

TABLE 4-8. STRUCTURES OF ASYMMETRIC ROTORS WHICH HAVE BEEN OBTAINED FROM MICROWAVE SPECTRA (Concluded)

Molecule	Structure	Reference
HN_3		[427]
H_2S		[783]
$\text{O}_2\text{S} (\text{SO}_2)$		[647] [565]
O_3		[875]

advent of high-resolution microwave spectroscopy. A large number have now been worked out by microwave techniques, and it seems feasible to solve the rotational spectrum of any asymmetric rotor which does not have serious complications due to internal motions (*cf.* Chap. 12) or an exceptionally complex hyperfine structure (*cf.* Chap. 6). The Stark effect has been extremely valuable in identifying and working out this type of spectrum (*cf.* Chap. 10). The structures of asymmetric rotors which have been obtained from microwave results are given in Table 4-8.

CHAPTER 5

ATOMIC SPECTRA

While most microwave spectra have their origin in absorption by molecules, certain types of atomic spectra may fall in the microwave region. Atomic theory is important even for molecular spectroscopy because it is often convenient to consider a molecule as being composed of atoms whose properties are not too greatly different from their properties in the free state. Moreover, many molecular phenomena are sufficiently analogous to phenomena in atoms so that it is worthwhile to study first the simpler atomic case.

This chapter will present a summary of those parts of the theory of atomic spectra which are needed for microwave spectroscopy. More extensive treatments are given in the several books devoted to the subject (*e.g.*, A. C. Candler [79], G. Herzberg [124], L. Pauling and S. Goudsmit [23], H. E. White [53], and for a more advanced, quantum-mechanical treatment, E. U. Condon and G. H. Shortley [56]).

5-1. The Hydrogen Atom. The simplest atom is that of hydrogen, consisting of a single proton and an electron. It is described by the wave equation

$$\nabla^2 \psi + \frac{8\pi^2\mu}{h^2} (W - V)\psi = 0$$

or, in spherical coordinates,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{8\pi^2\mu}{h^2} (W - V)\psi = 0 \quad (5-1)$$

where the nucleus, or more exactly the center of mass of the electron and nucleus, is taken as the origin of coordinates, and $\mu = mM/(M + m)$ is the reduced mass of the atom. W is the total energy of the atom, $V = -Ze^2/r$ is the potential energy, Z is the nuclear charge in units of the proton charge, and e is the proton charge.

By a process of separating the variables similar to that used for the diatomic molecule (Chap. 1), the wave equation may be solved [62], giving

$$\psi = R(r)\Theta(\theta)\Phi_m(\phi) \quad (5-2)$$

where

$$\Phi_M = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (5-3)$$

$$\Theta_{Ml} = \left[\frac{(2l+1)(l-|m|)!}{2(l+|m|)!} \right]^{\frac{1}{2}} P_l^{|m|}(\cos \theta) \quad (5-4)$$

$$R_{nl} = \sqrt{\frac{4(n-l-1)!Z^3}{[(n+l)!]^3 n^4 a_0^3}} \left(\frac{2Zr}{na_0} \right)^l e^{-Zr/na_0} L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) \quad (5-5)$$

and where $n = 1, 2, \dots$ is the principal quantum number
 $l = 0, 1, 2, \dots, (n-1)$ is the orbital quantum number
 $m = -l, -l+1, \dots, l-1$, l is the magnetic quantum number and should not be confused with the same symbol used for the mass of the electron

$P_l^{|m|}$ = associated Legendre polynomial

L_{n+l}^{2l+1} = associated Laguerre polynomial

$a_0 = h^2/4\pi^2\mu e^2$ is the radius of the first orbit of the hydrogen atom in the Bohr theory

It may be observed that Eq. (5-1) for the hydrogen atom is exactly the same as the wave equation (1-11) for a diatomic molecule with the potential $V(r)$ replacing the molecular potential $U(r)$. The hydrogen atom may, in fact, be regarded as a diatomic molecule with the proton and electron as the two atoms. The parts of the wave function (5-3) and (5-4) which depend on angle are identical with those for a diatomic or linear molecule (1-5) and (1-6). They are the same for any spherically symmetric potential, since these functions represent conservation of total angular momentum (l or J) and of the projection of the angular momentum (m or M) on a chosen axis. Unlike the diatomic molecule, the dependence of the potential on r in this atomic case is very simple and the radial wave function (5-5) can be determined. In more complex atoms, the potential for a single electron may often be considered spherically symmetric, so that the angular parts of the wave function are unchanged. However, the dependence of the potential on r is usually very difficult to determine, so that the radial wave function and energy cannot be exactly obtained.

Figures 5-1, 5-2, and 5-3 show the radial and angular distribution of the electrons. The s electron wave function is seen to be the only one which does not vanish at the center of the nucleus. The s electron is also the only one which has a spherical charge distribution.

The allowed energy levels for the hydrogen atom are given by

$$W = -\frac{2\pi^2\mu e^4 Z^2}{n^2 h^2} = -Rhc \frac{Z^2}{n^2} \quad (5-6)$$

where $R = 2\pi^2\mu e^4/c\hbar^3$ is the Rydberg constant in cm^{-1} . W is in ergs; to convert to cm^{-1} , divide by $\hbar c$. On this model of the hydrogen atom,

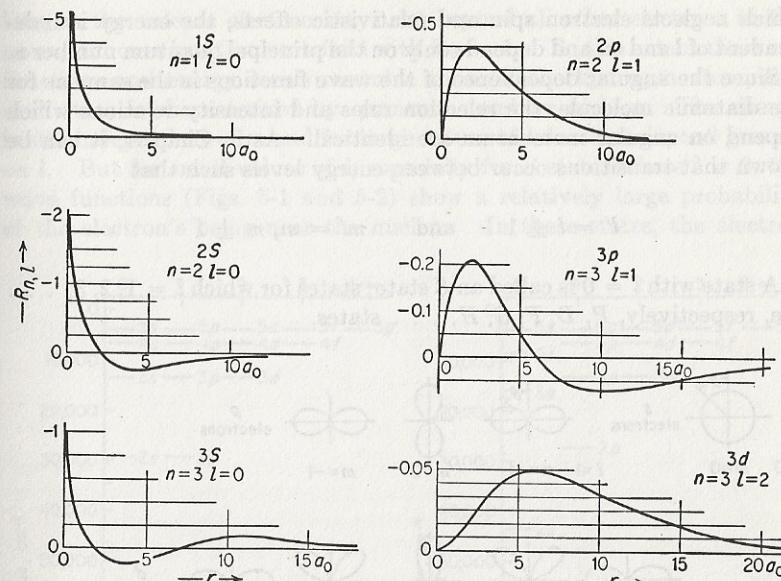


FIG. 5-1. The radial part of the hydrogen electronic wave function R_{nl} plotted as a function of the distance between the electron and the nucleus.

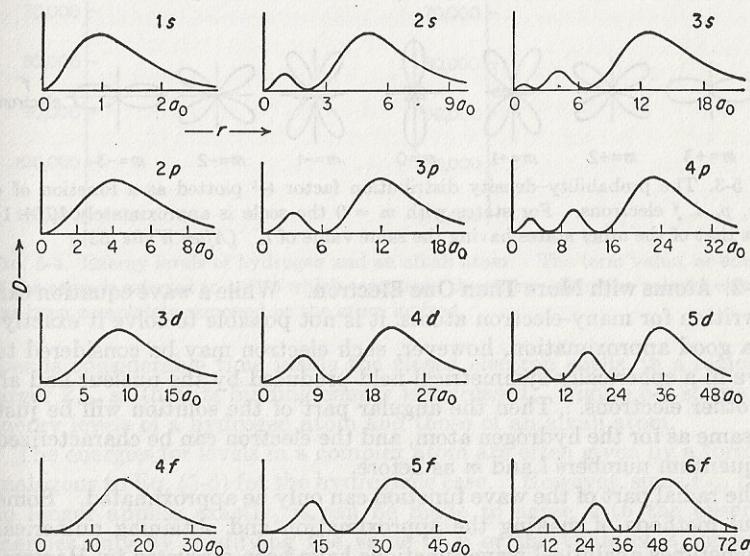


FIG. 5-2. The electronic density distribution $r^2(R_{nl})^2$ is plotted as a function of the electron-nuclear distance for several states of the hydrogen atom. The ordinate shows the probability of finding the electron between spherical shells of radii r and $r + dr$.

which neglects electron spin and relativistic effects, the energy is independent of l and m , and depends only on the principal quantum number n .

Since the angular dependence of the wave functions is the same as for the diatomic molecule, the selection rules and intensity relations which depend on angular momentum are identical. As in Chap. 1, it can be shown that transitions occur between energy levels such that

$$l' = l \pm 1 \quad \text{and} \quad m' = m, m \pm 1$$

A state with $l = 0$ is called an S state; states for which $l = 1, 2, 3, \dots$ are, respectively, P, D, F, G, H, \dots states.

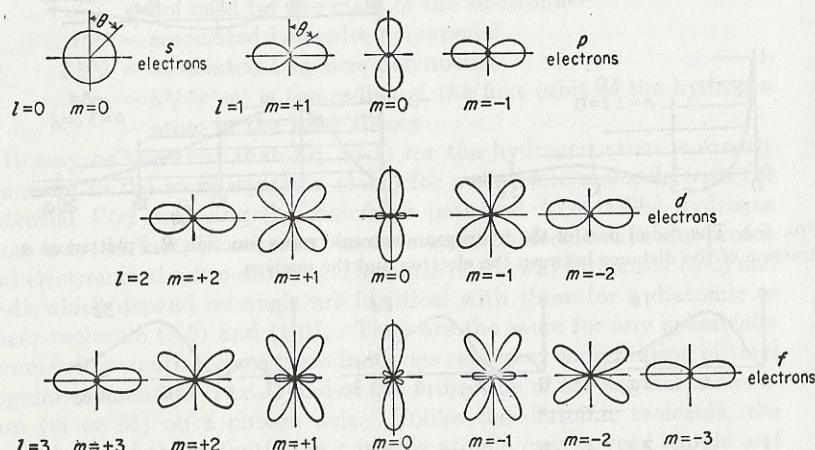


FIG. 5-3. The probability-density distribution factor Θ^2 plotted as a function of θ for s, p, d, f electrons. For states with $m = 0$ the scale is approximately $l(l+1)$ times that of the other states having the same value of l . (After White [53].)

5-2. Atoms with More Than One Electron. While a wave equation can be written for many-electron atoms, it is not possible to solve it exactly. To a good approximation, however, each electron may be considered to move in a spherically symmetrical field produced by the nucleus and all the other electrons. Then the angular part of the solution will be just the same as for the hydrogen atom, and the electron can be characterized by quantum numbers l and m as before.

The radial part of the wave function can only be approximated. Some useful methods of making the approximation and obtaining numerical or sometimes analytical wave functions have been discussed by Hartree, Fock, Fermi, Thomas, Slater, and others [305].

