34-kev gamma ray. There is no clear evidence for other gamma rays in this region except for the fact that the valleys between peaks do not drop as low as would be expected from the assumption that the peaks should show a Gaussian-type shape.

Analysis of the measured peak areas to obtain relative gamma-ray intensities indicates that, if an intensity of unity is assumed for the 134-kev gamma ray, the 81-kev line will be 0.287; the 0.695-Mev gamma, 0.116; the 1.48-Mev gamma, 0.0226; and the 2.185-Mev gamma, 0.0589.

Errors in these values can arise because of an inability to determine the exact base and shape for the total absorption peak and because of counting rate statistics. These errors are present both in the spectrum under observation and in the experimental determination of the peak to total ratios. Experience gained in the analysis of a considerable number of gamma-ray spectra has led to the conclusion that the uncertainty in the value quoted for the 0.695, 1.48, and 2.185 Mev quanta is about ± 8 percent and for the 81 kev quantum about ± 15 percent.

If it is assumed that 22 percent of the Ce^{144} disintegrations produce the 134-kev transition[2,3] and that 6.6 percent of the Ce^{144} disintegrations are internally converted in the 134-kev transition[2] (leaving 15.4 percent of the transitions as photon radiation), then the 0.695-Mev gamma ray occurs following 1.79 percent of the Pr^{144} disintegrations, the 1.48-Mev gamma ray follows 0.35 percent of the transitions and the 2.185-Mev gamma ray, in 0.91 percent of the transitions. This would be indicative that Pr^{144} decays through the 2.28-Mev beta group 1.44 percent of the time, and the 0.80-Mev group 1.26 percent, differing somewhat from the figures proposed by Emmerich *et al.*[3]

From the fact that only the 81- and 134-kev transitions are distinctly evident in the low-energy photon spectrum as well as being most prominent in the internal conversion spectrum,[2,3] we find no evidence contradictory with the decay scheme proposed for Ce^{144} by Emmerich *et al.*,[3] except that the 223-kev beta transition may have an intensity of as much as six percent.

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Nuclear Quadrupole Spectra in Solids*

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Numerical values for the energy levels, Zeeman splitting parameters, and intensity parameters of the pure quadrupole spectrum are given for ten values of the asymmetry parameter for spins 5/2, 7/2, and 9/2. The intensity parameters for the $m \rightarrow -m$ transition in a magnetic field for large asymmetric quadrupole interaction are given. They show that the corresponding lines should be observable. A method of increasing the accuracy of perturbation calculations is presented for the Zeeman splitting case and the strong magnetic field case.

INTRODUCTION

SINCE the first observations of nuclear quadrupole spectra in solids by Pound[1] and by Dehmelt and Kruger,[2] it has become abundantly clear that such observations provide a powerful means of investigation of the structure of solids. The theory of nuclear quadrupole interactions in solids has two aspects: first, the purely formal task of describing spectra in terms of interaction parameters; and second, the calculation of the interaction parameters or, conversely, the drawing of inferences about structure from experimental observations. It is toward the first aspect that this paper is addressed, in the hope of providing a broader theoretical basis for experiments which stress the second aspect.

The present state of the spectrum theory may be summarized as follows: (1) Pound has discussed the Hamiltonian; (2) Bersohn treated the broadening of a magnetic resonance line by a small quadrupole interaction;[3] (3) Pound gave third order perturbation formulae for the splitting of the magnetic resonance line by nuclear quadrupole interaction with a symmetric field gradient;[4] Bersohn treated the general case to third order; Volkoff *et al.*, have discussed the explicit orientational dependence of the first and second order formulas;[5] (4) Explicit numerical formulas giving the effect of small asymmetry on the pure quadrupole

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spectrum exist in the literature for $I=5/2$,[3] 3,[6] 7/2,[7] and 9/2;[8] Bersohn has given the general formula for small asymmetry; (5) Kruger[9] and Dean[10] have investigated the first order Zeeman effect for spin 3/2 for which the pure quadrupole spectrum can be obtained exactly for arbitrary asymmetry; Bersohn has given the effect of small asymmetry on the first order Zeeman splitting for spin 5/2; (6) Weiss[11] has studied a spin 3/2 nucleus in a symmetric electric field and simultaneously in a magnetic field of various strengths and orientations; Lamarche and Volkoff[12] have studied in detail the case of spin 5/2 in a particular asymmetric electric field for given orientation and arbitrary strength of magnetic field.

