orbit into a higher unoccupied p-orbit ($p{\rightarrow}p'$; P_0 mode).

From angular momentum considerations, we know the relative contributions of these two modes of excitation between $p_{1/2}$- and $p_{3/2}$-states of the doublet

$$R_{mj} = R_{mj}(p{\rightarrow}p'; P_0) + R_{mj}(s{\rightarrow}s'), \quad (70\text{a})$$

$$R_{m3/2}(p{\rightarrow}p'; P_0) = R_{m1/2}(p{\rightarrow}p'; P_0), \quad (70\text{b})$$

$$R_{m3/2}(s{\rightarrow}s') = -5\theta R_{m1/2}(s{\rightarrow}s'). \quad (70\text{c})$$

Since there are two Eqs. (69)—for $p_{1/2}$- and $p_{3/2}$-states—we can solve for the two independent polarization terms $R_m(p{\rightarrow}p'; P_0)$ and $R_{m1/2}(s{\rightarrow}s')$.

In an earlier work[9] we defined the quantities $\beta_{1/2}, \beta_{3/2}$[10] as the fractional contribution of the ($s{\rightarrow}s'$) excitation to the dipole hfs in a $^2P_{1/2}$- or a $^2P_{3/2}$-state. These are related to $R_m(s{\rightarrow}s')$ by

$$\beta_{1/2} = R_{m1/2}(s{\rightarrow}s')/(1+R_m).$$

The values of $\beta_{1/2}$ deduced for p-doublets under the assumption that $R_m = R_m(s{\rightarrow}s')$ can be deduced solely from the measured ratios $a_{1/2}/a_{3/2}$ and the theoretical values of θ. Values for several atoms are shown in Fig. 4.

Most interesting are the values of $R_m(p{\rightarrow}p'; P_0)$ deduced according to (69, 70). Table II gives values of polarization correction terms $R_m(p{\rightarrow}p'; P_0)$—deduced by using our calculated one-electron dipole integrals— and $\beta_{1/2}, \beta_{3/2}$—calculated from our earlier formulas (see reference 9) that assume $R_m = R_m(s{\rightarrow}s')$. The $p_{1/2}$-state of bromine has not been measured; and the exchange correction to the fine structure in boron is so large that we have not been able to determine $R_m(p{\rightarrow}p'; P_0)$, which should be identically zero for this atom. Also finite nuclear size effects (a few percent in Tl) have been ignored. Except in the case of iodine,[11] all the uncertainties here result from the inaccurate determination of the exchange correction to the calculated one-electron fine structure. It is remark-
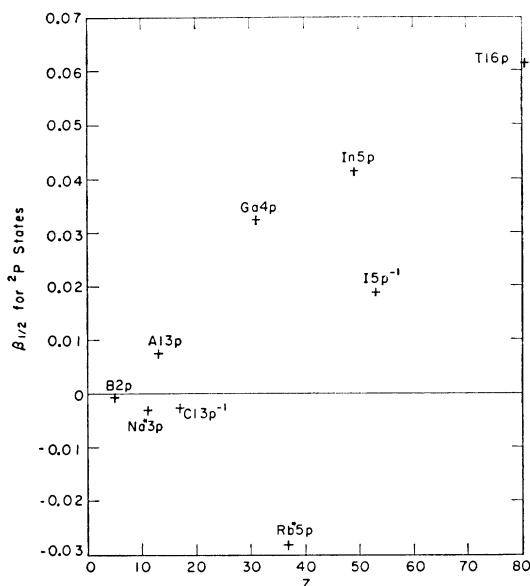

Fig. 4. Fractional contribution of s-electrons to the dipole hfs in $p_{1/2}$-states, calculated by ignoring all other polarization effects, in accordance with Eq. (3) of reference 9. It is interesting to note the trends of $\beta_{1/2}$ versus Z for each of the configurations s^2p (B, Al, Ga, In, Tl), s^2p^5 (Cl, I) and s^2p^6p' (Na*, Rb*). Experimental data on Rb* $5p$ from I. I. Rabi and B. Senitzky, Phys. Rev. 103, 315 (1956).