Particularly simple are the alkali-type atoms which have one electron outside a spherically symmetrical core of "closed electron shells." As

long as the valence electron stays out beyond all other electrons in the atom, it moves in a Coulomb field with $Z_{\text{eff}} = 1$. To this extent the wave functions and energy levels resemble those of the hydrogen atom, and each state is characterized by quantum numbers n, l, m . The energy is still independent of m and for large values of l does not depend greatly on l . But for small values of l , especially for S states where $l = 0$, the wave functions (Figs. 5-1 and 5-2) show a relatively large probability of the electron's being near the nucleus. In these states, the electron

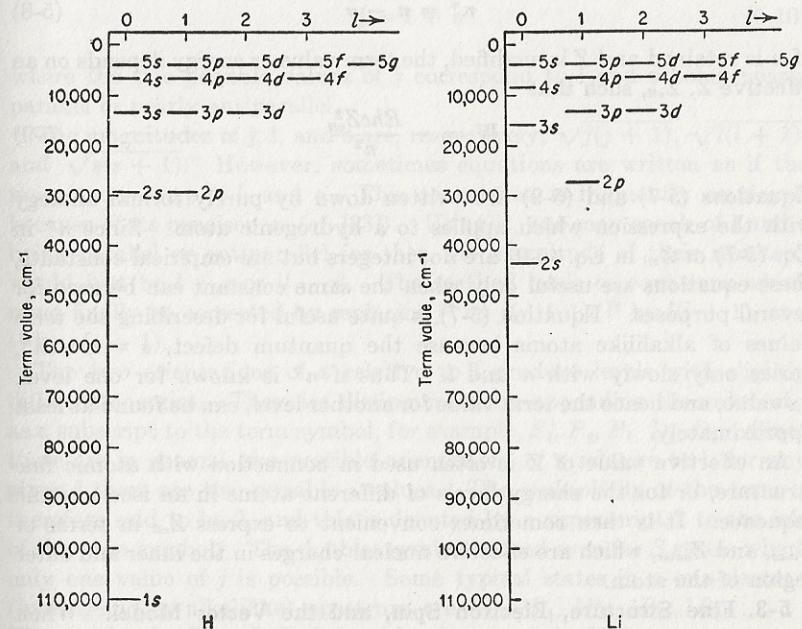


FIG. 5-4. Energy levels of hydrogen and an alkali atom. The term value, or energy, of the atom is referred to a zero which represents the energy after the valence electron has been completely removed or the atom ionized.

spends considerable time inside the closed electron shells, in a region of larger Z_{eff} , so that its binding energy is increased. Figure 5-4 shows the energy levels of a hydrogen atom and those of an alkali atom.

The energies for levels in a complex atom are often given by a formula analogous to Eq. (5-6) for the hydrogenic case. However, since Eq. (5-6) no longer applies exactly, it can be made to agree with the observed energies only by modifying the value of n or the value of Z , or both. Thus for the first case,

$$W = -\frac{RhcZ_o^2}{n^{*2}} = -\frac{RhcZ_o^2}{(n-\sigma)^2} \quad (5-7)$$

where R = Rydberg constant

Z_o = effective nuclear charge in the outer region of the atom.

$Z_o = 1$ for alkali atoms, but may be 2, 3, 4, . . . for ionized alkali-like atoms such as Be^+ , B^{++} , C^{+++} , etc.

n^* = effective principal quantum number; not an integer

n = principal quantum number, and is an integer

σ = quantum defect

From Eq. (5-7) it is seen that

$$n^* = n - \sigma \quad (5-8)$$

If n is retained and Z is modified, the term value or energy depends on an effective Z , Z_{eff} , such that

$$W = - \frac{RhcZ_{\text{eff}}^2}{n^2} \quad (5-9)$$

Equations (5-7) and (5-9) are written down by purely formal analogy with the expression which applies to a hydrogenic atom. Since n^* in Eq. (5-7) or Z_{eff} in Eq. (5-9) are not integers but are empirical constants, these equations are useful only when the same constant can be used for several purposes. Equation (5-7) is quite useful for describing the term values of alkali-like atoms because the quantum defect, $\sigma = n - n^*$, varies only slowly with n and l . Thus if n^* is known for one level, its value, and hence the term value for another level, can be found at least approximately.

An effective value of Z is often used in connection with atomic fine structure, or for the energy levels of different atoms in an isoelectronic sequence. It is then sometimes convenient to express Z_{eff} in terms of Z_{inner} and Z_{outer} , which are effective nuclear charges in the inner and outer region of the atom.

5-3. Fine Structure, Electron Spin, and the Vector Model. When spectral lines are examined with instruments of moderate resolving power, they are found to have a structure, i.e., to consist of several components. This "fine structure" is explained by attributing to the electron a spin angular momentum and a magnetic moment. The angular momentum is related to a spin quantum number s , and its magnitude is given by $\sqrt{s(s+1)}$ in units $h/2\pi$. For a single electron s always has the value $\frac{1}{2}$. This s should not be confused with the same letter used to denote a state with $l = 0$. The corresponding spin magnetic moment is $1 + (\alpha/2\pi)$, in units of the Bohr magneton* $he/4\pi mc$, where m is the electron mass. The fine structure constant α is $2\pi e^2/hc$ and approximately equals $1/37$. A further quantum number $m_s = \pm \frac{1}{2}$ is required to describe the projec-

* The Bohr magneton is usually taken as a positive quantity even though the electron charge is negative. Regardless of this convention, it should be remembered that the electron magnetic moment is opposite to the direction of its spin.

tion of s on some fixed direction, just as m_l gives the projection of the orbital angular momentum on a fixed direction.

The electron's orbital angular momentum and spin angular momentum are vectors and will therefore add in some way similar to the ordinary rules of vector addition to form a resultant denoted by \mathbf{j} . The magnitude of \mathbf{j} is also quantized. It is specified by the total-angular-momentum quantum number j which has the values $j = l + s$ and $j = |l - s|$ (when $s = \frac{1}{2}$). The corresponding vector equation is

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \quad (5-10)$$

where the two possible values of j correspond to \mathbf{l} and \mathbf{s} being nearly parallel or nearly antiparallel.

The magnitudes of \mathbf{j} , \mathbf{l} , and \mathbf{s} are, respectively, $\sqrt{j(j+1)}$, $\sqrt{l(l+1)}$, and $\sqrt{s(s+1)}$. However, sometimes equations are written as if the magnitudes were j , l , and s . This convention is frequently employed because of its conciseness (cf. [23]). Using it, one may speak of \mathbf{l} and \mathbf{s} being parallel or antiparallel for then the magnitude of their resultant would just be $l + s$ or $|l - s|$. The method leads to equations which must finally be corrected by replacing j^2 by $j(j+1)$, l^2 by $l(l+1)$, and s^2 by $s(s+1)$.

The two orientations of \mathbf{s} relative to \mathbf{l} produce levels with slightly different energies. They are distinguished by appending the value of j as a subscript to the term symbol, for example, $S_{\frac{1}{2}}$, $P_{\frac{1}{2}}$, $D_{\frac{3}{2}}$, $D_{\frac{5}{2}}$. Since there are in general two possible orientations of \mathbf{s} relative to \mathbf{l} , for any given l there are two possible j values. The multiplicity of the term is therefore said to be 2, and this is denoted by a superscript 2 to the left of the term symbol. The doublet symbol is used even for S states where only one value of j is possible. Some typical states in a one-electron (hydrogenic or alkali-like) spectrum are ${}^2S_{\frac{1}{2}}$, ${}^2P_{\frac{1}{2}}$, ${}^2P_{\frac{3}{2}}$, ${}^2D_{\frac{3}{2}}$, ${}^2D_{\frac{5}{2}}$, The two levels ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$ form a fine-structure doublet term.

The splitting between the two levels with different values of j which occurs when l is not zero is caused primarily by the magnetic interaction between the electron spin and electron orbital magnetic moments. This interaction can be derived from the magnitude of the magnetic field at the electron caused by the relative motion of the nucleus with respect to the electron. The splitting, however, is reduced by another contribution to the energy exactly half as large and in the opposite direction which is connected with a precession of the electron axis due to relativistic effects [7]. When both are taken into account, the energy level for a hydrogenic atom with nuclear charge Z is displaced by an amount

$$W_s = \frac{1}{2} \frac{e^2 h^2 Z}{4\pi^2 m^2 c^2} \left(\frac{1}{r^3} \right)_{\text{av}} s l \cos(\mathbf{s}, \mathbf{l}) \quad (5-11)$$

where e = electron charge

m = mass of the electron

c = velocity of light

h = Planck's constant

$(1/r^3)_{av}$ = average of the inverse cube of the distance between nucleus of charge Z and the electron.

Two values of $\cos(s,l)$ are possible corresponding to s being "parallel" or "antiparallel"; i.e., the quantum number j can equal $l + s$ or $l - s$. The quantity $sl \cos(s,l)$ appearing in (5-11) can be evaluated from the vector model. Figure 5-5 shows how the vectors l and s combine to form a resultant j . From the trigonometric relation between the sides and angles of a triangle in the diagram

$$sl \cos(s,l) = \frac{|\mathbf{j}|^2 - |\mathbf{s}|^2 - |\mathbf{l}|^2}{2}$$

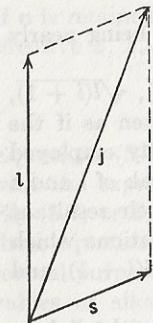


FIG. 5-5. Vector addition of l and s to form resultant j .

This method of adding vectors trigonometrically and then correcting the square of their magnitudes can be applied to any quantum vectors. It will be found useful for the addition of nuclear angular momenta to atomic or molecular angular momenta.

The vector model, which treats angular momenta as classical vectors except for quantum conditions imposed on their magnitudes, is very helpful because it permits easy calculation and visualization of many quantum-mechanical results. It always gives correctly the results of a true quantum-mechanical calculation if only the cosines between vectors or their projections on arbitrary directions are of importance. It is not directly applicable, however, when more complicated functions are required, such as the squares of cosines of angles between vectors.

Substituting the expression (5-12) for $sl \cos(s,l)$ into (5-11), the displacements of the two levels $j = l \pm s = l \pm \frac{1}{2}$ are given by

$$W_s = \frac{1}{2} \frac{e^2 h^2}{4\pi^2 m^2 c^2} \left(\frac{Z}{r^3} \right)_{av} \frac{\pm(l + \frac{1}{2}) - \frac{1}{2}}{2}$$

The + sign corresponds to $j = l + \frac{1}{2}$. The splitting or energy difference between the two levels is then

$$\Delta\nu = R\alpha^2 a_0^3 \left(\frac{Z}{r^3} \right)_{av} (l + \frac{1}{2}) \quad \text{cm}^{-1} \quad (5-13a)$$

For a hydrogenic orbit, Z is constant and

$$\left(\frac{1}{r^3} \right)_{av} = \frac{Z^3}{n^3 a_0^3 l(l + \frac{1}{2})(l + 1)} \quad (5-13b)$$

so that

$$\Delta\nu = \frac{R\alpha^2 Z^4}{n^3 l(l + 1)} \quad (5-13c)$$

where $R = 2\pi^2 me^4 / ch^3 \text{ cm}^{-1}$ [Eq. (5-6)]

$\alpha = 2\pi e^2 / hc$ is the fine-structure constant

$a_0 = h^2 / 4\pi^2 me^2$ is the Bohr radius of hydrogen

For an alkali-type atom a similar formula might be expected to hold approximately. The quantum number n in (5-13) must again be modified to an effective value $n^* = n - \sigma$. In addition, the Z^4 is not a simply determinable quantity since the electron is affected by Z_o , or Z_{outer} , when it is very far from the nucleus, and Z_i , or Z_{inner} , when it is inside the shells of other electrons and close to the nucleus. A good empirical expression, which can also be justified theoretically, is

$$\Delta\nu = \frac{R\alpha^2 Z_i^2 Z_o^2}{(n^*)^3 l(l + 1)} = \frac{5.83 Z_i^2 Z_o^2}{(n^*)^3 l(l + 1)} \quad \text{cm}^{-1} \quad (5-14)$$

n^* is the effective principal quantum number which may be evaluated from the term energy and from (5-7). Z_o is the same Z_o as in (5-7), which is the net charge on the atom after removing the valence electron. Z_i , the effective value of Z near the nucleus, may be taken as approximately 4 less than the nuclear charge Z for p electrons. Methods of approximating $\Delta\nu$ and appropriate values of Z_i are discussed by White [53].