A detailed derivation and discussion of the Hamiltonian, of various aspects of the spectrum theory, and of the calculation of interaction parameters has been given by the author.[13] For an introduction to the subject of nuclear quadrupole resonance, see the paper of Dehmelt.[14]

Experimentally, spins 7/2 and 9/2 are of importance, for example, in the study of ferroelectrics.[15] Further, inspection of the above summary shows that there is a need for the study of the pure quadrupole spectrum and its first order Zeeman splitting for electric fields of arbitrary asymmetry. Section I of this paper consists, then, of a review of the Hamiltonian; Sec. II gives a numerical analysis of the pure quadrupole spectrum for spins 5/2, 7/2, 9/2 in electric fields of arbitrary asymmetry; and Sec. III deals with the first order Zeeman splitting of that spectrum. For splittings of the magnetic resonance line as great as those observed by Knight and Cotts for Nb in $KNbO_3$,[15] third order calculations are not adequate. For that reason, Sec. IV contains a method of obtaining fourth order accuracy from third order calculations. A similar method of increasing the accuracy of calculations of the first order Zeeman splitting of the pure quadrupole spectrum is also presented.

Much of the work in this paper can be applied directly to the study of ferroelectrics and antiferroelectrics by nuclear resonance techniques.[15] For such substances the quadrupole coupling can be large, the field gradients asymmetric, and the orientation of the principal axes of primary importance.

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TABLE I. Secular equations.

I	Secular equation	Units of E
5/2	$E^3-7(3+\eta^2)E-20(1-\eta^2)=0$ [a]	$2L$
7/2	$E^4-42(1+\eta^2/3)E^2-64(1-\eta^2)E+105(1+\eta^2/3)^2=0$ [b]	$3L$
9/2	$E^5-11(3+\eta^2)E^3-44(1-\eta^2)E^2+\frac{44}{3}(3+\eta^2)^2E+48(3+\eta^2)(1-\eta^2)=0$	$6L$

[a] See reference 3.
[b] See reference 7.

I. HAMILTONIAN

We are concerned here with that part of the interaction energy between a nucleus and its environment which depends explicitly on the nuclear spin. For our purposes, we may characterize the nucleus completely by its spin I, its g-factor, and its quadrupole moment Q. The environment is specified by a constant magnetic field $\mathbf{H}_0$ and by $\partial E_i/\partial x_j$, the gradient of the electrostatic field at the nucleus produced by all charge exterior to the nucleus ($\nabla\cdot\mathbf{E}=0$). The relevant part of the Hamiltonian is

$$\mathcal{H}=-g\beta\mathbf{H}_0\cdot\mathbf{I}-K\sum_{\mu=-2}^{2}F_\mu Q_{-\mu}, \tag{1}$$

$$K=eQ/4I(2I-1), \tag{2}$$

$$F_0=\frac{\partial E_z}{\partial z},\quad F_{\pm1}=(2/3)^{\frac{1}{2}}\left(\frac{\partial E_z}{\partial x}\pm i\frac{\partial E_z}{\partial y}\right), \tag{3}$$

$$F_{\pm2}=\frac{1}{\sqrt{6}}\left(\frac{\partial E_x}{\partial x}-\frac{\partial E_y}{\partial y}\pm 2i\frac{\partial E_x}{\partial y}\right).$$

The operators Q_μ are such that the nonzero matrix elements of $\mathcal{H}$ in the representation diagonalizing I_z are

$$(m|\mathcal{H}|m)=-g\beta H_0{}^z m-KF_0[3m^2-I(I+1)], \tag{4a}$$

$$(m\pm1|\mathcal{H}|m)=-\tfrac{1}{2}g\beta(H_0{}^x\mp iH_0{}^y)\times[I(I+1)-m(m\pm1)]^{\frac{1}{2}}-KF_{\mp1}(3/2)^{\frac{1}{2}}\times(2m\pm1)[I(I+1)-m(m\pm1)]^{\frac{1}{2}}, \tag{4b}$$

$$(m\pm2|\mathcal{H}|m)=-KF_{\mp2}(3/2)^{\frac{1}{2}}\times[I(I+1)-(m\pm1)(m\pm2)]^{\frac{1}{2}}\times[I(I+1)-m(m\pm1)]^{\frac{1}{2}}. \tag{4c}$$

