From Nuclear Moments by N. Ramsey, 1953.

# INTRODUCTION TO NUCLEAR MOMENTS AND STATISTICS

## A. General Characteristics

The gross features of atomic spectra correspond to transitions between the energy levels of electrons moving in the Coulomb field of a positively charged nucleus of negligibly small dimensions. In this case and for Russell-Saunders coupling, the most closely adjacent energy levels are usually those of atomic states which differ in the relative orientation of orbital and electron spin angular momenta. The separation of this "fine structure" varies from less than one-tenth to several thousand wave numbers.

However, if this fine structure is examined more closely, it is often found that each line of the fine structure can in turn be resolved into further lines or "hyperfine structure" with a separation of the order of 1 cm-'. It was first suggested by Pauli (P4) that the hyperfine structure might be due to the action of a magnetic moment of the nucleus on the motion of the electrons.

Since this first suggestion, the effects of nuclear moments have been studied by a number of different methods. However, as will be described in detail subsequently, all observations so far are consistent with the following assumption@ concerning atomic nuclei:

(a) A nucleus whose mass number is odd obeys Fermi statistics (the sign of the wave function is reversed if two such identical nuclei are interchanged), and a nucleus whose mass number is even obeys Bose statistics (wave function unaltered on interchange).

(b) A nucleus has a spin angular momentum capable of being represented by a quantum-mechanical angular momentum vector a with all the properties [1] usually associated with such vectors. In nuclear moment work it is most convenient to use a dimensionless quantity I to measure the angular momentum in units of h where I is, therefore, defined by

$$a = \hbar I \tag{1}$$

[1] A good discussion of the properties of quantized angular momentum vectors is given by Condon and Shortley (C16).

The spin I of the nucleus is defined as the maximum possible component of I in any given direction.

(c) Tho nuclear spin I is half-integral if the mass number is odd and integral if the mass number is even.

(d) A nucleus has a magnetic moment $\mu_I$ which can be represented as

$$\mu_I = \gamma_I \hbar \mathbf{I} = g_I \mu_{NM} \mathbf{I} \tag{2}$$

where $\gamma_I$ and $g_I$ are defined by the above equations and are called the nuclear gyromagnetic ratio and the nuclear g factor, respectively. $\mu_{NM}$ is the nuclear magneton defined as $e\hbar/2Mc$, where M is the proton mass; $\mu_{NM}$ has the numerical value $5.04929 \times 10^{-24}$ erg·gauss$^{-1}$.[1] The quantity which measures the magnitude of $\mu_I$ and is called the nuclear magnetic moment, $\mu_I$, is

$$\mu_I = \gamma_I \hbar I \tag{3}$$

With this, Eq. (2) can be written

$$\mu_I = (\mu_I/I)\mathbf{I} \tag{4}$$

(e) Many nuclei with spin 1 or greater possess an electrical quadrupole moment, i.e., have electrical charge distributions which depart from spherical symmetry in a manner appropriate to an electrical quadrupole moment. (See Section 2 for a precise definition of an electrical quadrupole moment.)

(f) The nucleus instead of being infinitely heavy and of negligibly small dimensions has a finite mass and size. Corrections for these give rise to two different types of isotope shifts that will be discussed in the following sections.

(g) The nucleus has a finite polarizability nnd can he polarized by a strong electric field (K32, B43, G33).

Values of the above nuclear properties for the different nuclei are given in Section 4. Methods of measuring these properties are given in Section 3. Since many of these methods depend on the interactions of the nuclear moments with the rest of the atom or molecule, these interactions are discussed first in Section 2. Applications of nuclear moment techniques to chemistry and solid state physics are given in Section 5.

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[1] In the literature of the subject of nuclear moments there is considerable confusion in notation. In some papers $\mu_0$ or $\mu_n$ designates the nuclear magneton, whereas in other papers $\mu_0$, $\mu_1$, and $\beta$ designate the Bohr magneton $e\hbar/2mc$. Here $\mu_{NM}$ will be used for the nuclear magneton and $\mu_0$ for the Bohr magneton. Also, in many papers g or $g_I$ is written as agove for $\mu_I/(I\mu_{NM})$, but in others g is written for $\mu_I/(I\mu_0)$.

# 2

## INTERACTION OF A NUCLEUS WITH ATOMIC AND MOLECULAR FIELDS

### A. Electrostatic Interaction

The general electrostatic interaction between a charged nucleus and the charged electrons and nuclei of the remainder of the atom or molecule is as follows if the finite extension of the nucleus is taken into account :

$$\mathfrak{H}_{el} = +\int_{\tau_e}\int_{\tau_n} \frac{\rho_e(\mathbf{r}_e)\rho_n(\mathbf{r}_n)\,d\tau_e\,d\tau_n}{r} \tag{5}$$

where $\rho_e(\mathbf{r}_e)$ is the charge density of the electrons and of the other nuclei in the volume element $d\tau_e$ at position $\mathbf{r}_e$ relative to the center of the nucleus concerned, $\rho_n(r_n)$ is the nuclear charge density of the nucleus concerned in the volume element $d\tau_n$ at position $\mathbf{r}_n$ relative to the center of the nucleus, and $r$ is the magnitude of the radius vector $\mathbf{r}$ joining $d\tau_e$ and $d\tau_n$ as shown in Fig. 1. The definition of $\rho_e(\mathbf{r}_e)$ is such that it is negative for electrons and positive for positive charges.

If $\theta_{en}$ is the angle between $\mathbf{r}_e$ and $\mathbf{r}_n$ and if $r_e$ is greater than $r_n$, as may be assured by limiting consideration to electronic charges more distant than the radius $\boldsymbol{R}$ of the nucleus, $1/r$ may be expressed as follows from the cosine law of trigonometry and then expanded in the well-known fashion in a power series in m/r, [cf. (MS, p. 96)]:



Fig. 1. Electrostatic interactions with nucleus in atoms and molecules.

$$\frac{1}{r} = \frac{1}{\sqrt{r_e^2 + r_n^2 - 2r_e r_n \cos\theta_{en}}} = \frac{1}{r_e} + \frac{r_n}{r_e^2}P_1 + \frac{r_n^2}{r_e^3}P_2 + \cdots \tag{6}$$
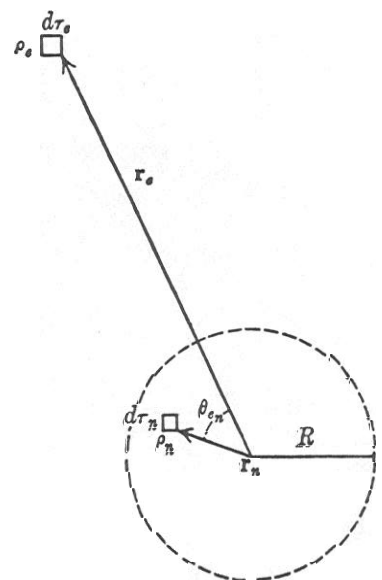
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where $P_l$ is the Legendre polynomial of $\cos\theta$, so that

$$P_1 = \cos\theta_{en}$$
$$P_2 = \tfrac{1}{2}(3\cos^2\theta_{en} - 1) \tag{7}$$

The term involving $P_l$ is said to arise from the multipole moment of order 2'. Thus the first term corresponds to a monopole or single charge, the second to the electric dipole moment, and the third to the electric quadrupole moment.

The first term is the one already used in normal atomic theory and consequently is of no interest in a discussion of nuclear moments. The second term corresponding to an electrical dipole moment, should be zero for reasons of symmetry to be discussed shortly and has indeed been experimentally found to be zero for all nuclei so far studied. Electric moments higher than electrical qundrupole momenta have so far been too small to be observed. Consequently, in **the** study of nuclear moments the only important electrostatic term is the quadrupole one. If **the** above equations are combined in evaluating the interaction energy, functions of the cosine of the angle $\theta$ between $\mathbf{r}_n$ and $\mathbf{r}_e$ must be integrated over all directions of $\mathbf{r}_n$ and of $\mathbf{r}_e$. This might lead one to expect a very complicated result. However, as shown in Section 2C, if full advantage is taken of the symmetry properties of the nucleus, the electrostatic quadrupole interaction term reduces to (C5, C6, K8)

$$\mathfrak{H}_Q = \frac{e^2 q_J Q}{2I(2I-1)J(2J-1)}\left[3(\mathbf{I}\cdot\mathbf{J})^2 + \frac{3}{2}\mathbf{I}\cdot\mathbf{J} - \mathbf{I}^2\mathbf{J}^2\right] \tag{8}$$

where Q is the single arbitrary nuclear constant required to describe the quadrupole interaction and is called the magnitude of the electrical qundrupole moment and is defined by