Although (5-14) represents as accurate an expression as can usually be obtained for many-electron atoms, the hydrogen case can be treated much more completely. A more exact theory for the hydrogenic case will be discussed below.

5-4. Atoms with More Than One Valence Electron. Many atoms have more than one valence electron, each one of which is characterized by quantum numbers n , l , and s . The angular momenta l and s may be coupled in several different ways by the interactions between the electrons. The most common coupling scheme, and one that applies for all light atoms, is known as *LS* or Russell-Saunders coupling. For this scheme the individual l 's are coupled so that they add vectorially to form a resultant L , and the spins couple to form a resultant S . Finally L and S add vectorially to form a total angular momentum J . To the vectors L , S , and J correspond quantum numbers L , S , and J , while their magnitudes are, respectively, $\sqrt{L(L+1)}$, $\sqrt{S(S+1)}$, and $\sqrt{J(J+1)}$. The state of the atom as a whole is represented by a term symbol quite analogous to that used for the hydrogen atom. In fact the hydrogenlike atoms may be regarded as especially simple cases of *LS* coupling. A

capital letter S, P, D, F, \dots gives the value of L , corresponding, respectively, to $L = 0, 1, 2, 3, \dots$. A subscript to the right gives the value of J , while $2S + 1$ is given by a superscript to the left. $2S + 1$ is called the "multiplicity" of the state. This is because, as long as $L \geq S$, J may assume any of the values $L + S, L + S - 1, \dots, L - S$, or $2S + 1$ different J states are possible. For example, the states $^3P_2, ^3P_1, ^3P_0$ have the same L and S , but different J 's; they constitute a triplet.

In compounding the angular momenta of the individual electrons, it is usually necessary to consider only those electrons outside closed shells, because for all closed shells L, S , and J are zero. The number of electrons in a closed shell is governed by the Pauli exclusion principle.

In a strong electric or magnetic field, the interactions of the individual electrons with the field are stronger than their interactions with each other. Then in addition to n, l , and s , each electron has quantum numbers m_l and m_s which are, respectively, the projections of l and s on the field direction. m_l can have the values $l, l - 1, \dots, -l$, while in any one atom can have a given set of the five quantum numbers n, l, s, m_l, m_s . From this it follows that $2(2l + 1)$ electrons may have a given n and l . They form a closed subshell, with zero angular momentum and a spherical distribution of charge. For a given value of n, l may assume the values $0, 1, 2, \dots, n - 1$. Including all these possible values of $l, 2n^2$ electrons have the same value of n , and they constitute a closed shell.

5-5. Selection Rules and Intensities. The intensity of a transition between two states of an atom is proportional to the square of the matrix element of the electric dipole moments between the states, that is,

$$I \propto |\int \psi_2^* e z \psi_1 d\tau|^2 \quad (5-15)$$

and to the population of the initial state.

The value of the matrix element involves both the radial and the angular parts of the wave function. The radial part of the wave function depends on the quantum numbers n and l and on the particular atom in question. It is usually difficult to evaluate exactly. However, the angular part of the wave function depends only on the angular momentum quantum numbers and not on the details of the particular atom as long as the electron can be considered to move in a spherical potential. General selection rules may hence be found for the changes in angular momentum quantum numbers allowed during a radiative transition. They are very similar to the selection rules of Sec. 1-4 and may be written

$$L' = L \pm 1, L \quad (5-16)$$

$$J' = J \pm 1, J \text{ (but } J' \text{ and } J \text{ cannot both be zero)}$$

$$\Sigma l_i \text{ changes from odd to even or vice versa}$$

$$\Delta m_J = 0, \pm 1$$

Although these selection rules are very useful in predicting which transitions may occur, they give little information about the absolute or relative intensities of transitions, which often depend on the radial parts of the wave function.

In cases involving a group of transitions with the various initial states and the various final states differing among themselves only in the relative orientation of the angular momentum vectors \mathbf{L}, \mathbf{S} , and \mathbf{J} , the radial part of the matrix element (5-15) is constant. The relative intensities of such transitions then depend only on the angular momentum quantum numbers. A typical example of this type of case is a group of fine-structure components of "one" transition. Their relative intensities are given by [23], [53]:

For transitions $L \leftarrow L - 1$:

$$\begin{aligned} J \leftarrow J - 1, I &= \frac{B(L + J + S + 1)(L + J + S)(L + J - S)(L + J - S - 1)}{J} \\ J \leftarrow J, \quad I &= - \frac{B(L + J + S + 1)(L + J - S)(L - J + S)(L - J - S - 1)(2J + 1)}{J(J + 1)} \\ J \leftarrow J + 1, I &= \frac{B(L - J + S)(L - J + S - 1)(L - J - S - 1)(L - J - S - 2)}{(J + 1)} \end{aligned} \quad (5-17)$$

For transitions $L \leftarrow L$:

$$\begin{aligned} J \leftarrow J - 1, I &= - \frac{A(L + J + S + 1)(L + J - S)(L - J + S + 1)(L - J - S)}{J} \\ J \leftarrow J, \quad I &= \frac{A[L(L + 1) + J(J + 1) - S(S + 1)]^2(2J + 1)}{J(J + 1)} \\ J \leftarrow J + 1, I &= - \frac{A(L + J + S + 2)(L + J - S + 1)(L - J + S)(L - J - S - 1)}{(J + 1)} \end{aligned} \quad (5-18)$$

Expressions (5-17) and (5-18) for the relative intensities take into account both the squares of the matrix element (5-15) and the relative populations of the different levels, assuming that the populations are proportional to the statistical weights or M degeneracy.

In Appendix I, these relative intensities have been tabulated. It should be noted that the lines whose intensities are to be compared must be close together in frequency for Eqs. (5-17) and (5-18) to apply. Otherwise the intensity should be multiplied by a frequency factor which is ν^4 for optical emission lines, or ν^2 for microwave absorption.

These formulas and tables depend only on the magnitude and direc-

tions of the vectors which have been added, and not on the specific form of interaction between the vectors. They may therefore be used for transitions in which angular momentum vectors other than \mathbf{L} , \mathbf{S} , and \mathbf{J} are involved if appropriate changes are made in the symbols.

For example, if the nucleus has an angular momentum I , it can interact with the electronic angular momentum J to give a new total angular momentum quantum number F . The energy separations between levels with different values of F give rise to hyperfine structure, which will be considered shortly. Then the relative intensities of different transitions in a hyperfine-structure pattern are given by the same equations (5-17) and (5-18), provided we replace J by F , L by J , and S by I . Here the symbol I should not be confused with the same letter used to denote intensity in Eqs. (5-17) and (5-18).

The general behavior of the relative intensities of fine-structure components may be readily understood. The radiation fields act primarily on the orbital angular momentum and change L by one unit without changing S . This is because the force of the electric component of the field on the electron charge is much greater than magnetic forces acting on the electron spin. If L is increased during the transition to $L + 1$ and S is unaffected in magnitude or direction, then J would be expected to change in approximately the same way as L , or to increase to $J + 1$. It will be observed that the stronger transitions in Appendix I tend to be those for which the change in J has the same value as the change in L . This is most notably true for large values of L , where quantum-mechanical results most closely approximate classical expectations.

5-6. Fine Structure—More Exact Treatment. Although most atoms are so complex that a theoretical calculation of fine structure which is much more exact than the expressions (5-13) and (5-14) given above is very difficult and even uncertain, the hydrogen atom and hydrogenlike one-electron ions are sufficiently simple to allow a considerably more exact treatment. Because of this simplicity, the hydrogen spectrum, and the hydrogen fine structure in particular, has been much used as a testing ground for atomic theory. Several different treatments of the hydrogen fine structure have met with temporary success, but each in turn has required modification as experimental techniques and theoretical knowledge advanced. The basis of the modern treatment of the hydrogen atom and its fine structure was given in 1928 by Dirac. He proposed a relativistic form of quantum mechanics which inherently provides the electron with the properties previously postulated separately as a spin and magnetic moment.

According to the Dirac theory, the energy levels of a hydrogenlike atom are given by

$$W = mc^2 \left\{ \left(1 + (\alpha Z)^2 [n - |K| + (K^2 - \alpha^2 Z^2)^{\frac{1}{2}}]^{-2} \right)^{-\frac{1}{2}} - 1 \right\} \quad (5-19)$$

where $|K| = j + \frac{1}{2}$. It may be seen from Eq. (5-19) that the levels with the same value of n and j are degenerate. If this equation is expanded in powers of αZ , it gives

$$\frac{W_{nj}}{hc} = -\frac{Z^2 R}{n^2} - \frac{\alpha^2 Z^4 R}{n^3} \left[(j + \frac{1}{2})^{-1} - \left(\frac{3}{4n} \right) \right] + \dots \quad (5-20)$$

so that the fine-structure doublet separation between the ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$ levels is

$$\Delta\nu = \frac{R\alpha^2 Z^4}{n^3 l(l+1)} \quad (5-21)$$

which agrees with the previous result [Eq. (5-13)], although here it is evident that terms in higher orders of αZ have been neglected. Figure

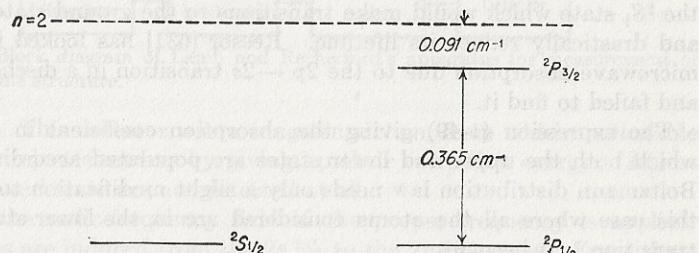


FIG. 5-6. Fine structure of $n = 2$ levels of hydrogen (Dirac theory). The dotted line indicates the position the levels would have according to the Bohr theory, which does not consider fine structure.

5-6 shows the $n = 2$ levels of the hydrogen atom according to the Dirac theory.

Optical spectroscopic measurements of the fine structure of the hydrogen H_α line ($n = 3$ to $n = 2$), indicated that the structure of the $n = 2$ level of hydrogen was in reasonable, although not precise, agreement with the predictions of the Dirac theory. However, because hydrogen is such a light gas, the atoms have large thermal velocities which, through the Doppler effect, cause considerable broadening of the lines. The resultant blurring of the pattern was sufficient even at liquid-air temperatures to make the disagreement uncertain. There was some indication that the ${}^2S_{\frac{1}{2}}$ level was displaced upward with respect to the P levels by about 0.03 cm^{-1} , or 1000 Mc [80], [88], [89]. On the other hand, the apparent shifts were attributed by some [97] to impurities in the light source.

As early as 1928 Grotrian [9] had pointed out that the selection rules permitted transitions between states with the same value of n , and that radio waves might be used to induce such transitions. Several attempts were made [31], [60] to observe transitions between the $2s \ {}^2S_{\frac{1}{2}}$ and $2p \ {}^2P_{\frac{1}{2}}$ levels which on the Dirac theory should be separated by $\Delta\nu = 0.365 \text{ cm}^{-1}$,

or 10,950 Mc. Spark-gap oscillators were used, and the radiation was passed through a hydrogen gas discharge tube. Betz reported absorptions of about 25 per cent at wavelengths of 3, 9, and 27 cm, but these absorptions seem to be impossibly large. Haase [60] found no resonant absorption at all.