[9] C. Schwartz, Phys. Rev. 99, 1035 (1955).
[10] Not to be confused with the atomic potential parameter β, which will not be referred to again.
[11] The value $\Delta\nu(^2P_{1/2}, \text{I}^{127}) = 0.673 \text{ cm}^{-1} \pm 2\%$ was measured by R. Onaka of the Spectroscopy Laboratory, M.I.T. (private communication).

TABLE II. Deduced values of polarization correction factors for dipole hfs in ^2P states; contributions from the excitation of s- and p-core electrons.

	$a_{1/2}/5a_{3/2}$	θ	$\beta_{1/2}$	$\beta_{3/2}$	$R_m(p\to p'; P_0)$
B $2p$	0.9985	1.0019	−0.00057	+0.0028	...
Al $3p$	1.065	1.015_1	+0.00773	−0.0412	+0.028±0.019
Ga $4p$	1.403	1.103	+0.0329	−0.231	+0.023±0.008
In $5p$	1.887	1.303	+0.0413	−0.390	+0.034±0.005
Tl $6p$	16.109[a]	2.416	+0.0616	−4.96	+0.050±0.003
Cl $3p^5$	1.012	1.029_4	-0.0027_3	+0.0138	+0.030±0.015
Br $4p^5$	...	1.143	...	...	...
I $5p^5$	1.55±0.08[b]	1.382	+0.0135±0.006	−0.104±0.05	+0.040±0.022

[a] See reference 13. [b] See reference 11.

able how small and uniform all of these deduced values for the $p\to p'$; P_0 excitation are. The only comparable values calculated by Sternheimer are +0.17 for aluminum and +0.47 for chlorine. Reasons for the large discrepancy in the results for these "antishielding" terms will be discussed in the next section.

We cannot conclude anything from our present calculations about the magnitude of all other modes of excitation, e.g., $(s\to d)$, $(p\to f)$, $(p\to p'; P_2)$, and so on. However, our earlier phenomenological theory of $s\to s'$ effects[1,9] is based on the assumption that all other modes are negligible. This theory has been so successful in predicting the g_I perturbation (see I) and the relative magnitude of the hfs anomalies in $p_{1/2}$- and $p_{3/2}$-states[12,13] that it appears that probably all polarization effects for dipole hfs in ^2P-states are negligible except for the $s\to s'$ excitation which can be handled by our empirical analysis.

DISCUSSION OF POLARIZATION TERMS

Sternheimer's calculations of the $s\to s'$ polarization contribution to dipole hfs in boron and chlorine give values about six times too large,[2] as determined by comparison with the experimental values of $a_{1/2}/a_{3/2}$. This error is believed to be a result of the inaccuracies of the particular mathematical approach used by Sternheimer. However, in the case of the $p\to p'$; P_0 excitations—which are frequently described as a radial redistribution of core charge—much more can be said regarding the difference between the large terms calculated by Sternheimer and the small values we have deduced.

First, it should be pointed out that the values of $R_m(p\to p'; P_0)$ which we derived were based on the values of the calculated dipole integrals fixed by comparing our calculated fine-structure splittings with the experimental fine structure. We have tacitly assumed the absence of any polarization contributions to the one-electron fine structure. Sternheimer does find a $p\to p'$; P_0 polarization contribution to the fine structure of just the same size as those he finds for the dipole hfs, and he also has the same term contributing to the quadrupole hfs. Thus, Sternheimer finds[2] very little or

no relative $p\to p'$; P_0 polarization correction in ratios of these quantities. The last statement is essentially in agreement with our results and gives support to the statement that in comparing dipole hfs to fine structure only the $s\to s'$ configuration mixing is important. In comparing quadrupole hfs to dipole hfs we cannot make such a general statement, since there are the terms in the quadrupole polarization problem—the classical angular redistribution of core charge—that are not present in the dipole or fine-structure problems. We therefore suggest the following modification of well-known formulas for the determination of nuclear quadrupole moments.[14] For atomic states $p^x(x=\pm1)$ $^2P_{3/2}$,

$$Q=\pm\frac{b\mu F_{\frac{3}{2}}0.269}{a_{\frac{3}{2}}IRC(1-\beta_{\frac{3}{2}})}\text{ barns,} \tag{71}$$

where b is the measured quadrupole hfs, a is the dipole hfs, μ is the nuclear dipole moment in nuclear magnetons, I is the nuclear spin, F/R is the ratio of relativistic correction factors, and β is the fractional contribution of s electrons to the hfs[15] $[(1-\beta)^{-1}=(1+R)]$. C is Sternheimer's quadrupole polarization correction factor as calculated by the Thomas-Fermi or his equivalent method.[2] It is, of course, understood that this formula should be replaced by the results of thorough going calculations with polarized atomic wave functions. Calculations of this sort must be consistent with all experimental data and Sternheimer's present results are not.

