Zeeman Splitting of Nuclear Quadrupole Resonances*

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The theory of the Zeeman splitting of the pure quadrupole energy levels for nuclei of half-integral spin is given in a form that is correct for any electric field gradient. The splitting of the spectra is discussed, and also the simplifications that can be made in the theory when the magnetic field is parallel to any of the three principal axes of the electric field gradient. For spin 3/2 it is shown that the deviation of the gradient from cylindrical symmetry can be determined from the Zeeman spectrum, and detailed calculations are given for this case, along with a discussion of their experimental application.

WHEN there is a strong electric quadrupole coupling between a nuclear species and the gradients of the electric fields at those nuclei due to nearby charges, and when the sample is a crystalline solid so that the average field gradients are constant in time and are the same at equivalent nuclei throughout the sample, we can observe the spectra corresponding to transitions of this species of nucleus between the various energy levels specified by that coupling ("pure quadrupole resonances").[1,2] Since the gradient of the electric field at a given nucleus is produced primarily by the valence electrons belonging to that atom, the details of these resonances provide important information about the way in which the atoms are bound in the solid.[3]

If a homogeneous external magnetic field is applied to such a solid, it will interact with the magnetic dipole moments of the nuclei that we are considering and thereby introduce an additional coupling.[1,4,5] In this paper we shall be concerned with the effect of this additional coupling for small magnetic fields (Zeeman region), in which case each resonance line for a given nucleus is split into either two or four components. The splitting depends on the orientation of the magnetic field with respect to the electric field gradient at that nucleus. In a polycrystalline sample the result is to smear the resonance over a band of frequencies, since there are in effect all possible relative orientations present. However if the sample is a single crystal, we should observe at most as many different Zeeman spectra as there are sites for that species of nucleus in the unit cell. An analysis of such a spectrum for selected magnetic field orientations will determine the orientation of the electric field gradient at each nucleus of the given species, and give additional data on the structure of the sample.[6]

The theory of the Zeeman effect is complicated by the twofold degeneracy of the pure quadrupole energy levels, the complications being most severe for the cases of nuclei of half-integral spin. Calculations for the latter cases have been published for electric field gradients with cylindrical symmetry and for those whose deviation from cylindrical symmetry is small enough to be handled satisfactorily by perturbation theory.[4,5] In the theory given here the magnetic field is again treated only to first order, but the asymmetry of the electric field gradient is treated exactly.

From experimental work[6] it appears that one of the major tasks of the theory is to provide some means of visualizing as a whole all possible cases of Zeeman splitting for a given quadrupole resonance line, since then it is a simple task of recognition to identify approximately the orientation and properties of each electric field gradient from a fairly cursory examination of the splittings due to a sequence of magnetic field orientations. The general form of the Zeeman splitting of the energy levels is given in C, together with a consideration of methods for abbreviating the specific calculations that are required for any one set of electric field gradient parameters. In applying these calculations it is very helpful to plot contours of constant Zeeman splitting of the energy levels, the stereographic net being an excellent chart for this purpose. The contours of constant splitting of the α and β components of the spectra can be obtained from these by graphical addition and subtraction. From such contours for the two extreme cases alone ($\eta=0$ and $\eta=1$) it is possible to get a good part of the over-all picture that is desired.

The case of nuclei of spin $\frac{3}{2}$ is unique in that the two parameters that characterize the electric field gradient cannot be separately determined from the pure quadrupole spectrum alone. However a complete analysis can be made from the Zeeman spectrum, and in section E we consider the theory for this case in detail.

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A. THE QUADRUPOLE EIGENSTATES

The Hamiltonian for the interaction between the electric quadrupole moment of a nucleus and the charges surrounding the nucleus has been derived elsewhere.[1,5] In this Hamiltonian the effect of the surrounding charges is expressed in terms of the symmetric tensor composed of the second derivatives of the electrostatic potential that they produce at the nucleus, $V_{x_ix_j}=\partial^2V/\partial x_i\partial x_j$. Only that part of the potential that is generated by charges outside of the nucleus is involved; hence Laplace's equation holds and $V_{xx}+V_{yy}=-V_{zz}$. We consider here only those coordinate systems in which the tensor is diagonal. We define the principal coordinate system by requiring that $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$, and we introduce the quantities $eq\equiv V_{zz}$ and $\eta\equiv(V_{xx}-V_{yy})/V_{zz}$. In the principal coordinate system we have $0\leq\eta\leq1$, and η is a measure of the deviation of the tensor from cylindrical symmetry around the z axis.

The principal coordinate system is uniquely defined by this convention except in the case $\eta=0$, in which the distinction between the x and the y axes disappears, and in the case $\eta=1$. In the latter case we have $V_{xx}=0$ and $V_{zz}=-V_{yy}$, and it is apparent that by interchanging the z and the y axes and reversing the sign of eq we obtain a new coordinate system which also satisfies our definition of the principal coordinate system; here it is the x axis that is unique.