$$eQ \equiv \int \rho_n(\mathbf{r}_n)_{m_I=I}(3z_n^2 - r_n^2)\,d\tau_n \tag{9}$$

where the subscript indicates the integral is carried out for the nuclear state whose magnetic quantum number $m_I = I$. Q has the dimension of square centimeters. Since $\rho_n(\mathbf{r}_n)$ is proportional to the nuclear charge Z, this definition of Q (which is the conventional one) carries an implicit factor of Z, e.g., if two nuclei were of the same size and shape their quadrupole moments would be proportional to their nuclear charges Z. Likewise

$$eq_J \equiv \int_{r_e>R} \rho_e(\mathbf{r}_e)_{m_J=J}(3\cos^2\theta_{ez}-1)\frac{1}{r_e^3}\,d\tau_e \tag{10}$$

where $\theta_{ez}$ is the angle between $\mathbf{r}_e$ and the $z$ axis relative to which this state has $m_J = J$ and where it usually is possible to allow $\mathbf{R}\to\mathbf{0}$ after the integration is completed. In the classical limit of large $I$ and $J$, Eq. (8) reduces to the more familiar classical expression

$$\mathfrak{H}_Q = \frac{e^2 q_J Q}{4}\frac{1}{2}(3\cos^2\theta_{IJ}-1) = \frac{e^2 q_J Q}{4}P_2(\cos\theta_{IJ}) \tag{11}$$

where $\theta_{IJ}$ is the angle between I and J. The $\mathbf{I}\cdot\mathbf{J}$ term in Eq. (8) is purely a quantum-mechanical one corresponding to the fact that the quantum-mechanical analogue of $\cos^2\theta$ is not $(\mathbf{I}\cdot\mathbf{J})^2/\mathbf{I}^2\mathbf{J}^2$.

Although the above form for the quadrupole interaction is the one most frequently used in discussions of the quadrupole interaction in atoms, it is less suited to treatment of quadrupole interactions in linear $^1\Sigma$ molecules. This arises from the fact that $q_J$, as indicated by the subscript $J$, for $^1\Sigma$ molecules is dependent on the magnitude of the rotational quantum number $J$ of the molecule. This dependence results from the state $m_J = J$ having its J much more nearly parallel to the $z$ axis when $J$ is large than when $J$ is small. For discussions of such molecules it is, therefore, desirable to re-express Eq. (8) in a form such that all the $J$ dependence is explicitly indicated. As shown in Section 2C, this can be done by replacing $q_J$ by

$$q_J = -\frac{J}{2J+3}\frac{1}{e}\frac{\partial^2 V^e}{\partial z_0^2} \tag{12}$$

where $V^e$ is the potential from the charges external to a small sphere surrounding the nucleus (as emphasized by the superscript e) and $z_0$ is along the axis of symmetry of the molecule.[1] With this replacement Eq. (8) becomes

$$\mathfrak{H}_Q = -\frac{eQ(\partial^2 V^e/\partial z_0^2)}{2I(2I-1)(2J+3)(2J-1)}\left[3(\mathbf{I}\cdot\mathbf{J})^2 + \frac{3}{2}\mathbf{I}\cdot\mathbf{J} - \mathbf{I}^2\mathbf{J}^2\right] \tag{13}$$

Although this equation is applicable only to linear molecules, it can easily be modified to apply to symmetrical top molecules, as done in Section 2C and as discussed in greater detail in Section 3G.

[1] There is much notational confusion in the literature on this **point**. **Kellogg**, **Rabi, Ramsey, and Zacharias** (**K8**) use the symbol $q$ for what is here **called** $q_J$. Bardeen and **Townes** (**B4**), on the other hand, use q to represent the quantity here represented by $\partial^2 V^e/\partial z_0^2$, and Feld (F7) and others use $\partial^2 V/\partial z^2$ for this quantity. Also, Nordsieck (**N11**) and Ramsey (**R11**) have sometimes used the still different quantity $q'$, which is **related to the above** by $q' = (1/2e)(\partial^2 V^e/\partial z_0^2)$.

Whm the interaction between the vectors I and J is large compared to the interaction of either with any other field, Eq. (13) can be expressed in an alternative form. Let the angular momentum which is the vector sum of I and J be F = I + J with quantum number **F.** Then I· J can be evaluated from

$$\mathbf{F}^2 = (\mathbf{I} + \mathbf{J})^2 = \mathbf{I}^2 + \mathbf{J}^2 + 2\mathbf{I}\cdot\mathbf{J} \qquad (14)$$

so

$$\mathbf{I}\cdot\mathbf{J} = \tfrac{1}{2}(\mathbf{F}^2 - \mathbf{I}^2 - \mathbf{J}^2) = \tfrac{1}{2}[F(F+1) - I(I+1) - J(J+1)] \equiv \tfrac{1}{2}C$$

$$(15)$$

This can be used in Eq. (13), whence the quadrupole energy $E_Q$ **is**

$$E_Q = -\frac{eQ(\partial^2 V^e/\partial z_0{}^2)}{I(2I-1)(2J+3)(2J-1)}$$
$$\times [\tfrac{3}{8}C(C+1) - \tfrac{1}{2}I(I+1)J(J+1)] \qquad (16)$$

The above electrical quadrupole interaction occurs in general along with various magnetic interactions often of comparable magnitude. Consequently the determination of the energy levels in most actual problems depends on solving a secular equation of a matrix of a Hamiltonian one of whose terms is **similar** to the above. Therefore in the solution of most problems both the diagonal and non-diagonal matrix elements of the above interaction must be evaluated. This can be done from Eq. (61). Alternatively, a table evaluating these has been Published by Kellogg, Rabi, Ramsey, and Zacharias (KS), and it is often of value in actual problems. Their paper also provides a detailed example of the application of the above quadrupole interaction expressions to a practical problem, the evaluation of the quadrupole moment of the deuteron.

In order that the electrical quadrupole moment Q may be experimentally determined from the observed interaction energy, it is necessary according to Eq. (8) or (13) to have a determination of the atomic or molecular constant $q_J$ or $\partial^2 V^e/\partial z_0{}^2$. Various methods for estimating these quantities have **been** devised. For many atoms, $q_J$ can be evaluated (C5, K29) in terms of the experimentally measured fine structure constant for the atom, since the latter, like $q_J$, is also dependent on the mean value of $1/r_e{}^3$. Illustrative of such results is the following value of $q_J$ which applies when $q_J$ is due to a single electron in a $^2P_{3/2}$ state:

$$q_J = \frac{2}{5}\frac{6}{\mu_0{}^2 Z_i}\eta \qquad (17)$$

where 6 is the experimentally observed optical fine (not hyperfine) structure separation, $Z_i$ is the effective nuclear charge introduced by Landé (L2, W8) into the theory of **fine** structure, and $\eta$ is a correction factor which is approximately unity and is evaluated by Casimir (C6). Recently Davis, Feld, Zabel, and Zacharias (D7) in studies of atomic chlorine have used their experimentally observable magnetic hyperfine structure splitting and the known nuclear magnetic moment to determine the mean value of $1/r_e{}^3$ as discussed subsequently in Sections 2B and 2E. With this determination and the assumption of the separability of the angular and radial electron wave function, $q_J$ is directly determined and can be combined with their own determination of the quadrupole interaction of the same atom to yield the value of the nuclear quadrupole moment. This measurement is particularly direct and effective since it does not depend on such correction factors as $Z_i$ and $\eta$. However, it has recently been pointed out by Sternheimer (S46) that the inner electron shells of an atom partially shield the nucleus from the gradient of the electric field from the outer charged particles. Consequently, gradients calculated from the latter alone are likely to be in error by approximately 4 to 45 percent and thus lead to errors in the measured quadrupole moments of this amount. Sternheimer's correction, however, does not apply to the quadrupole moment of the deuteron since in this case the effects of all the electrons are included in the calculation. However, the measurements of all other nuclear quadrupole moments have an uncertainty due to this phenomenon.

In the important case of molecular $D_2$, Nordsieck (N11) and Newell (N7) have directly calculated $q_J$ from the molecular wave function. Extension of this method to other molecules is numerically quite difficult. However, Townes (T22) has suggested for heavy atoms covalently bonded in molecules with $p$-orbitals that $\partial^2 V^e/\partial z_0{}^2$ can be calculated from atomic fine structure separations in the same way as from atomic spectra, as discussed in much greater detail in Section 5B.