One important lesson that has been learned from the rather confusing history of this polarization problem is that in speaking of a polarization correction factor we should state for which initially unpolarized description we are correcting. Sternheimer generally starts a calculation by using the available Hartree, not Hartree-Fock, wave functions for an atom; sometimes he has to start with the given wave functions for an ion containing one electron more or less than the atom he is interested

12 A. Lurio and A. G. Prodell, Phys. Rev. 101, 79 (1956).
13 G. Gould, Phys. Rev. 101, 1828 (1956).

14 This is essentially Sternheimer's Eq. (59a), in the third of references 2; his $(1+R_m)$ has been replaced by our $(1-\beta_{3/2})^{-1}$; and the Thomas-Fermi (modified) factor C replaces his $(1+R)$, in accordance with Sternheimer's discussion.
15 The factor $(1-\beta)^{-1}$ in Eq. (71) is most important for indium, in which it reduces the previously given values of Q by 28%; A. K. Mann and P. Kusch, Phys. Rev. 77, 427 (1950).

in. In Sternheimer's work, the large $p \rightarrow p'$; P_0 term is mainly a readjustment of the radial wave function of the valence p-electron by virtue of the exchange interaction between core and valence electrons that was neglected in the wave functions taken at the start. Hence, we claim that these are not polarization effects of consequence to hfs[16]; indeed these terms cancel out in ratios of dipole and quadrupole hfs and fine structure.

A formal analysis of the Hartree-Fock method shows that in this scheme two excitations, which give the major part of Sternheimer's $p \rightarrow p'$; P_0 terms,[17] are identically zero:

(A) Excitation of an electron from a closed nl-shell of the core into the valence $n'l$-shell.

(B) Excitation of an electron from the valence $n'l$-shell into an unoccupied $n''l$-shell.

These "selection rules" reflect a stability of the Hartree-Fock wave functions, in that we cannot improve the radial wave functions of the occupied nl-shells by attempting to mix states, since they have already been determined to be the best possible as a consequence of the variational principle on which the Hartree-Fock procedure is based. Indeed, in the most general Hartree-Fock procedure,[18] when we do not impose the restrictions of the shell structure, this stability becomes so extreme that there will be no (first-order) polarization corrections of any sort. However, the solution of this generalized Hartree-Fock problem is at least as difficult as that of the ordinary approach; e.g., modified (shell model) Hartree-Fock, plus polarizations as perturbation effects. There are alternative restrictions[19] on the generalized Hartree-Fock procedure that give 0th-order wave functions which, in the polarization calculation, have still different selection rules regarding the nature of admixed configurations. All of these different starting points should (must) lead to the same final results, and the decision as to which program will be used depends upon the ease and reliability of calculation.

OCTOPOLE MOMENTS

In determining the nuclear magnetic octopole moments, we have made several improvements on the earlier work. First, the problem of deriving the purely octopole interaction by calculating the second-order dipole-quadrupole effect is very nearly solved (see Appendix), at least for $^2P_{3/2}$-states. Our conclusion is that there is only one small, easily calculable addition

to be made to the doublet perturbing terms calculated in I.