With the electric field gradient expressed in this manner, the nonzero matrix elements of the Hamiltonian for the quadrupole interaction are

$$(m_z|\,\mathcal{H}_e|\,m_z)=A[3m_z^2-I(I+1)],$$
$$(m_z\pm2|\,\mathcal{H}_e|\,m_z)=A(\eta/2)f_I(\pm m_z)f_I(1\pm m_z),$$

where

$$f_I(m)=f_I(-m-1)=[(I-m)(I+m+1)]^{\frac{1}{2}},$$
$$A=[e^2qQ/4I(2I-1)], \tag{1}$$

and where I is the spin of the nucleus and m_z is the component of spin along the z axis of the principal coordinate system of the electric field gradient. The quantity eQ is the electric quadrupole moment of the nucleus, defined by $eQ\equiv\langle\rho(3z^2-r^2)\rangle_{\text{Av}}$, in which ρ is the charge density of the nucleus and z and r describe the locations of the elements of charge density that are incorporated into the average; the averaging is performed for the nuclear state $m=I$.

This Hamiltonian links only alternate spin states. For the case of half-integral spins with which this paper deals it is readily seen that the two independent submatrices which can be identified are identical except for a reversal of the signs of m involved, and it can be seen that this reversal of sign does not change the matrix elements. It follows that the twofold degenerate energy eigenstates can be divided into two groups which involve identical sets of transformation coefficients and energy levels, $E_{m'}{}^0$:

$$A_{m'}=(1/2|\,m')\psi_{\frac{1}{2}}+(3/2|\,m')\psi_{-\frac{1}{2}}+(5/2|\,m')\psi_{\frac{3}{2}}+\cdots,$$
$$B_{m'}=(1/2|\,m')\psi_{-\frac{1}{2}}+(3/2|\,m')\psi_{\frac{3}{2}}+(5/2|\,m')\psi_{-\frac{3}{2}}+\cdots. \tag{2}$$

The number m' is taken as the value of $|m|$ that applies to the state as $\eta\rightarrow0$.

The above formulation is generally chosen in these problems because of the resulting simplicity of the case $\eta=0$. However the form of the Hamiltonian matrix is unchanged if we use as a basis the states $\psi(I,m_x)$ or $\psi(I,m_y)$ instead of the set $\psi(I,m_z)$. We choose the phase relations between the sets of spin eigenfunctions to correspond to cyclic permutations of the x, y, and z axes, and we introduce the quantities F and G, in which we retain the parameters eq and η to describe the electric field gradient:

$$\begin{aligned} F_x&=-\tfrac{1}{2}A(1-\eta), & G_x&=-\tfrac{1}{4}A(3+\eta),\\ F_y&=-\tfrac{1}{2}A(1-\eta), & G_y&=+\tfrac{1}{4}A(3-\eta),\\ F_z&=A, & G_z&=\tfrac{1}{2}A\eta. \end{aligned} \tag{3}$$

With this notation the Hamiltonian matrix elements for all three cases can be written

$$(m_i|\,\mathcal{H}_e|\,m_i)=F_i[3m_i^2-I(I+1)],$$
$$(m_i\pm2|\,\mathcal{H}_e|\,m_i)=G_if_I(\pm m_i)f_I(1\pm m_i), \tag{4}$$

in which $i=x$, y, or z denotes the chosen axis of spin quantization. Since the form of the Hamiltonian is the same in each of these formulations, a choice of eigenstates can be made for each with the form given in (2), these alternative sets of states being different linear combinations of the twofold degenerate levels.

The nuclear quadrupole resonances that are observed are all due to magnetic dipole transitions, since it is impossible to produce rf electric fields with gradients at the nuclei that are strong enough to cause appreciable transition probabilities. For $\eta=0$ we observe only the transitions with $\Delta m=\pm1$, which are produced by rf fields in the xy plane. However, because of the mixing of the spin states, we must consider other $\Delta m'$ values and all orientations of the rf field for large values of η. We shall not discuss the pure quadrupole spectra further except for the case $I=\frac{3}{2}$, which is treated in Sec. E. In the remainder of this paper we deal with the splitting of the individual lines of these spectra which is produced by a magnetic field.

We note at this point that the values of the two electric field gradient parameters can be evaluated separately from experimental pure quadrupole spectra for all values of nuclear spin except $\frac{3}{2}$. The coefficients of the secular equation for either submatrix of the Hamiltonian provide $(I+\frac{1}{2})$ equations relating the $(I+\frac{3}{2})$ unknowns, $E_{m'}{}^0$ and η. For $I\geq5/2$ there are two or more pure quadrupole resonance frequencies; the ratios of pairs of these frequencies can be equated to the proper ratios of differences between energy levels, and with these additional relations the unknowns can be evaluated to any desired accuracy. In contrast to

these cases, that of $I=\frac{3}{2}$ provides only a single experimental datum, and the complete analysis is impossible.