From Eq. (5) it might appear that an electric multipole moment of order $2^l$ would be possible for any integral value of $l$ greater than or equal to zero. However, by quite general arguments it can be shown that the orders of the possible multipoles are considerably restricted. The proofs of these restrictions are given in Section 2D, and the results only are summarized immediately below. Provided that the nuclear states are not degenerate in $I$, provided that all electrical effects arise from electrical charges, and provided that nuclear forces conserve parity, all odd ($l$ odd) electric multipole moments vanish. This is the theorem used above to justify omitting electric dipole momenta from consideration. The proof in Section 2D is essentially the same as in

the atomic case (Vi) nnd depends on the parity properties of the wave functions.     In the nuclear case there is no reason to expect a degeneracy of levels (as in the hydrogen atom) which would give rise to exceptions to the general rule, since the energy separations of the different nuclear energy levels are in general very large compared to any of electric interaction energies within the atoms or molecules. However, Purcell and Ramsey (P28) have recently pointed out that this proof depends on the assumption that the electrical effects of 8 nucleus arise only from electrical charges or a related parity assumption and that these assumptions are not necessarily self-obvious in the case of little-understood particles like nucleons and nuclei. They have, therefore, searched with high precision for an electrical dipole moment for the neutron.     In an experiment with J. Smith, they find (S-15) that, if such a dipole moment exists, its magnitude must be less than the charge on the electron multiplied by a distance $D = 5 \times 10^{-21}$ cm.

In addition to the above restriction on $l$ it may be shown, as in Section 2D,[1] that for a nuclear spin of $I$ it is impossible to observe a multipole moment of order $2^l$ greater than that corresponding to $l = 2I$. In other words, for a qundrupole moment to be observable the spin must be at least $Z = 1$. This result is very reasonable indeed, for, if the spin were $\frac{1}{2}$ and the nuclear charge distribution were spheroidal in shape with the spin axis being the spheroid's axis of symmetry, the quadrupole moment would stilt be experimentally undetectable since only two values for $m_I$ of $\pm\frac{1}{2}$ are allowed and for these two the charge distribution is essentially the same. Similar restrictions to the above apply to the angular momentum of the atom with which the nuclear multipole moment interacts   Thus, if $J$ is less than 1, an electric quadrupole interaction with a nucleus will not show up experimentally even though the nucleus may have a large electric quadrupole moment.

There is one electrostatic effect in atoms which is often experimentally important even though it is not directly concerned with nuclear moments. This is the so-called isotope shift of heavy nuclei. As stated, earlier, the expansion in Eq. (6) is valid only if $r_e > r_n$; it is incorrect to assume the simple $1/r_e$ dependence for the spherically symmetric term of Eq. (6) for $r_e < R$, the nuclear radius. Approximate calculations of the shift produced by this effect of the finite size of the nucleus have been made (B36, R8, K29). This effect is particularly important with penetrating outer orbits and heavy nuclei. With heavy elements, since diierent isotopes of the same element have nuclei of slightly different size, the effect is different for different isotopes. This is the origin

[1] An alternative simple proof based an the Hamilton-Cayley equation is given by Nierenberg *et al.* (N9).

of its name, isotope shift. Recently Fierz (F9a), Brix (B44), Kopfermann (K32, Bff), Breit (B43), A. Bohr (B30), and others have suggested that studies of the isotope shift may yield valuable information about nuclear charge distribution and perhaps about the polarization of nuclei by atomic electrons since the electrical polarizabilities of the isotopes may be different.

B. Magnetic Interaction

The magnetic interaction of a nucleus, with its associated atom or molecule and with any externally applied magnetic field, can be expanded in a multipole series closely analogous to Eq. (6). Also, analogous parity and angular momentum arguments apply to limit the allowed multipole orders 2'. For magnetic multipole moments the limitations are that $l$ must be odd and $l$ must be less than or equal to $2I$, where I is the spin of the nucleus concerned.

The lowest order of magnetic interaction is therefore magnetic dipole, the next higher being magnetic octupole  So far no magnetic octupole or higher magnetic multipole interaction has been definitely observed. Tolansky (T13) has suspected octupole effects in iodine. However, Casimir and Karreman (C8) have developed a detailed theory of magnetic octupole interactions. They find that an unreasonably large octupole moment would be required to give Tolansky's results. Consequently consideration of magnetic interactions will here be limited to magnetic dipole moments for which the interaction energy is

$$\mathfrak{H}_M = -\mu_I \cdot (\mathbf{H}_J + \mathbf{H}_0) \qquad (18)$$

where $\mu_I$ is the nuclear magnetic moment, $\mathbf{H}_0$ the externally applied magnetic field, and $\mathbf{H}_J$ the magnetic field at the nucleus arising from the rest of the atom or molecule which has angular momentum J in units of h. This form of magnetic interaction implies the assumption that the electron current distribution inside the nucleus does not contribute appreciably to the interaction energy. It can be shown (C6, B29) that this contribution is only a few percent even in the wont case -heavy nuclei and $S$ electrons.

As stated in Section 1, the magnetic moment vector of a nucleus can be taken (C16, W10, P5) as proportional to its spin angular momentum, which proportionality can be written as

$$\mu_I = \left(\frac{\mu_I}{0I}\right)\mathbf{I} \qquad (19)$$

with the notation of Section 1.

From Eqs. (18) and (19) the magnetic interaction energy may be written

$$\mathfrak{H}_M = -\left(\frac{\mu_I}{I}\right) \mathbf{I} \cdot (\mathbf{H}_J + \mathbf{H}_0) \tag{20}$$

If $\mathbf{H}_J$ is zero, as in S states or $^1\Sigma$ states of non-rotating molecules, $\mu_I$ may readily be evaluated from a measurement of the energy levels, from a knowledge of the applied field $\mathbf{H}_0$, and from Eq. (20). However, in other atoms where the contribution of $\mathbf{H}_J$ is important it is necessary to evaluate $\mathbf{H}_J$ theoretically. Just as $\mu_I$ in Eq. (19) above could be taken as proportional to I, so here $\mathbf{H}_J$ can be taken as proportional to J for matrix elements diagonal in $J$, so that, if the external field Hc is zero, Eq. (20) becomes

$$\mathfrak{H}_M = a\mathbf{I} \cdot \mathbf{J} \tag{21}$$

where a contains all the proportionality constants and is defined by

$$a = -\left(\frac{\mu_I}{I}\right)\frac{\mathbf{H}_J}{\mathbf{J}} = -\left(\frac{\mu_I}{I}\right)\frac{\mathbf{H}_J \cdot \mathbf{J}}{\mathbf{J} \cdot \mathbf{J}} \tag{22}$$

The value of $\mathbf{I} \cdot \mathbf{J}$ obtained in Eq. (15) may be used here with the result that

$$\mathfrak{H}_M = \frac{a}{2}[F(F + 1) - I(I + 1) - J(J + 1)] \tag{23}$$

In order that $g_I$ may be experimentally determined from the energy levels it is necessary according to Eqs. (23) and (22) to have an estimate for $\mathbf{H}_J$, the effective magnetic field at the nucleus due to the rest of the atom. For hydrogen-like atoms this effective field has been calculated by Fermi, Goudsmit, and others (F8, G18, K29). A simplified version of these calculations is given in Section 2E. The results are that for an $S$ electron

$$a = \frac{16\pi}{3}\mu_0\frac{\mu_I}{I}|\psi_{n0}(0)|^2 = \frac{8}{3}\frac{2\pi\hbar c\ \mathrm{Ry}\ \alpha^2 Z^3 g_I}{n^3(M/m)}. \tag{24}$$

and for an electron of orbital angular momentum $L \neq 0$

$$a = \frac{2\pi\hbar c\ \mathrm{Ry}\ \alpha^2 Z^3 g_I}{n^3(L + \frac{1}{2})J(J + 1)(M/m)} \tag{25}$$

where Ry is the Rydberg constant $(2\pi^2 m e^4/h^3 c\ cm\text{-}')$, $\alpha$ is the fine structure constant $e^2/(\hbar c)$, $M/m$ is the ratio of the proton to the electron mass, and $\psi_{n0}(0)$ is the wave function of the electron at the position of zero radius. Small corrections to the above have been intro-

duced by Breit (B32, B41, B42) and Margenau (M9) to allow for the reduced mass effect of the nucleus and for the relativistic effects of the atomic electron. The reduced mass effect introduces an extra factor of $(1 + m/M)^{-3}$ into Eq. (24). Low and Salpeter (L10b) have recently introduced a small additional reduced mass correction corresponding to recoil of the nucleus from the virtual photons that are interchanged. An approximate formula for the calculation of the interaction constant in alkali metals has been calculated by Goudsmit (G19) and is identical with Eq. (25) except that $Z^3$ is replaced by $Z_0^2 Z_i$ and $n$ is replaced by nc, where $Z_i$ is the effective charge when the valence electron is inside the core of closed electron shells, Zc is the effective charge when it is outside the core, and $n_0$ is the effective principal quantum number outside the core. Therefore, for alkali atoms;

$$a = \frac{2\pi\hbar c\ \mathrm{Ry}\ \alpha^2 Z_0^2 Z_i(\mu_I/I\mu_{NM})}{n_0^3(L + \frac{1}{2})J(J + 1)(M/m)} \tag{26}$$

If the fine structure separation 6 of the same term is known, it can be used empirically to eliminate the $Z_0$ and $n_0$ dependence, since by atomic theory

$$\delta = \frac{2\pi\hbar c\ \mathrm{Ry}\ \alpha^2 Z_0^2 Z_i^2}{n_0^3 L(L + 1)} \tag{27}$$

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$$a = \frac{\delta L(L + 1)}{(L + \frac{1}{2})J(J + 1)Z_i(M/m)} \tag{28}$$

Various corrections to Eq. (213) have been calculated by Fermi and Segrè (F9), Breit (B34), Racah (R7), Goudsmit and Bacher (G17) and Wills (B37), and the results have been summarized by Kopfermann (K29). In addition to the relation (26) applying for alkali atoms with 1 valence electron, it can also be used for halogens where just 1 electron is missing from the outer shell. It can further be applied approximately tc atoms of the aluminum group, since the first two valence electrons form a more or less closed shell. More complicated relationships hold for 2 valence electrons such as alkaline earths. These have been summarized by Kopfermann (K29).