Second, our calculations give new values for one-electron octopole integrals that are quite different from the Casimir-styled evaluation of I. For evaluating the nuclear octopole moment Ω from the corrected octopole interaction constant c, we use a formula similar to (71). For $p^{\pm 1}$ $^2P_{3/2}$,

$$\Omega = \frac{c\mu F_{\frac{3}{2}} 1.96 \times 10^8}{a_{\frac{3}{2}} I T(1 - \beta_{\frac{3}{2}}) Z^2} \text{ nmb}, \qquad (72)$$

(where 1 nmb $\equiv$ 1 nuclear magneton barn $= e\hbar/2Mc$ $\times 10^{-24}$ cm^2), and the existent data are summarized in Table III, wherein we give the measured and corrected values of c $(=A_3$ defined in I) as well as values for Ω deduced from (72) with our new calculated values of T/F (Fig. 1). The errors given in Table III are experimental errors for c_{meas}, plus the estimated theoretical error in the second-order correction $(\lesssim 1\%)$ for c_{corr}. No error has been given to the theoretical evaluation of the octopole moment Ω from the corrected interaction constant. The one-electron part of this—which is all we have used—is believed to be accurate within a few (<5) percent.

The new octopole data, obtained after the publication of I, is on the chlorine isotopes. In this light element, the second-order correction is extremely important; it reverses the sign of the apparent octopole effect. Furthermore, the nuclear shell model predicts, for a $d_{3/2}$-proton, $\Omega \approx -0.008$ nmb, which is a very small octopole moment on account of the mutual cancellation of the spin and orbital contributions. The values of Ω for the chlorine isotopes given in Table III are somewhat unique in that they fall outside the Schmidt-like lines in Fig. 2 of I.

The unanswered question is "What about polarization corrections to the one-electron octopole interaction?" It has been thought that, analogous to the dominant configuration interaction contributions of s-electrons to dipole hfs, the most important modes of core excitation for the octopole problem will be $p \rightarrow p'$ and $s \leftrightarrow d$. Both of these modes involve the delta-func-

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[16] It may be claimed that these really are independent "spin polarizations" caused by separating "direct" and exchange phenomena. However, in the very important aspect of describing several electrons in the same (equivalent) orbit no separation like this is meaningful.

[17] P_0 means, in the notation of atomic spectroscopy, that only those parts of matrix elements of configuration interaction involving the Slater integral F^0 are considered.

[18] L. Brillouin, Actualités Sci. et Ind. No. 71 (1933); No. 159 (1934).

[19] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

TABLE III. Octopole data.

	c_{meas} (cps)	c_{corr} (cps)	Ω (nmb)[e]
Cl^{35}	9.30±1.2[a]	−6.95±1.2	−0.0188±0.0003
Cl^{37}	5.35±1.2[a]	−5.41±1.2	−0.0146±0.0003
Ga^{69}	50.2±3.3[b]	93.0 ±3.4	0.137 ±0.005
Ga^{71}	86.0±3.3[b]	121.9 ±3.4	0.180 ±0.005
In^{115}	82±32[c]	1682 ±40	0.475 ±0.011
I^{127}	2870±370[d]	2010 ±520	0.181 ±0.047

[a] J. H. Holloway, Ph.D. thesis, Department of Physics, Massachusetts Institute of Technology, 1956 (unpublished).
[b] R. T. Daly, Jr. and J. H. Holloway, Phys. Rev. **96**, 539 (1954).
[c] P. Kusch and T. G. Eck, Phys. Rev. **94**, 1799 (1954); experimental data corrected slightly in accordance with a private communication from P. Kusch.
[d] Jaccarino, King, Satten, and Stroke, Phys. Rev. **94**, 1798 (1954).
[e] Ω is given in units of nuclear magneton barns (10^{-24} cm^2).

tion form of the radial operator,

$$r^{-5} \rightarrow r^{-4} \delta(r),$$

that gives the numerically largest contribution.

Pursuing the analogy, we thought that the relative importance of polarization effects to the octopole interaction in a $^2P_{3/2}$-state might be similar to that of $s \rightarrow s'$ effects in the dipole hfs of a $^2S_{1/2}$-term. However, this dipole effect is surprisingly large, for example, in the lighter alkali atoms. If we calculate $\psi^2(0)$ from Hartree-Fock functions for the valence electron in Li, Na, and K, we find, in comparison with the experimental value of $\Delta\nu/\mu$, apparent polarization correction factors of 40–60%. It should be the first requirement of any program for calculating polarization effects in hfs to give the correct result for the simple Li atom.[3] However, until more is known about these polarization effects, we should probably not trust the values of nuclear magnetic octopole moments given here for more than qualitative comparison with nuclear models.