B. THE ZEEMAN PERTURBATION

If a magnetic field is applied to the system that we have been discussing, the interaction between it and the magnetic dipole moment of the nucleus must be added to the Hamiltonian.[4,5,7] These additional matrix elements can be written

$$\begin{aligned}(m_z|\,\mathcal{H}_m|\,m_z)&=2m_z\xi\cos\theta,\\ (m_z+1|\,\mathcal{H}_m|\,m_z)&=\xi\sin\theta e^{-i\phi}f_I(m_z),\\ \xi&=(\gamma\hbar H/2),\end{aligned}\tag{5}$$

where H is the magnitude of the magnetic field and θ and ϕ are its orientation expressed in polar coordinates that are based on the principal coordinate system, $f_I(m)$ is the function defined in (1), and γ is the gyromagnetic ratio of the nucleus. The magnetic coupling is assumed to be small compared to the quadrupole energies.

We review first the results when the electric field gradient has cylindrical symmetry.[4,8] The states $\psi(I,m_z)$ are correct to first order for $|m|\neq\frac{1}{2}$, but the submatrix $m_z=\frac{1}{2}$, $-\frac{1}{2}$ must be diagonalized for the remaining pair of levels. The energies are

$$\begin{aligned}E_m&=A[3m^2-I(I+1)]\pm 2m\xi\cos\theta,\quad |m|\neq\tfrac{1}{2}\\ E_{\frac{1}{2}\pm}&=A[\tfrac{3}{4}-I(I+1)]\pm\xi[(I+\tfrac{1}{2})^2\sin^2\theta+\cos^2\theta]^{\frac{1}{2}}.\end{aligned}\tag{6}$$

The required mixtures of the $\frac{1}{2}$, $-\frac{1}{2}$ states are given by

$$\begin{aligned}E_{\frac{1}{2}+}:&\quad(\tfrac{1}{2}|+)=\cos\Theta e^{-i\phi/2},\\ &\quad(-\tfrac{1}{2}|+)=\sin\Theta e^{i\phi/2};\\ E_{\frac{1}{2}-}:&\quad(\tfrac{1}{2}|-)=\sin\Theta e^{-i\phi/2},\\ &\quad(-\tfrac{1}{2}|-)=-\cos\Theta e^{i\phi/2};\\ &\tan(2\Theta)=(I+\tfrac{1}{2})\tan\theta.\end{aligned}\tag{7}$$

The specification of Θ in terms of θ comes from the requirement that the matrix element connecting the new states be zero.

For the general case it is necessary to investigate the mixing of each degenerate pair of states $A_{m'}$, $B_{m'}$. We start from the expressions (2) for the exact pure quadrupole states. By definition $\mathcal{H}_e$ is diagonal in this system, with eigenvalues $E_{m'}{}^0$ which can be calculated when necessary from (1). The transformed matrix elements of the magnetic interaction (5) which we need are

$$\begin{aligned}(A_{m'}|\,\mathcal{H}_m|\,A_{m'})&=-(B_{m'}|\,\mathcal{H}_m|\,B_{m'})=\xi a_{m'}\cos\theta,\\ (A_{m'}|\,\mathcal{H}_m|\,B_{m'})&=\xi\sin\theta(b_{m'}e^{-i\phi}+c_{m'}e^{i\phi}),\end{aligned}\tag{8}$$

in which we use the Zeeman parameters a, b, c defined by

$$\begin{aligned}a_{m'}&=[(1/2|\,m')^2-3(3/2|\,m')^2+5(5/2|\,m')^2-\cdots],\\ b_{m'}&=(I+1/2)(1/2|\,m')^2+2f_I(3/2)(3/2|\,m')(5/2|\,m')\\ &\quad+2f_I(7/2)(7/2|\,m')(9/2|\,m')+\cdots,\\ c_{m'}&=2f_I(1/2)(1/2|\,m')(3/2|\,m')\\ &\quad+2f_I(5/2)(5/2|\,m')(7/2|\,m')+\cdots.\end{aligned}\tag{9}$$

[7] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
[8] B. Feld and W. E. Lamb, Phys. Rev. **67**, 15 (1945).

The quadratic secular equations arising from each such pair of states yield the Zeeman energy levels for the general case:

$$E_{m'\pm}=E_{m'}{}^0\pm\xi[a_{m'}{}^2\cos^2\theta+(b_{m'}{}^2+c_{m'}{}^2+2b_{m'}c_{m'}\cos2\phi)\sin^2\theta]^{\frac{1}{2}}.\tag{10}$$

The Zeeman parameters are defined above in terms of the pure quadrupole transformation coefficients. However they may also be evaluated in part from the terms linear in ξ which occur in expansions of the special solutions for a magnetic field parallel in turn to each of the three major axes. For these orientations (10) becomes

$$E_{m'\pm}=E_{m'}{}^0\pm\begin{cases}\xi|\,a_{m'}|&H\|z\\ \xi|\,b_{m'}+c_{m'}|&H\|x.\\ \xi|\,b_{m'}-c_{m'}|&H\|y\end{cases}\tag{11}$$

The required terms are just the derivatives $(\partial E/\partial\xi)_{\xi=0}$, and exact formulas for them may be found by implicit differentiation of the secular equations for the three special cases. The only limitation on the accuracy of the results in this method is the accuracy of the energy values $E_{m'}{}^0$ that are subsequently inserted in the formulas.

