HYPERFINE STRUCTURE AND HIGHER NUCLEAR MOMENTS

by

CHARLES LEON SCHWARTZ

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Signature of Author . . . Signature redacted . . .
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Certified by. . . . Signature redacted . . .
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ABSTRACT

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Considering the classical electric and magnetic interactions between atomic electrons and the nucleus, we arrive at a representation of the hyperfine interactions in terms of a multipole expansion of the field potentials. Treating these non-central interactions in first order perturbation theory we can give the form of the general interval structure and analyze for the multipole interaction constants using Racah coefficients. Pertinent matrix elements for a single valence electron are calculated relativistically. Some second order terms of the dipole and quadrupole interactions are calculated as they affect the interpretation of the first order octupole interaction. In this work we also take into account quantitatively the effect of some electronic configuration interaction. Finally the values of nuclear magnetic octupole moments expected according to different models are calculated and compared with the experimental data thus far collected. Generally the measured octupole moments are in as good agreement with the values predicted by the single particle shell model as are the corresponding dipole moments. In the appendices are given respectively a sample calculation of the octupole interaction in a complex electronic state, a non-relativistic analysis of the hyperfine interactions, and a discussion of the various approximations made in this study.

Thesis Supervisor: V.F. Weisskopf

Title: Professor of Physics

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I. INTRODUCTION

The recent very accurate measurements by Jaccarino et al$^{(1)}$ on the hyperfine structure of the ground state of I^{127} showed that the theory of dipole and quadrupole interactions as previously developed was insufficient to describe the level structure to this new high precision. In order to learn how finer details of the level structure could be interpreted in terms of higher nuclear moments, it was decided to review the entire theory of hyperfine structure.

First, treating the nucleus as a stationary non-relativistic quantum mechanical system, we derive a multipole expansion for the electric and magnetic fields produced by the nuclear charge and current distributions. In this development the electromagnetic potentials are expressed in terms of scalar and vector spherical harmonics. When these potentials are put into the Dirac hamiltonian for the electrons, the terms of different orders of symmetry can be identified as tensor operators, so that one can write down the form of the generalized "interval rule" in terms of Racah coefficients. This analysis proves to have not only formal, but also practical computational advantages over the formulations given in the prior literature.

The interaction constant A_k for each multipole order k is the product of the nuclear moment of that order and an electronic matrix element. The general electronic matrix elements are evaluated for the case of a single valence electron using the techniques of Racah(2) for the spin-angular integrals, and following the method of Casimir(3), Racah(4), and Breit(5) for the radial integrals.

The magnitude of the hyperfine interaction energies decreases rapidly with order: The magnetic octupole interaction is weaker than the magnetic dipole by about 10^{-5}. Thus in the perturbation theory second order terms (mixing in excited electron states) in the dipole and quadrupole interactions give contributions which may appear as first order magnetic octupole (and electric 2^4 pole) interactions. This effect is calculated using so far only the perturbation of the nearby doublet level. In this work the dipole contribution of s-electrons in mixed configurations is allowed for by quantitative analysis depending on the measured dipole interaction constants in both states of the doublet.

After all the electronic contributions have been extracted from the observed octupole interaction constant, the value of the nuclear magnetic octupole moment is finally revealed. We have calculated the values of these moments to be expected according to the individual particle shell model for the nucleus. The results, for various single particle orbits, are represented on a diagram similar to the Schmidt plot for dipole moments; and the octupole moments of the few nuclei already investigated take approximately the same positions on this new diagram as they do on the Schmidt plot.

The measurement of higher nuclear moments may also prove to be a valuable test of the Bohr-Mottelson collective nuclear model. In their "strong-coupling" scheme the observable magnitude of an octupole moment is decreased from the single particle value of the simpler theory by a factor as small as 1/35.

II. The Hyperfine Structure

In the absence of external fields an atom may be described very accurately in terms of a compact charged nucleus and an electron system arranged in the central Coulomb field produced by the nucleus. If, however, the electrons have some resultant angular momentum $J > 0$ and the nucleus also has a spin $I > 0$, there will be further interactions between the two systems, described as magnetic dipole, electric quadrupole, etc. We then denote by hyperfine structure (h.f.s.) the different energy eigenvalues associated with the various total angular momentum states of the combined systems characterized by the quantum number F

$$|I - J| \leq F \leq I + J$$

The major part of the electron-nuclear (non-central) interaction is the magnetic dipole term which is characteristically of the order of magnitude

$$\mu_0 \mu_N \left\langle \frac{1}{r_e^3} \right\rangle = \frac{e\hbar}{2mc} \frac{e\hbar}{2Mc} \left\langle \frac{1}{r_e^3} \right\rangle$$

where m is the electron mass, M the proton mass, and r_e the radial coordinate of the electron from the nucleus. This may be compared with the fine-structure (f.s.) spacing of the electronic energy levels, which is of the order

$$\left(\frac{\hbar}{2mc}\right)^2 Ze^2 \left\langle \frac{1}{r_e^3} \right\rangle$$

where Z is the atomic number.

The ratio of these two

$$\frac{\text{h.f.s.}}{\text{f.s.}} \sim \frac{m}{MZ} \sim 10^{-4} - 10^{-5}$$

is then a measure of the approximation to which we may use the various orders of perturbation theory to calculate the h.f.s. levels. We want to compare with this number the ratio of the energies associated with successive multipole orders. The ratio of octupole to dipole is roughly

$$\langle r_n^2 \rangle \langle r_e^{-5} \rangle / \langle r_e^{-3} \rangle$$

where r_n is the nuclear coordinate and r_e the electronic coordinate. $\langle r_n^2 \rangle$ is approximately R_o^2, where R_o is the nuclear radius; and the ratio $\langle r_e^{-5} \rangle / \langle r_e^{-3} \rangle$ is approximately $(Z/a_o)^2$ (a_o = Bohr radius) because the interactions involved take place near the nucleus where the scale of the electronic wave function is a_o/Z, not just a_o. The octupole/dipole ratio is then

$$(ZR_o/a_o)^2 \sim 10^{-4} - 10^{-6}$$

comparable to the ratio of h.f.s./f.s. We shall start by considering the h.f.s. interactions in first order and later turn our attention to the effect of second order terms on the higher moments.

First, the non-central interactions between electrons and the nuclear particles, whatever these interactions may be, will be expanded in a series of tensor operators. The perturbation hamiltonian H_1 is written

$$H_1 = \sum_k T_e^{(k)} \bullet T_n^{(k)} \tag{1}$$

$T_e^{(k)}$ is a tensor operator of rank k which operates in the space of the electronic coordinates only; its rank is defined by the fact that it commutes with the total angular momentum operator of the same space, $\vec{J}$, just as do the spherical harmonics of order k. $T_n^{(k)}$ operates on the coordinates of the nucleons in the same manner; and the terms in the series (1) are the scalar products of these two tensors, thus are invariants in the combined space.[†] We now wish to calculate the first order energy expectation values of H_1 in states described as having J of the electron and I of the nucleus coupled to the resultant F.

$$W_F = \langle IJF | H_1 | IJF \rangle = \sum_k \langle IJF | T_e^{(k)} \bullet T_n^{(k)} | IJF \rangle \tag{2}$$

These matrix elements are independent of the magnetic quantum number M_F, so it will be ignored. According to a well-known theorem of Racah(2) the dependence on F of each of the matrix elements in (2) can be separated out as follows

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[†] The heavy dot $\bullet$ will be used to denote the scalar product of two tensor operators

$$T^{(k)} \bullet U^{(k)} = \sum_\mu T_\mu^{(k)} U_{-\mu}^{(k)} (-1)^\mu$$

while the light dot $\cdot$ will denote the scalar product of two cartesian vectors

$$\vec{V} \cdot \vec{W} = V_x W_x + V_y W_y + V_z W_z$$

$$\langle IJF | T_e^{(k)} \cdot T_n^{(k)} | IJF \rangle = (-1)^{I+J-F} W(IJIJ;Fk) \langle I \| T_n^{(k)} \| I \rangle \langle J \| T_e^{(k)} \| J \rangle \quad (2)$$

where W, the Racah coefficient, is a known algebraic function of its six arguments; and the double-barred matrix elements, called the reduced matrix elements, are independent of any magnetic quantum numbers which may be assigned to the states indicated.

We shall write the h.f.s. term energy as

$$W_F = \sum_k A_k M(IJ;F;k) \quad (3a)$$

with the normalization

$$M(IJ;I+J;k) = 1 \quad (3b)$$

which gives directly

$$A_k = \langle T_e^{(k)} \rangle_{JJ} \langle T_n^{(k)} \rangle_{II} \quad (4a)$$

with the relation

$$\langle T^{(k)} \rangle_{JJ} = \frac{(2J)!}{\sqrt{(2J-1)!(2J+k+1)!}} \langle J \| T^{(k)} \| J \rangle \quad (4b)$$

Our A's are related to the usual$^{(1)}$ h.f.s. interaction constants as follows:

$$\begin{aligned} A_1 &= IJa \\ A_2 &= 1/4b \\ A_3 &= c \end{aligned} \quad (4c)$$

The coefficient M is given by the formula

$$M(IJ;F;k) = \frac{(2I-k)!}{(2I)!}\,\frac{(2J-k)!}{(2J)!}\,\frac{(I+J-F)!(J-I+F)!(I-J+F)!}{(I+J+F+1)!}\left[k!\right]^2$$

$$\sum_z (-1)^{z+I+J-F}\,\frac{(2I+2J+1-z)!}{z!(2I-k-z)!(2J-k-z)!\left[(I+J-F-z)!(k+F-I-J+z)!\right]^2} \qquad (5)$$

where the sum extends over all integral values of z for which no factorial has a negative argument.

It has been customary to express M in terms of the cosine factor

$$K = F(F+1)-I(I+1)-J(J+1)$$

The formulas for the first four orders of M in terms of K are the following

$$M(IJ;F;1) = \frac{1}{2IJ}\,K \qquad (6a)$$

$$M(IJ;F;2) = \frac{6}{(2I)(2I-1)(2J)(2J-1)}\left[K(K+1)-\frac{4}{3}I(I+1)J(J+1)\right] \qquad (6b)$$

$$M(IJ;F;3) = \frac{20}{(2I)(2I-1)(2I-2)(2J)(2J-1)(2J-2)}\Big[K^3+4K^2 \qquad (6c)$$
$$+\frac{4}{5}K\left\{-3I(I+1)J(J+1)+I(I+1)+J(J+1)+3\right\} -4I(I+1)J(J+1)\Big]$$

$$M(IJ;F;4) = \frac{70}{(2I)(2I-1)(2I-2)(2I-3)(2J)(2J-1)(2J-2)(2J-3)}\,\cdot$$

$$\Big[\,K^4 + 10K^3 + \frac{4}{7}K^2\left\{-6I(I+1)J(J+1)+5I(I+1)+5J(J+1)+39\right\}$$
$$+\frac{4}{7}K\left\{-34I(I+1)J(J+1)+12I(I+1)+12J(J+1)+18\right\} \qquad (6d)$$
$$-\frac{24}{35}I(I+1)J(J+1)\left\{-2I(I+1)J(J+1)+4I(I+1)+4J(J+1)+27\right\}\Big]$$

It should be pointed out that formulas (6c,d) are quite unwieldy for numerical evaluation and it is frequently easier to work directly from (5). For example, if $2J = k$, we have

$$M(IJ;F;2J) = (-1)^{I+J-F} \frac{(2J)!(2I+2J+1)!(I-J+F)!}{(2I)!(I+J+F+1)!(I+J-F)!(J-I+F)!} \quad (7a)$$

or if $k = 2J-1$

$$M(IJ;F;2J-1) = (-1)^{I+J-F} \frac{(2J-1)!(2I+2J)!(I-J+F)!}{(2I)!(I+J+F+1)!(I+J-F)!(J-I+F)!} \cdot$$

$$\cdot\ 2\left[F(F+1)-I(I+1)+J^2\right] \quad (7b)$$

The following sum rule is also of help in checking numerical work

$$\sum_F (2F+1)M(IJ;F;k) = 0 \qquad (k>0)$$

Aside from the physical content of the operators (1) this analysis gives us the selection rule that the series (3a) terminates at the term $k = 2J$ or $2I$, whichever is smaller. One then has $2J$ (or $2I$) interaction constants A_k to be solved for from the $2J$ (or $2I$) measured energy intervals. Due to an orthogonality sum of the Racah coefficients one can solve (3a) analytically for the A_k.

$$A_k = (2k+1)\frac{\left[(2I)!(2J)!\right]^2}{(2I-k)!(2I+k+1)!(2J-k)!(2J+k+1)!} \sum_F (2F+1)\cdot M(IJ;F;k)W_F \quad (8)$$

III. Electromagnetic Potentials

We shall now describe the electric and magnetic static interactions between the nuclear and electronic systems in a multipole expansion.