INTERPRETATION OF hfs ANOMALIES

The hfs anomaly for a particular atomic state is defined as the defect in the following ratio between measured quantities for a pair of isotopes.

$$\Delta = \frac{a_1 \mu_2 I_1}{\mu_1 a_2 I_2} - 1, \tag{73}$$

where a is the dipole hfs interaction constant measured in that state, μ is the nuclear magnetic dipole moment, I is the nuclear spin, and subscripts 1, 2 refer to the two isotopes (convention: 2 heavier than 1). This effect has several sources, each of which is of physical interest, and it may be a difficult problem to separate them from the total measured Δ.

The reason that Δ is small is that the relation (for an s-electron, for example)

$$a = \mu \psi^2(0) \tag{74}$$

is very nearly correct and $\psi^2(0)$ is very nearly the same for two isotopes. Corrections to $\psi^2(0)$ come from the following sources:

(A) The electron's reduced mass $m^{-1} \rightarrow m^{-1}(1+m/AM)$ controls the scale of the electronic wave function; hence a factor $(1+m/AM)^{-3}$ in Eq. (74) (and the $\langle r^{-3} \rangle$ terms) contribute to Δ, since the masses (AM) of the two isotopes differ.

(B) The finite size of the nuclear charge distribution implies that the electron sees a non-Coulombic field at distances $r < R$, where R is the nuclear radius (B-R effect). Since R may change between two isotopes, this distortion of the electronic wave function gives a contribution to Δ.

Corrections to the nature of the dipole interaction come from:

(C) A reduced mass factor $1/m \rightarrow 1/m(1+m/AM)$ enters into the orbital (not spin) g-factor for p, and higher l-electrons, and it will contribute differently in the two isotopes. There are also "specific reduced mass" terms that contribute to orbital hfs which are of the form:

$$\frac{e}{AMc} \sum_{i \neq j} \frac{\mathbf{\mu}_N \cdot (\mathbf{r}_i \times \mathbf{p}_j)}{r_i^3}, \tag{75}$$

where i, j refer to two different electrons. This term has exchange matrix elements (for $L > 0$) which, on account of the nuclear mass factor AM, can contribute to Δ.

(D) Because the nuclear magnetism is not concentrated in a point, a part of the total dipole hfs interaction occurs when the electron penetrates the nuclear matter (B-W effect). This part of the interaction is not represented by the nuclear moment μ, which is measured with the field of completely external sources. This effect is probably the most interesting, as far as information on nuclear structure is concerned, but only its differential between two isotopes is seen in Δ.

In their contributions to Δ, the effects that depend on the nuclear size (B) are important for heavy nuclei, while the mass effects (A), (C) are important for light nuclei; this is similar to the situation in the spectroscopic isotope shift studies. The B-W effect (D) may be larger or smaller than these other effects for any nuclear mass and size, depending upon the magnetic structure of the two isotopes.

Moreover, there may be contributions to Δ from second-order hfs. That is, in addition to the usual first-order formula (74), there may be second-order terms coming from the mixing of higher electronic (and possibly nuclear) excited states by the hfs interactions. These second-order terms have the product of two matrix elements of electric (E) or magnetic (M) hfs interactions in the form EE, MM, ME; and they may give contributions to several multipoles when the experimental data are interpreted according to the first-order interval rules. Second-order contributions to the apparent dipole interaction constant, a, may come from nearby atomic states. This part is easily calculated, say for a perturbing doublet, and the value is generally quite small. Probably more important are the contributions from the very highly excited (continuum) electronic state. These terms can be estimated in a very crude way by techniques analogous to those used in the appendix for the particular problem of the $M1E2$ second-order pseudo-octopole term.

The EE terms do not contribute to the dipole hfs but may influence the even multipoles.[20] The MM terms give contributions that appear to be about $am/M \sim 10^{-5}$ times the first-order dipole term; thus, they are generally negligible. The ME terms, however, may give results

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[20] Gunther-Mohr, Geschwind, and Townes, Phys. Rev. 81, 289 (1951).

as large as 1% of the first-order dipole, and might con-
tribute to Δ.

These estimates of second-order effects are very
rough and considerably more analysis is needed before
too much trust can be placed in the current interpreta-
tions of hfs anomalies.