All the states of a single hyperfine structure group have the same values of the quantum numbers Z and $J$ in Eq. (23) while $F$ takes on values from $Z + J$ to $|Z - J|$. *The energy* difference between a state with $F = F$ and $F = F - 1$ is, according to Eq. (23).

$$\mathfrak{H}_M(F) - \mathfrak{H}_M(F - 1) = aF \tag{29}$$

This regularity is called the interval rule, and for this reason $a$ is often called the interval factor. However, even with magnetic dipole inter-actions, exceptions to this rule can occur if two atomic states of different $J$ are separated by an amount which is not large compared to the hyper-fine structure, in which case $J$ in Eq. (23) is no longer a good quantum number nnd second-order perturbations must be taken into account. Calculations of the effect of perturbations have been made by Fermi and Segrè, Casimir Goudsmit, and Bacher (F9, C4, G20).

If $J = \frac{1}{2}$, the separation, $2\pi\hbar\,\Delta\nu$, of the hyperfine structure levels is

$$2\pi\hbar\,\Delta\nu = aF = a\left(I + \frac{1}{2}\right) = a\,\frac{2I + 1}{2} \qquad (30)$$

The quantity $\Delta\nu$ defined in this way is frequently referred to as the hyperfine structure separation, or the hfs $\Delta\nu$.

So far in the detailed discussion of Eq. (20) it has been assumed either that there was no intramolecular interaction or that the external mag-netic field was zero. However, in many of the practical cases which arise in nuclear moment measurements the magnetic interactions of the electrons and the nuclei with each other and of one or both with the external field are of comparable importance.

The effect of an external magnetic field on the hyperfine structure of a spectral line illustrates such a combined interaction. In this case, if the interaction energy of the electrons as well as the nucleus with ex-ternal magnetic field is included and if $\mu_J$ is the resultant electronic magnetic moment defined analogously to Section 1, Eqs. (20) and (22) become

$$\mathfrak{H}_M = a\,\mathbf{I}\cdot\mathbf{J} - \frac{\mu_J}{J}\,\mathbf{J}\cdot\mathbf{H}_0 - \frac{\mu_I}{I}\,\mathbf{I}\cdot\mathbf{H}_0 \qquad (31)$$

If the magnetic field is very weak, corresponding to a weak field Zeeman effect, the term $a\,\mathbf{I}\cdot\mathbf{J}$ in the above is the largest, so that I and J are tightly coupled together to form a resultant F as in Fig. 2. As a consequence, only the components of the electron and nuclear magnetic moments along F are effective, since the perpendicular components average to zero and the above becomes approximately

$$\mathfrak{H}_M = a\,\mathbf{I}\cdot\mathbf{J} - \frac{\mu_J}{J}\,\mathbf{J}\cdot\frac{\mathbf{F}}{|\mathbf{F}|}\frac{\mathbf{F}}{|\mathbf{F}|}\cdot\mathbf{H}_0 \qquad (32)$$

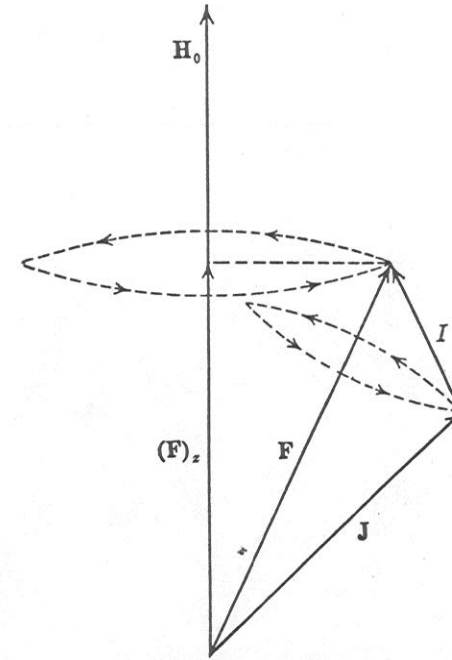where the nuclear moment's interaction with the external field is neg-

Fig. 2. Coupling of nuclear angular momentum **I** and electronic angular momentum J in weak magnetic field $H_0$.

lected because of the small size of both the nuclear moment and the field. But

$$\mathbf{I}\cdot\mathbf{I} = (\mathbf{F} - \mathbf{J})\cdot(\mathbf{F} - \mathbf{J}) = |\mathbf{F}|^2 + |\mathbf{J}|^2 - 2\mathbf{J}\cdot\mathbf{F} \qquad (33)$$

so the energy for the state specified by quantum numbers $F$ and $m$, where $m$ is the magnetic quantum number for $F$, is

$$
\begin{aligned}
W_M(F, m) &= (F, m|\,\mathfrak{H}_M\,|F, m)\\
&= a(F, m|\,\mathbf{I}\cdot\mathbf{J}\,|F, m)\\
&\quad - \frac{\mu_J}{J}\,\frac{[F(F+1) + J(J+1) - I(I+1)]}{2F(F+1)}\\
&\quad \times (F, m|\,\mathbf{F}\cdot\mathbf{H}_0\,|F, m)\\
&= \frac{a}{2}\,[F(F+1) - I(I+1) - J(J+1)]\\
&\quad - \frac{\mu_J}{J}\,\frac{[F(F+1) + J(J+1) - I(I+1)]}{2F(F+1)}\,H_0 m \qquad (34)
\end{aligned}
$$

In the limit of a very strong magnetic field corresponding to a Paschen-Back effect, on the other hand, I and J will each separately precess rapidly about H as in Fig. 3, so that $F$ is no longer a good quan-
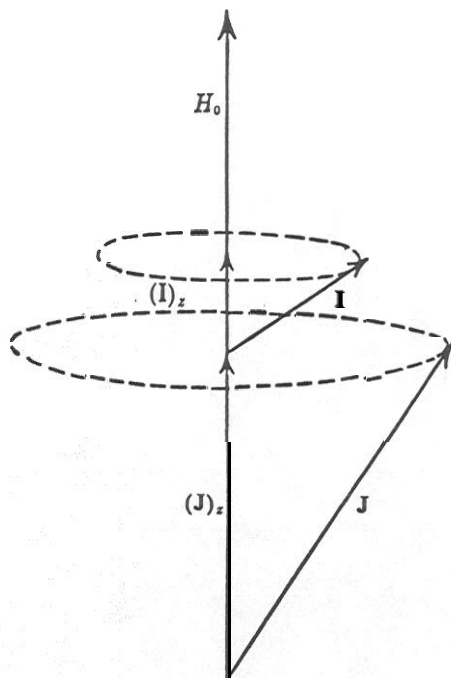


**Fig. 3. Coupling of nuclear angular momentum I and electronic angular momentum J in strong magnetic field H₀.**

tum number but instead the good quantum numbers are the magnetic quantum numbers, $m_I$ and $m_J$, of I and J separately.

Then from Eq. (31)

$$W_M(m_I, m_J) = (m_I m_J | \mathfrak{H}_m | m_I m_J)$$

$$= a(m_I m_J | (I)_x (J)_x + (I)_y (J)_y + (I)_z (J)_z | m_I m_J)$$

$$- \frac{\mu_J}{J} H m_J - \frac{\mu_I}{I} H m_I$$

$$= - \frac{\mu_J}{J} H m_J - \frac{\mu_I}{I} H m_I + a m_I m_J \qquad (35)$$

since the diagonal elements of $I_x$ and I, are zero.