II. PURE QUADRUPOLE SPECTRUM

A. Energy Levels

In this case, the magnetic field vanishes and it is convenient to work in the principal axis system of the tensory $\partial E_i/\partial x_j$. Then $F_0=-eq$, $F_{\pm1}=0$, $F_{\pm2}=-(1/\sqrt{6})eq\eta$, where η is called the asymmetry parameter. If the axis are chosen so that $|\partial E_x/\partial x|\leq|\partial E_y/\partial y|\leq|\partial E_z/\partial z|$, then $0\leq\eta\leq1$. Now $(-m'|\mathcal{H}|-m)=(m'|\mathcal{H}|m)$, and $(m'|\mathcal{H}|m)=0$ unless $\Delta m=0$, ±2, so that the secular equation factors into two identical ones of degree $I+\frac{1}{2}$. We shall speak of each set of $I+\frac{1}{2}$ levels as a group of levels. If we denote E_m as that eigenvalue which goes over continuously into $-L[3m^2-I$

TABLE II. Eigenvalues E^0 and Zeeman-splitting parameters A, B, C of the pure quadrupole Hamiltonian.

I	m	η	E^0	A	B	C
5/2	5/2	0.1	5.00278	6.2469	—	—
		0.2	5.01113	6.2375	0.0002	—
		0.3	5.02512	6.2215	0.0011	—
		0.4	5.04481	6.1982	0.0035	0.0002
		0.5	5.07034	6.1670	0.0086	0.0007
		0.6	5.10185	6.1268	0.0179	0.0018
		0.7	5.13952	6.0767	0.0332	0.0039
		0.8	5.18353	6.0154	0.0567	0.0075
		0.9	5.23412	5.9417	0.0907	0.0136
		1.0	5.29150	5.8545	0.1379	0.0229
	3/2	0.1	−0.985095	2.2206	0.1565	0.0026
		0.2	0.941470	2.1387	0.5870	0.0182
		0.3	0.872088	2.0202	1.1959	0.0510
		0.4	0.781033	1.8830	1.8751	0.0942
		0.5	0.672723	1.7416	2.5387	0.1353
		0.6	0.551343	1.6048	3.1340	0.1620
		0.7	0.420564	1.4768	3.6373	0.1652
		0.8	0.283469	1.3587	4.0435	0.1399
		0.9	0.142591	1.2496	4.3583	0.0846
		1.0	0	1.1480	4.5918	—
	1/2	0.1	−4.01768	0.2409	9.0955	−1.1827
		0.2	4.06966	0.2162	9.3570	2.2692
		0.3	4.15303	0.1824	9.7237	3.1952
		0.4	4.26378	0.1464	10.1289	3.9390
		0.5	4.39762	0.1131	10.5222	4.5125
		0.6	4.55051	0.0850	10.8752	4.9437
		0.7	4.71895	0.0626	11.1772	5.2640
		0.8	4.90006	0.0454	11.4283	5.5010
		0.9	5.09153	0.0325	11.6339	5.6771
		1.0	5.29150	0.0230	11.8008	5.8086
7/2	7/2	0.1	7.00233	12.2467	—	—
		0.2	7.00935	12.2369	—	—
		0.3	7.02106	12.2203	—	—
		0.4	7.03753	12.1966	—	—
		0.5	7.05881	12.1656	0.0002	—
		0.6	7.08501	12.1265	0.0005	0.0001
		0.7	7.11622	12.0786	0.0013	0.0002
		0.8	7.15260	12.0210	0.0030	0.0004
		0.9	7.19432	11.9521	0.0063	0.0009
		1.0	7.24157	11.8704	0.0121	0.0020
	5/2	0.1	1.00834	6.2360	0.0005	—
		0.2	1.03351	6.1925	0.0078	0.0003
		0.3	1.07589	6.1154	0.0386	0.0019
		0.4	1.13601	5.9991	0.1183	0.0078
		0.5	1.21447	5.8383	0.2762	0.0228
		0.6	1.31176	5.6295	0.5395	0.0527
		0.7	1.42809	5.3736	0.9249	0.1035
		0.8	1.56325	5.0765	1.4331	0.1784
		0.9	1.71652	4.7485	2.0456	0.2762