It does appear possible to detect this fine-structure splitting by direct microwave absorption. Hydrogen atoms may be excited to the $2s\ ^2S_{\frac{1}{2}}$ or $2p\ ^2P_{\frac{1}{2}}$ states in an electrical discharge in wet hydrogen. From the $^2P_{\frac{1}{2}}$ state they decay rapidly, since this state has a natural lifetime τ_p of only 1.6×10^{-9} sec. The $2s\ ^2S_{\frac{1}{2}}$ state is metastable, however, so that atoms tend to accumulate in it and they may absorb microwave energy by making a transition to the $2p\ ^2P_{\frac{1}{2}}$ state. On the other hand, a relatively small electric field may be expected to produce a Stark effect in the $^2S_{\frac{1}{2}}$ state which would make transitions to the ground state possible and drastically reduce its lifetime. Reesor [631] has looked for direct microwave absorption due to the $2p \leftarrow 2s$ transition in a discharge tube and failed to find it.

The expression (1-49) giving the absorption coefficient in a gas for which both the upper and lower states are populated according to the Boltzmann distribution law needs only a slight modification to apply to this case where all the atoms considered are in the lower state of the transition. It becomes

$$\gamma = \frac{8\pi^2 N}{3hc} \frac{|er|^2 \nu \Delta\nu}{(\nu - \nu_0)^2 + (\Delta\nu)^2} \quad (5-22)$$

where γ is the absorption coefficient for microwave radiation of frequency ν , ν_0 is the resonant frequency, and $|er|$ is the dipole moment matrix element, or e times the matrix element of the coordinate vector r of the atomic electron for the transition $2s\ ^2S_{\frac{1}{2}} \rightarrow 2p\ ^2P_{\frac{1}{2}}$. The square of the matrix element $|er|^2$ for the transition can be calculated as $6a_0^2e^2$, where $a_0 = h^2/4\pi^2me^2$ is the radius of the first Bohr orbit for hydrogen. If broadening of the resonance absorption due to collisions can be ignored then there is no appreciable broadening of the $^2S_{\frac{1}{2}}$ state and the half width is just $1/(4\pi\tau_p)$, where τ_p is the natural lifetime of the $^2P_{\frac{1}{2}}$ state, 1.6×10^{-9} sec. This short lifetime gives a half width of about 50 Mc. The number of atoms N in the $2s\ ^2S_{\frac{1}{2}}$ state is very difficult to calculate. However, a rough estimate gives $N = 5 \times 10^{10}$ atoms/cm³ under optimum conditions [484], so that the absorption coefficient becomes, from (5-22),

$$\gamma = 1.6 \times 10^{-4} \text{ cm}^{-1} \quad (5-23)$$

This is a large absorption coefficient by microwave spectroscopic standards, but its detection would be made more difficult by the large half width of the line, which is $1/(4\pi\tau_p) \approx 50$ Mc. The effective absorption might be reduced by transitions in the reverse direction if the $^2P_{\frac{1}{2}}$ state is appreciably populated. A further complication is the back-

ground of continuous absorption by free electrons in the discharge tube. This might be of the order of 10^{-4} cm^{-1} in a typical case.

While it seems that the hydrogen fine structure could probably be detected by direct absorption, no experiment of this type has yet been done. An alternative experiment, which is very suitable for an accurate measurement of this resonance, is the atomic-beam method of Lamb and Rutherford [484]. Figure 5-7 is a block diagram of their apparatus.

Hydrogen was dissociated in an oven, and collimated by slits to form an atomic beam. Some of the atoms were excited to the metastable $2s\ ^2S_{\frac{1}{2}}$ state by an electron bombarder. Then the beam passed through a region in which a radio-frequency field was applied and finally hit a

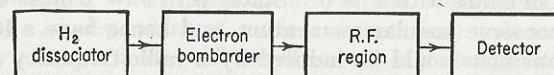


FIG. 5-7. Block diagram of Lamb and Rutherford's apparatus for measurement of hydrogen fine structure.

detector. This detector was a tungsten ribbon, from which metastable atoms can eject electrons by giving up their excitation energy. Atoms in the ground state are not detected at all.

When the radio-frequency field of the proper frequency is applied, transitions are induced from the $2s\ ^2S_{\frac{1}{2}}$ to the $2p\ ^2P_{\frac{1}{2}}$ state. From there the atoms quickly decay to the ground state. Since the density in the beam is low there is little imprisonment of resonance radiation to increase the $2p\ ^2P_{\frac{1}{2}}$ population.

To avoid the necessity for varying the radio frequency over a wide range which would make difficult the maintenance of constant radio-frequency power, the transition region was placed in a variable magnetic field. Then the Zeeman effect of the transition was observed and the frequency for zero field was found by extrapolation.

The fine structure of singly ionized helium was also studied by Lamb and Skinner [381], [485]. In this case the decay of the metastable atoms on application of the microwave field was detected by observation of the ultraviolet photons emitted in the transition to the ground state.

In both hydrogen and helium the $2s\ ^2S_{\frac{1}{2}}$ level was found to be higher than the $2p\ ^2P_{\frac{1}{2}}$. However the separation between the levels $2p\ ^2P_{\frac{1}{2}}$ and $2p\ ^2P_{\frac{3}{2}}$ in hydrogen agreed fairly well with expression (5-21) [790]. For hydrogen the measured separation between $2s\ ^2S_{\frac{1}{2}}$ and $2p\ ^2P_{\frac{1}{2}}$ was 1057.777 ± 0.10 Mc [876]; while in ionized helium the shift was $14,020 \pm 100$ Mc for the corresponding level [485]. To achieve this precision in the measurement of the center frequency of a broad line requires a careful consideration of the factors affecting the shape and position of the line [790], [876].

The apparent upward shifts of the $2s\ ^2S_{\frac{1}{2}}$ levels are now explained fairly

well by the interaction between the atomic electron and its radiation field [177]. The calculation is very difficult to carry out accurately, but the calculated shift for hydrogen agrees within about 0.5 Mc with the observed shift [876].

Probably the simplest atom from the theoretical point of view is positronium. It consists of a positron and electron only, so that there is no complication from the short-range forces associated with heavy nucleons. This atom is not stable, decaying in about 10^{-8} sec with the annihilation of the particles and emission of either two or three γ rays. Consequently, it is not easy to study experimentally, and was discovered only recently by Deutsch [568a]. Two γ rays are emitted in opposite directions from states with $J = 0$. States with $J = 1$ must emit three photons to conserve angular momentum, and hence have a longer lifetime. If transitions could be induced by a radio-frequency field from the $J = 1$ to the $J = 0$ states, triplet positronium would be converted to singlet, and the transition detected by the increase in double quantum annihilation. For this direct experiment, a frequency near 2×10^5 Mc would be needed.

However, lower frequencies can be used to measure the fine structure of positronium with the aid of the Zeeman effect. In a magnetic field the $J = 1$ state is split into $M = 0$ and $M = \pm 1$ components. The $M = 0$ state acquires some singlet character, so that double quantum annihilation can occur from it. Weinstein, Deutsch, and Brown [997a] have used the annihilation radiation to detect microwave induced transitions from the $J = 1, M = \pm 1$ to the $M = 0$ levels. Since this Zeeman splitting depends in part on the ratio of magnetic field to the singlet-triplet separation, this measurement determined the fine structure splitting between the $J = 0$ and 1 states as $(2.0338 \pm 0.0004) \times 10^5$ Mc. The calculated value of 2.0337×10^5 Mc [712a] is in excellent agreement.

A few other fine-structure splittings in atoms can probably be studied by microwave techniques. However, in many cases the fine structure is so large that transition frequencies do not lie in the microwave region, or in other cases the lifetimes of both states are so small that application of microwave techniques is difficult.

5-7. Hyperfine Structure. Atomic nuclei have radii near 10^{-12} cm, and hence are very small compared with the size of electron orbits, which are approximately 10^{-8} cm. Nuclei are also some 10^4 times heavier than electrons. To a good approximation electronic energies can therefore be obtained by considering nuclei to be positive point charges of infinite mass. However, effects on electronic energy levels due to the finite size and mass of nuclei, although small, often appear on careful observation of atomic spectra. They are called hyperfine structure because they produce a very small splitting of atomic lines, usually much smaller than the fine structure.

If the nucleus is to be considered other than a point charge, it must be recognized that the nucleus involves a charge distribution and that this charge distribution may be in motion, producing magnetic fields and giving the nucleus an angular momentum. As for an atom or any other quantum-mechanical system, the angular momentum of the nucleus must be $I\hbar/2\pi$, where I is an integer or half integer and is usually called the nuclear spin.

A number of types of hyperfine interactions between nuclei and electrons are independent of the relative orientation of nuclear spin I and electronic angular momentum J . These include the small shifts due to the finite nuclear mass, variation of the electron potential from a coulomb potential when electrons are within the nuclear radius, and isotropic (*i.e.*, independent of nuclear orientation) polarization of the nucleus by electron fields. These effects slightly change each electronic energy level but can usually be detected only by examining their variation between two or more isotopes, and hence are called "isotope effects." Thus a given chemical element may produce a number of slightly different superimposed spectra, each associated with a particular isotope of the element. Since the "isotope effects" do not represent small splittings of the energy levels of any one atomic system, but rather small differences between the spectra of different systems, they are not generally observed by microwave spectroscopy.

On the other hand, hyperfine interactions which vary with nuclear orientation give small splittings of electronic energy levels and are often observed with microwave or radio-frequency techniques. These effects may be either electric or magnetic in origin. Although the magnetic effects are usually most prominent in atoms, electric effects predominate in molecules. The electric interactions will be discussed first.

Hyperfine Structure Due to Electric Charge Distribution in the Nucleus. Motion of the center of mass of the nucleus is unchanged for the various possible nuclear orientations; hence it is the natural origin in considering a nucleus of finite size. Let V_0 be the electrostatic potential produced at the nuclear center of mass by all electronic charges in the atom, and $\partial V_0/\partial x$ represent its derivative evaluated at the same point. The electrostatic energy of a charge $\rho(x,y,z) \Delta x \Delta y \Delta z$, where ρ represents the nuclear charge density, is $\Delta W = \rho \Delta x \Delta y \Delta z V(x,y,z)$.

Expanding V as a series and writing the volume element $\Delta x \Delta y \Delta z = \Delta\tau$

$$\begin{aligned} \Delta W = \rho \Delta\tau & \left[V_0 + x \frac{\partial V_0}{\partial x} + y \frac{\partial V_0}{\partial y} + z \frac{\partial V_0}{\partial z} + \frac{1}{2}x^2 \frac{\partial^2 V_0}{\partial x^2} + \frac{1}{2}y^2 \frac{\partial^2 V_0}{\partial y^2} \right. \\ & + \frac{1}{2}z^2 \frac{\partial^2 V_0}{\partial z^2} + xy \frac{\partial^2 V_0}{\partial x \partial y} + yz \frac{\partial^2 V_0}{\partial y \partial z} + zx \frac{\partial^2 V_0}{\partial x \partial z} \\ & \left. + \dots + \frac{x^n y^m z^p}{n! m! p!} \frac{\partial^{n+m+p} V_0}{\partial x^n \partial y^m \partial z^p} + \dots \right] \quad (5-24) \end{aligned}$$

Integrating over the entire nuclear volume,

$$W = \int \rho(x,y,z) \left[V_0 + x \frac{\partial V_0}{\partial x} + y \frac{\partial V_0}{\partial y} + z \frac{\partial V_0}{\partial z} + \frac{1}{2}x^2 \frac{\partial^2 V_0}{\partial x^2} + \frac{1}{2}y^2 \frac{\partial^2 V_0}{\partial y^2} + \frac{1}{2}z^2 \frac{\partial^2 V_0}{\partial z^2} + xy \frac{\partial^2 V_0}{\partial x \partial y} + yz \frac{\partial^2 V_0}{\partial y \partial z} + zx \frac{\partial^2 V_0}{\partial z \partial x} + \dots \right] dv \quad (5-25)$$