The ease of intermediate coupling is of particular importance In nuclear moment research, even though it is more difficult to work out

the energy levels since a secular equation must be solved as in the corresponding fine structure case (C16). The result of a straight-forward solution of the secular equation in the case $J = \frac{1}{2}$ and for **any I** is (B35, M17)

$$W_M(F, m) = - \frac{AW}{2(2I + 1)} - \frac{\mu_I}{I} Hm \pm \frac{\Delta W}{2} \sqrt{1 + \frac{4m}{2I + 1} x + x^2} \quad (36)$$

where

$$\Delta W \equiv \frac{a}{2}(2I + 1) \equiv 2\pi\hbar \, \Delta\nu \qquad x = \frac{(-\mu_J/J + \mu_I/I)H}{AW} \qquad (37)$$
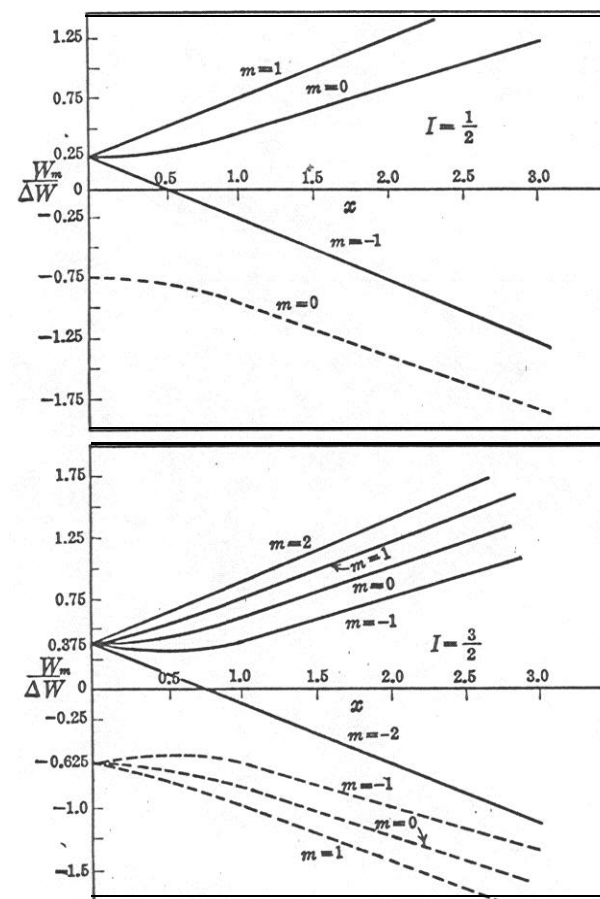


**Fig. 4. Variation of the energy with the magnetic field. Nuclear moment assumed positive The dotted lines are the magnetic levels arising from the $F = I - \frac{1}{2}$ state (R4).**

and the + is  used for $F = I + \frac{1}{2}$ and the $-$ for $F = I - \frac{1}{2}$.  This energy  dependence  for  the  case  of  I = $\frac{1}{2}$ and $\frac{3}{2}$ is plotted in Fig. 4. Tho quantity  $\Delta\nu$ is the "hyperfine structure $\Delta\nu$" or  the hyperfine  struc-ture separation of Eq. (30).

## C. Appendix A. Form of Nuclear Electrical  Quadrupole Moment Inter-action

From Eqs. (5) and (6),

$$\mathfrak{H}_Q = \int_{\tau_e}\int_{\tau_n} r_n{}^2\rho_n(\mathbf{r}_n)\frac{1}{2}(3\cos^2\theta_{en} - 1)\frac{\rho_e{}^e(\mathbf{r}_e)}{r_e{}^3}d\tau_n\,d\tau_e \tag{38}$$

The superscript $e$ is used to indicate the charge density external to the nucleus  concerned, since the  expansion is valid only for  $r_e > r$ The above can readily be expanded in Cartesian  coordinates by use of the relation  that  $r_n r_e \cos\theta_{en}$ equals $\sum x_{ni}x_{ei}$.  With this expansion Eq. (38) becomes

$$\mathfrak{H}_Q = \int_{\tau_e}\int_{\tau_n}\rho_n(\mathbf{r}_n)\left[\frac{3}{2}\sum_{ij}x_{ni}x_{nj}x_{ei}x_{ej} - \frac{1}{2}r_n{}^2r_e{}^2\right]\frac{\rho_e{}^e(\mathbf{r}_e)}{r_e{}^3}d\tau_n\,d\tau_e$$

On the other hand, if Eq. (39) below is directly expanded with the first form Of Eq. (40) and the second form of Eq. (41). the same equation is also obtained.   Therefore  Eq. (38) can be expressed in the  alternative tensor form

$$\mathfrak{H}_Q = -\tfrac{1}{6}\sum_{ij}Q_{ij}(\nabla E^e)_{ij} \tag{39}$$

where

$$Q_{ij} = \int_{\tau_n}\rho_n(\mathbf{r}_n)(3x_{ni}x_{nj} - \delta_{ij}r_n{}^2)\,d\tau_n$$

$$= \int_{\tau_n}\rho_n(\mathbf{r}_n)(3\frac{x_{ni}x_{nj} + x_{nj}x_{ni}}{2} - \delta_{ij}r_n{}^2)_n \tag{40}$$

and

$$(\nabla E^e)_{ij} = -\int_{\tau_e}\rho_e{}^e(\mathbf{r}_e)\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\left(\frac{1}{r_e}\right)d\tau_e$$

$$= -\int_{\tau_e}\frac{\rho_e{}^e(\mathbf{r}_e)}{r_e{}^5}(3x_{ei}x_{ej} - \delta_{ij}r_e{}^2)\,d\tau_e$$

$$= -\int_{\tau_e}\frac{\rho_e{}^e(\mathbf{r}_e)}{r_e{}^5}(3\frac{x_{ei}x_{ej} + x_{ej}x_{ei}}{2} - \delta_{ij}r_e{}^2)\,d\tau_e \tag{41}$$

The  final forms above of Eqs. (40) and (41) arise from the fact  that he components of $\mathbf{r}$ commute among themselves $(x_ix_j = x_jx_i)$, whence

the tensors are symmetric; this manner 'of writing explicitly exhibits the symmetric character of the tensor.  It is also immediately apparent that the traces (diagonal sums) of Eqs. (40) and (41) are zero.

The next step of the proof is most simply taken from group theory. However, it may also be shown directly from simple **matrix** multiplica-tions.  Since the  later  proof,  though  numerically  tedious,  is  con-ceptually  simpler  and is  not  conveniently  available  in the  published literature, it is outlined in the addendum on page 21.  This proof also automatically  provides  a  numerical  evaluation  of  the  quantum-mechanical matrix elements of the quadrupole interaction.  The theorem which can be proved either by group theory (W14) or as in the addendum applies to all second-rank tensors of, say, the form (40) which (a) are constructed  in the same  manner  from  vectors  satisfying  the  same com-mutation rules with respect to I, $(b)$ are symmetric, and (c) have a zero trace.  This  theorem  states  that  the  quantum-mechanical  matrix ele-ments diagonal in I of all such tensors have the  same dependence on the magnetic quantum number $m_I$.

The  above theorem shows that, as concerns the  $m_I$ dependence of matrix elements  $(Im|\,Q_{ij}\,|Im')$ diagonal in I of Eq. (40), $Q_{ij}$ may be replaced by

$$Q_{ij} = C\left[3\frac{(I)_i(I)_j + (I)_j(I)_i}{2} - \delta_{ij}I^2\right] \tag{42}$$

since this tensor satisfies the above three conditions.  The arbitrary constant C can he expressed in terms of the scalar quantity $Q$, which is conventionally called the nuclear quadrupole  moment and is defined by

$$Q \equiv \frac{1}{e}\int\rho_{nm_I=I}[3z_n{}^2 - r_n{}^2]\,d\tau_n = (II|\,Q_{33}\,|II)$$

$$= C(II|\,3(I)_z{}^2 - I^2\,|II) = C[3I^2 - I(I+1)]$$

$$= CI(2I - 1) \tag{43}$$

Hence

$$Q_{ij} = \frac{eQ}{I(2I - 1)}\left[3\frac{(I)_i(I)_j + (I)_j(I)_i}{2} - \delta_{ij}I^2\right] \tag{44}$$

Likewise, for matrix elements diagonal in $J$,

$$(\nabla E^e)_{ij} = \frac{eq_J}{J(2J - 1)}\left[3\frac{(J)_i(J)_j + (J)_j(J)_i}{2} - \delta_{ij}J^2\right] \tag{45}$$

where

$$q_J = \frac{1}{e}\int\frac{3z_e{}^2 - r_e{}^2}{r_e{}^5}\rho_{e,m_J=J}\,d\tau_e \tag{46}$$