The electrostatic potential set up in space by a distribution of charges in the nucleus is

$$V(r) = \int \frac{\rho(r')}{|r-r'|}\, dv' \tag{9}$$

where $\rho = e\Psi^* \sum_i g_{\ell_i} \Psi$ is the density of electric charge of all the nucleons; g_ℓ is +1 for protons and zero for neutrons. Now expanding the Green's function in terms of spherical harmonics

$$\frac{1}{|r-r'|} = \sum_k r_<^k \; r_>^{-k-1} \; C^{(k)}(\theta,\varphi)\cdot C^{(k)}(\theta',\varphi') \tag{10}$$

where

$$C^{(k)}_\mu(\theta,\varphi) = \sqrt{\frac{4\pi}{2k+1}}\, Y_{k\mu}(\theta,\varphi)$$

we have the desired multipole operators of the electric interaction. The functions $C^{(k)}$ are tensor operators of rank k with parity $(-1)^k$.

The vector potential for the magnetic field set up by the nuclear currents and spins is not quite so simple; it will be expressed in terms of vector spherical harmonics$^{(6)}$. We choose the form

$$\vec{A} = \sum_{k\mu} \vec{L}C_{\mu}^{(k)}(\theta,\varphi)h_{k,\mu}(r) \qquad (11)$$

where $\vec{L} = -i\vec{r}\times\mathrm{grad}$, which assures the gauge $\mathrm{div}\vec{A} = 0$. The operator $\vec{L}$ commutes with any function of r and also with the Laplacian so that the equation $\nabla^2\vec{A} = -\frac{4\pi}{c}\vec{j}$ becomes

$$\sum_{k\mu} \vec{L}C_{\mu}^{(k)}(\theta,\varphi)\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{k(k+1)}{r^2}\right]h_{k,\mu}^{(r)} = -\frac{4\pi}{c}\vec{j} \qquad (12)$$

Now using the orthogonality of the vector spherical harmonics over the unit sphere

$$\int\left[\vec{L}C_{\mu}^{(k)}\right]^{*}\cdot\left[\vec{L}C_{\mu'}^{(k')}\right]d\Omega = \delta_{kk'}\,\delta_{\mu\mu'}\frac{4\pi}{2k+1}k(k+1) \qquad (13)$$

we get

$$\left[\frac{1}{r}\frac{d^2}{dr^2}r - \frac{k(k+1)}{r^2}\right]h_{k,\mu}(r) = -\frac{1}{c}\frac{2k+1}{k(k+1)}\int\left[\vec{L}C_{\mu}^{(k)}(\theta,\varphi)\right]^{*}\cdot\vec{j}\,d\Omega$$

The Green's function for the left-hand side is

$$\frac{1}{2k+1}r_{<}^{k}\;r_{>}^{-k-1}$$

so finally we have the solution

$$h_{k,\mu}^{(r)} = \frac{1}{c}\frac{1}{k(k+1)}\int\left[\vec{L}r_{<}^{k}\;r_{>}^{-k-1}C_{\mu}^{(k)}(\theta,\varphi)\right]^{*}\cdot\vec{j}\,dv \qquad (14)$$

The nuclear currents $\vec{j}$ consist of two parts: the convection current

$$\vec{j}_c = e\Psi^{*}\sum_i g_{l_i}\vec{v}_i\,\Psi$$

and the spin current

$$\vec{j}_s = \mathrm{curl}\,\Psi^{*}\sum_i g_{s_i}\frac{e\hbar}{2m_i}\vec{S}_i\Psi$$

The convection current should be a symmetrized combination, but it is easily shown that the two terms give just the same contributions under the integral (14).

For the convection current term in (14) we can write

$$\left[\vec{L}(\ )\right]^{*}\cdot\vec{j}_c = i\vec{r}\times\vec{\nabla}(\ )^{*}\cdot\vec{j}_c = -i\vec{\nabla}(\ )^{*}\cdot(\vec{r}\times\vec{j}_c)$$

and get its contribution to (14) in the convenient form

$$\frac{-i}{k(k+1)}\int\left[\vec{\nabla}\, r_<^{k}\ r_>^{-k-1}C_{\mu}^{(k)}{}^{*}(\theta,\varphi)\right]\cdot\Psi^{*}2g_{\ell}\mu_N\vec{L}\Psi dv \qquad (15)$$

with the shorthand notation

$$2g_{\ell}\mu_N\vec{L} \equiv \sum_i g_{\ell_i}\frac{e\hbar}{m_i c}\vec{L}_i$$

For the spin current term we use the identity

$$\vec{r}\times\text{curl} = \text{grad}\,\vec{r}\cdot-(r\frac{\partial}{\partial r}+1)$$

and by partial integrations we have the spin contribution to (14)†.

$$\frac{-i}{k(k+1)}\int\left[\vec{\nabla}(r\frac{\partial}{\partial r}+1)r_<^{k}\ r_>^{-k-1}C_{\mu}^{(k)}{}^{*}(\theta,\varphi)\right]\cdot\Psi^{*}g_s\mu_N\vec{S}\Psi dv \qquad (16)$$

where again

$$g_s\mu_N\vec{S} \equiv \sum_i g_{s_i}\frac{e\hbar}{2m_i c}\vec{S}_i$$

Finally we can write the solution for the vector potential

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† There are surface terms left over from these partial integrations but they exactly cancel each other.

$$\vec{A} = \sum_k \frac{-i\mu_N}{k(k+1)}\left[\vec{L}C^{(k)}(\theta,\varphi)\right]\bullet\left[r^{-k-1}\int_0^r \Psi^*(\vec{\nabla} r'^{k}C^{(k)}(\theta',\varphi')\circ\right.$$

$$\circ\,(2g_\ell\vec{L} + (k+1)g_s\vec{S})\Psi\,dv' + r^k\int_r^\infty \Psi^*(\vec{\nabla} r'^{-k-1}C^{(k)}(\theta',\varphi')\circ$$

$$\left.(2g_\ell\vec{L} - kg_s\vec{S})\Psi\,dv'\right] \qquad (17)$$

In what follows we shall consider the nucleus as a point source and use only that part of the potentials corresponding to an observation point outside the nuclear matter. The error made this way affects only the magnitude of interaction observed, not its multipolarity. This error, involved in the h.f.s. anomaly(7) is appreciable only for 2^k-pole magnetic interaction with an electron in a state $j = k/2$, and then for various orders the effect varies as $1/k+1$; for the dipole ($k=1$) this effect is only a few per cent in the heaviest atoms.

We can now define the integrals occurring in (9) and (17) as the general nuclear electric and magnetic multipole moments

$$Q_k^\mu = e\int \Psi^* g_\ell r^k C_\mu^{(k)*}(\theta,\varphi)\Psi\,dv \qquad (18a)$$

$$M_k^\mu = \mu_N\int \Psi^*(\vec{\nabla} r^k C_\mu^{(k)*}(\theta,\varphi)\circ(g_\ell\frac{2}{k+1}\vec{L} + g_s\vec{S})\Psi\,dv \qquad (18b)$$

and write

$$V = \sum_k r^{-k-1}C^{(k)}(\theta,\varphi)\bullet Q_k \qquad (19a)$$

$$\vec{A} = \sum_k \frac{-i}{k}\, r^{-k-1}(\vec{L}C^{(k)}(\theta,\varphi))\bullet M_k \qquad (19b)$$

We also note that the operator Q_k has parity $(-1)^k$ while M_k has parity $(-1)^{k+1}$ so that the only static electric moments are of even order and the only static magnetic moments are of odd order if we assume that the nuclear wave function has a well-defined parity.

IV. Electronic Matrix Elements

We now investigate the interaction of a single electron (charge $-e$) with the nuclear fields just described. The electron wave function Ψ obeys the Dirac equation

$$\left[\vec{\alpha} \cdot (c\vec{p} + e\vec{A}) + \beta mc^2 - eV\right]\Psi = E\,\Psi \tag{20}$$

and for the zero order solutions in only the central part of the electrostatic potential, V_c, we put $\Psi = \begin{pmatrix}\psi \\ \phi\end{pmatrix}$ where ψ is the large component and ϕ the small component of the four-spinor Ψ. Now introducing quantum numbers we have the separations

$$\psi_{\ell jm} = f(r)/r\, \mathcal{Y}_{\ell jm}$$

$$\phi_{\ell jm} = g(r)/ir\, \mathcal{Y}_{\underline{\ell} jm}$$

where $\underline{\ell} = \ell \pm 1$

$j = \ell \pm 1/2 = \underline{\ell} \mp 1/2$

$$\mathcal{Y}_{\ell jm} = \sum_{m_\ell m_s} (1/2\ m_s\, \ell\, m_\ell | 1/2\, \ell\, jm)\, Y_\ell^{m_\ell}(\theta,\varphi)\, \chi_{1/2 m_s} \tag{21}$$

and χ is a two-component spinor.