APPENDIX: THE SECOND-ORDER CORRECTIONS TO THE OCTOPOLE INTERACTION

In I, we calculated the second-order pseudo-octopole
corrections caused by mixing of the doublet $p_{1/2}$-state
and estimated the further contributions of the higher np
levels as negligible. The two other classes of terms con-
tributing to the dipole×quadrupole (DQ) matrix-ele-
ment product, which were ignored in I, have now been
estimated. First, the contributions of almost all excited
states formed by raising an electron out of the closed
shells vanish.

The ground state core system has total angular mo-
ments $J_c = 0$ (in the absence of polarization effects); we
shall characterize the excited states by the angular
momentum J_c', which is formed by coupling the spin
of the excited core electron to the spin of the hole in
the core. J_c' is then coupled to the spin of the valence
electron(s) to form the total electronic angular mo-
mentum of the intermediate state. The second-order
hfs contribution comes from products of matrix ele-
ments of the form

$$\langle J_c = 0 | D | J_c' \rangle \langle J_c' | Q | J_c = 0 \rangle;$$

but, since D is a vector operator and Q is a second-rank
tensor operator, we have the two incompatible selection
rules: $J_c' = 1$, $J_c' = 2$. There are thus no DQ cross
products from these types of excitations. The only
exception to this analysis is the case of the core particle
excited into the valence shell; then, the Pauli principle
forbids this arbitrary angular momentum coupling
scheme. For these special terms, we can easily calculate
the contribution. A good approximation gives the value
of this part of the DQ pseudo-octopole correction rela-
tive to the main DQ term from the doublet $p_{1/2}$-state as

$$+\frac{1}{5} \sum_{\text{filled } np \text{ shells}} \frac{\delta_{np}}{E_{np}}, \qquad (A16)$$

where the values of δ_{np}, the fine-structure splittings,
and E_{np}, the term values, can be obtained from x-ray
data. This correction is approximately 0.2% for chlo-
rine, and increases to about 5% for iodine. As the
importance of the main second-order term (from $p_{1/2}$)
decreases for heavier atoms, the increase of this relative
correction with increasing Z is not at all serious, and
it can be ignored completely. The only possibly serious
approximation in this analysis is the neglect of con-
figuration mixing for other than the doublet per-
turbation.

The second and final class of excited states—in which

a valence electron is excited to high continuum states—
can be estimated by a more careful application of the
closure approximation attempted in Appendix I of I.
The scheme is to evaluate the second-order sum as
follows:

$$\sum_n \frac{\langle i | D | n \rangle \langle n | Q | i \rangle}{\Delta E_n} \rightarrow \frac{1}{\Delta E_{\text{Av}}} \langle i | DQ | i \rangle. \qquad (A17)$$

When $| i \rangle$ is a $p_{3/2}$-state, it is seen that the operator
product DQ is excessively singular at $r \rightarrow 0$. One then
applies a cutoff at $r = R_n$, the nuclear radius, since the
singular form of these operators is correct only for the
electron coordinate outside the nuclear coordinate. If we
did not cut off, in this way, the left-hand side of (A17)
would also diverge in the sum over the very highly
excited states. Since the $\sum_n$ is increasing up to the high
value of the momentum of excited continuum states
corresponding to the coordinate cutoff,

$$k_{\text{max}} = 1/R_n,$$

we can fairly approximate ΔE_{Av} by the excitation energy
at this cutoff:

$$E_{\text{Av}} \sim \hbar c / R_n \text{ (relativistic)}.$$

We then proceed to evaluate (A17) relative to the first-
order octopole interaction, and it is seen that this is an
effect of less than 1%.

ERRATA IN PREVIOUS PAPERS

In Eq. (30) of reference 1, the factor in square brackets should read:

"$[k(2\kappa+k)(2\kappa+k-1)-4\alpha^2Z^2(1-k)]$."

In reference 9, the last line of paragraph 4 should read: "(-0.80 ± 0.16), while we predict $-5.3/(1.7+5.3) = -0.76$."

The definition of the correction factor ζ (Eq. (47) of I) is incorrect since it neglects the effect of s electrons on the diagonal dipole matrix element.[21] The proper formula for ζ can be evaluated with formulas given in

[21] This error was pointed out to the author by Dr. Thomas Eck in private communication.