The degeneracy of the quadrupole interaction is easily dealt with in the three special cases needed above, for in each case the complete Hamiltonian can again be split into two independent parts neither of which is itself degenerate. In one method of doing this we choose the axis of spin quantization in (4) to be the one parallel to the magnetic field; adding the proper magnetic elements for these states we obtain

$$\begin{aligned}(m_i|\,\mathcal{H}_e+\mathcal{H}_m|\,m_i)&=F_i[3m_i{}^2-I(I+1)]+2\xi m_i,\\ (m_i\pm2|\,\mathcal{H}_e+\mathcal{H}_m|\,m_i)&=G_if_I(\pm m_i)f_I(1\pm m_i),\end{aligned}\tag{12}$$

in which $i=x$, y, or z, according to the direction of the magnetic field. Although this method of handling the case $H\|x$ or y is useful in dealing with arbitrary values of η, it is not suitable for perturbation calculations even when η is small, since the off-diagonal quadrupole elements are the same order of magnitude as the diagonal ones.

In an alternate procedure for the case $H\|x$ we use the sum and difference states,

$$\psi_{m\pm}=2^{-\frac{1}{2}}[\psi(I,m_z)\pm\psi(I,-m_z)],\quad m_z=\tfrac{1}{2},\tfrac{3}{2},\cdots I.$$

The Hamiltonian elements for this case then become

$$\begin{aligned}(m_\pm\|m_\pm)&=A[3m^2-I(I+1)]\pm\delta_{m,\frac{1}{2}}\xi f_I(-\tfrac{1}{2}),\\ ((m+1)_\pm\|m_\pm)&=\pm\delta_{m,\frac{1}{2}}A(\eta/2)f_I(-\tfrac{1}{2})f_I(\tfrac{1}{2})+\xi f_I(m),\\ ((m+2)_\pm\|m_\pm)&=A(\eta/2)f_I(m)f_I(m+1).\end{aligned}\tag{13}$$

Since the sum and difference states are correct for $\eta=0$, this formulation is useful for perturbation calculations.

For $H\|y$ apparently we should rotate the sum and difference states 90° about the z axis. However the only distinction between the x and y axes is that $|V_{xx}|$

$\leq |V|_{vv}$ or, equivalently, that $\eta \geq 0$. Therefore the transformation is accomplished in effect by changing the sign of η wherever it occurs. Similar sum and difference states can also be constructed from the bases $\psi(m_x)$ or $\psi(m_y)$ to provide independent nondegenerate submatrices for magnetic fields parallel to the other pairs of the coordinate axes. These states, however, are not useful for perturbation calculations, and they hold no advantage over the simple spin states for the work that we are considering here.

As an illustration we calculate the Zeeman parameters to the first power of η. We take the energies to second order from Eqs. (13) for $H\|x$; we reverse the sign of η in this result to obtain the case $H\|y$; we use the diagonal elements from (12) with $i=z$ for $H\|z$; from these expressions we identify the Zeeman parameters according to the prescription in (11). We find (see Bersohn's results, reference 5)

$$\begin{gathered} a_{m'}=2m', \\ b_{\frac{1}{2}'}=(I+\tfrac{1}{2}), \quad b_{m'}=0 \quad \text{for } m'>\tfrac{1}{2}, \\ c_{\frac{1}{2}'}=-c_{\frac{3}{2}'}=-(I-\tfrac{1}{2})(I+\tfrac{1}{2})(I+\tfrac{3}{2})(\eta/6), \\ c_{m'}=0 \quad \text{for } m'>\tfrac{3}{2}. \end{gathered} \tag{14}$$

C. THE ZEEMAN SPECTRUM

From the general formulation of the energy levels given above, we can see that the dependence of the Zeeman splitting of the spectrum on the orientation of the magnetic field is formally the same for every quadrupole resonance. For the transition $m_1' \leftrightarrow m_2'$, we have

$$\nu=\nu_0 \pm (\xi/h)([m_1']\pm[m_2']), \tag{15}$$

where ν_0 is the appropriate unperturbed frequency and

$$[m]\equiv+[a_m{}^2\cos^2\theta+(b_m{}^2+c_m{}^2+2b_mc_m\cos 2\phi)\sin^2\theta]^{\frac{1}{2}}.$$

We label the pair with the smaller splitting, i.e., with $([m_1']-[m_2'])$, the α components, and the other pair the β components. Additional resonances are possible here, corresponding to the transitions $A_{m'} \leftrightarrow B_{m'}$,[1] but for small magnetic fields they would occur at very low frequencies. They will not be discussed in this paper.