The interaction hamiltonian is

$$H_1 = -e(V - V_c) + e\vec{\alpha} \cdot \vec{A} \tag{22}$$

and we will need the general matrix elements

$$\int \Psi^* H_1\, \Psi' \, dv$$

For the electric 2^k-pole matrix element ($k > 0$) these are

$$-e\langle Q_k\rangle\cdot\int_0^\infty r^{-k-1}dr\Big[ff'(1/2\,\ell\, jm|C^{(k)}|1/2\,\ell' j'm')$$

$$+\ gg'(1/2\,\underline{\ell}\, jm\,|\,C^{(k)}\,|\,1/2\,\underline{\ell}' j'm')\Big]$$

Now the matrix elements of $C^{(k)}$ in the $1/2\,\ell\, jm$ scheme are independent of the quantum numbers ℓ except for the parity selection ($\ell+\ell'+k$ even). Hence for the reduced matrix elements of electric multipoles we have

$$-e\,\langle\|Q_k\|\rangle\int_0^\infty r^{-k-1}(ff'+gg')dr(1/2\,\ell\, j\,\|\,C^{(k)}\,\|\,1/2\,\ell' j') \tag{23}$$

For the magnetic multipole we have the general matrix elements

$$e\frac{1}{ik}\langle M_k\rangle\cdot\Big[\int\psi^*_{\ell jm}\,\vec{\sigma}\circ(\vec{L}r^{-k-1}C^{(k)})\phi_{\underline{\ell}' j'm'}dv$$

$$+\int\phi^*_{\underline{\ell} jm}\,\vec{\sigma}\circ(\vec{L}r^{-k-1}C^{(k)})\psi_{\ell' j'm'}dv\Big]$$

But we can write

$\vec{\sigma}\cdot(\vec{L}r^{-k-1}C^{(k)}_{\mu})\phi = \vec{\sigma}\cdot\vec{L}(r^{-k-1}C^{(k)}_{\mu}\phi)-r^{-k-1}C^{(k)}_{\mu}(\vec{\sigma}\cdot\vec{L}\phi)$ and also by the hermiticity of $\vec{\sigma}\cdot\vec{L}$

$$\int\psi^*\vec{\sigma}\cdot\vec{L}(r^{-k-1}C^{(k)}_{\mu}\phi)dv=\int(\vec{\sigma}\cdot\vec{L}\psi)^*r^{-k-1}C^{(k)}_{\mu}\phi\,dv$$

Now the functions ψ, ϕ are eigenfunctions of the operator $\vec{\sigma}\cdot\vec{L}$ belonging to the eigenvalues $\kappa-1$, $\underline{\kappa}-1$, respectively; where κ is the Dirac quantum number

$$\kappa=\begin{cases}(j+1/2) & j=\ell+1/2\\ -(j+1/2) & j=\ell-1/2\end{cases}$$

referred to the large component and $\underline{\kappa}=-\kappa$.

We thus get for the reduced matrix elements of the magnetic multipoles

$$-e/k \,\langle \| M_k \| \rangle\, (\kappa + \kappa') \int_0^\infty r^{-k-1}(fg' + gf')dr \cdot$$

$$\cdot\, (1/2\,\ell\, j \,\|\, C^{(k)} \,\|\, 1/2\,\ell' j') \tag{24}$$

which have the parity selection ($\ell + \ell' + k$ odd). The general reduced matrix elements of the $C^{(k)}$ can be calculated best with the techniques of Racah.(2) The result is (using a formula of Schwinger(8))

$$(1/2\,\ell\, j \,\|\, C^{(k)} \,\|\, 1/2\,\ell' j') = 1/2(1+(-1)^{\ell+\ell'+k})\,\Delta(jj'k)(-1)^{\frac{j'-j+s-1}{2}} \tag{25}$$

$$\frac{(j+j'+s)!!}{(j+j'-s)!!(j-j'+s-1)!!(j'-j+s-1)!!}$$

$$\text{where } s = \begin{cases} k & j+j'+k \quad \text{even} \\ k+1 & j+j'+k \quad \text{odd} \end{cases}$$

and

$$\Delta(abc) = \left[\frac{(a+b-c)!(b+c-a)!(c+a-b)!}{(a+b+c+1)!}\right]^{1/2}$$

For the first order hyperfine interactions only the diagonal matrix elements are needed and we get for the interaction constants

$$A_k = -Q_k e \int_0^\infty r^{-k-1}(f^2+g^2)dr(-1)^{k/2}\,\frac{(k-1)!!}{k!!}\,\frac{(2j)!}{(2j+k)!!(2j-k-1)!!} \tag{26a}$$

$$k \text{ even}, > 0$$

$$A_k = -M_k \frac{e}{k} 4\kappa \int_0^\infty r^{-k-1} fg\,dr(-1)^{\frac{k-1}{2}}\,\frac{k!!}{(k-1)!!}\,\frac{(2j)!}{(2j+k+1)!!(2j-k)!!}$$

$$k \text{ odd} \tag{26b}$$

in terms of the specific nuclear moments

$$Q_k = \langle Q_k^o \rangle_{II} \quad M_k = \langle M_k^o \rangle_{II} \tag{27}$$

The preceding analysis was for a single electron bound to the nucleus. It is also correct to describe the interaction of a single valence electron outside closed sub-shells of other electrons.[†] For configurations such as p^5, d^9 in L-S coupling, or $(3/2)^3$, $(5/2)^5$ in j-j coupling where there is just one electron less than the number needed to fill a shell, only very slight modifications are needed to give the correct matrix elements: the even (electric multipole) interactions are just (-1) times the values for a single electron while the odd (magnetic multipole) ones are the same.

In the case of more complex electronic configurations one must know the coupling scheme of the several angular momenta involved; then the techniques of Racah(2) show how to calculate the appropriate "projection" factors. An example is worked out in Appendix 1.

[†] This assumes that one can write the total wave function for all the electrons in the form of products where the coordinates of the valence electron are separated from those of the core electrons.

V. Radial Integrals

With the separation of variables (21) the Dirac equation (20) for the radial functions f and g reads

$$\left(\frac{d}{dr} - \frac{\kappa}{r}\right) f = \frac{1}{\hbar c}(mc^2 + E + eV_c) g$$

$$\left(\frac{d}{dr} + \frac{\kappa}{r}\right) g = \frac{1}{\hbar c}(mc^2 - E - eV_c) f \qquad (28)$$

For a many-electron atom the best solution consistent with the assumption of the preceding footnote is obtained from a Hartree-Fock treatment. However, to obtain simple analytical results we make the assumption, following Casimir(3), that the important contribution to the integrals (26) comes from the region of small values of r. This should be an excellent approximation for the cases $j = \ell + 1/2 = k/2$ (magnetic dipole in $s_{1/2}$ state, magnetic octupole in $p_{3/2}$ state, etc.) where the non-relativistic treatment gives the interaction as due entirely to the electron density at the nucleus (r=0). For orbits of larger ℓ, however, the wave function is concentrated farther out and is more slowly rising near the origin so this approximation worsens. At small value of r the major contribution to the potential is from the nucleus. Setting $V_c = \frac{Ze}{r}$ and with the approximation of zero binding energy $|mc^2 - E| \ll V_c$ we get from (28) the solutions in terms of Bessel functions

$$f = C\left[\frac{x}{2} J_{2\rho+1}(x) - (\rho + \kappa) J_{2\rho}(x)\right]$$

$$g = C\alpha Z J_{2\rho}(x) \qquad (29)$$

where $x = \sqrt{8Zr/a_0}$ $\quad \rho = \sqrt{\kappa^2 - \alpha^2 Z^2}$ $\quad a_0 = \frac{\hbar^2}{me^2}$ $\quad \alpha = \frac{e^2}{\hbar c}$

With these functions the radial integrals (26) can be evaluated(9) to give the following results

$$\int_0^\infty r^{-k-1}(f^2+g^2)dr = C^2\left(\frac{2Z}{a_0}\right)^k \frac{(2k-2)!}{k!(k-1)!} \frac{k(2\kappa+k)(2\kappa+k-1)-4\alpha^2Z^2(3k-1)}{(2\rho+k)(2\rho+k-1)\ldots(2\rho-k)} \tag{30}$$

$$\int_0^\infty r^{-k-1}fg\,dr = C^2\,\frac{\hbar}{2mc}\left(\frac{2Z}{a_0}\right)^{k+1} \frac{(2k-1)!}{k!(k-1)!} \frac{(-k-2\kappa)}{(2\rho+k)(2\rho+k-1)\ldots(2\rho-k)} \tag{31}$$

The normalization constant C, which gives the density at the nucleus of the wave function of the outer valence electron, is best evaluated in terms of the fine-structure separation (for non-s electrons) between the states $j = \ell + 1/2$ and $j = \ell - 1/2$, which have almost identical wave functions for larger values of r. Here and subsequently we shall use the notation of a single dash ' to identify a quantity as relating to the state $j = \ell + 1/2$, and a double dash '' for the state $j = \ell - 1/2$. The resulting identification is(3), (4),(5)

$$C' \cong -C'' \qquad C^2 = \frac{\delta}{2.911}\,\frac{\ell(\ell+1)}{2HZ^3}\,\frac{1}{a_0} \tag{32}$$

where δ is the doublet splitting in cm^{-1}, and H is a relativistic correction factor. More accurate approximations for the ratio $|C''/C'|$ will be termed normalization corrections and will be of concern in the following section. Casimir(3) gives the estimate

$$\left|\frac{C''}{C'}\right|^2 = 1 + \frac{3\alpha^2 Z^2}{2\ell(\ell+1)n^*} \qquad (33)$$

involving the "effective quantum number" n^*. However, an explicit calculation by Breit for the case of Thallium ($Z = 81$) gives a value for $|C''/C'|^2 = 1.65$ compared to the 1.18 of (33). We shall use Casimir's formula (33) for lighter nuclei ($Z \lesssim 50$) for which these corrections are not very large anyway. For the integrals of greatest interest we shall write the results in the following forms.

Magnetic dipole: $$\int_0^\infty r^{-2} fg\,dr = C^2 \frac{\hbar}{2mc}\left(\frac{2Z}{a_0}\right)^2 \frac{F}{(2\ell+1)\left[\mp(2\ell+1)-1\right]} \qquad (34a)$$

$\mp$ as $j = \ell \pm 1/2$

Electric quadrupole: $$\int_0^\infty r^{-3}(f^2+g^2)\,dr = C^2\left(\frac{2Z}{a_0}\right)^2 \frac{R}{\ell(2\ell+1)(2\ell+2)} \qquad (34b)$$

Magnetic octupole:

$$\int_0^\infty r^{-4} fg\,dr = C^2 \frac{\hbar}{2mc}\left(\frac{2Z}{a_0}\right)^4 \frac{10\ T}{(2\ell+3)(2\ell+2)(2\ell+1)(2\ell)(2\ell-1)\left[\mp(2\ell+1)-3\right]} \qquad (34c)$$

$\mp$ as $j = \ell \pm 1/2$

F and R are the same relativistic correction factors given by Casimir$^{(3)}$; T is the corresponding correction factor for the octupole integral and is given by

$$T = \frac{(2j+4)!}{(2j-3)!}\,\frac{(2\rho-4)!}{(2\rho+3)!} \qquad (35)$$

All these factors, along with H, are plotted as functions of Z in Fig. I for the case $\ell = 1$.

VI. Second-Order Effects

So long as we consider only first order effects of the h.f.s. interactions, the multipoles can be separated from one another unambiguously by the orthogonality of the "interval rules" for different orders (8). However in second order we get the energy given by the square of a matrix element. Thus if, in second order, we consider the matrix element from the state IJF to the (different) state I'J'F of the h.f.s. interactions of various orders, we get a dependence on F which goes as the Racah coefficient

$$(-1)^F\ W(I'J'IJ;Fk)$$

In the square of the matrix element there will be such products as

$$W(I'J'IJ;Fk_1)W(I'J'IJ;Fk_2)$$

and if we want to know what part of this looks like the first order term of an interaction of rank k we multiply by

$$(-1)^F\ W(IJIJ;Fk)\ (2F+1)$$

and sum over F. This sum is well known in the theory of Racah coefficients and gives a result proportional to

$$W(Ik_1Ik_2;I'k)\ W(Jk_1Jk_2;J'k)$$

which is non zero only if

$$|k_1 - k_2| \leq k \leq k_1 + k_2$$

Thus in second order the square of the dipole term can influence at most the quadrupole; the cross dipole-quadrupole term can affect up to the octupole; and the square of the quadrupole term can reach to the 2^4 pole.