Therefore

$$\mathfrak{H}_Q = \frac{1}{6}\frac{e^2 q_J Q}{I(2I-1)J(2J-1)}\sum_{ij}\left[3\frac{(I)_i(I)_j + (I)_j(I)_i}{2} - \delta_{ij}I^2\right]$$
$$\times\left[3\frac{(J)_i(J)_j + (J)_j(J)_i}{2} - \delta_{ij}J^2\right] \quad (47)$$

Equation (47) can be expressed in an alternative form which is often more convenient for calculations. This can be done by considering typical terms of the equation. Thus, as I and J commute with each other,

$$\sum_{ij}(I)_i(I)_j(J)_i(J)_j = \left\{\sum_i (I)_i(J)_i\right\}\left\{\sum_j (I)_j(J)_j\right\} = (I\cdot J)^2$$

Likewise

$$\sum_{ij}(I)_i(I)_j\,\delta_{ij}J^2 = \left[\sum_i (I)_i^2\right]J^2 = I^2 J^2$$

and

$$\sum_{ij}\delta_{ij}I^2 J^2 = 3I^2 J^2$$

The only complicated terms are

$$\sum_{ij}(I)_j(I)_i(J)_i(J)_j = \sum_{ij}(I)_i(I)_j(J)_j(J)_i$$

In this, from the usual commutation rules (C16) for angular momentum operators, we can write

$$(I)_i(I)_j = (I)_j(I)_i + i(I)_{i\times j}$$

where the subscript $i \times j$ indicates the component perpendicular to the $i$ and j components as in a vector product. Therefore

$$\sum_{ij}(I)_i(I)_j(J)_j(J)_i = \sum_{ij}(I)_j(I)_i(J)_j(J)_i + i\sum_{ij}(I)_{i\times j}(J)_j(J)_i$$
$$= (I\cdot J)^2 + i\sum_{iJ}(I)_{i\times j}(J)_j(J)_i$$

**But**

$$(J)_j(J)_i = \frac{(J)_j(J)_i + (J)_i(J)_j}{2} = \frac{(J)_j(J)_i + (J)_i(J)_j + i(J)_{j\times i}}{2}$$

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$$i\sum_{ij}(I)_{i\times j}(J)_j(J)_i = \frac{i}{2}\sum_{ij}(I)_{i\times j}[(J)_j(J)_i + (J)_i(J)_j] - \frac{1}{2}\sum_{ij}(I)_{i\times j}(J)_{j\times i}$$

However, the terms of the first sum on the right are antisymmetric in $i$ and j and the sum vanishes. Therefore

$$i\sum_{ij}(I)_{i\times j}(J)_j\cdot(J)_i = -\tfrac{1}{2}\sum_{ij}(I)_{i\times j}(J)_{j\times i} = \tfrac{1}{2}\sum_{ij}(I)_{i\times j}(J)_{i\times j}$$
$$= \tfrac{1}{2}\sum_k 2(I)_k(J)_k = I\cdot J$$

Therefore

$$\Sigma(I)_i(I)_j(J)_j(J)_i = (I\cdot J)^2 + I\cdot J$$

**and**

$$\mathfrak{H}_Q = \frac{1}{6}\frac{e^2 q_J Q}{I(2I-1)J(2J-1)}\left\{\frac{9}{2}(I\cdot J)^2 + \frac{9}{2}[(I\cdot J)^2 + (I\cdot J)]\right.$$
$$\left. - 3I^2 J^2 - 3I^2 J^2 + 3I^2 J^2\right\}$$
$$= \frac{e^2 q_J Q}{2I(2I-1)J(2J-1)}\left[3(I\cdot J)^2 + \frac{3}{2}I\cdot J - I^2 J^2\right] \quad (48)$$

which is the form of the quadrupole interaction used above.

Although Eq. (48) is the one conventionally used for discussing quadrupole interactions in atoms, it is less convenient for quadrupole moments of $^1\Sigma$ linear molecules rotating with different rotational angular momentum quantum numbers $J$. This is true because the quantity $q_J$ is dependent on the magnitude of $J$. Hence it is desirable in the molecular case to replace $q_J$ by a quantity which is expressed in terms of the molecule's axis instead of an axis fixed in space, since such a quantity will be the same for molecules which differ only in $m_J$ and $J$.

For this transformation let $z_0$ be along the axis of symmetry of the molecule and let $\theta_e$ and $\phi_e$ be the angular spherical polar coordinates of a point in the molecule relative to an external $z$ axis while 8,' and $\phi_e'$ are the coordinates relative to the molecular axis of symmetry $z_0$. Also let $\theta''$ and $\phi''$ be the angles expressing the position of the $z_0$ axis relative to the $z$ axis. Then, by the spherical harmonic addition theorem as summarized by Condon and Shortley (C16, p. 54),

$$3\cos^2\theta_e - 1 = \tfrac{1}{2}(3\cos^2\theta'' - 1)(3\cos^2\theta_e' - 1) + \text{terms involving } e^{i\phi''}$$
$$(49)$$

Now, however, by Condon and Shortley (C16, p. 51), the wave function for a rotating molecule in the rotational state $m_J = J$ is

$$\psi_{JJ}(\theta'', \phi'') = \frac{(-1)^J}{\sqrt{2\pi}}\sqrt{\frac{(2J+1)!}{2}}\frac{1}{2^J J!}\sin^J\theta'' e^{iJ\phi''} \quad (50)$$

Therefore, the average of Eq. (49) over the rotational state can be found by multiplying Eq. (49) by $\psi_{JJ}|^2$ and integrating over all angles with $d\Omega = \sin\theta\,d\theta\,d\phi$. From this and the use of Peirce's integral 483 (P8) the following is ohtsined immediately:

$$<3\cos^2\theta_e - 1>_{m_{J-J}} = -\frac{J}{2J+3}(3\cos^2 8,' - 1)$$

Therefore

$$q_J = \frac{1}{e}\int \frac{3z_e^2 - r_e^2}{r^5}\rho^e_{e,m_{J-J}}\,d\tau$$

$$= \frac{1}{e}\int \frac{3\cos^2\theta_e - 1}{r_e^3}\rho^e_{e,m_{J-J}}\,d\tau$$

$$= -\frac{J}{2J+3}\frac{1}{e}\int \frac{3\cos^2\theta_e' - 1}{r_e^3}\rho^e\,d\tau'$$

$$= -\frac{J}{2J+3}\frac{1}{e}\frac{\partial^2 V^e}{\partial z_0^2} \tag{51}$$

where

$$\frac{\partial^2 V^e}{\partial z_0^2} = \int \frac{3\cos^2\theta_e' - 1}{r_e^5}\rho^e\,d\tau' \tag{52}$$

As is apparent from the form of this expression, $V^e$ can be interpreted as the potential from all charges external to a small sphere surrounding the nucleus

It is important to emphasize that $V^e$ i n not the potential $V$ of all electrical charges from the rest o f the molecule including the electron density of the molecule inside the nuclear radius. The difference between these two can readily be evaluated. Let $\rho_1$ be the electronic charge density at the nucleus, and assume that in the immediate vicinity of the nucleus it is spherically symmetric. Then, as $V - V^e$ arises solely from the spherically symmetric charge distribution $\rho_1$, from Poisson's equation

$$\frac{\partial^2(V - V^e)}{\partial x^2} + \frac{\partial^2(V - V^e)}{\partial y^2} + \frac{\partial^2(V - V^e)}{\partial z^2} = 4\pi\rho_1 = 3\frac{\partial^2(V - V^e)}{\partial z^2} \tag{53}$$

so

$$\frac{\partial^2 V}{\partial z^2} = \frac{\partial^2 V^e}{\partial z^2} + \frac{4\pi}{3}\rho_1 \tag{54}$$

Owing to its spherical symmetry the $\rho_1$ term does not affect the nuclear quadrupole interaction.