The total intensity of the four components of the Zeeman multiplet is that of the corresponding unsplit pure quadrupole resonance. For the case $\eta=0$, the relative intensities of these four components are easily derived from the approximate states given in (7, 8). Only rf magnetic fields in the xy plane are effective. For transitions between levels with $|m| \neq \frac{1}{2}$ only the α components can be observed, with intensities that are equal and that do not depend on the orientation of the Zeeman field. On the other hand, the mixing of the states $m=\pm\frac{1}{2}$ means that the single pure quadrupole line corresponding to transitions between the states $|m|=\frac{1}{2}, \frac{3}{2}$ splits into four components whose intensities do depend on the orientation of the Zeeman field, according to the rules

$$\begin{aligned} &\alpha\colon \quad W(\tfrac{3}{2},\tfrac{1}{2}+) \doteq W(-\tfrac{3}{2},\tfrac{1}{2}-) \sim \cos^2\Theta, \\ &\beta\colon \quad W(\tfrac{3}{2},\tfrac{1}{2}-) \doteq W(-\tfrac{3}{2},\tfrac{1}{2}+) \sim \sin^2\Theta. \end{aligned} \tag{16}$$

Because of the general mixing of states by the asymmetry and by the Zeeman field, both the α and the β components may be observable for each pure quadrupole line when η is large. Although we shall not attempt a detailed discussion of relative intensities here, we shall set up the machinery for obtaining certain useful selection rules. We consider the set of nine cases: Zeeman field (H_0) parallel to x, y, or z, together with the rf field (H_1) parallel to x, y, or z. For $H_0\|z$ we imagine the states $\psi(I,m_z)$ arrayed in such a fashion that the submatrix containing the A states of equation (2) is grouped separately from the one with the B states.

In this diagram we consider the locations of the nonzero elements of I_x, I_y, and I_z, whose squares are proportional to the transition probabilities for H_1 parallel in turn to x, y, and z. For selection rules we find that $H_1\|z$ can at most cause transitions between states lying within the same submatrix (transitions which we designate together as $[AA]$), while $H_1\|x$ or y can at most cause transitions for which one state is in A and the other is in B (designated $[AB]$). For $H_0\|x$ or y we use the states $\psi(I,m_x)$ or $\psi(I,m_y)$; the above arguments can be duplicated step by step, and for the selection rules we permute cyclically the names x, y, and z.

These qualitative results are quite general, holding for any relative strength of the dipole and the quadrupole couplings and for any value of the parameter η. For the Zeeman region it is apparent that in these particular cases we shall observe at most either the α components alone or the β components alone.

For a few quadrupole transitions it can be readily determined which of the pairs of components, α or β, is represented by $[AA]$ and by $[AB]$, respectively. In the case $H_0\|z$ with η small, it can be seen from (6) that for transitions between quadrupole states in which $\Delta m'$ is odd, $[AA]$ and $[AB]$ correspond, respectively, to the β and the α Zeeman components, while for the transitions with $\Delta m'$ even the situation is reversed.

Because the levels $m'>\frac{3}{2}$ are unsplit by a Zeeman field parallel to x or y in the second order calculation we cannot so readily investigate the general selection rules for the α and β components except for the transitions $\frac{1}{2}' \leftrightarrow \frac{3}{2}'$. The submatrices of the sum and difference states of (13) are equivalent to the A and B submatrices based on $\psi(I,m_x)$; therefore, we may use second-order energies to show that, for the transitions $\frac{1}{2}' \leftrightarrow \frac{3}{2}'$ with $H_0\|x$, the $[AA]$ pair comprise the α components while the $[AB]$ pair are the β components. For $H_0\|y$ these identifications are reversed.

Although the above identifications were derived on the basis of small η, an intuitive argument leads us to accept them tentatively for all values of η. We have seen by a rigorous argument that only one pair of

Zeeman components can be seen in any of these cases. If we then assume that our various results are continuous functions of the parameter η, we find that a given one of the identifications that we have made for small η can be reversed only for values of η at which either the intensity of the quadrupole resonance becomes zero or the α and the β components coalesce.

It is of interest to note finally that the nuclear induction apparatus of Bloch *et al.*[9] can detect the Zeeman-split quadrupole resonances although it cannot detect the unsplit pure quadrupole lines. In such a spectrometer the transmitter coil bathes the sample in a linearly polarized rf magnetic field. The receiver coil in the apparatus views this field as the sum of two fields with opposite senses of circular polarization, and the essential experimental question which it answers is whether at any given frequency one circular component interacts more strongly with the sample than does the other. In the pure quadrupole resonances both senses of circular polarization are treated alike by the sample, mainly because of the $\pm m$ degeneracy of the system. The Zeeman splitting lifts this degeneracy, and it can be shown that certain of the Zeeman components should be detected by the nuclear induction equipment if the numerous orientations involved in the experiment are favorable.

D. REMARKS ON $\eta=1$

In applying the foregoing theory to obtain an over-all picture of the solutions for a given value of nuclear spin we would desire at least the particular solutions for the end points of the range $0\leq\eta\leq1$. The point $\eta=0$ is easily treated, and nearby values of η can be handled satisfactorily by perturbation theory. We now point out briefly the properties of the problem for $\eta=1$ which simplify the other set of calculations.