We shall now calculate the off-diagonal matrix elements for the dipole and quadrupole operators from the state in which the measurement is being made (assumed to be $j = \ell + 1/2$) to the near-by doublet level of the electron ($j = \ell - 1/2$).

For the dipole term the matrix element (always diagonal in F) is from (24)

$$W(IJIJ-1;F1)(-1)^{I+J-F-1}\langle I\|M_1\|I\rangle(-e).$$

$$\cdot(\kappa+\kappa')\int_0^\infty r^{-2}(f'g''+g'f'')dr(1/2\ell J\|C^{(1)}\|1/2\underline{\ell}J-1)$$

and from (25)

$$(1/2\ell J\|C^{(1)}\|1/2\underline{\ell}J-1) = \sqrt{\frac{(2J+1)(2J-1)}{4J}} \text{ also } \kappa+\kappa' = 1.$$

The form of the Racah coefficient is

$$W(IJIJ-1;F1)(-1)^{I+J-F-1} = \sqrt{\frac{(I+J-F)(J-I+F)(I-J+F+1)(I+J+F+1)}{(I+1)(2I+1)2I(2J+1)2J(2J-1)}}$$

and the nuclear term is

$$\langle I\|M_1\|I\rangle = \sqrt{\frac{(I+1)(2I+1)}{I}}\,M_1$$

So that the entire matrix element is

$$\frac{-eM_1}{4IJ}\int_0^\infty r^{-2}(f'g''+g'f'')dr\sqrt{(I+J-F)(J-I+F)(I-J+F+1)(I+J+F+1)} \qquad (36)$$

The radial integral yields

$$\int_0^\infty r^{-2}(f'g''+g'f'')dr = C'C''\frac{\hbar}{2mc}\left(\frac{2Z}{a_0}\right)^2\frac{-4\Gamma(\rho'+\rho''-1)}{\Gamma(\rho''-\rho'+2)\Gamma(\rho'-\rho''+2)\Gamma(\rho'+\rho''+2)}$$

$$\equiv -C'C''\frac{\hbar}{2mc}\left(\frac{2Z}{a_0}\right)^2\frac{G}{\ell(2\ell+1)(2\ell+2)} \qquad (37)$$

The ratio of this to the diagonal term in the state $j=\ell+1/2$ is

$$\int_0^\infty r^{-2}(f'g''+g'f'')dr \Big/ \int_0^\infty r^{-2}f'g'dr = \frac{C''}{C'}\frac{1}{\ell}\frac{G}{F'} \equiv -\frac{1}{\ell}\xi \tag{38}$$

The off-diagonal quadrupole matrix element is from (23)

$$W(IJIJ-1;F2)(-1)^{I+J-F-1}\langle I\,\|Q_2\|\,I\rangle(-e)\int_0^\infty r^{-3}(f'f''+g'g'')dr$$

$$(1/2\ell J\,\|\,C^{(2)}\,\|\,1/2\ell J-1)$$

and from (25)

$$(1/2\ell J\,\|\,C^{(2)}\,\|\,1/2\ell J-1) = \sqrt{\frac{3(2J+1)(2J-1)}{16J(J+1)(J-1)}}$$

The form of the Racah coefficient is

$$W(IJI\;J-1;F2)(-1)^{I+J-F-1} =$$

$$\sqrt{\frac{3(I+J-F)(J-I+F)(I-J+F+1)(I+J+F+1)}{4J(J+1)(J-1)(2J-1)(2J+1)(2I+3)(2I+1)(2I-1)I(I+1)}}\;\cdot$$

$$\cdot\left[F(F+1)-I(I+1)-J^2+1\right]$$

and the nuclear term is

$$\langle I\,\|Q_2\|\,I\rangle = \sqrt{\frac{(2I+3)(2I+1)(I+1)}{I(2I-1)}}\;Q_2$$

So the entire matrix element is

$$-eQ_2\int_0^\infty r^{-3}(f'f''+g'g'')dr\sqrt{(I+J-F)(J-I+F)(I-J+F+1)(I+J+F+1)}\;\cdot$$

$$\cdot\left[F(F+1)-I(I+1)-J^2+1\right]\times\frac{3}{8J(J+1)(J-1)I(2I-1)} \tag{39}$$

The radial integral gives

$$\int_0^\infty r^{-3}(f'f''+g'g'')dr=C'C''\left(\frac{2Z}{a_0}\right)^2 \frac{2\Gamma(\rho'+\rho''-2)}{\Gamma(\rho'+\rho''+3)\Gamma(\rho'-\rho''+3)\Gamma(\rho''-\rho'+3)}$$

$$\Big\{12\left[\alpha^2Z^2+(\rho'+\kappa')(\rho''+\kappa'')\right]+(\rho'+\rho''-1)(\rho'+\rho''-2)(\rho'-\rho''+2)(\rho''-\rho'+2)$$

$$-3(\rho'+\kappa')(\rho'+\rho''-2)(\rho'-\rho''+2)-3(\rho''+\kappa'')(\rho'+\rho''+2)(\rho''-\rho'+2)\Big\} \tag{40}$$

$$\equiv -C'C''\left(\frac{2Z}{a_0}\right)^2 \frac{S}{\ell(2\ell+1)(2\ell+2)}$$

The ratio of this to the diagonal integral in the $j=\ell+1/2$ state is

$$\int_0^\infty r^{-3}(f'f''+g'g'')dr \Big/ \int_0^\infty r^{-3}(f'^2+g'^2)dr = -\frac{C''}{C'}\frac{S}{R'} \equiv \eta \tag{41}$$

Collecting all the terms we can now write the second order energy as follows

$$W_F^{(2)}=\frac{1}{\Delta E}(I+J-F)(J-I+F)(I-J+F+1)(I+J+F+1)\cdot$$

$$\cdot\left[-\frac{3(F(F+1)-I(I+1)-J^2+1)}{2J(J-1)(2J-1)I(2I-1)}\eta A_2' - \frac{J+1}{2IJ(2J+1)(2J-1)}\xi A_1'\right]^2 \tag{42}$$

in terms of the first order interaction constants in the state $j = \ell+1/2$ (we might also have referred to the state $j = \ell +1/2$)s ΔE is $-\delta$ (the fine-structure splitting) if the $j = \ell + 1/2$ state is the lower state (in energy), or $+\delta$ if $j = \ell - 1/2$ is lower.

VII. Effects of Configuration Interaction

We now go on to consider the effect of some configuration interaction of the sort discussed by Fermi and Segrè$^{(10)}$ and calculated in a particular case by Koster$^{(11)}$. For configurations $s^2\ell j$ (or $s^2\ell^{-1}j$) we include the possibility of one of the s electrons being raised to a higher s-state s'. The wave function in L-S coupling will be written - for both $j = \ell + 1/2$ and $j = \ell - 1/2$ levels

$$\Psi_j = a_0(s^2(S=0)\,{}^2L_j) + a_1(ss'(S=1)\,{}^2L_j) + a_2(ss'(S=0)\,{}^2L_j) \qquad (43)$$

with normalization $a_0^2 + a_1^2 + a_2^2 = 1$, where S is the resultant angular momentum of the two s electrons' spins which then couples to the spin of the ℓ electron to give the doublet. In what follows we shall approximate only that $a_1^2 \ll 1$ (Koster finds $a_1^2 = .001$ for Gallium, Z = 31).

For the wave function (43) the octupole and quadrupole matrix elements, as well as the fine-structure are essentially the same (to order a_1^2) as those one would get from considering only the valence ℓ electron alone. We are interested in the effect of the s-electrons in the first and second order dipole interactions as these influence the interpretation of the purely octupole interaction from the h.f.s. data. We shall find an explicit evaluation for a correction factor which should be multiplied into A_1^I in formula (42) just to take account of the dipole interaction of these s-electrons.

First, with the total dipole operator written as a sum of an operator $T_\ell^{(1)}$ (of rank 1) acting on the valence ℓ

electron and another $T_s^{(1)}$ acting on the s electrons, the general reduced matrix element becomes (to order $a_1^2 \ll 1$)

$$(J \| T_\ell^{(1)} + T_s^{(1)} \| J') = (J \| T_\ell^{(1)} \| J') + \Delta_{JJ'} \qquad (44)$$

where $\Delta_{JJ'}$ is a sum of matrix elements between various terms of (43), all of the form

$$\Delta_{JJ'} \sim (S1/2,\ 1/2\ell,\ J \| T_s^{(1)} \| S'1/2,\ 1/2\ell,\ J')$$

$$= W(1/2J1/2J';\ell 1)\ \sqrt{2J+1}\ \sqrt{2J'+1}\ (-1)^{\ell-1/2+J} \cdot$$

$$\cdot\ (S1/2,\ 1/2 \| T_s^{(1)} \| S'1/2,\ 1/2)$$

That is, without actually calculating $\Delta_{JJ'}$ we have gotten its dependence on J and J'. Now putting $J = \ell + 1/2$ we get the ratios

$$\frac{\Delta_{JJ-1}}{\Delta_{JJ}} = \sqrt{\frac{2J-1}{J+1}} \qquad (45a)$$

$$\frac{\Delta_{J-1\ J-1}}{\Delta_{JJ}} = -\sqrt{\frac{(J-1)(2J-1)}{(J+1)(2J+1)}} \qquad (45b)$$

Also the ratio of the off-diagonal to diagonal ($J=\ell+1/2$ state) reduced dipole matrix elements of the ℓ electron is

$$-\xi\ \frac{\sqrt{(J+1)(2J-1)}}{(2J+1)(2J-1)} \qquad (46)$$

The desired correction factor ξ is given by

$$\xi = \frac{(\ell J \| T_\ell^{(1)} \| \ell J') + \Delta_{JJ'}}{(\ell J \| T_\ell^{(1)} \| \ell J')} \qquad (47)$$

and from now on we will understand $J = \ell + 1/2$, $J' = \ell - 1/2 = J-1$.

One must calculate Δ_{JJ} by taking the discrepancy between the observed interaction constant A_1' and that amount calculated for the valence ℓ-electron alone. If the h.f.s. is measured in the $J' = \ell - 1/2$ state as well, one can get a better check on Δ by solving the two simultaneous equations of the form (44) with the measured interaction constants A_1' and A_1''. Using (45b) and the relation

$$(\ell J\text{-}1 \| T_\ell^{(1)} \| \ell J\text{-}1) = \sqrt{\frac{(J+1)(2J-1)}{(J-1)(2J+1)}}\,(\ell J \| T_\ell^{(1)} \| \ell J) \qquad (48)$$

$$\Theta = \frac{F''}{F'} \left|\frac{C''}{C'}\right|^2$$

we get

$$M_1 \Delta_{JJ} = \frac{\Theta A_1' - \frac{J}{J+1} A_1''}{\Theta + \frac{J-1}{J+1}} \sqrt{\frac{(J+1)(2J+1)}{J}} \qquad (49a)$$

$$M_1 (\ell J \| T_\ell^{(1)} \| \ell J) = \frac{\frac{J-1}{J} A_1' + A_1''}{\Theta + \frac{J-1}{J+1}} \sqrt{\frac{J(2J+1)}{(J+1)}} \qquad (49b)$$

and finally

$$\zeta = 1 + \frac{1}{\xi} \frac{\frac{J}{J+1} A_1'' - \Theta A_1'}{A_1'' + \frac{J-1}{J} A_1'} \quad \frac{(2J+1)(2J-1)}{(J+1)J} \qquad (49c)$$

The calculations carried out here also find application in the study of the Zeeman effect in h.f.s. as used to measure directly the nuclear g-factor. When an atom of spin $J = 1/2$ (for $I > 1/2$) is placed in a uniform magnetic field H, there are according to the Breit-Rabi formula pairs of lines arising from the h.f.s. the difference of whose frequencies gives directly the quantity $2g_I \mu_N H$.