		1.0	1.88669	4.4025	2.7277	0.3900
	3/2	0.1	−2.96971	2.1575	0.9293	−0.0138
		0.2	2.88628	1.9362	3.0617	0.0618
		0.3	2.76651	1.6823	5.3001	0.0564
		0.4	2.62743	1.4480	7.0760	+0.1041
		0.5	2.48217	1.2436	8.3145	0.4516
		0.6	2.33975	1.0632	9.1305	0.9604
		0.7	2.20609	0.8998	9.6656	1.5779
		0.8	2.08487	0.7493	10.0346	2.2449
		0.9	1.97813	0.6112	10.3166	2.9078
		1.0	1.88669	0.4870	10.5589	3.5256
7/2	1/2	0.1	−5.04097	0.2220	16.6392	−3.8223
		0.2	5.15658	0.1512	18.1007	6.7962
		0.3	5.33044	0.1023	19.6395	8.7475
		0.4	5.54610	0.0607	20.8895	9.9385
		0.5	5.79112	0.0349	21.8100	10.6626
		0.6	6.05702	0.0198	22.4699	11.1165
		0.7	6.33822	0.0112	22.9450	11.4133
		0.8	6.63098	0.0063	23.2926	11.6162
		0.9	6.93270	0.0036	23.5518	11.7604
		1.0	7.24157	0.0020	23.7490	11.8664
9/2	9/2	0.1	6.00143	20.2463	—	—
		0.2	6.00572	20.2319	—	—
		0.3	6.01289	20.2166	—	—
		0.4	6.02297	20.1902	—	—
		0.5	6.03598	20.1557	—	—
		0.6	6.05199	20.1125	—	—
		0.7	6.07105	20.0602	—	—
		0.8	6.09323	19.9977	0.0001	—
		0.9	6.11864	19.9242	0.0003	—
		1.0	6.14738	19.8382	0.0008	0.0001
	7/2	0.1	2.00467	12.2369	—	—
		0.2	2.01870	12.1973	—	—
		0.3	2.04218	12.1301	0.0005	—
		0.4	2.07524	12.0332	0.0028	0.0002
		0.5	2.11809	11.9033	0.0105	0.0009
		0.6	2.17102	11.7354	0.0308	0.0031
		0.7	2.23440	11.5227	0.0760	0.0089
		0.8	2.30867	11.2568	0.1648	0.0219
		0.9	2.39434	10.9286	0.3222	0.0480
		1.0	2.49193	10.5297	0.5783	0.0952
	5/2	0.1	−0.989724	6.2123	0.0060	0.0001
		0.2	0.958469	6.0899	0.0919	0.0031
		0.3	0.905221	5.8615	0.4324	0.0212
		0.4	0.829081	5.5122	1.2157	0.0767
		0.5	0.730171	5.0528	2.5141	0.1840
		0.6	0.610259	4.5232	4.2069	0.3252
		0.7	0.472749	3.9750	6.0338	0.4426
		0.8	0.322087	3.4495	7.7273	0.4615
		0.9	0.163016	2.9670	9.1118	0.3227
		1.0	0	2.5310	10.1240	—
	3/2	0.1	−2.96512	2.0395	3.3607	0.0329
		0.2	2.87966	1.6461	9.0311	0.1116
		0.3	2.77647	1.2968	13.0116	0.9467
		0.4	2.67805	1.0101	15.3151	2.4522
		0.5	2.59608	0.7637	16.7710	4.2783
		0.6	2.53541	0.5518	17.9117	6.0693
		0.7	2.49670	0.3794	18.9414	7.6018
		0.8	2.47833	0.2493	19.8877	8.8013
		0.9	2.47766	0.1578	20.7274	9.6920
		1.0	2.49193	0.0970	21.4437	10.3376
	1/2	0.1	−4.05126	0.1885	27.4244	9.0014
		0.2	4.18630	0.0957	31.5395	14.3040
		0.3	4.37338	0.0417	34.5446	16.8182
		0.4	4.59107	0.0176	36.3957	18.0484
		0.5	4.82782	0.0075	37.5463	18.7207
		0.6	5.07734	0.0033	38.2989	19.1300
		0.7	5.33599	0.0014	38.8170	19.4010
		0.8	5.60149	0.0006	39.1894	19.5917
		0.9	5.87231	0.0003	39.4661	19.7318
		1.0	6.14738	0.0001	39.6770	19.8380

$\times(I+1)]$ as η goes to zero, then $E_m=E_{-m}$ for all η. Here $L=e^2qQ/4I(2I-1)$.