(a) The calculation of the energy levels of the quadrupole system involves in general the solution of a secular equation for the $E_{m'}{}^0$ whose order is $(I+\frac{1}{2})$. However for $\eta=1$ it can be shown[6] that the energy levels are symmetric around the value $E=0$, and that the secular equation can be reduced to one involving only powers of $(E_{m'}{}^0)^2$, with an additional single root $E_{m'}{}^0=0$ factored out in those cases where there is an uneven number of values of $|m|$. This situation can be understood on physical grounds by recalling that here we have $V_{xx}=0$ and $V_{yy}=-V_{zz}$. This case can therefore be considered either as the limit of the case where $V_{zz}=eq$ and $-(eq/2)\geq V_{yy}\geq-eq$ (as we do in the principal coordinate system), or as the limit of the case where $V_{yy}=eq'=-eq$ and $-(eq'/2)\geq V_{zz}\geq-eq'$ (as we would in the alternate coordinate system that satisfies our definition of a principal coordinate system in this one case). Because of this the set of energy eigenvalues for $V_{yy}=-V_{zz}$ must be unchanged by a reversal of the sign of the energy unit, e^2qQ.

[9] Bloch, Hansen, and Packard, Phys. Rev. **70**, 474 (1946).

(b) Let us consider the extended range $0\leq\eta\leq3$. An inspection of the defining equation $\eta=(V_{xx}-V_{yy})/V_{zz}$ shows that, whereas $\eta=0$ signifies cylindrical symmetry around the z axis, $\eta=3$ signifies it around the y axis, and the preceding paragraph shows that $\eta=1$ can be considered as the midpoint of the transition from one symmetry case to the other.

From (a) and (b) we can see that the Zeeman splitting of the state $m'=\frac{1}{2}+k$ as a function of the direction of the magnetic field when $\eta=1$ must be the same function as the splitting of the state $m'=I-k$ except for a rotation of 90° around the x axis. Similar relations hold for such functions as the Zeeman splitting of the spectrum and the transition probabilities as functions of the Zeeman and the rf magnetic fields. Also we note that the variations of these functions as η passes through the value 1 must be such as to match the appropriate alternate functions that are based on the rotated coordinate system, providing proper account is taken of the unsymmetrical way in which η describes the two sides of the point $\eta=1$.

E. DETAILS FOR $I=3/2$

Here much of the basic computation can be performed exactly. We begin by listing the principal results for the energy levels in terms of the usual parameter, η. In this case the secular equations from (4) are quadratic, and the exact energy levels are

$$\begin{aligned}&E=-\xi\pm E_0[1+4(\xi^2-\xi F)/E_0{}^2]^{\frac{1}{2}},\quad\text{(states }A\text{)}\\&E=+\xi\pm E_0[1+4(\xi^2+\xi F)/E_0{}^2]^{\frac{1}{2}},\quad\text{(states }B\text{)}\\&E_0=F^2+(4G/3)=A(1+\tfrac{1}{3}\eta^2)^{\frac{1}{2}}.\end{aligned}\tag{17}$$

Identifying the states by the limiting values of $|m_z|$ as η, $\xi\rightarrow0$, we find the approximate energies for small value of ξ to be

$$\begin{aligned}E_{\frac{3}{2}'}&=E_0\pm(1+2F/E_0)\xi,\\E_{\frac{1}{2}'}&=-E_0\pm(1-2F/E_0)\xi,\end{aligned}\tag{18}$$

Inserting in turn the proper values for F_i, we find the Zeeman parameters from (18) and (11):

$$\begin{aligned}&a_{\frac{3}{2}'}=-1-2/\rho,\quad a_{\frac{1}{2}'}=-1+2/\rho,\\&b_{\frac{3}{2}'}=1-1/\rho,\quad b_{\frac{1}{2}'}=1+1/\rho,\\&c_{\frac{3}{2}'}=\eta/\rho,\quad c_{\frac{1}{2}'}=-\eta/\rho,\\&\rho=(1+\tfrac{1}{3}\eta^2)^{\frac{1}{2}}.\end{aligned}\tag{19}$$

The energy levels for any value of η and correct to first order in the magnetic field are now given by

$$\begin{aligned}&E_{\frac{3}{2}'\pm}=E_0\pm\xi[\tfrac{3}{2}'],\quad E_{\frac{1}{2}'\pm}=-E_0\pm\xi[\tfrac{1}{2}'],\\&[m]\equiv[a_m{}^2\cos^2\theta+(b_m{}^2+c_m{}^2+2b_mc_m\cos2\phi)\sin^2\theta]^{\frac{1}{2}}.\end{aligned}\tag{20}$$

It can be seen that the radical $[m]$ multiplying ξ does not vanish for any values of (θ,ϕ) except in the singular case $\eta=0$ for which $[3/2]$ is zero along the locus $\theta=90°$.