Foley(12) has shown that for a $p_{1/2}$ electron state second order contributions involving the doublet $p_{3/2}$ level can change the apparent value of g_I - as compared with the value measured directly by nuclear resonance methods. His formula is

$$R^{-1} = \frac{g_I(\text{atomic beam = h.f.s.})}{g_I(\text{nuclear resonance})} = 1 - \frac{1837\,\Delta\nu}{6(2I+1)g_I\delta} \qquad (50)$$

where $\Delta\nu$ is the h.f.s. interval in the $p_{1/2}$ state at zero field and δ is the fine-structure separation. Clendenin(13) has done the calculation relativistically and he gets formula (50) with the factor G/F" included in the second term.

What enters in (50) is just the off-diagonal matrix element of the h.f.s. interactions between the $p_{1/2}$ and $p_{3/2}$ states times the matrix element of the electron's magnetic moment operator between the same two states. There are three effects not considered by these other authors which we can now include: the normalization correction factor; the off-diagonal quadrupole term; the effect of configuration interaction on the off-diagonal dipole term. Using (42) we get the result

$$R^{-1} = 1 - \frac{1837}{g_I\delta}\left[\frac{\Delta\nu}{6(2I+1)}\,\zeta\,\frac{\xi}{\theta} - \frac{b}{I(2I-1)}\,\eta\right] \qquad (51)$$

b is the usual quadrupole interaction constant ($b=4A_2$) measured in the $p_{3/2}$ state and all other factors in (51) are as earlier defined. The sign of the correction term above is correct only when the $p_{1/2}$ state is lower in energy than the $p_{3/2}$ state.

We shall compare the calculated and measured values of this discrepancy for the ground states of Gallium and Indium.

Gallium(14) $Z = 31 \quad \delta = 24.8\ 10^6$ mc/sec. $\quad n^* = 1.51$

$$\left|\frac{C''}{C'}\right|^2 = 1.02_5 \qquad \xi = 1.02 \qquad \eta = 1.04 \qquad \theta = 1.10_5$$

$$\zeta = 1.58 \qquad A_1''/A_1' = 2.34$$

Ga^{69}: $\Delta\nu = 2677$ mc/sec. $\quad b = 62.5$ mc/sec. $\quad g_I = 1.34$

$$R^{-1} = 1 - .0078$$

to be compared with the experimental value

$$1 - .0079 \pm .0023$$

Ga^{71}: $\Delta\nu = 3402$ mc/sec. $\quad b = 39.4$ mc/sec. $\quad g_I = 1.70$

$$R^{-1} = 1 - .0084$$

with the experimental value

$$1 - .0077 \pm .0017$$

Indium(15) $Z = 49 \quad \delta = 66.5\ 10^6$ mc/sec. $\quad n^* = 1.53$

$$\left|\frac{C''}{C'}\right|^2 = 1.06 \qquad \xi = 1.04 \qquad \eta = 1.11 \qquad \theta = 1.30$$

$$\zeta = 1.84 \qquad A_1''/A_1' = 3.12$$

In^{115}: $\Delta\nu = 11{,}330$ mc/sec. $\quad b = 450$ mc/sec. $\quad g_I = 1.22$

$$R^{-1} = 1 - .0060$$

and the experimental value is

$$1 - .0062 \pm .0005$$

VIII. Nuclear Moments

The nuclear moments are defined as the following expectation values (evaluated in the state $m_I = I$).

$$Q_k = \langle e g_\ell r^k C^{(k)}(\vartheta,\varphi) \rangle_{II} \qquad (52a)$$

for electric moments (k even)

$$M_k = \langle \mu_N (\vec{\nabla} r^k C^{(k)}(\vartheta,\varphi)) \cdot (g_\ell \frac{2}{k+1} \vec{L} + g_s \vec{S}) \rangle_{II} \qquad (52b)$$

for magnetic moments (k odd)

The magnetic multipole moments (52b) can also be written in the form

$$M_k = -\int r^k C^{(k)}(\vartheta,\varphi) \operatorname{div} M dv$$

where M is the magnetization density (in the state $m_I=I$) defined as in Blatt and Weisskopf$^{(6)}$ Chapter I. These are related to the usually defined moments as follows

$\mu = M_1$ Magnetic Dipole Moment

$Q = 2Q_2$ Electric Quadrupole Moment

and we shall define the Magnetic Octupole Moment Ω as

$$\Omega = -M_3$$

It can be seen from the phase factors in Eqs. (26a,b) that the moments of a given type, electric or magnetic, have a natural oscillation in sign as one proceeds to higher orders. The minus sign is introduced in the definition of Ω so that a nucleus with a positive dipole moment is most likely to have a positive octupole moment as well.

It is of interest to calculate the moments expected of a single odd nucleon in an orbit of spin I. From (25) and (4b) we get directly the electric moments

$$Q_2 = \frac{1}{2}Q = -\frac{1}{2}\,\frac{2I-1}{2I+2}\,eg_\ell \langle r^2\rangle \qquad (53a)$$

$$Q_4 = \frac{3}{8}\,\frac{(2I-1)(2I-3)}{(2I+4)(2I+2)}\,eg_\ell \langle r^4\rangle \qquad (53b)$$

For a nuclear configuration of n (odd) equivalent nucleons in the expected ground state we have the relation

$$Q_k(j^n I=j) = \frac{2j+1-2n}{2j-1}\,Q_k(j) \qquad (53c)$$

giving the moment of the several particles in terms of the value for a single particle.

The calculation of the magnetic multipole expectation values (52b) is slightly more involved. With extensive use of the Racah techniques we have derived the following general formula for matrix elements of this type in single-particle orbits; g is any function of r.

$$\begin{aligned}
&(\ell\,1/2\,j \,\|\, (\vec{\nabla} g C^{(k)})\circ(g_\ell \vec{L} + g_s \vec{S}) \,\|\, \ell'\,1/2\,j') = \tfrac{1}{2}\left(1-(-1)^{\ell+\ell'+k}\right)\\
&\Big\{ g_\ell\, 1/2\; g/r\,(-1)^{j'-1/2+k}\Big[k(k+1) - \Big((j+1/2)+(-1)^{j+j'+k}(j'+1/2)\Big)\\
&\quad \Big((j+1/2)+(-1)^{j+j'+k}(j'+1/2)+(-1)^{\ell+1/2+j}\Big)\Big] + g_s\, 1/2\,(-1)^{\ell'+j+j'}\\
&\quad \Big[(-1)^{\ell+1/2+j}\,\frac{d}{dr}g - g/r\Big((j+1/2)+(-1)^{j+j'+k}(j'+1/2)\Big)\Big]\Big\}\,\Delta(jj'k)\\
&\quad (-1)^{\frac{j'+j+s}{2}+1}\,\frac{(j+j'+s)!!}{(j+j'-s)!!\,(j-j'+s-1)!!\,(j'-j+s-1)!!}
\end{aligned} \qquad (54)$$

with s and $\Delta()$ defined as in (25).

For the diagonal matrix elements in the state $M_I=I$, using (4b) and (54) we get

$$\mu = M_I = \mu_N I \begin{cases} g_\ell + \dfrac{g_s-g_\ell}{2I} & I = \ell + 1/2 \\ g_\ell - \dfrac{g_s-g_\ell}{2I+2} & I = \ell - 1/2 \end{cases} \tag{55}$$

the usual Schmidt values; and for the octupole

$$\Omega = -M_3 = +\mu_N \frac{3}{2} \frac{(2I-1)}{(2I+4)(2I+2)} \langle r^2 \rangle \begin{cases} (I+2) \\ (I-1) \end{cases} \cdot$$

$$\cdot \begin{cases} \left[(I-3/2)g_\ell + g_s\right] & I = \ell + 1/2 \\ \left[(I+5/2)g_\ell - g_s\right] & I = \ell - 1/2 \end{cases} \tag{56}$$

One can make a plot of these values of the single-particle octupole moments very much like the Schmidt plot for dipoles. In Fig. II are the lines for $I = \ell + 1/2$ and $I = \ell - 1/2$ of the quantity

$$\frac{\Omega}{\mu_N \langle r^2 \rangle} \text{ as a function of } I \ (\geqslant 3/2)$$

for an odd proton ($g_\ell = +1$, $g_s = 5.58$); a similar plot can be drawn for an odd neutron ($g_\ell = 0$, $g_s = -3.83$).

For nuclear configuration of several equivalent particles in the ground state $I = j$ we get for the magnetic multipole moments

$$M_k(j^n I=J) = M_k(j) \tag{57}$$

If (as in an odd-odd nucleus for example) we have a configuration of two particles (or two separate groups of particles) with separate spins j_1 and j_2 coupled to a resultant I, any multipole moment of the total system is made up out of the moments of the two particles as follows.

$$(j_1 j_2 I m_I = I \| T_1^{(k)} + T_2^{(k)} \| j_1 j_2 I m_I = I) = \frac{(2I+1)!}{\left[(2I-k)!(2I+k+1)!\right]^{1/2}}$$

$$\left[\frac{\sqrt{(2j_1-k)!(2j_1+k+1)!}}{(2j_1)!} (j_1 m_1 = j_1 \| T_1^{(k)} \| j_1 m_1 = j_1) \cdot \right.$$

$$\cdot W(j_1 I j_1 I; j_2 k)(-1)^{j_2 - j_1 - I + k} + \frac{\sqrt{(2j_2-k)!(2j_2+k+1)!}}{(2j_2)!} \cdot \tag{58}$$

$$\left. \cdot (j_2 m_2 = j_2 \| T_2^{(k)} \| j_2 m_2 = j_2) W(j_2 I j_2 I; j_1 k)(-1)^{j_1 - j_2 - I + k} \right]$$

We can make one interesting and simple remark concerning the interpretation of nuclear moments in A. Bohr's asymmetric core model. In the strong-coupling situation where the valence nucleons are alligned with respect to a permanently distorted nuclear core we must reduce all the moments by a projection factor P_k which allows for the transformation of the necessary operators into the body frame of the core. This projection factor, in the nuclear ground state where the valence nucleon is alligned with the core axis, is given by

$$P_k = (2I+1) \frac{\left[(2I)!\right]^2}{(2I-k)!(2I+k+1)!} \tag{59}$$

It is interesting that the higher P_k's can be quite small numbers if I is small ($I \sim k/2$). For the octupole, for example,

$$P_3 = 1/35 \qquad I = 3/2$$

$$5/42 \qquad I = 5/2$$

while the smallest P_1 is 1/3 (for I = 1/2) and the smallest P_2 is 1/5 (for I = 3/2).

The contrast between the asymmetric core effects in quadrupole and octupole moments is further intensified by the fact that while it is the large numerical charge of the core which, in spite of the projection factor, creates a large quadrupole moment, the total magnetization of the core is only of the order of that produced by a single particle. The conclusion is that if the strong-coupling situation exists for nuclei with small spins (3/2, 5/2) the octupole moment should be much smaller than the expected single particle value.