From Eqs. (48) and (52) it follows immediately that

$$\mathfrak{H}_Q = -\frac{eQ(\partial^2 V^e/\partial z_0^2)}{2I(2I-1)(2J+3)(2J-1)}\left[3(\mathbf{I}\cdot\mathbf{J})^2 + \frac{3}{2}\mathbf{I}\cdot\mathbf{J} - \mathbf{I}^2\mathbf{J}^2\right] \tag{55}$$

If the molecule instead of being a linear molecule is a symmetric top, the above can easily be extended to include this case. For a symmetric-top molecule the angular momentum is no longer exactly perpendicular to the molecular axis; therefore, to define the situation, an extra quantity $(J)$,, must be introduced which measures the component of $J$ *along* the axis of the molecule so that, if $\theta'''$ is the angle between $J$ and the internuclear axis.

$$\cos\theta''' = \frac{(\mathbf{J})_{z_0}}{|\mathbf{J}|} \tag{56}$$

For a symmetric-top molecule a procedure analogous to that for Eq. (49) therefore directly yields the relation

$$\mathfrak{H}_Q = -\frac{eQ(\partial^2 V^e/\partial z_0^2)}{2I(2I-1)(2J+3)(2J-1)}\left[1 - \frac{3(\mathbf{J})_{z_0}^2}{\mathbf{J}^2}\right]$$
$$\times [3(\mathbf{I}\cdot\mathbf{J})^2 + \tfrac{3}{2}\mathbf{I}\cdot\mathbf{J} - \mathbf{I}^2\mathbf{J}^2] \tag{57}$$

Addendum. The theorem used in the derivation of Eq. (42) is most easily proved by group theory methods (W10, W14). However, it may be derived in a less subtle though more tedious fashion from the matrix elements of a vector and the laws of matrix multiplication. Let T be any vector associated with the nucleus and satisfying the same commutation rules with respect to I as $\mathbf{r}$ or I. Let $\alpha$ represent all the quantum numbers except I and $m_I$ that are associated with the nucleus in an I, $m_I$ representation, and let $m$ temporarily be written for $m_I$. Then the matrix elements that are desired are

$$\left(\alpha I m\left|3\frac{T_iT_j + T_jT_i}{2} - \delta_{ij}T^2\right|\alpha I m'\right) \tag{58}$$

However, the matrix of a product equals the product of the matrices; thus, for example,

$$(\alpha I m|\,T_iT_j\,|\alpha I m') = \sum_{\alpha''I''m''}(\alpha I m|\,T_i\,|\alpha''I''m'')(\alpha''I''m''|\,T_j\,|\alpha I m') \tag{59}$$

Hence the desired matrix can be calculated from the matrices of the components of the corresponding vector T. Note, however, that, although only matrix elements of $T_iT_j$ diagonal in I are desired, they

depend on matrix elements of $T_i$ that are non-diagonal in I. It is this dependence on non-diagonal elements of the vector that makes the proof lengthy instead of trivial.

The well-known matrix elements (C16, P5) for a vector are

$$(\alpha I m|\ T\ |\alpha' I + 1 m \pm 1) = \mp T_{\alpha I;\,\alpha' I+1}\tfrac{1}{2}\sqrt{(I\pm m+1)(I\pm m+2)}(\mathbf{i}\pm i\mathbf{j})$$

$$(\alpha I m|\ T\ |\alpha' I + 1 m) = T_{\alpha I;\,\alpha' I+1}\sqrt{(I+1)^2 - m^2}\,\mathbf{k}$$

$$(\alpha I m|\ T\ |\alpha' I m \pm 1) = T_{\alpha I;\,\alpha' I}\tfrac{1}{2}\sqrt{(I\mp m)(I\pm m+1)}(\mathbf{i}\pm i\mathbf{j}) \quad (60)$$

$$(\alpha I m|\ T\ |\alpha' I m) = T_{\alpha I;\,\alpha' I}\,m\,\mathbf{k}$$

$$(\alpha I m|\ T\ |\alpha' I - 1 m \pm 1) = \pm T_{\alpha I;\,\alpha' I-1}\tfrac{1}{2}\sqrt{(I\mp m)(I\mp m-1)}(\mathbf{i}\pm i\mathbf{j})$$

$$(\alpha I m|\ T\ |\alpha' I - 1 m) = T_{\alpha I;\,\alpha' I-1}\sqrt{I^2 - m^2}\,\mathbf{k}$$

From Eqs. (59) and (60) the matrix elements of Eq. (58) can be directly calculated These expressions can be simplified by the use of various algebraic identities such as

$$\sqrt{(I \pm m + 1)(I \pm m + 2)([j + 1]^2 - [m \pm 1]^2)}$$
$$= (I \pm m + 2)\sqrt{(I \pm m + 1)(I \mp m)}$$

The matrix elements of Eq. (58) then directly become

$$\left(\alpha I m \left| 3\frac{T_i T_j + T_j T_i}{2} - \delta_{ij}T^2 \right| \alpha I m'\right)$$

$$= \left\{\sum_{\alpha'} [-\tfrac{3}{2}T_{\alpha I;\,\alpha' I+1}T_{\alpha' I+1;\,\alpha I} - \tfrac{3}{2}T_{\alpha I;\,\alpha' I-1}T_{\alpha' I-1;\,\alpha I}\right.$$

$$\left. + \tfrac{3}{2}T_{\alpha I;\,\alpha' I}T_{\alpha' I;\,\alpha I}]\right\}\{[\sqrt{(I\mp m)(I\mp m-1)(I\pm m+1)(I\pm m+2)}]\cdot$$

$$X\ \tfrac{1}{2}[\delta_{i1}\delta_{j1} - \delta_{i2}\delta_{j2} \pm i(\delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1})]\delta_{m'm\pm 2}$$

$$+ [(2m\pm 1)\sqrt{(I\mp m)(I\pm m+1)}\,]\tfrac{1}{2}[\delta_{i3}\delta_{j1} + \delta_{i1}\delta_{j3}$$

$$\pm i(\delta_{i3}\delta_{j2} + \delta_{i2}\delta_{j3})]\delta_{m'm\pm 1} + \sqrt{\tfrac{2}{3}}[3m^2 - I(I+1)]$$

$$X\ \sqrt{\tfrac{2}{3}}[\delta_{i3}\delta_{j3} - \tfrac{1}{2}\delta_{i1}\delta_{j1} - \delta_{i2}\tfrac{1}{2}\delta_{j2}]\delta_{m'm}\} \quad (61)$$

Since all the constants $T_{\alpha I;\,\alpha' I'}$ combine in the above to make a common factor with all the $m$ dependence being contained in the other factor,

the $m$ dependence of the above tensor components are the same for all such tensors regardless of the different relative values of the constants $T_{\alpha I;\,\alpha' I'}$ possessed by different vectors T. This then gives the desired theorem. Equation (61) also provides the $m$ dependence of the matrix elements, and this is of value in the analysis of any problem in detail.

## D. Appendix B. Theoretical Restrictions on the Orders of Electrical Multipoles

1. Parity Restrictions. From parity considerations it will first be shown that, if all nuclear electrical effects arise from electrical charges and if the nuclear Hamiltonian is unaltered by an inversion of the coordinate system, no odd ($l$ odd) nuclear electrical multipole moment can exist.

For the proof of this, consider the parity operator $R$ which inverts the space coordinates, i.e., reverses the signs of the components of a vector $\mathbf{r}_n$. If $\mathfrak{H}$ is the Hamiltonian of the nuclear system, by assumption $\mathfrak{H}$ and $R$ commute, whence if there is no degeneracy the eigenfunctions of $\mathfrak{H}$ are also eigenfunctions of $R$. Hence, if $R'$ is the eigenvalue of the operator $R$ and if $\psi(\mathbf{r})$ is a non-degenerate eigenfunction of $\mathfrak{H}$,

$$R\psi(x_n, y_n, z_n) = R'\psi(x_n, y_n, z_n) = \psi(-x_n, -y_n, -z_n) \quad (62)$$

Then

$$R^2\psi(x_n, y_n, z_n) = R\psi(-x_n, -y_n, -z_n)$$
$$= \psi(x_n, y_n, z_n) = R'^2\psi(x_n, y_n, z_n) \quad (63)$$

Hence

$$R'^2 = 1 \quad (64)$$

or

$$R' = \pm 1 \quad (65)$$

Therefore, with the above assumptions, all states must be of either even or odd parity, i.e., must have eigenfunctions that are multiplied by either $+1$ or $-1$ on inversion of coordinates. In either case $\psi^*\psi$ is unaltered on inversion of coordinates; therefore

$$\rho_n(x_n, y_n, z_n) = \text{d-z.,} \quad -y_n, -z_n) \quad (66)$$

However, from Eqs. (5) and (6) it is apparent that, in so far as the nuclear coordinates are concerned, the multipole of order 2 is proportional to

$$\int_{\tau_n} r_n^l \rho_n(x_n, y_n, z_n)P_l\,d\tau_n \quad (67)$$

An inversion of coordinates in polar coordinates corresponds to $\theta \to \pi - \theta$, $\phi \to \pi + \phi$, and $r \to r$, so $P_l$ has its sign changed on inversion if $l$ is odd and is unaltered if $l$ is even; therefore

$$P_l(-x_n, -y_n, -z_n) = (-1)^l P_l(x_n, Y", z_n) \tag{68}$$

Therefore, from Eqs. (66) and (67) if $l$ is odd, the contribution from $-x_n, -y_n, -z_n$ in the integral (G7) just cancels the contribution from $x_n, y_n, z_n$. Therefore the integral vanishes and no odd electrical multipole moment can bc observed.