An alternate formulation of this problem yields simple expressions for the eigenstates and the matrix

elements required for dipole transition probabilities. We write the pure quadrupole states in the automatically orthogonal form:

$$\begin{aligned} A_1&=\cos(\alpha/2)\psi_{\frac{1}{2}}-\sin(\alpha/2)\psi_{-\frac{3}{2}},\\ A_3&=\sin(\alpha/2)\psi_{\frac{1}{2}}+\cos(\alpha/2)\psi_{-\frac{3}{2}},\\ B_1&=\cos(\alpha/2)\psi_{-\frac{1}{2}}-\sin(\alpha/2)\psi_{\frac{3}{2}},\\ B_3&=\sin(\alpha/2)\psi_{-\frac{1}{2}}+\cos(\alpha/2)\psi_{\frac{3}{2}},\\ \tan\alpha&=(2G/\sqrt{3}F). \end{aligned} \tag{21}$$

The subscripts are the value of $|2m|$ for $\alpha=0$. α is specified by the requirement that the off-diagonal quadrupole elements vanish. The diagonal quadrupole elements express the unperturbed energies as

$$\begin{aligned} (A_3\|A_3)=(B_3\|B_3)&=-(A_1\|A_1)=-(B_1\|B_1)\\ &=E_0=F\sec\alpha=(2G/\sqrt{3})\csc\alpha. \end{aligned} \tag{22}$$

For the moment let us employ the parameters F_z, G_z of (3), but allow η to take all values $-\infty\leq\eta\leq\infty$; this is equivalent to choosing one of the normal coordinates axes at random as the z axis and discussing all possible ratios of V_{xx}, V_{yy}, and V_{zz} in this one coordinate system. We find

$$\tan\alpha=(2G_z/\sqrt{3}F_z)=(\eta/\sqrt{3}). \tag{23}$$

For a small magnetic field always parallel to what we are at present calling the z axis, the perturbation of the energy levels is given by the diagonal elements. Adding these to (22) we find

$$\begin{aligned} (A_1\|A_1)&=-E_0+\xi(2\cos\alpha-1),\\ (B_1\|B_1)&=-E_0-\xi(2\cos\alpha-1),\\ (A_3\|A_3)&=E_0-\xi(2\cos\alpha+1),\\ (B_3\|B_3)&=E_0+\xi(2\cos\alpha+1). \end{aligned} \tag{24}$$

For magnetic dipole transition probabilities we need the matrix elements of I_x, I_y, and I_z; for completeness we include those for the low-frequency transitions:

$$\begin{aligned} &(A_1|2I_x|B_1)=1-2\sin(\alpha-30^\circ),\\ &(A_3|2I_x|B_3)=1+2\sin(\alpha-30^\circ),\\ &(A_1|2I_x|B_3)=(A_3|2I_x|B_1)=2\cos(\alpha-30^\circ),\\ &(A_1|2I_y|B_1)=-i[1+2\sin(\alpha+30^\circ)],\\ &(A_3|2I_y|B_3)=-i[1-2\sin(\alpha+30^\circ)],\\ &(A_1|2I_y|B_3)=(A_3|2I_y|B_1)=i[2\cos(\alpha+30^\circ)],\\ &(A_1|2I_z|A_3)=-(B_1|2I_z|B_3)=2\sin(\alpha). \end{aligned} \tag{25}$$

The foregoing solutions are formally correct for all three of the matrices $i=x$, y, or z, obtained from (4). However, for our working formulas we want these solutions couched in terms appropriate to the principal coordinate system which we have adopted as the standard way to describe a given physical case. Denoting by subscripts the parameters defined by (21) when we use F_x, G_x or F_y, G_y, we can show that

$$\alpha_x=\alpha+60^\circ,\quad \alpha_y=\alpha-60^\circ, \tag{26}$$

where η is given by (23) in terms of the principal coordinate system. To identify the energy levels in terms of the nomenclature appropriate to $\psi(I,m_z)$ we assume e^2qQ to be positive and list the levels for the three cases in order of decreasing energy (the fact that the Zeeman levels do not cross for intermediate orientations of the magnetic field is shown by the nonvanishing of $[m]$ in (20)):

	$H\|\|z$ $\psi(m_z)$	$H\|\|x$ $\psi(m_x)$	$H\|\|y$ $\psi(m_y)$
$E_{\frac{3}{2}+}$	B_3	B_1	A_1
$E_{\frac{3}{2}-}$	A_3	A_1	B_1
$E_{\frac{1}{2}+}$	A_1	B_3	B_3
$E_{\frac{1}{2}-}$	B_1	A_3	A_3

(27)

For the spin matrix elements between these states for $H\|x$ or y the letters x, y, and z are permuted cyclically in (25) and α is modified as shown in (26).

The Zeeman parameters are easily evaluated from (9) and (21):

$$a=-1\pm2\cos\alpha,\quad b=1\pm\cos\alpha,\quad c=\mp\sqrt{3}\sin\alpha. \tag{28}$$

Here the upper and lower signs refer to $m'=\frac{1}{2}$ and $\frac{3}{2}$, respectively.