The first term may be easily integrated to give ZeV_0 , where Z is the atomic number of the nucleus and Ze its total charge. This is the term which is independent of nuclear size or shape. The second term may be written

$$\frac{\partial V_0}{\partial x} \int \rho(x,y,z)x dv$$

where the integral is the nuclear dipole moment in the x direction. If this nuclear dipole is not produced by an external field, such as that of the electrons, but is a property only of the nucleus, it can be shown to be zero except in very rare cases. Suppose the wave function and hence the charge distribution for a nucleus is known and the dipole moment in the x direction, $\int \rho x dx dy dz$, has the value μ_x . If the positive directions of the nuclear coordinates x , y , and z are now reversed, a new wave function can be found and a new charge density which is just the same function of the new coordinates x' , y' , z' as it was of the old coordinates x , y , z . This is possible because, for all known forces within the nucleus, the Hamiltonian or wave equation turns out to depend only on even powers of the coordinates and hence remains unchanged when the signs of all coordinates are reversed. The charge density at x will be replaced by a similar charge density at x' or $-x$. However, the direction of the angular momentum does not change on reversing all coordinates. In the new coordinate system, the dipole moment $\mu_{x'}$ has the same value as before but is oppositely directed, that is, $\mu_{x'} = -\mu_x$. Other nuclear properties, however, including the nuclear angular momentum, will have remained unchanged. We must conclude, therefore, that if the nucleus has a dipole moment in one direction with respect to its angular momentum, there must be a degenerate nuclear state, or one of the same energy, with an oppositely directed dipole. Normally, such identical or degenerate states of the nucleus are not encountered, and hence the nucleus has no inherent dipole moment.* If a nucleus has angular momentum I , there are

* A similar proof may be applied to any system, showing that no dipole moments may exist in nature without degeneracy. What is ordinarily referred to as the permanent dipole moment of a molecule in fact does not give a molecule an average dipole moment in one direction unless there is degeneracy or an external field. The dipole moment of a large macroscopic collection of charges may be regarded as existing only because of the very close spacing, and hence effective degeneracy, of the rotational energy levels of such a large system.

$2I + 1$ different possible states having the same energy, corresponding to the different values of M_I , the projection of I on a fixed direction. It might be thought that this is a degeneracy which allows a dipole moment. However, since the angular momentum operator is similar to the Hamiltonian in that it does not change sign when all coordinates are reversed, an argument similar to that above shows that no dipole moment can exist unless the system has two states of the same energy and the same value of M_I . It can thus be shown that all terms of (5-25) involving odd powers of the coordinates will normally be zero. However, terms such as $\int \frac{1}{2}\rho x^2 dv$ and $\int \rho xy dv$ are not necessarily zero because they do not change sign with reversal of direction of all coordinates. These terms are associated with the quadrupole moment of the nucleus.

Before reexpressing these terms in a more convenient form, it is interesting to note their approximate magnitude. The potential V produced by the electron is e/r_e , where r_e is the distance between electron and nucleus. Hence $\partial^2 V / \partial x^2$ is roughly e/r_e^3 . The integral $\int \frac{1}{2}\rho x^2 dv$ is of the order $\int \rho r_n^2 dv = Zer_n^2$, where r_n is the nuclear radius. Hence the term $\partial^2 V / \partial x^2 \int \frac{1}{2}\rho x^2 dv \approx Ze^2 r_n^2 / r_e^3$. This might be compared with the first term in our expansion, $ZeV = Ze^2/r_e$, giving the electrostatic energy for a point nucleus. The ratio of the two is r_n^2/r_e^2 , or 10^{-8} if r_n is 10^{-12} cm and an average value of 10^{-8} cm is taken for r_e . The usual electrostatic energy is of the order 10^6 cm^{-1} , so the energy associated with the small correction terms of this type is expected to be 0.001 cm^{-1} , or 30 Mc. Still higher-order terms in the expansion (5-24) which are nonzero involve fourth powers of the coordinates [that is, $x^4(\partial^4 V / \partial x^4)$, etc.] They are associated with the nuclear hexadecapole (16-pole) and are expected to be still smaller than the quadrupole terms by a factor of roughly 10^8 . In most cases this makes them only a few cycles per second, and too small for present experimental accuracy to detect.

Part of the energy due to terms of (5-25) containing second derivatives of the potential does not vary with nuclear orientation. To eliminate this part we subtract

$$\int \frac{1}{6}\rho(x^2 + y^2 + z^2) \left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} \right) dv \text{ or } \nabla^2 V \int \frac{1}{6}\rho r^2 dv$$

If electrons do not penetrate the nucleus, then $\nabla^2 V$ is zero everywhere ρ is not zero, and this energy integral vanishes. If the electrons do penetrate the nucleus, then this energy represents a deviation from a Coulomb field within the nuclear radius, and is an important part of the atomic isotope shift.

The Electric Quadrupole Moment. Eliminating then the parts of (5-25) which are independent of nuclear orientation and the dipole terms, which have been shown to vanish, the remaining terms are attributable to a

nuclear electric quadrupole and may be written

$$W_Q = \frac{1}{6} \int \rho \left[(3x^2 - r^2) \frac{\partial^2 V}{\partial x^2} + (3y^2 - r^2) \frac{\partial^2 V}{\partial y^2} + (3z^2 - r^2) \frac{\partial^2 V}{\partial z^2} + 6xy \frac{\partial^2 V}{\partial x \partial y} + 6yz \frac{\partial^2 V}{\partial y \partial z} + 6zx \frac{\partial^2 V}{\partial z \partial x} \right] dv \quad (5-26)$$

or

$$W_Q = -\frac{1}{6} Q : \nabla E \quad (5-27)$$

which is the inner product between the quadrupole moment dyadic

$$Q = \int (3rr - r^2 I) \rho dx dy dz \quad (5-28)$$

and the gradient of the electric field due to the electrons.

The properties of dyadics may be found in [105] or [63]. A dyadic \mathbf{AB} is formed from the two vectors $\mathbf{A} = A_x \mathbf{i} + A_y \mathbf{j} + A_z \mathbf{k} = \sum_n A_n \mathbf{e}_n$.

$\mathbf{B} = B_x \mathbf{i} + B_y \mathbf{j} + B_z \mathbf{k} = \sum_m B_m \mathbf{e}_m$, where \mathbf{e}_n represents one of the three unit vectors \mathbf{i} , \mathbf{j} , or \mathbf{k} . The dyadic has nine components and may be written $\sum_{nm} A_n B_m \mathbf{e}_n \mathbf{e}_m$. The unit dyadic I is $ii + jj + kk$, and is said to be diagonal because no "cross terms" of the type ij or jk occur. The inner product of two dyadics $\mathbf{AB} : \mathbf{CD}$ is the scalar quantity $\sum_{nm} A_n B_m C_n D_m$,

which is analogous to the scalar product of two vectors.

By a proper choice of axes any symmetric dyadic such as the quadrupole moment dyadic may be diagonalized. This eliminates all terms except those multiplying ii , jj , or kk .

The charges in the nucleus are rotating very rapidly about the direction of the nuclear spin. If an average is made over a time long enough for the nuclear particles to rotate many times, but so short that the electrons or charges outside the nucleus have not appreciably changed position, the electric field gradient may be considered constant and the nuclear charge distribution cylindrical. Using a new coordinate system with z_n in the direction of the nuclear spin, all nondiagonal terms of Q become zero, and the diagonal terms are simply related;

$$\int \rho (3x_n^2 - r^2) dv = \int \rho (3y_n^2 - r^2) dv = -\frac{1}{2} \int \rho (3z_n^2 - r^2) dv \quad (5-29)$$

The entire quadrupole moment dyadic may hence be expressed in terms of one constant, called "the" nuclear quadrupole moment

$$Q = \frac{1}{e} \int \rho (3z_n^2 - r^2) dx dy dz \quad (5-30)$$

where e is the charge of one proton. From (5-30) it can be seen that a nucleus whose charge distribution is spherical has zero quadrupole

moment, for then the average value of $3z_n^2$ is just equal to the average value of $r^2 = x_n^2 + y_n^2 + z_n^2$. The quadrupole moment may be considered then a measure of the deviation of the nuclear charge from spherical shape. If the charge distribution is somewhat elongated along the nuclear axis z_n , then Q is positive; if it is flattened along the nuclear axis, Q is negative. From (5-26) the quadrupole energy becomes

$$W_Q = \frac{e}{6} Q \left[\frac{\partial^2 V}{\partial z_n^2} - \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} \right) \right] \quad (5-31)$$

If the potential V is due entirely to charges outside the nucleus, then

$$\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} = -\frac{\partial^2 V}{\partial z_n^2}$$

from Laplace's equation, and

$$W_Q = \frac{e}{4} Q \frac{\partial^2 V}{\partial z_n^2} \quad (5-32)$$

The potential V is produced by electrons which are in rapid motion, so rapid that the nuclear axis z_n may be considered stationary during the time that the electrons traverse their entire orbits, or take up all possible positions. Hence, (5-31) may be averaged over all possible electron positions

$$W_Q = \frac{e}{6} Q \left[\frac{\partial^2 V}{\partial z_n^2} - \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_n^2} + \frac{\partial^2 V}{\partial y_n^2} \right) \right]_{av} \quad (5-33)$$

or, using Laplace's equation again

$$W_Q = \frac{e}{4} Q \left(\frac{\partial^2 V}{\partial z_n^2} \right)_{av} \quad (5-34)$$

If the average electron charge density is spherical, then

$$\frac{\partial^2 V}{\partial x_n^2} = \frac{\partial^2 V}{\partial y_n^2} = \frac{\partial^2 V}{\partial z_n^2} \quad \text{and} \quad W_Q = 0$$

Since only s electrons, which have spherically symmetric distributions, have large probabilities of being found within the nucleus, it is customary to set

$$W_Q = \frac{e}{4} Q \left(\frac{\partial^2 V'}{\partial z_n^2} \right)_{av} \quad (5-35)$$

where V' is the potential due only to the electronic distribution outside a small sphere surrounding the nucleus. This gives a small error, because p or d electrons, which are not spherically distributed, have a finite, though small, probability of being inside the nucleus. The density of a nonspherically distributed p electron must, however, be zero at the center of the nucleus, and its average density within the

nucleus is given in order of magnitude by $e(r^2/r_e^5)$, where r is the distance from the center of the nucleus and r_e is the radius of the electron orbit. Hence from Poisson's equation $(\partial^2 V/\partial x_n^2)$ or $(\partial^2 V/\partial y_n^2)$ due to this p -electron cannot be much greater than $e(r_n^2/r_e^5)$. The neglected contribution to the energy is therefore of the order

$$eQ \frac{er_n^2}{r_e^5} \approx \frac{e^2 r_n^4}{r_e^5}$$

which is of the size of the hexadecapole energy discussed above and usually unobservably small. We shall henceforth define the quadrupole energy without this small contribution as

$$\frac{eQ}{4} \left(\frac{\partial^2 V'}{\partial z_n^2} \right)_{av}$$

or, omitting the prime,

$$\frac{eQ}{4} \left(\frac{\partial^2 V}{\partial z_n^2} \right)_{av}$$

We turn now to an examination of the gradient of the electric field, $(\partial^2 V/\partial z_n^2)_{av}$, along the nuclear axis produced by the electrons. About an axis parallel to the electronic angular momentum, $J(h/2\pi)$ or J , the average electric field is cylindrically symmetric, and the dyadic or tensor $(-\nabla E)_{av}$ is hence diagonal with components

$$\left(\frac{\partial^2 V}{\partial x_1^2} \right)_{av} = \left(\frac{\partial^2 V}{\partial y_1^2} \right)_{av} = \left(-\frac{1}{2} \frac{\partial^2 V}{\partial z_1^2} \right)_{av}$$