I, and the result can be written for a ^2P state (replacing Eq. (62) of I) as follows:

$$\zeta = 1 - \beta_{3/2}\left(1+\frac{16}{5\xi}\right),$$

where $\beta_{3/2}$ is defined in reference 9 and some values are given in Table II of this paper. The octopole data in Table III have been corrected for this error.

Similarly, in Eq. (51) of I, the factor $[\Delta\nu/6(2I+1)]$ $\times\zeta(\xi/\theta)$ should be replaced by $(5/12)\xi\zeta a_{3/2}$, using this new formula for ζ. The correctly calculated values of R^{-1} still agree with the measured values within the experimental uncertainties.

Electron g Value in the Ground State of Deuterium*†

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The ratio of the electron g_J in the deuterium ground state to the proton g_p in a cylindrical mineral oil sample has been measured. The measurement was made using the microwave magnetic resonance absorption method and apparatus which Beringer and Heald used to determine $-g_J/g_p$ for hydrogen. The three strong-field Zeeman transitions having $\Delta m_J = \pm 1$, $\Delta m_I = 0$ were observed at a frequency of 9200 Mc/sec. The accuracy was limited by the minimum observed line widths of 20 parts per million resulting principally from magnetic field inhomogeneities. When one uses the Breit-Rabi formula, the unweighted mean of 68 observations yields $-g_J(\text{D})/g_p = 658.2162$ with an assigned error of ± 0.0008. The ratio of this value to the value of $-g_J(\text{H})/g_p$ obtained by Beringer and Heald, who used an identical mineral oil sample is $g_J(\text{D})/g_J(\text{H}) = 0.9999983 \pm 0.0000015$, and to the value of $-g_J(\text{H})/g_p$ of Koenig, Prodell, and Kusch, after suitable diamagnetic corrections, is $g_J(\text{D})/g_J(\text{H}) = 0.9999997 \pm 0.0000023$. These values are in agreement with the theoretically expected value of $g_J(\text{D})/g_J(\text{H}) = 1$ and with the less precise direct measurement of Nelson and Nafe.

1. INTRODUCTION

THE spin magnetic moment of the electron in the ground state of the hydrogen atom relative to the proton magnetic moment (or, in terms of the g value ratios, $g_J(\text{H})/g_p$) has been measured in recent years[1,2] to a precision of about 1 part per million (ppm). The quantity of theoretical interest is the ratio of the spin magnetic moment of the free electron to the orbital magnetic moment of the free electron (g_s/g_L). The experimental value of $g_J(\text{H})/g_L$ is obtained as the ratio of the value of $g_J(\text{H})/g_p$ to the value of g_L/g_p, which is measured by comparing the cyclotron frequency of a free electron with the proton resonance frequency.[3] The quantity g_s/g_L is obtained from $g_J(\text{H})/g_L$ by making the

theoretical relativistic bound state correction[4,5] $g_s = g_J(\text{H})(1-\frac{1}{3}\alpha^2)$ in which α is the fine structure constant. The measurement of g_L/g_p has been made to an accuracy of only 12 ppm and thus limits the accuracy of the experimental value of g_s/g_L to about 12 ppm. The experimental values so obtained[1,2] are in agreement with the theoretical value[6] for the electron spin magnetic moment, which includes quantum electrodynamic radiative corrections to order α^2.

One of the early radio-frequency measurements of electronic magnetism was a comparison of the electron spin magnetic moment in the ground states of hydrogen and deuterium by the atomic-beam magnetic resonance method.[7] To within the experimental accuracy of 10 ppm, the ratio $g_J(\text{H})/g_J(D)$ was found to be 1. In view

[1] Koenig, Prodell, and Kusch, Phys. Rev. 88, 191 (1952).
[2] R. Beringer and M. A. Heald, Phys. Rev. 95, 1474 (1954).
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[6] J. Schwinger, Phys. Rev. 73, 416 (1948); R. Karplus and N. M. Kroll, Phys. Rev. 77, 536 (1950). A further correction of order α^3 to the magnetic moment of the electron in the hydrogen atom has been computed by E. H. Lieb, Phil. Mag. 46, 311 (1955).
[7] E. B. Nelson and J. E. Nafe, Phys. Rev. 76, 1858 (1949).