The factored secular equations, listed in Table I, have been solved numerically for ten values of η for spins 5/2, 7/2, 9/2. The resulting eigenvalues are listed in Table II under E^0. Values for E^0 for spin 9/2 have been obtained previously to five significant figures.[13]

B. Intensities

Each line in the spectrum is a superposition of the four transitions $\pm m \leftrightharpoons \pm m'$. The sum of the four

transition probabilities will be proportional to

$$WH'^2=\sum_{(\pm)}|(\pm m'|\mathbf{H}'\cdot\mathbf{I}|\pm m)|^2, \quad (5)$$

where $\mathbf{H}'$ is the rf-field exciting the transitions. If θ and ϕ are the polar angles of $\mathbf{H}'$ with respect to the principal axes, then

$$W=2D\cos^2\theta+\tfrac{1}{2}\sin^2\theta[G+2J\cos2\phi], \quad (6)$$

$$D=(I_{m,m'}{}^z)^2, \quad G=(I_{-m,m'}{}^+)^2+(I_{-m,m'}{}^-)^2,$$

$$J=(I_{-m,m'}{}^+)(I_{-m,m'}{}^-). \quad (7)$$

In the above formulas we have taken m and m' to be one of the two pairs belonging to the same group among the four levels $\pm m$, $\pm m'$ and have set $I^\pm=I^x\pm iI^y$.

We note that W contains all of the orientation dependence of the intensity of a given line. Hence, fitting the observed dependence on orientation of the relative intensity of a line to Eq. (6) will serve as a check on the assignment of mm' values to that line.

Values of D, G, and J are given in Table III for the transitions of observable intensity. In selecting the transition listed in the table, ν^2W has been used as a measure of the signal to noise ratio of a line and hence its observability. Also tabulated are the averaged transition probabilities $\overline{W}$ appropriate to a polycrystalline or powdered sample:

$$\overline{W}=\tfrac{2}{3}D+\tfrac{1}{3}G. \quad (8)$$

The results embodied in Table III show that the allowed transitions, $|\Delta m|=1$, are dominant for all values of η. There are several "forbidden" transitions for which the breakdown of the selection rule $|\Delta m|=1$ may be sufficiently strong to permit observation. These are the (5/2,1/2) transition for $I=5/2$, 7/2, 9/2, and the (7/2,3/2) transition for $I=7/2$, 9/2, both for various values of η. Similar results have been obtained in the special case considered by Lamarche and Volkoff.[12] For all lines except those with $I=9/2$, $(m,m')=(1/2, 5/2)$, $\eta\geq0.5$, the intensity is a maximum when $\mathbf{H}'$ is parallel to the x axis and for the exceptional cases when $\mathbf{H}'$ parallels the y axis.

If the observed frequency ratios of a pure quadrupole spectrum are drawn as horizontal lines on a plot of calculated frequency ratios *vs* η, one set of their intercepts with the calculated curves should lie on a vertical line. One thus obtains η and then qQ. Observations of the directional dependence of intensities in a single crystal yields the orientation of the principal axes. One can then determine the frequency of, and optimum orientation of $\mathbf{H}'$ for the "forbidden" lines if these are not observed at first.

III. ZEEMAN SPLITTING

A study of the Zeeman splitting of the pure quadrupole spectrum in a single crystal as a function of the orientation of the magnetic field will yield simply and immediately the orientation of the crystalline field axes[10] as well as a check on the assignment of transitions in the zero field pattern. The large quadrupole moments of some nuclei, e.g., Ta, have prevented the measurement of their magnetic moments by the usual magnetic resonance or induction techniques. The Zeeman splitting[16] can probably give the magnetic moment to greater accuracy than can be obtained at present by optical means.[17] The case of the symmetric field gradient is by far the simplest to analyze. The results for $\eta\neq0$ presented below will be useful, however, when the nucleus in question cannot be found in a site of tetragonal, hexagonal, or rhombohedral symmetry.