Here z_1 is along the axis of electronic angular momentum. These quantities, which are elements of a tensor, can easily be transformed to the nuclear coordinate system. If θ is the angle between I and J or z_n and z_1 , and if x_1 and x_n are chosen parallel to each other,

$$\begin{aligned} \left(\frac{\partial^2 V}{\partial z_n^2} \right)_{av} &= \sin^2 \theta \left(\frac{\partial^2 V}{\partial y_1^2} \right)_{av} + \cos^2 \theta \left(\frac{\partial^2 V}{\partial z_1^2} \right)_{av} \\ &= \frac{3 \cos^2 \theta - 1}{2} \left(\frac{\partial^2 V}{\partial z_1^2} \right)_{av} \end{aligned} \quad (5-36)$$

defining $(\partial^2 V/\partial z_1^2)_{av} \equiv q_J$, the quadrupole energy becomes

$$W_Q = \frac{eq_J Q}{4} \frac{3 \cos^2 \theta - 1}{2} \quad (5-37)$$

Expression (5-37) is the correct classical expression for quadrupole energy, but since the quantum numbers I and J are usually small, only a quantum-mechanical derivation, first given by Casimir [70], can be relied on for an accurate expression. To treat the energy quantum-mechanically, the Hamiltonian may be taken from Eq. (5-27) as

$$H = -\frac{1}{6} Q : \nabla E$$

Q and ∇E can be replaced by operators having known eigenvalues for the usual nuclear and electronic wave functions by the following method. The operator $\frac{3}{2}(II + \widetilde{II}) - I^2 I$ has the same angular dependence with respect to nuclear orientation as Q , which is proportional to $3rr - r^2 I$. Hence its matrix elements between states of various orientations must be identical with Q except for a proportionality constant.*

$$(Im_I | Q | Im_I) = \text{const} [Im_I | \frac{3}{2}(II + \widetilde{II}) - I^2 I | Im_I] \quad (5-38)$$

where I, m_I are quantum numbers for the nuclear spin and the component of the nuclear spin in a direction z fixed in space. The symmetrized expression $\frac{3}{2}(II + \widetilde{II})$, where \widetilde{II} indicates the transpose of II , is used because Q is a symmetric operator. To evaluate the proportionality constant, consider the zz component for the state $m_I = I$

$$\begin{aligned} (II | Q_{zz} | II) &= \text{const} (II | 3I_z^2 - I^2 | II) \\ &= \text{const} [3I^2 - I(I+1)] \end{aligned} \quad (5-39)$$

from the known expectation values for I_z^2 and I^2 . The quantity

$$(II | Q_{zz} | II)$$

corresponds at least approximately to the classical quadrupole moment eQ , and will be so defined. Hence $eQ = \text{const} I(2I-1)$, or

$$Q_{op} = \frac{eQ}{I(2I-1)} [\frac{3}{2}(II + \widetilde{II}) - I^2 I] \quad (5-40)$$

Similarly, it can be shown that

$$(\nabla E)_{op} = \frac{q_J}{J(2J-1)} [\frac{3}{2}(JJ + \widetilde{JJ}) - J^2 I] \quad (5-41)$$

where $q_J = (JJ | \frac{\partial^2 V}{\partial z^2} | JJ)$. Expression (5-41) applies only to the common case where J is a "good" quantum number.

Since the electronic potential at the nucleus due to charge e is

$$\frac{e}{r} = \frac{e}{\sqrt{x^2 + y^2 + z^2}}$$

where r is the distance from nucleus to charge,

$$\frac{\partial^2 V}{\partial z^2} = e \frac{3z^2 - r^2}{r^5} = e \frac{3 \cos^2 \theta - 1}{r^3}$$

where θ is the angle between the z axis fixed in space and the radius vector r . This gives

$$q_J = \int \rho_{JJ} \frac{3 \cos^2 \theta - 1}{r^3} d\tau = \left(\frac{\partial^2 V}{\partial z_1^2} \right)_{av} \quad (5-42)$$

* For a more complete discussion, see [969a], p. 16.

where ρ_{JJ} indicates the electron charge density for a state $m_J = J$. If only one electron of wave function ψ is included,

$$q_J = e \int \psi_{JJ}^* \frac{3 \cos^2 \theta - 1}{r^3} \psi_{JJ} d\tau \quad (5-43)$$

The operator for the quadrupole energy is $W_{op} = -\frac{1}{6}Q_{op}:(\nabla E)_{op}$. In case J is a constant or "good" quantum number, this becomes from (5-40) and (5-41) and use of the commutation rules for the components of angular momenta

$$\frac{1}{2} \frac{eq_J Q}{I(2I-1)J(2J-1)} [3(I \cdot J)^2 + \frac{3}{2}(I \cdot J) - I^2 J^2] \quad (5-44)$$

If terms off diagonal in J must be considered, the basic form of W_{op} above must be used. It is easily shown that, if I and J are allowed to be very large, (5-44) becomes equivalent to the classical expression (5-37), since $I \cdot J$ becomes $IJ \cos \theta$.

The total angular momentum of the system in units $\hbar/2\pi$ may be written $\mathbf{F} = \mathbf{I} + \mathbf{J}$ and is of course constant, as is its projection

$$m_F = m_I + m_J$$

on the fixed axis. A representation F, m_F is hence appropriate, and in this representation I^2, J^2 , and $\mathbf{I} \cdot \mathbf{J}$ are diagonal so that the expectation values of (5-44) can be easily determined. The diagonal elements for these operators are $I(I+1)$, $J(J+1)$, and $C/2$, respectively, where

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

Hence

$$W_q = \frac{1}{2} \frac{eq_J Q}{I(2I-1)J(2J-1)} [\frac{3}{4}C(C+1) - I(I+1)J(J+1)] \quad (5-45)$$

From expression (5-45) hyperfine splitting of energy levels due to nuclear quadrupole effects may be calculated. The magnitude of the quadrupole effects determined by the quadrupole coupling constant eqQ , which involves both the nuclear quadrupole moment Q , and q_J , the second derivative of the potential along the axis of electronic angular momentum. This coupling constant may vary from zero to a few tenths of a wave number, or thousands of megacycles, and of course can be either positive or negative. Evaluation of the quantity q_J will be discussed at some length in Chap. 9. If q_J is known, then determination of the quadrupole coupling constant allows a determination of the nuclear constant Q .

Nuclear Polarizability. Another type of electrostatic interaction is an electric polarization of the nucleus. The strong electrostatic fields due to atomic electrons induce a small electric dipole moment on the nucleus which slightly increases the force of attraction between electron and

nucleus, thus lowering the electronic energy levels by an amount which depends on the nuclear polarizability and the square of the electric field strength.

The nuclear polarizability α_z along the spin axis is not necessarily the same as its polarizability α_x perpendicular to this axis. Hence the energy depends on the orientation of the spin with respect to the electric field. Since the polarizability is a symmetric tensor just as is the quadrupole moment, it is not difficult to show that the energy of polarization has the same dependence on nuclear orientation as that due to a quadrupole moment. Gunther-Mohr, Geschwind, and Townes [583] have given the variation of energy of polarization with angle as

$$W_A = \frac{e}{3} \frac{(\alpha_z - \alpha_x)p_J}{I(2I-1)J(2J-1)} [\frac{3}{4}C(C+1) - I(I+1)J(J+1)] \quad (5-46)$$

This expression is very similar to the energy (5-45) due to a quadrupole moment. Here p_J corresponds to q_J , and is defined in analogy with (5-42) as

$$p_J = \int \rho_{JJ} \frac{3 \cos^2 \theta - 1}{r^4} d\tau = \frac{2}{e} (E_z^2 - E_x^2)_{av} \quad (5-47)$$

The coupling constant $ep_J(\alpha_z - \alpha_x)$ is equivalent to $\frac{3}{2}eq_J Q$, and in many cases these two are experimentally indistinguishable. The difference $\alpha_z - \alpha_x$ in classical polarizabilities can be expressed quantum-mechanically as

$$\alpha_z - \alpha_x = \frac{2I(I+1)}{2I-1} \sum_n \frac{|\mu_{0n}|_{M=I}^2 - |\mu_{0n}|_{M=I-1}^2}{W_n - W_0} \quad (5-48)$$

where $|\mu_{0n}|$ is the z component of the electric dipole matrix element between the ground state of energy W_0 and an excited state of energy W_n . Subscripts $M = I$ and $M = I - 1$ indicate that the matrix elements are states with the projection M of \mathbf{I} on the z direction equal to I and $I - 1$, respectively.

If the nuclear matrix elements and energy levels were known, the polarizabilities could be easily calculated. However, generally only rough magnitudes for these quantities are known. $|\mu_{0n}|$ may be taken approximately equal to one protonic charge times one nuclear radius, and $W_n - W_0$ as 1 Mev to roughly evaluate $\alpha_z - \alpha_x$. The quantity $\alpha_z - \alpha_x$ may also be taken as approximately equal to the nuclear volume. From such estimates and evaluation of p from Hartree wave functions, it may be shown that the anisotropic polarization effects are usually about 1 per cent of the nuclear quadrupole effects, hence generally not larger than a few megacycles. They can be experimentally distinguished from nuclear quadrupole effects only because they depend in a different way on the electron-nuclear distance r . Thus the relative size of quadrupole coupling and polarization energy will be different in different electronic

states. If precision measurements of hyperfine-structure splittings could be made in several electronic states of an atom with two isotopes, the ratio of the splittings for the two isotopes would vary from state to state. Because it is not usually possible to measure precisely the hyperfine structure of excited states, this method is not very practical.

However, in different types of molecules the electronic configuration about a given atom may be quite different. Then if nuclear polarization is appreciable the apparent quadrupole coupling ratio between two isotopes would depend on the molecule in which it is measured. Certain variations in the ratios of quadrupole moments for Cl^{35} and Cl^{37} have been observed but cannot clearly be attributed to nuclear polarizability ([575], [760]).

Magnetic Hyperfine Structure. Another type of hyperfine structure which depends on the nuclear orientation is connected with magnetic interactions between the nucleus and atomic electrons. If the structure of the nucleus and the possibility of having circulating charges within the nucleus is considered, it is not surprising that this magnetic hyperfine structure shows that a magnetic dipole moment μ must be attributed to the nucleus. Each possible orientation of the nuclear spin has a slightly different energy due to interaction between the nuclear magnetic moment and the magnetic field at the nucleus produced by the spins and orbital motions of surrounding electrons.

The electrons precess about their total angular momentum \mathbf{J} so that the currents and magnetic fields must on the average be cylindrically symmetric about the direction of \mathbf{J} , and hence the magnetic field they produce at the nucleus is parallel to \mathbf{J} . For similar reasons the magnetic moment μ_I of the nucleus is parallel to its spin \mathbf{I} . The energy of interaction is $\mu_I H \cos \theta$ or $\mathbf{\mu}_I \cdot \mathbf{H}$, which may be written

$$W = a\mathbf{I} \cdot \mathbf{J} \quad (5-49)$$

since $\mathbf{\mu}_I$ is parallel to \mathbf{I} and \mathbf{H} to \mathbf{J} . The quantity a is a constant for a given electronic state and nucleus, and is known as the interval factor.

The quantity $\mathbf{I} \cdot \mathbf{J}$ involves the cosine of the angle between \mathbf{I} and \mathbf{J} , and can easily be obtained from the vector model [cf. Eq. (5-12)], so that

$$W = \frac{a}{2} [F(F+1) - J(J+1) - I(I+1)] \quad (5-50)$$

where F is the magnitude of the vector $\mathbf{F} = \mathbf{I} + \mathbf{J}$. F may take on the values $I+J, I+J-1, \dots, |I-J|$. The total number of different values of F is $2I+1$ if $I < J$, or otherwise $2J+1$.