IX. Examples: $P_{3/2}$ Electrons

For an electron state with a single valence electron in a $p_{3/2}$ orbit there will be (for $I \geqslant 3/2$) four h.f.s. levels with the following M(IJ;Fk) coefficients (6), (7):

	k=1	k=2	k=3
F=I+3/2	1	1	1
F=I+1/2	$\frac{I-3}{3I}$	$\frac{-(2I-1)(I+3)}{I(2I-1)}$	$-3\ \frac{2I+4}{2I}$
F=I-1/2	$\frac{-I-4}{3I}$	$\frac{-(2I+3)(I-2)}{I(2I-1)}$	$+3\ \frac{(2I+4)(2I+3)}{(2I)(2I-1)}$
F=I-3/2	$\frac{-3I-3}{3I}$	$\frac{(2I+3)(I+1)}{I(2I-1)}$	$-\ \frac{(2I+4)(2I+3)(2I+2)}{(2I)(2I-1)(2I-2)}$

If we let x, y, z be the measured intervals between the F=I+3/2-F=I+1/2; F=I+1/2-F=I-1/2; F=I-1/2-F=I-3/2 levels respectively, then we get for the interaction constants (8);

$W_{I-3/2}=0$; $W_{I-1/2}=z$; $W_{I+1/2}=(y+z)$; $W_{I+3/2}=(x+y+z)$

$$A_1=\frac{9}{10}\,\frac{I(I+2)x}{(I+1)(2I+1)}x++\frac{3}{10}\,\frac{(2I-1)(2I+3)}{(I+1)(2I+1)}\,y+\frac{9}{10}\,\frac{(I-1)}{(2I+1)}\,z \tag{60a}$$

$$A_2=\frac{1}{2}\,\frac{I(2I-1)(I+2)}{(2I+1)(I+1)(2I+3)}\,x-\frac{1}{2}\,\frac{(2I-1)}{(2I+1)(I+1)}\,y-\frac{1}{2}\,\frac{(I-1)}{(2I+1)}\,z \tag{60b}$$

$$A_3=\frac{1}{10}\,\frac{I(I-1)(2I-1)}{(2I+3)(2I+1)(I+1)}\,x-\frac{1}{10}\,\frac{(I-1)(2I-1)}{(2I+1)(I+1)}\,y+\frac{1}{10}\,\frac{(I-1)}{(2I+1)}\,z \tag{60c}$$

We should subtract from the above formula for A_3 the amount due to the second order corrections (42), this comes to (using (8) to find the octupole-like part):

$$\frac{1}{\Delta E}\,\frac{3}{10}\,\frac{I-1}{I}\,\eta\,A_2'\left[\frac{8}{2I-1}\,\eta\,A_2'-\frac{5}{6}\,\xi\,\zeta\,A_1'\right] \tag{61}$$

with

$$\rho = 1 + \frac{16}{\xi} \frac{3/5A''_1/A'_1 - \theta}{3A''_1/A'_1 + 1} \qquad (62)$$

The formula for A_3 in terms of the octupole moment is

$$A_3 = \mu_0 \frac{\Omega\, 16}{5\cdot7\cdot9} \frac{T}{H} \frac{Z}{a_0^5} \frac{\delta}{2.911} \qquad (63)$$

or

$$\Omega = A_3 \frac{H}{T} \frac{3.36\ 10^{-17}}{\delta\ \ Z}$$

in units of

Ω - nuclear magneton cm^2

A_3 - mc./sec.

δ - cm^{-1}

For the ground state of Iodine$^{(1)}$: $n^* = 1.14$ I^{127}: $Z = 53$, $\delta = 7600$ cm^{-1}, $A'_1 = 3100$ mc/sec., $A'_2 = 286.6$ mc/sec.

$$\left|\frac{C''}{C'}\right|^2 = 1.10 \qquad \xi = 1.05 \qquad \eta = 1.13$$

No measurements have been made on the $p_{1/2}$ state, but it is expected that there will be considerably less configuration interaction in the halogens than in the corresponding Group III elements due to the tighter binding of the s-electrons. We will thus assume $\rho = 1$. The formula for A_3 with corrections is

$$A_3 = \frac{1}{5\cdot7\cdot16}\left[5x - 16y + 14z\right] - .00053 \text{ mc/sec.}$$

$$= (.00287 \pm .00037 - .00053) \text{mc/sec.}$$

where we have taken the square root of the sum of the squares of the experimental errors in x, y, z (weighted as above) as the total error. Using (63) with H = 1.07, T = 1.22 we get $\Omega_{127} = (0.17 \pm 0.03)10^{-24}$ nuclear magneton cm^2.

With the value for the radial integral taken roughly as

$$\langle r^2 \rangle = 3/5\, R_o = 3/5(.135A^{1/3})^2 10^{-24}\text{cm}^2$$

we get the value (0.62±0.10) on the octupole diagram (~1/4 the expected single particle value).

For the metastable $p_{3/2}$ state of Indium^{115} Kusch$^{(16)}$ has remeasured the intervals with extreme accuracy. Using the correction factors already worked out we get for A_3

$$A_3 = \frac{7}{2200}\left[6x-16y+11z\right] + .00109 \text{ mc/sec.}$$

$$= (.000011 \pm .000032 + .00109)\text{mc/sec.}$$

With H = 1.065 and T = 1.19 the octupole moment is

$$\Omega_{115} = (.31 \pm .01)10^{-24} \text{ nuclear magneton cm}^2$$

Approximating as above for $\langle r^2 \rangle$ we get the value (2.1±0.1) on the octupole plot (~1/2 the single particle value).

Daly$^{(17)}$ has measured the h.f.s. of the $p_{3/2}$ state for the two stable isotopes of Gallium. The several correction factors have already been quoted; we have

$$\underline{Ga}^{69}: \quad A_3 = \frac{1}{400}[x-4y+5z] + .0000336 \text{ mc/sec.}$$

$$= (50.2 \pm 3 + 33.6)10^{-6} \text{ mc/sec.}$$

$\underline{Ga^{71}}$: $A_3 = \frac{1}{400}\left[x-4y+5z\right] + .0000285$

$= (85.8 \pm 3 + 28.5)10^{-6}$ mc/sec.

with $H = 1.02_5$, $T = 1.06_5$ we get the octupole moments

$\Omega_{69} = (0.107 \pm .004)10^{-24}$ nuclear magneton cm^2

$\Omega_{71} = (0.146 \pm .004)10^{-24}$ nuclear magneton cm^2

Estimating $\langle r^2 \rangle$ as before we get the values (.58) for Ga^{69} and (.77) for Ga^{71} on the octupole plot.

The values of the quantity $\Omega/\mu_N\langle r^2 \rangle$ for these six nuclides are displayed in Fig. II, and it is striking to see the similarity between the distribution of points on this diagram and that on the Schmidt plot for dipole moments. Any strong conclusions about the quantitative aspects of this comparison may as yet be unjustified since the rough estimate

$$\langle r^2 \rangle = \tfrac{3}{5}R_o^2, \; R_o = 1.35\ A^{1/3}10^{-13}\text{cm}.$$

should be replaced by the analytical evaluations of some reasonable shell model. However it is interesting to compare the sizes of the octupole moments for the isotopic pair $Ga^{69,71}$. The heavier nucleus has larger dipole and octupole moments and smaller quadrupole moment, thus is consistently closer to the pure single-particle picture.

Appendix I

As an examplie in computing the multipole moment in a complex electron configuration we shall work out the problem of the octupole interaction in the ground state of an element of Group V, As, Sb, Bi. The electron configuration in these is p^3 and the ground state is denoted $^4S_{3/2}$. In pure L-S coupling such a state, because of its spatial symmetry, could have no octupole or quadrupole moment even though the total spin 3/2 is large enough. The state is actually described in terms of an intermediate coupling scheme and for the heavier elements comes very close to pure j-j coupling.

Following Breit$^{(5)}$ we shall describe such a state, for J = 3/2, in terms of the allowed states in j-j coupling, made up of $p_{1/2}$ and $p_{3/2}$ states for each single electron. The wave function is written

$$\Psi_{3/2} = c_1 \left(\tfrac{3}{2}\,\tfrac{3}{2}\,\tfrac{3}{2}\right)_{3/2} + c_2 \left(\tfrac{3}{2}\,\tfrac{3}{2}\,\tfrac{1}{2}\right)_{3/2} + c_3 \left(\tfrac{3}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}\right)_{3/2} \tag{A1}$$

For the first component of (A1) the state J = 3/2 is the only allowed state for the three equivalent electrons of spin 3/2; for the second component the two equivalent 3/2 electrons are coupled to a resultant spin of 2, which then couples to the third electron of spin 1/2 to form the resultant J = 3/2; in the third component of (A1) the two 1/2 electrons must couple to spin zero.

Now to compute the octupole matrix element in the state (A1) we shall use only the fact that we are working with a tensor operator of rank three, and compare the result with that to be expected of a single $p_{3/2}$ electron state. First, note that there are no cross terms since a tensor of rank 3 cannot have matrix elements between states of spin 1/2 and 3/2 (for the individual electrons). The third component is exactly the state of a single $p_{3/2}$ electron and the first component gives the same matrix element since it represents the state of one $p_{3/2}$ electron missing from a closed shell.

Only the second component requires use of the Racah algebra$^{(2)}$. The calculation is as follows

$$\left(\left(\tfrac{3}{2}\,\tfrac{3}{2}\right) 2,\ 1/2\ 3/2 \,\|\, T^3 \,\|\, \left(\tfrac{3}{2}\,\tfrac{3}{2}\right) 2,\ 1/2\ 3/2\right)$$

$$= 4W(2\ 3/2\ 2\ 3/2;\ 1/2\ 3)\left(\tfrac{3}{2}\,\tfrac{3}{2}\ 2 \,\|\, T^3 \,\|\, \tfrac{3}{2}\,\tfrac{3}{2}\ 2\right)$$

since T^3 has zero matrix element for the 1/2 electron state. Next

$$\left(\tfrac{3}{2}\,\tfrac{3}{2}\ 2 \,\|\, T^3 \,\|\, \tfrac{3}{2}\,\tfrac{3}{2}\ 2\right) = -\ 2\cdot 5\cdot W(3/2\ 2\ 3/2\ 2;\ 3/2\ 3)\left(\tfrac{3}{2} \,\|\, T^3 \,\|\, \tfrac{3}{2}\right)$$

where the factor 2 accounts for the fact that both $\frac{3}{2}$ electrons contribute equally while the subsequent factors represent the contribution of just one.

Putting these results together we have

$$\left(\Psi_{3/2} \,\|\, T^3 \,\|\, \Psi_{3/2}\right) = \left(p_{3/2} \,\|\, T^3 \,\|\, p_{3/2}\right)\Big[\, C_1^2 + C_3^2$$

$$-40C_2^2 W(2\ 3/2\ 2\ 3/2;\ 1/2\ 3)W(3/2\ 2\ 3/2\ 2;\ 3/2\ 3)\Big]$$

Now evaluating the Racah coefficients and using the normalization

$$C_1^2 + C_2^2 + C_3^2 = 1$$

we have the ratio

$$\left(\Psi_{3/2} \| T^3 \| \Psi_{3/2}\right) \Big/ \left(p_{3/2} \| T^3 \| p_{3/2}\right) = 1 - 9/5\ C_2^2 \tag{A2}$$

The constants C_1, C_2, C_3 may be evaluated from the observed multiplet structure and also from the atomic g_J value. For Bismuth, Breit and Wills$^{(5)}$ give $C_2 = 0.345$ so the factor (A2) is 0.786.