2. Upper Limit to Electrical Multipole Order. It can next be shown that for a nuclear spin Z it is impossible to observe a nuclear electrical multipole moment of order $2^l$ greater than that corresponding to $l = 21$, where I is the nuclear spin.

For the proof of this, consider the $2^l$ multipole interaction term which, from Eq. (67) can be written as proportional to

$$\int_{\tau_n} r_n{}^l \psi_n{}^* P_l \psi_n \, d\tau_n \tag{69}$$

However, by the assumption that the nuclear spin is I, $\psi_n$ and $\psi_n{}^*$ are each eigenfunctions corresponding to an angular momentum I. Since $r_n{}^l$ has no angular dependence, $r_n{}^l \psi_n{}^*$ is **also** an eigenfunction of angular momentum $I$. However, as is well known (C16), $P_l$ is also an eigenfunction of an angular momentum and corresponds to angular momentum 1. Therefore the product of $P_l$ and $\psi_n$ corresponds to a wave function in which the angular moments I and $l$ are combined. By the vector model for combining angular momentum,' $P_l \psi_n$ will therefore correspond to an angular momentum between $l + I$ and $| l - Z |$. However, in the integral (69), $r_n{}^l \psi_n{}^*$ and $P_l \psi_n$ will be orthogonal and the integral will vanish unless they correspond to eigenfunctions with the same angular momentum eigenvalues. Therefore, in order that Eq. (69) may not vanish, I must lie between $l + I$ and $| l - I |$. As this can occur only if $l \leq 2I$, the above statement is proved.

### E. Appendix C. Magnetic Hyperfine Structure Constants

What **is** desired is a calculation of the constant a in Eq. (21). By Eq. (22) this can be obtained if the magnetic field $H_J$ arising from the electrons can be evaluated at the nucleus. For a hydrogen-like atom, $H_J$ can be calculated from the following simple classical considerations

'For a detailed justification of this use of the vector model see Condon and Shortley (C16, pp. 57. 58).

illustrated in Fig. 5. The electron's magnetic field arises from the combination of the field $H_L$, due to the electron's orbital motion, and the field $H_S$, due to the electron's spin magnetic moment; therefore

$$H_J = H_L + H_S \tag{70}$$

But, classically, if $\mathbf{v}$ is the electron's velocity, $\mathbf{r}$ the position of the elec-
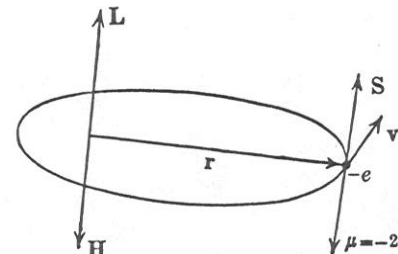


Fig. 5 Schematic diagram of the interaction of the nucleus with the orbital and spin magnetic fields of the electron in an atom.

tron relative to the nucleus, and L the electron's orbital angular momentum in units of h

$$H_L = \frac{-e\mathbf{v} \times (-\mathbf{r})}{cr^3} = \frac{-\mathbf{r} \times m\mathbf{v}}{r^3} \frac{e}{mc} = -2\mu_0 \frac{L}{r^3} \tag{71}$$

where $\mu_0$ is the Bohr magneton $e\hbar/2mc$. Likewise, from expressions for the field of a classical magnetic dipole, $\mu = -2\mu_0 S$,

$$H_S = -\frac{1}{r^3}\left[\mu - \frac{3(\mu \cdot \mathbf{r})\mathbf{r}}{r^2}\right] = \frac{2\mu_0}{r^3}\left[S - \frac{3(S \cdot \mathbf{r})\mathbf{r}}{r^2}\right] \tag{72}$$

Then

$$H_J \cdot J = (H_L + H_S) \cdot J = -\frac{2\mu_0}{r^3}\left[L - S + 3\left(S \cdot \frac{\mathbf{r}}{r}\right)\frac{\mathbf{r}}{r}\right] \cdot (L + S) \tag{73}$$

Only the value of this expression averaged over the electron's motion is of interest, so that, after the scalar multiplication is made, the terms may be averaged over the electron's motion. Terms with a factor $L \cdot \mathbf{r}/r$ may be omitted since they equal zero. Then, if $<l/r?>$ indicates the averaged value of $1/r^3$, the average value of $H_J \cdot$ J is

$$H_J \cdot J = (H_L + H_S) \cdot J = -2\mu_0 \left\langle \frac{1}{r^3}\right\rangle\left[L(L+1) - S(S+1)\right.$$
$$\left. + 3\left(S \cdot \frac{\mathbf{r}}{r}\right)^2\right] \tag{74}$$

But $\mathbf{S} \cdot \mathbf{r}/r$ is just the component  of S in the direction $\mathbf{r}/r$.  Therefore for an electron  with spin $\frac{1}{2}$ it is $\pm \frac{1}{2}$, so that the square of this quantity is necessarily $+\frac{1}{4}$. With this  and $S = \frac{1}{2}$, Eq. (74) becomes

$$\mathbf{H}_J \cdot \mathbf{J} = -2\mu_0 < \frac{1}{r^3} > L(L + 1) \tag{75}$$

For hydrogen-like atoms, $< 1/r^3 >$ is well known [1] and is

$$< \frac{1}{r^3} > = \frac{Z^3}{a_0{}^3 n^3 (L + 1)(L + \frac{1}{2})L} \tag{76}$$

where $a_0$ is the radius of the  first Bohr orbit of  a hydrogen atom or $\hbar^2/me^2$. Therefore, from  Eq. (22),

$$a = \frac{2\mu_0 (\mu_I/I) Z^3}{a_0{}^3 n^3 (L + \frac{1}{2}) J (J + 1)} = \frac{2\pi \hbar c \text{ Ry } \alpha^2 Z^3 g_I}{n^3 (L + \frac{1}{2}) J (J + 1)(M/m)} \tag{77}$$

where  the  last form  is  expressed  in  terms of  the  Rydberg constant $\text{Ry} = me^4/4\pi \hbar^3 c$ and  the  fine  structure constant $\alpha = e^2/\hbar c$. This equation  is  the  result  used  in Eq. (25).   It  should  be  noted  that this discussion is not rigorous when applied to an $S$ state, since then Eq. (76) becomes infinite and  Eq. (75) indeterminate.  Nevertheless, if in Eq. (77) the values $L = 0$ and $J = \frac{1}{2}$ are substituted, the result is

$$a = \frac{8}{3} \frac{2\pi \hbar c \text{ Ry } \alpha^2 Z^3 g_I}{n^3 (M/m)} \tag{78}$$

which is just the result of Eq. (2.1) that has been calculated  in a rigorous relativistic wave-mechanical  manner by Fermi (F8) and others.

[1] See, for example, Condon  and Shortley  (C16, p. 117).

# 3

## EXPERIMENTAL  METHODS  OF  MEASURING  NUCLEAR

## MOMENTS  AND  STATISTICS

### A.  Hyperfine Structure in Optical Atomic Spectra

The experimental techniques for the optical study of hyperfine struc-ture are those of ordinary optical spectroscopy. However, because of the very close spacing ($\Delta \nu \sim 0.05$ cm-') of many hyperfine  structure lines, highly refined techniques must commonly be used. Carefully made Fabry-Perot  etalons are often used to resolve the lines.  Special light sources have been developed by Schiiler and others which can be well cooled to reduce Doppler broadening and which are designed to reduce absorption broadening; use is often made of hollow cathode dis-charges in which the cathode is  a hollow cylinder, as illustrated in Fig. 6, which can be well cooled, often with liquid air. Jackson and Kuhn (J5), Minkowski (M23), Meissner (M14), Paul (P3), and others have designed their light sources so the emitting atoms are in a directed atomic beam which can be viewed transversely to reduce Doppler effect, as in Fig. 7. Fuller  descriptions und summaries of the optical techniques employed and of the detailed methods of term analysis have been given by Tolansky  (T1) and by  Kopfermann (K29).

The spin can be determined from hyperfine structure studies in sev-eral different ways.  The easiest way, when applicable, is merely to use the number of components of the spectral line.  If the hyperfine struc-ture of one of the set of states concerned in the transition is negligibly small compared to the other, the number of hyperfine structure lines will be either $2J + 1$ or $2I + 1$ according as $I > J$ or $J > I$.   Conse-quently, if $J$ is sufficiently  large, $I$ can be obtained merely by counting the number of lines.  Even if the hyperfine structure of one state is not negligibly small, this procedure can be used if  a term analysis of the spectrum is possible, in which case  all that is necessary is to determine the multiplicity of a term for which $J > I$.

Even if measurements cannot be made on a state for which $J > I$, the spin can sometimes be determined by measuring the relative spacing of the components of a term and using the interval rule, Eqs. (23) and (29), todetermine the different $F$ values and consequently to determine I. However, great care must be exercised in using this method to make