If the angular momenta of a number of electrons add up vectorially to a resultant angular momentum of zero, as in the case of a closed shell of electrons, then the average magnetic field at the nucleus is zero. Hence in evaluating the constant a , it is necessary to take into account

only the unfilled shell of electrons, which in many common cases may consist of only one electron, or a closed shell minus one electron. Although a nonrelativistic treatment of the magnetic field H at the nucleus gives a good approximation for hyperfine structure produced by electrons with orbital angular momentum, for s electrons relativistic theory (summarized in [67]) is necessary. Hyperfine structure is particularly important and large for s electrons, since they penetrate most closely to the nucleus.

For non- s electrons (*i.e.*, with $l > 0$) in a hydrogenic atom,

$$a = \frac{2\mu_I\mu_0}{I} \left(\frac{1}{r^3} \right)_{av} \frac{l(l+1)}{j(j+1)} = \frac{g(I)}{1836} \frac{e^2 h^2}{8\pi^2 m^2 c^2} \left(\frac{1}{r^3} \right)_{av} \frac{l(l+1)}{j(j+1)} \quad (5-51)$$

where $g(I)$ is the "nuclear g factor," *i.e.*, the ratio of the nuclear magnetic moment in nuclear magnetons to its angular momentum in units of $h/2\pi$. One nuclear magneton = $h e_P / 4\pi M_P c$, where M_P is the mass of the proton and e_P its charge. Since M_P is 1836 times the mass of the electron, the nuclear magneton is 1836 times smaller than the Bohr magneton.

Substituting the quantum-mechanical value of $\left(\frac{1}{r^3} \right)_{av}$ [Eq. (5-13b)]

$$\begin{aligned} a &= \frac{g(I)}{1836} \frac{R\alpha^2 Z^3}{n^3(l+\frac{1}{2})j(j+1)} \\ &= \frac{g(I)}{1836} \frac{\Delta\nu l(l+1)}{Z(l+\frac{1}{2})j(j+1)} \end{aligned} \quad (5-52)$$

where $\Delta\nu$ is the fine-structure doublet splitting given by Eq. (5-13c).

Expression (5-52) follows either from a nonrelativistic calculation which treats the electrons as point particles with electric charge and a magnetic dipole moment, or from a semirelativistic calculation which neglects the electron's binding energy in comparison with its rest mass. A more exact relativistic treatment [19], [28] gives

$$a = \frac{g(I)}{1836} \frac{\Delta\nu l(l+1)}{Z(l+\frac{1}{2})j(j+1)} \frac{\kappa}{\lambda} \quad (5-53)$$

$$\text{where } \kappa = \frac{4j(j+\frac{1}{2})(j+1)}{(4\rho^2 - 1)\rho}$$

$$\rho = \sqrt{(j+\frac{1}{2})^2 - (\alpha Z_i)^2}$$

$$\lambda = \left[\frac{2l(l+1)}{(\alpha Z_i)^2} \right] \{ [(l+1)^2 - (\alpha Z_i)^2]^{\frac{1}{2}} - 1 - [l^2 - (\alpha Z_i)^2]^{\frac{1}{2}} \}$$

The values of λ and κ are tabulated by Goudsmit [41].

Since ρ depends on j , κ is quite different for $p_{\frac{1}{2}}$ and $p_{\frac{3}{2}}$ states. Thus the relativistic correction makes the constant larger for a $p_{\frac{1}{2}}$ electron than for a $p_{\frac{3}{2}}$ electron. This is because, in a relativistic treatment, spin and orbital angular momentum are not sharply separated. Thus a $p_{\frac{1}{2}}$ electron has some of the character of an $s_{\frac{1}{2}}$ electron (the only other type for which

$j = \frac{1}{2}$). We shall see that an $s_{\frac{1}{2}}$ electron has a large interaction constant. The relativistic theory shows that for an s electron

$$a = \frac{g(I)}{1836} \frac{e^2 h^2}{3\pi m^2 c^2} \psi^2(0) \kappa \quad (5-54)$$

$\psi^2(0)$ is the electron density at the nucleus, or the square of the non-relativistic Schrödinger wave function at $r = 0$, the center of the nucleus. For a hydrogenic atom $\psi^2(0) = Z^3 / \pi a_o^3 n^3$, so that

$$a = \frac{g(I)}{1836} \frac{e^2 h^2 Z^3 \kappa}{3\pi^2 m^2 c^2 a_o^3 n^3} \quad (5-55)$$

$$a = \frac{g(I)}{1836} \frac{8R\alpha^2 Z^3 \kappa}{3n^3} \quad (5-56)$$

It is interesting that this expression for an s electron is just what would be obtained by more or less arbitrarily using expression (5-52) for a and setting $l = 0$, $j = \frac{1}{2}$, assuming the relativistic correction κ is unity.

Interaction between atomic magnetic fields and a nuclear magnetic octupole moment has recently been detected by Jaccarino, King, Satten, and Stroke [942]. A rough estimate of the magnitude of magnetic octupole interaction would indicate that it is smaller than the dipole interaction by the square of the ratio of nuclear radius to the distance between nucleus and electron [cf. discussion of hexadecapole moment above]. However, the magnetic octupole actually gives effects somewhat larger than such an estimate. In the case of atomic I and In the effects are many kilocycles in size and have been detected by molecular beam techniques [942] [953].

General Considerations about the Existence of Nuclear Moments. If a nucleus has spin I , the pole of highest order which can occur is given by $2^{|I|}$. Thus, for $I = 0$, no dipole or quadrupole moment may exist, but only a monopole (charge). If $I = \frac{1}{2}$, a dipole moment may exist, but not a quadrupole moment, which occurs only if $I \geq 1$. This limit to the order of poles which may occur can be proved quite generally, but we shall only attempt an indication of why it occurs. In an external field, a nucleus of spin I can have $2I + 1$ different orientations or states and hence $2I + 1$ different energies. In order to specify these energies completely, only $2I + 1$ different constants of the nucleus need be given. Thus, if $I = 0$, there is no need for more than one constant, the monopole strength or electric charge (no magnetic "charge" exists). If $I = \frac{1}{2}$, two states occur, and one need specify only the monopole and dipole strength. When $I \geq 1$, a quadrupole moment is needed, etc. Additional discussion of this limit can be found in [969a].

Poles of various orders alternate between electric and magnetic type for reasons of symmetry. Thus, as shown above, electric monopoles and quadrupoles exist, but ordinarily electric dipoles do not occur. However, magnetic dipoles and octupoles are permitted.

5-8. Penetrating Orbita. If the state of an electron is not well approximated by a hydrogenlike wave function, as in the cases of valence electrons which penetrate a closed shell of electrons around the nucleus, an exact expression for the interval factor a is very difficult to calculate. However, on the basis of some approximate models, the following expressions for a may be obtained for these cases.

For a non- s electron [41]:

$$a = \frac{g(I)}{1836} \frac{\Delta\nu}{Z_i} \frac{l(l+1)\kappa}{(l+\frac{1}{2})j(j+1)\lambda} \quad (5-57)$$

and for an s electron [40]

$$a = \frac{g(I)}{1836} \frac{8R\alpha^2 Z_i Z_o^2}{3n^{*3}} \kappa \left(1 - \frac{d\sigma}{dn}\right) \quad (5-58)$$

where n^* is the effective principal quantum number and $\sigma = n - n^*$ is the quantum defect. If the energy levels of the atom satisfy a Rydberg-Ritz equation,

$$T = \frac{RZ_o^2}{(n - \alpha - \beta T)^2} \quad (5-59)$$

where α and β are constants, T is the term value, and R is the Rydberg constant, then [359]

$$\frac{d\sigma}{dn} = \frac{\beta}{\beta - n^*/2T} \quad (5-60)$$

In the above equations, for s electrons $Z_i = Z$, the nuclear charge. The equation then works well for elements of medium weight but gives values of a which may be 10 to 20 per cent high for very light or very heavy elements. For heavy elements an additional correction for the finite radius of the nucleus should be made, and with this addition the formula is quite accurate [359].

For p electrons, it is usual to put $Z_i = Z - 4$ in place of Z in (5-52). This works well in the equation for $\Delta\nu$, the fine-structure splitting, but is not so good for hyperfine structure where the average of a different power of Z is involved [cf. [364]]. If the nuclear moment and so $g(I)$ is known, it is also possible to use the observed hyperfine-structure interval factor, a , to evaluate $(1/r^3)_{av}$ [67]. For a non- s electron, from Eq. (5-53), with relativistic corrections,

$$\left(\frac{1}{r^3}\right)_{av} = \frac{1836}{g(I)} \frac{8\pi^2 m^2 c^2}{e^2 h^2} \frac{j(j+1)}{l(l+1)} \frac{\lambda}{\kappa} a \quad (5-61)$$

This value of $(1/r^3)_{av}$ may then be used in evaluation of nuclear quadrupole moments from observed quadrupole coupling energies.

5-9. Zeeman Effects for Atoms. When an atom is placed in a magnetic field, the energy levels undergo a splitting known as the Zeeman

effect (cf. Chap. 11 for Zeeman effects on molecules). It is convenient to distinguish three cases: (a) a weak magnetic field, where this splitting is considerably less than the hyperfine structure, (b) a strong field, where the splitting is much larger than the hyperfine structure, and (c) intermediate fields.

In the weak-field case, the nuclear spin \mathbf{I} remains coupled to the electronic angular momentum \mathbf{J} , and their resultant \mathbf{F} has $2F + 1$ possible values of the component, M_F , along the field direction. Then the energy due to magnetic hyperfine structure and interactions with the magnetic field is [cf. (11-13)]

$$\begin{aligned} W(F, M_F) = & \frac{a}{2} [F(F+1) - I(I+1) - J(J+1)] \\ & - \left\{ \frac{\mu_I}{I} [I(I+1) + F(F+1) - J(J+1)] \right. \\ & \left. + \frac{\mu_J}{J} [F(F+1) + J(J+1) - I(I+1)] \right\} \frac{M_F H}{2F(F+1)} \quad (5-62) \end{aligned}$$

where a is a constant which gives the strength of the magnetic hyperfine structure, μ_I is the nuclear magnetic moment, μ_J the atomic (electron spin and orbital combined) magnetic moment, and H the applied magnetic field.

In a very strong field, I and J interact more strongly with the field than with each other. Then

$$W(I, J, M_I, M_J) = aM_I M_J - \frac{\mu_J}{J} HM_J - \frac{\mu_I}{I} HM_I \quad (5-63)$$

where M_I and M_J are the quantum numbers for the projection of \mathbf{I} and \mathbf{J} , respectively, on H . The intermediate field case is generally more complicated. For the important special case of $J = \frac{1}{2}$ (e.g., hydrogen, the alkalis, silver, gold, indium, thallium) the energies are given by Breit and Rabi [19a]

$$W(F, M_F) = -\frac{\Delta W}{2(2I+1)} - \frac{\mu_I}{I} HM_F \pm \frac{\Delta W}{2} \sqrt{1 + \frac{4M_F}{2I+1} x + x^2} \quad (5-64)$$

where $\Delta W \equiv (a/2)(2I+1) \equiv h \Delta\nu$, and $\Delta\nu$ is the zero-field hyperfine structure splitting

$$x = \frac{(-\mu_J/J + \mu_I/I)}{\Delta W} H$$

Zeeman effects in atoms are often relatively large (several megacycles per gauss). It is then possible to measure transitions between Zeeman components of several hyperfine levels by varying the applied magnetic field until the transitions coincide with a given microwave frequency.

When a resonant cavity spectrograph is employed, this possibility is especially useful.