Appendix II. Sketch of the Non-Relativistic Theory

For a non-relativistic study the hyperfine interactions may be conveniently described directly in terms of the two charge-current densities, without using the intermediary fields. Thus for the electric interaction we write the energy (to first order)

$$W_e = \iint \frac{\rho_1 \rho_2}{r_{12}} \, dv_1 dv_2$$

and with the assumption that system 1 is outside system 2 se get the multipole expansion

$$W_e = \sum_k \int \rho_1 r^{-k-1} C^{(k)} dv_1 \bullet \int \rho_2 r^k C^{(k)} dv_2 \qquad (A3)$$

Then identifying ρ as e times the wave function product $\psi^* \psi$ (A3) can be read as the product of two matrix elements.

For the magnetic interaction between two current systems the interaction is

$$W_m = \frac{-1}{c^2} \iint \frac{\vec{j}_1 \cdot \vec{j}_2}{r_{12}} \, dv_1 dv_2 \qquad (A4)$$

However because of the vector nature of the currents $\vec{j}$ we cannot immediately make a multipole expansion of this expression, (A4). We first express each current density $\vec{j}$ in terms of a magnetization density $\vec{M}$

$$\vec{j} = c \operatorname{curl} \vec{M}$$

Then a series of partial integrations reduces (A4) to

$$W_m = \iint \frac{\operatorname{div} M_1 \operatorname{div} M_2}{r_{12}} dv_1 dv_2 \qquad (A5)$$

provided the two systems 1 and 2 do not overlap anywhere. Now we can make the usual expansion to get

$$W_m = \sum_k \int \operatorname{div} M_1 r^{-k-1} C^{(k)} dv_1 \bullet \int \operatorname{div} M_2 r^k C^{(k)} dv_2 \qquad (A6)$$

The analysis of the angular dependence of the h.f.s. interactions is just as before and we get for the interaction constants

$$A_k = e^2 \left\langle r^{-k-1} C^{(k)} g_\ell \right\rangle_{JJ} \left\langle r^k C^{(k)} g_\ell \right\rangle_{II} \qquad (A7)$$

electric multipole, k even

$$A_k = \left\langle r^{-k-1} C^{(k)} \operatorname{div} M_1 \right\rangle_{JJ} \left\langle r^k C^{(k)} \operatorname{div} M_2 \right\rangle_{II}$$

magnetic multipole, k odd

The magnetic terms are not yet in the desired form ψ^* operator ψ. Using vector identities and carrying out some partial integrations (see ref. (6)) one can re-express the magnetization in terms of convection and spin currents through the operators $\vec{L}$ and $\vec{S}$. The final result for the magnetic multipoles is

$$A_k = \mu_0 \mu_N \left\langle \left(\vec{\nabla} r^{-k-1} C^{(k)}\right) \cdot \left(\frac{-2}{k} g_\ell \vec{L} + g_s \vec{S}\right) \right\rangle_{JJ} \cdot$$

$$\cdot \left\langle \left(\vec{\nabla} r^k C^{(k)}\right) \cdot \left(\frac{2}{k+1} g_\ell \vec{L} + g_s \vec{S}\right) \right\rangle_{II} \qquad (A8)$$

For single electron states $1/2\ell J$ the matrix elements occurring in (A7) and (A8) can be evaluated using formulas (25) and (54) respectively. For the first four orders the results are ($g_\ell = -1$, $g_s = -2$ for electron)

$$A_1 = IJa = \mu_o \frac{2\ell(\ell+1)}{J+1} \langle r^{-3} \rangle M_1 \qquad \text{(A9)}$$

$$A_2 = 1/4b = e^2 \frac{(2J-1)}{2(2J+2)} \langle r^{-3} \rangle Q_2 \qquad \text{(A10)}$$

$$A_3 = c = -\mu_o \frac{8\ell(\ell-1)(\ell+1)(\ell+2)}{(2J+2)(2J+3)(2J+4)} \langle r^{-5} \rangle M_3 \qquad \text{(A11)}$$

$$A_4 = d = -e^2 \, \frac{3}{8} \, \frac{(2J-1)(2J-3)}{(2J+2)(2J+4)} \langle r^{-5} \rangle Q_4 \qquad \text{(A12)}$$

where we have used the nuclear moments as defined in (18).

These formulas are invalid for the special case of magnetic 2^k pole interaction in an electron state $J = \ell + 1/2 = k/2$ -- dipole in $S_{1/2}$ state, octupole in $p_{3/2}$ state. For these cases an alternative analysis is carried out as follows. The vector potential

$$\vec{A}(2) = \frac{1}{c}\int \frac{\vec{j}(1)}{r_{12}} \, dv_1$$

is easily evaluated for the electron in the state $M = J$ considering the spin and convection current contributions to $\vec{j}$ in the usual way. Taking just the $k(=2\ell+1)$-pole term we find that the magnetic field which it represents can easily be written as the gradient of a scalar. That is

$$\vec{H} = \text{curl } \vec{A} = \text{grad } \varphi$$

$$\varphi = -\mu_o g(0)(-1)^\ell \frac{2(2\ell)!(2\ell+1)!(2\ell+2)!}{\ell! \, \ell! (4\ell+3)!} r^k C^{(k)} \qquad \text{(A13)}$$

where, if $f(r)$ is the normalized radial wavefunction,

$$g(r) = |r^{-\ell} f(r)|^2$$

Now a formula for the magnetic interaction equivalent to (A4) is

$$W_m = -\int \vec{H}\cdot\vec{M}\, dv$$

where $\vec{M}$ is the nuclear magnetization density. Putting in (A13) and performing one partial integration we have the effective evaluation of the electronic matrix element (A7) for these special cases. Thus for an $S_{1/2}$ electron

$$A_1 = \frac{2}{3}\mu_0 g(o) M_1 \qquad \text{(A14)}$$

and for a $p_{3/2}$ electron

$$A_3 = -\frac{4}{35}\mu_0 g(o) M_3 \qquad \text{(A15)}$$

This last result is identical with the evaluation given by Casimir and Karreman(18) in their original investigation of the octupole interaction in Iodine.

For the calculation of second order effects between doublet states the forms (A7), (A8) of the dipole and quadrupole operators are used. Assuming that both doublet states have identical radial wave functions the final result is just equation (42) with

$$\xi = \eta = 1.$$

Appendix III. Discussion of Approximations

In this section we shall discuss several approximations made in the theoretical analysis of this paper in order to arrive at an estimate of the accuracy of the terms calculated.

A: The assumption that a many-electron atom can be described as a core of closed shells plus a few valence electrons is the essential starting point for any study of atomic multiplet structure, fine structure and hyperfine structure. The corrections to this model, termed configuration interaction, include the admixture of excited states for the core electrons, brought about through the electrostatic interactions among all the electrons. The calculations of Sternheimer(19) have attempted to account for these effects in the dipole and quadrupole hyperfine interactions, the magnitude of his correction factors being of the order of 10 percent. Notwithstanding the difficulties of the labor involved, a calculation, similar to Sternheimer's, for the octupole interaction would be valuable.

B: In the evaluation of the radial integrals the use of unshielded coulomb wavefunctions is an excellent approximation for the octupole integral in a $p_{3/2}$ state; but for the dipole and quadrupole integrals of $\langle r^{-3} \rangle$ there may be a sizeable error, especially in the lighter elements. As an example, integrating $\langle r^{-3} \rangle$ with a Hartree wavefunction for Gallium from $r=0$ to $r=.05a_0$ one has only 50 percent of the entire $\langle r^{-3} \rangle$ integral while the strength of the central potential is already shielded by 20 percent. In calculating the second order corrections to the hyperfine structure only ratios of these $\langle r^{-3} \rangle$ integrals are needed so the major part of this error is eliminated. For the best evaluation of these terms one might take values for ξ and η somewhere between unity and the values given in the text.

The uncertainty in the value of the normalization constant C^2 is not easy to evaluate, but it must be at least of the order $|C''/C'|^2 - 1$. It would be interesting to check formulas (32) by carrying out the numerical solution of the Dirac radial equations with some reasonable approximation for the complex central field in several atoms.

The discussions A and B relate to the problem of getting the nuclear octupole moment from the corrected interaction constant, and as a figure of merit for the results used in Chapter IX we suggest a value of about 15 percent.

C: The accuracy of the second order calculation involving the doublet state should be very good. The error is probably no more than a couple of percent for the terms relating to the valence ℓ-electron (see B above) and very likely no more for the s-electron correction factor, all these quantities being derived from other experimental numbers with only slight theoretical corrections. The only check on these several terms is in the explanation of the g_I-discrepancy in a $p_{1/2}$ state, where at present the large experimental uncertainties prevent a closer verification.

D: The biggest question in evaluating the second order corrections is what about the contributions of other electronic levels besides the doublet state? One would like to rely on the larger energy denominators, ΔE_n, associated with all other terms of the perterbation sum to keep their contributions smaller by a factor $\delta / \Delta E_n$ than the contribution of the doublet level alone, but the total effect of the infinity of terms is not easily seen.

First, one can simplify the problem just a little with the following results. One can show in general that the octupole-like part of the (quadrupole)^2 term from a general $^2P_{3/2}$ state (in L-S coupling) to any other perturbing ^2L_J state is zero if one adds the contributions of both doublet states J=L+1/2 and J=L-1/2. The only residual contribution of such terms would be due to the slightly different energy denominators of the two doublet states, thus an order of magnitude smaller than any straightforward estimate.

The (quadrupole)^2 term is anyway smaller than the cross dipole-quadrupole term and it is the latter one that we must worry about now. One might think that a useful estimate of this problem could be gotten from a closure approximation. That is, one tries to represent the second order sum as follows

$$\sum_n \frac{|\langle i | H_1 | n \rangle|^2}{\Delta E_n} = \frac{1}{\Delta E_{ave}} \sum_n |\langle i | H_1 | n \rangle|^2 \qquad \text{(A16)}$$

where i refers to the initial state, n the intermediate states being summed over, and ΔE_{ave} is an average excitation energy for the particular problem.

For our problem, letting D and Q stand for the dipole and quadrupole operators, the second factor on the right-hand side of (A16) becomes the matrix element $\langle i|DQ|i\rangle$. The form of this operator is very much like the form of the octupole operator except that the product DQ has an extra factor e^2/r, which after taking the expectation value becomes a factor Ze^2/a_o. An upper limit for the evaluation of (A16) is gotten by setting $\Delta E_{ave} = \Delta E_{min} \sim e^2/a_o$, which gives a result larger by a factor Z than the first order octupole matrix element.

It must be pointed out that equating ΔE_{ave} to ΔE_{min} is an extremely bad approximation for our problem. The reason for this is that our operators are very strongly varying functions (r^{-3}) so that the correct average excitation energy ΔE_{ave} is some very high energy. By way of justifying this last statement we cite the example of a delta-function perturbation which requires an infinite value of ΔE_{ave} to make (A16) meaningful. We thus believe that the closure approximation is useless in our problem.