In the course of experimental work it was found that one of the most useful features of the Zeeman spectrum as a function of magnetic field orientation was the locus along which the α components are unsplit; this relatively strong resonance at the normal pure quadrupole frequency was easy to identify and to interpret. The condition for this locus is $[\frac{3}{2}']=[\frac{1}{2}']$, and by inserting the Zeeman coefficients that were derived above the locus can be explicitly written as the function $\theta_0(\phi)$. Here we shall derive $\theta_0(\phi)$ in a manner to show its importance for all magnitudes of the magnetic field when $I=\frac{3}{2}$. The secular equation for the general case in which any orientation of the magnetic field is allowed is

$$\begin{aligned} 0=E^4&-[2+(2\eta^2/3)+10\xi^2]E^2\\ &-(16\xi^2-24\xi^2\sin^2\theta+8\xi^2\eta\sin^2\theta\cos2\phi)E\\ &+1+2\eta^2/3+\eta^4/9-10\xi^2+12\xi^2\sin^2\theta+9\xi^4\\ &+2\eta^2\xi^2-4\xi^2\eta^2\sin^2\theta+8\xi^2\eta\sin^2\theta\cos2\phi. \end{aligned} \tag{29}$$

The energy unit $A=(e^2qQ)/[4I(2I-1)]$ is used here, so that $\xi=(\gamma\hbar H/2A)$. This equation reduces to a quadratic in E^2 when the coefficient of E is zero, which occurs when

$$\sin^2\theta=2/(3-\eta\cos2\phi). \tag{30}$$

The four solutions have the form

$$E=\pm(A\pm B)^{\frac{1}{2}},$$

and it is easy to verify from this that (30) must define the locus $\theta_0(\phi)$. For magnetic field strengths too large to be treated by first order calculations there will not be in general an unsplit line at the pure quadrupole

frequency, but at least one pair of spectral components will coalesce to a single line along this locus, making it readily identifiable experimentally.

We note finally the methods for determining η from experimental Zeeman data. One set of measurements for this purpose is the location of $\theta_0(\phi)$ of (30). The principal coordinate system for the field gradient under investigation is determined from the symmetry that the Zeeman splittings show as functions of the orientation of the magnetic field and from the fact that $\theta_0(\phi)$ has its maximum and minimum values in the xz and the yz planes, respectively. η is found from the formula:

$$\eta=\frac{3[\sin^2\theta_0(0°)-\sin^2\theta_0(90°)]}{\sin^2\theta_0(0°)+\sin^2\theta_0(90°)}. \tag{31}$$

As we have seen, this method of determining η can be adapted for use with magnetic fields of any magnitude. In this procedure the only precision measurements are those of the direction of the magnetic field; the spectrometer serves only as an indicator.

The other method that our theory provides for determining η requires the measurement of the amounts of splitting when the magnetic field is parallel to one of the principal axes of the field gradient in question. The differences in frequency between the Zeeman components and the unsplit quadrupole resonance, expressed in energy units, are found from (19):

	α	β	
$H\|\|z$	2ξ	$4\rho\xi$	
$H\|\|x$	$2(1-\eta)\rho\xi$	2ξ	(32)
$H\|\|y$	2ξ	$2(1+\eta)\rho\xi$.	

η is therefore found directly from a measurement of the splitting of the proper pair of Zeeman components along one of the principal axes. The magnetic field can be calibrated by measuring the splitting for one of the other pairs.

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Particle Derivation of Nuclear Rotation Properties Associated with a Surface Wave

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The dynamical conception of nuclear rotation in terms of a surface wave on a droplet of irrotational fluid has achieved some success in spite of the great differences between nucleons and the particles of a normal classical fluid. As a justification for the simplifying assumption of irrotational fluid flow, the collective rotational energy is here derived from a suitable set of nucleon wave functions in the approximation in which there is a rotating distortion, slow compared with the internal nucleon motions. The wave functions are those of a three-dimensional harmonic oscillator that is made anisotropic by having the force constant along one axis different from those along the other two in a rotating cartesian coordinate system. For the case of steady rotation about a fixed axis, the perturbation problem with first-order wave functions leads to a second-order rotational energy which agrees with the droplet-model result. The observed level spacings appear to lie between this result and that of a rigid rotator, and the discrepancy is probably to be attributed to higher orders. The result is also derived by another method without introducing a steady rotation.

INTRODUCTION

THE spectacular success of the (jj) coupling shell model,[1] in accounting particularly for the magic numbers and the succession of ground-state angular momenta J of the moderately heavy nuclei, leaves little doubt that the extrashellular nucleons have an independence of motion quite different from that of the molecules in a classical fluid. These particular successes were first achieved on the assumptions that the extrashellular nucleons move in a spherically symmetric potential, have large spin-orbit coupling, and interact with one another besides. The equally impressive success of the introduction of a nonsperical core,[2,3] in accounting for the large quadrupole moments and especially the ratios of certain low excitation energies,[4] gives the impression that the degree of freedom permitting distortion of the core is important to the external features of most nuclei without radically modifying the internal coupling of the nucleons as

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