Beringer and Heald [898] obtained an accurate measurement of the Zeeman splitting in atomic hydrogen, using a frequency near 9500 Mc and a variable magnetic field. The hydrogen was dissociated by a discharge just before passing through the cavity resonator. From their measurements, and the molecular-beam measurement of the zero field hyperfine structure splitting [737a], the electron-spin magnetic moment g factor is found to be $g_s = -2(1.001148 \pm 0.000006)$. The precision of this value was not limited by the microwave spectrum, but by the absolute calibration of magnetic fields in terms of proton resonance frequencies. A similar technique has been applied to the atoms O [739a], N [932a], and P [913b].

5-10. Microwave Studies of Atomic Hyperfine Structure. Since the separations between hyperfine-structure levels often lie in the microwave range, it is possible to use microwaves to induce transitions between these levels. The electric dipole matrix element between these states vanishes because they belong to the same electronic configuration. However, the magnetic dipole matrix element is not zero and it permits the transition to take place. The peak intensity for a transition in which $\Delta F = \pm 1$ is then given by Eq. (1-50), where in this case μ_{ij} is the appropriate matrix element for the magnetic dipole moment of the atom.

The transitions are most likely to be found in the microwave region for an atom in a ${}^2S_{\frac{1}{2}}$ ground state, because the largest number of atoms would occur in the ground state, and a ${}^2S_{\frac{1}{2}}$ state has a relatively large hyperfine structure. In that case, the matrix elements are ([56], pp. 64–72), for $F = I + \frac{1}{2} \leftarrow F = I - \frac{1}{2}$,

$$|\mu_{ij}|^2 = \frac{4[(I + \frac{1}{2})^2 - m_F^2]}{(2I + 1)^2} \mu_0^2 \quad \text{when } \Delta m_F = 0 \quad (5-65)$$

$$|\mu_{ij}|^2 = \frac{2(I + \frac{1}{2} \pm m_F)(I + \frac{3}{2} \pm m_F)}{(2I + 1)^2} \mu_0^2 \quad \text{when } \Delta m_F = \pm 1 \quad (5-66)$$

where m_F = projection of the total angular momentum, F , on a fixed direction

μ_0 = the Bohr magneton, $h/4\pi mc$.

The transitions with $\Delta m_F = \pm 1$ are polarized so that the magnetic vector is perpendicular to the fixed direction and those with $\Delta m_F = 0$ are polarized with the magnetic vector parallel to the fixed direction.

If the above matrix elements are substituted into (1-50) to obtain the absorption coefficient for each component of the transition ($\Delta m_F = 0$, $\Delta m_F = +1$, or $\Delta m_F = -1$), then $Nf/3$ in this formula must be interpreted as the number of atoms in the ground state of each component. In case the atom is in an external magnetic field, each value of m_F has a slightly different energy, and the intensity of individual components is

needed. If, however, there is no external magnetic field for one polarization of the incident radiation, then what is wanted is the average of all transitions for which $\Delta m_F = 0$ or $\Delta m_F = \pm 1$. This average, after multiplication by 3 to obtain the sum of the squares of the dipole matrix elements for all three directions of polarization, is

$$|\mu_{ij}|_{av}^2 = \frac{4(I+1)}{2I+1} \mu_0^2 \quad (5-67)$$

Expression (5-67) is the appropriate quantity to insert in the customary way into (1-50) if Nf is taken to be the fraction of atoms in the state $F = I - \frac{1}{2}$.

The hyperfine structure of the $^2S_{\frac{1}{2}}$ ground state of cesium was investigated by Roberts, Beers, and Hill [405]. In that case, using the notation of Eq. (1-50) and calculating the intensity of the entire transition,

$$Nf = 2.5 \times 10^{14} \text{ atoms/cm}^3 \text{ corresponding to a pressure of } 3 \times 10^{-2}$$

mm

$$T = 500^\circ\text{K}$$

$\Delta\nu = 1.5 \times 10^5$ cycles/sec (estimated roughly from kinetic theory)

$$\nu_0 = 9.2 \times 10^9 \text{ cycles/sec}$$

$$I = \frac{7}{2}$$

$$|\mu_{ij}|_{av}^2 = \frac{2}{3}\mu_0^2$$

so that $\gamma_{\max} = 6 \times 10^{-9} \text{ cm}^{-1}$ for an average component. The cesium was placed in a microwave resonant cavity which was used to control the frequency of a klystron oscillator. The cavity was in a variable magnetic field so that each component could be brought in turn to the resonant frequency of the cavity. As the magnetic field was varied to make a component of the line approach the resonant frequency of the cavity, this resonant frequency was slightly changed by the anomalous dispersion associated with the cesium resonance, and the consequent variation in frequency of the controlled oscillator was detected.

Few other atoms have been investigated by microwave absorption spectroscopy because of the relatively weak absorptions and the difficulty of obtaining many materials in atomic form. However, Shimoda and Nishikawa [642] obtained a measurement of transitions between hyperfine components of Na^{23} at 1772 Mc. Hyperfine interactions in H [737a], N [932a], and P [913b] have been obtained from microwave transitions between Zeeman components (see Sec. 5.9). A large number of atoms have been investigated by molecular-beam techniques (see [969a]), which are particularly suited for this purpose.

5-11. Microwave Spectra from Astronomical Sources. Microwave radiation due to transitions between the hyperfine components of atomic hydrogen in interstellar space was first detected by Ewen and Purcell [571] and independently discovered by Muller and Oort [621]. This radiation has a wavelength near 21 cm and penetrates the earth's ionosphere and gas and dust particles in interstellar space rather readily.

The frequency corresponding to the transition between hyperfine components of hydrogen has been measured in the laboratory as 1420.405 Mc [737a]. Near this frequency, hydrogen gas has a large enough absorption coefficient to be opaque for certain directions through our own galaxy, the Milky Way. Hence it also radiates an intensity corresponding to a black body at about 100°K , which is the effective temperature for the hyperfine levels of H in interstellar space.

In interstellar space, hydrogen atoms occur with a density near 1 atom/cm³, or a pressure of less than 10^{-19} atm. Since a collision between atoms is very rare, occurring only once in a number of years, the dominating source of broadening is the Doppler effect. The various parts of the Milky Way have random velocities as large as about $\pm 10 \text{ km/sec}$ with respect to each other so that the Doppler effect gives a line-width parameter $\Delta\nu$ of about $\frac{\nu}{3 \times 10^4}$, or 50 kc, for $\nu = 1420 \text{ Mc}$.

The total amount of power received by an antenna from the radiation by interstellar hydrogen is approximately $kT\Delta\nu$, where T is the temperature 100°K , and $\Delta\nu$ the line width of 50 kc. This amounts to slightly less than 10^{-16} watt but is enough to give a signal which is a few hundred times background noise in a carefully constructed radiometer of the type described in Chap. 15.

If the temperature of an object is measured by the intensity of radiation at a given frequency, the apparent temperature is given by

$$T = T_o(1 - e^{-\gamma L}) \quad (5-68)$$

where T_o = temperature of the object

L = thickness of the object

γ = absorption coefficient at the frequency of measurement

For an opaque object, $T = T_o$. For less opaque material the apparent temperature T of emission is reduced. It must be at least as large as about 1° for an emission line to be detectable. Temperature changes which are this small correspond to observation of a gas which is almost transparent, that is, $\gamma L \ll 1$. In this case the observed temperature is, from (5-68),

$$T \approx T_o \gamma L \quad (5-69)$$

Now the absorption coefficient γ for a gas is given by Eq. (1-50). For the ground atomic state of hydrogen, $f = 1$ and μ is approximately one Bohr magneton, since the transition involves a magnetic rather than an electric dipole moment. Inserting values of the constants, expression (5-69) becomes

$$T \approx 5 \times 10^{-19} \frac{NL}{\lambda} \quad (5-70)$$

Here $\nu/\Delta\nu = 3 \times 10^4$ due to Doppler effect has been used and λ is the wavelength. For a temperature change as large as 1°C , the number of molecules NL which must be in the path of observation is

$$NL = 2 \times 10^{18}\lambda \quad (5-71)$$

Since the longest dimension of the Milky Way is approximately 10^{23} cm, an interstellar gas must have a density as high as about $N = 2 \times 10^{-5}\lambda$ to be detected by microwave emission if the transition involved is due to a magnetic dipole moment. Since hydrogen has a density of approximately 1 atom/cm³ in interstellar space, its radiation is clearly observable. In fact, in this case γL is larger than unity in most directions through our galaxy, and the galaxy is opaque at the center of the hydrogen line. On the other hand, deuterium would be very difficult to observe, since it probably has a density of only 10^{-3} or 10^{-4} atom/cm³, and the transition between hyperfine levels falls at longer wavelengths.

If the transition is due to an electric dipole moment, then the dipole matrix element is approximately 1 debye, which is 100 times larger than the matrix element due to a magnetic dipole transition, and the minimum observable density of interstellar gas would be approximately

$$N = 2 \times 10^{-9}\lambda$$

A few molecules with dipole moments, such as the radical OH, are thought to have densities as high as $N = 10^{-6}$, and hence their spectra may possibly be observed.

Transitions between several other hyperfine levels in atoms may eventually be observed from astronomical objects. The hyperfine structure of N¹⁴ in several states of ionization may be sufficiently intense for observation since the density of nitrogen in interstellar gas is approximately 10^{-3} atom/cm³. However, frequencies for the hyperfine structure of N¹⁴ are known experimentally only for the ground state of the neutral atom. The hyperfine structure of N¹⁴ in high states of ionization may possibly also be observed in the sun's atmosphere.

The microwave line emitted by interstellar hydrogen has been particularly valuable for astronomy. For example, its observation has shown that, in certain directions through our galaxy, there are several strips of gas each moving systematically at velocities appropriate to the successive arms of a rotating spiral nebula. This seems to give the clearest evidence so far available that our galaxy is a spiral nebula.

CHAPTER 6

QUADRUPOLE HYPERFINE STRUCTURE IN MOLECULES

6-1. Introduction. In most atoms, the predominant hyperfine structure is due to interaction between a nuclear magnetic moment and magnetic fields of the atomic electrons. Effects of a nuclear quadrupole moment are smaller and give small deviations from the expected magnetic hyperfine intervals. However, for most molecules in the ground state, the magnetic fields due to various electrons almost completely cancel, giving zero or only very small magnetic fields at the nucleus. Electric quadrupole effects in molecules may still be sizable, however, and they become the dominating source of hyperfine structure.

The cancellation of magnetic fields in molecules due to electronic motions is simply because the electrons are paired; *i.e.*, for each electron with an angular momentum and hence magnetic field, there is another electron in a similar state but with oppositely directed angular momentum. The net electronic angular momentum for the electrons in the ground state of most molecules is indicated by the spectroscopic term ${}^1\Sigma_0$, which signifies that the net electronic spin and orbital angular momentum are both zero. It is not surprising that electronic momenta are paired off in a molecule if the nature of molecular bonds is considered. Generally an atom forms chemical bonds with each of its unpaired electrons, each one pairing with an electron from another atom in the molecule to give a net zero angular momentum. For the rare molecules such as NO, ClO₂ and NO₂ having an odd number of electrons, a complete pairing of electron spins is impossible. These molecules are hence paramagnetic and have large magnetic hyperfine structures. There are in addition a few cases of molecules having an even number of electrons in which the chemical bonds are unusual and the electron spins are not paired. The most notable example of this case is O₂, which is in a ${}^3\Sigma_1$ state, having two parallel electron spins.

For the overwhelming majority of molecules, however, magnetic hyperfine effects are extremely small, and it is electric quadrupole hyperfine structure that is evident when molecular spectra are examined with high resolution.

The discussion given in the preceding chapter of interaction between a nuclear electric quadrupole moment and a surrounding charge distribution is of course as valid for a molecular system as for an atomic system