We will now try to carry out part of the second order sum in an approximate manner. First, the matrix element from a p-state to an f-state are exceedingly small compared with the p-p matrix elements. The octupole part of the dipole-quadrupole matrix product from a $p_{3/2}$ state to a $p_{1/2}$ state is from (61)

$$-\frac{1}{4}\,\frac{I-1}{I}\,A_2A_1$$

and the corresponding contribution from the $p_{3/2}$-$p_{3/2}$ matrix elements turns out to be

$$+\frac{1}{5}\,\frac{I-1}{I}\,A_2A_1$$

where all the finer correction factors have been ignored. If we consider the two doublet levels of any perturbing ^2P state to have the same energy denominators, these two terms cancel strongly, leaving only 1/5 of the original $p_{3/2}$-$p_{1/2}$ term.

We must also take into account the poorer overlap of the radial wavefunctions as we proceed to higher perturbing levels. For bound states of a single valence electron Casimir gives the normalization constant C^2 for any level as proportional to $n^{*\,-3}$ where n^* is the effective quantum number for that level. Comparing the sum over all p-doublets up to zero energy with the value found in the ground state doublet alone we have to evaluate

$$\sum_{i=1}^{\infty}\left(\frac{n^*}{n^*+i}\right)^3$$

where n^* here refers to the ground state. This number is about 0.4 for n =1.5 and 0.2 for n =1. Combining these several factors we may estimate the value of the apparent octupole interaction due to all levels for the single electron up to E=0 as

$$1/5(0.4)\,\delta/\Delta E_{min}$$

times the correction obtained from the ground state doublet alone. Values of $\delta/\Delta E_{min}$ for several atoms are 1/300 for Al, 1/95 for Cl, 1/40 for Ga, 1/20 for Br, 1/13 for In, 1/9 for I, which result in corrections of less than one percent for all these atoms.

No attempt has been made to carry the perturbation sum further to cover the positive energy states. We will just try to guess at the additional contributions of exciting all the core electrons to their spectrum of bound states. Assuming that the matrix elements for these core excitations are about the same as those for the valence electron, we consider only the effect of their number - there are Z-1 of them - and their tighter binding. Counting outward from the nucleus, the i^{th} electron is bound by something like $(Z-i+1)^2$ Rydbergs compared with about one Rydberg for the valence electron. Summing then we have the factor

$$\sum_{i=1}^{Z} \frac{1}{(Z+1-i)}{}^{2} < 1.65$$

In summary, the discussions C and D relating to the accuracy of the second order corrections to the octupole interactions are still quite crude and incomplete. However, in view of the optimistic results which these discussions do suggest, we will guess an accuracy of about 5 percent for the corrections as calculated in chapter IX.

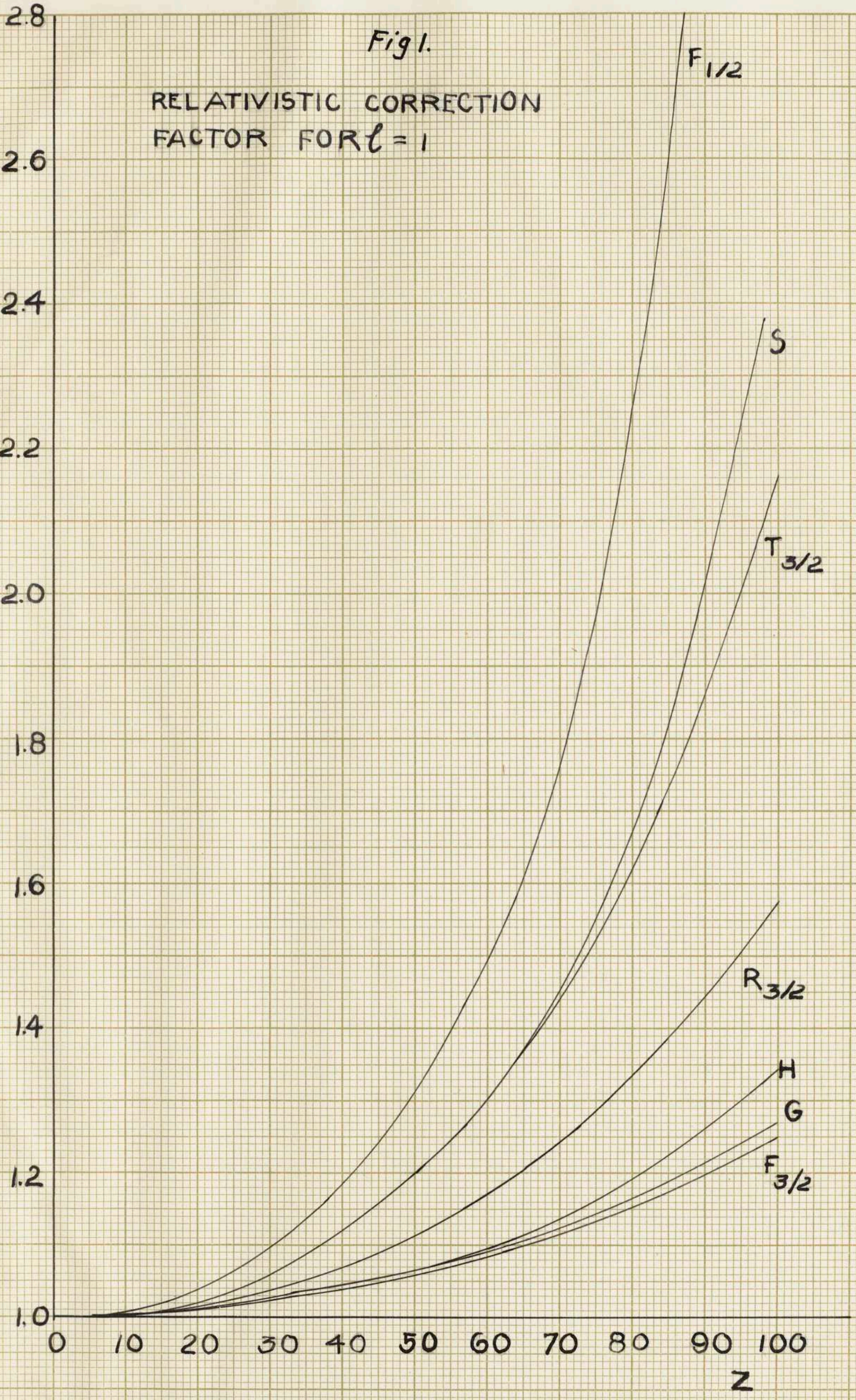
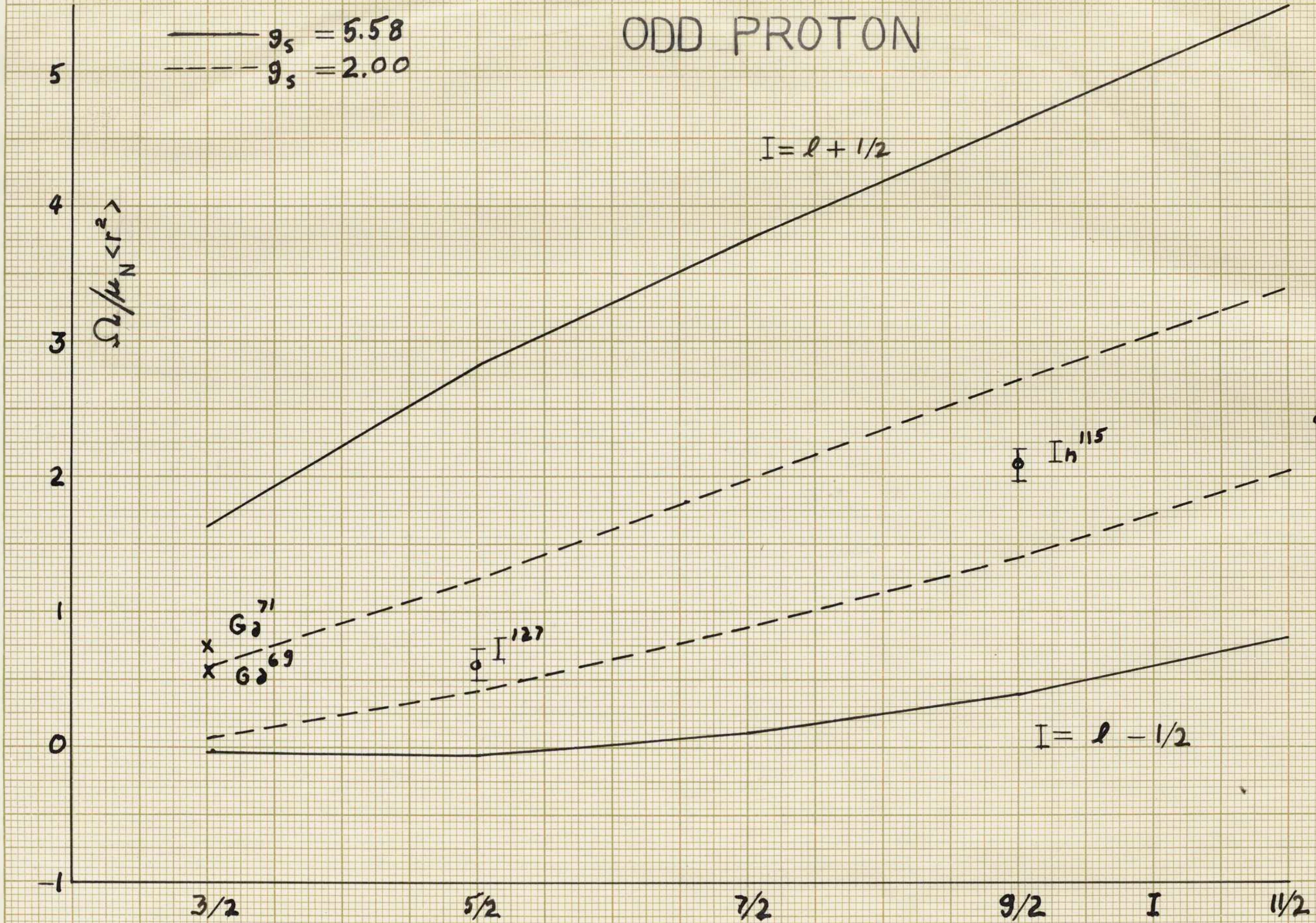


Fig 1.

RELATIVISTIC CORRECTION FACTOR FOR $l = 1$



ODD PROTON
$g_s = 5.58$
$g_s = 2.00$
$I = l + 1/2$
$I = l - 1/2$
$\Omega / \mu_N \langle r^2 \rangle$
Ga^{71}
Ga^{69}
I^{127}
In^{115}
5
4
3
2
1
0
−1
3/2
5/2
7/2
9/2
I
11/2

Fig 2.

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BIOGRAPHY

Charles Leon Schwartz was born in Brooklyn, New York on June 9, 1931. After attending public schools in New York City and Stamford, Connecticut, and also the Romford School, Washington, Connecticut, he entered the Massachusetts Institute of Technology in September, 1948. After receiving the degree of S.B. in Physics in June, 1952, he entered the graduate school of the Institute the following fall. During the two years of graduate study he held consecutively fellowships from the National Science Foundation and the Gulf Oil Corporation and, during the last summer, a research assistantship with the Department of Physics.

He has published the following papers in the Physical Review, 94 (1954).

"The Ground States of Odd-Odd Nuclei", p. 95.

"Many-Particle Configurations in a Central Field" (with A. de-Shalit), p. 1257.