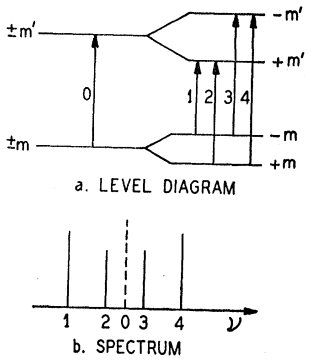

FIG. 1. Zeeman splitting of pure quadrupole spectrum.

A. Energy Levels

A magnetic field $\mathbf{H}_0$ at arbitrary orientation to the principal axes connects the degenerate states $\pm m$. Solution of the resulting secular problem yields, to first degree in the field strength,

$$E_{\pm m}=E_{\pm m}{}^0\mp g\beta H_0[A\cos^2\theta+\tfrac{1}{4}\sin^2\theta(B+2C\cos2\phi)]^{\frac{1}{2}}, \quad (9)$$

$$A=(I_{mm}{}^z)^2, \quad B=(I_{m,-m}{}^+)^2+(I_{m,-m}{}^-)^2,$$

$$C=I_{m,-m}{}^+I_{m,-m}{}^-. \quad (10)$$

In Eq. (9), θ and ϕ are the polar angles of $\mathbf{H}_0$. Values of A, B, and C are listed in Table II. Figure 1 shows schematically the fourfold splitting of each component of the pure quadrupole spectrum. The four members of the multiplet are symmetric about the original line in frequency and intensity.

B. Intensities

The intensity formulas for arbitrary orientation of the rf-field $\mathbf{H}'$ are extremely complicated. One can, however, show that the intensities of the Zeeman pattern are symmetric in the general case, as noted above. Examination of the general formulas shows that all lines of a multiplet are of comparable, but not necessarily equal, intensity. Hence those multiplets which contain allowed transitions $|\Delta m|=1$ are dominant.

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TABLE III. Intensity parameters, pure quadrupole spectrum.

$I=5/2$

Quantity	η	Transitions (1/2,3/2)	(3/2,5/2)	(1/2,5/2)
D	0.1	0.02	···	···
	0.2	0.07	···	···
	0.3	0.15	···	0.01
	0.4	0.24	0.01	0.02
	0.5	0.33	0.01	0.02
	0.6	0.41	0.02	0.03
	0.7	0.49	0.04	0.03
	0.8	0.56	0.07	0.04
	0.9	0.62	0.10	0.04
	1.0	0.68	0.14	0.05
G	0.1	7.87	4.99	0.01
	0.2	7.51	4.97	0.04
	0.3	7.01	4.95	0.08
	0.4	6.44	4.93	0.13
	0.5	5.88	4.92	0.17
	0.6	5.36	4.92	0.21
	0.7	4.91	4.93	0.23
	0.8	4.53	4.95	0.25
	0.9	4.21	4.99	0.26
	1.0	3.95	5.03	0.26
J	0.1	0.48	0.11	···
	0.2	0.90	0.22	···
	0.3	1.24	0.33	···
	0.4	1.47	0.44	0.01
	0.5	1.62	0.56	0.01
	0.6	1.70	0.67	0.02
	0.7	1.74	0.79	0.02
	0.8	1.74	0.91	0.03
	0.9	1.72	1.03	0.03
	1.0	1.70	1.16	0.04
$\bar{W}$	0.1	2.64	1.66	···
	0.2	2.55	1.66	0.02
	0.3	2.44	1.65	0.03
	0.4	2.31	1.65	0.05
	0.5	2.18	1.65	0.07
	0.6	2.06	1.66	0.09
	0.7	1.97	1.67	0.10
	0.8	1.88	1.70	0.11
	0.9	1.82	1.73	0.11
	1.0	1.77	1.77	0.12

$I=7/2$

Quantity	η	Transitions (1/2,3/2)	(3/2,5/2)	(5/2,7/2)	(1/2,5/2)	(3/2,7/2)
D	0.1	0.06	···	···	0.01	···
	0.2	0.21	0.01	···	0.02	···
	0.3	0.37	0.02	···	0.03	0.01
	0.4	0.52	0.06	···	0.05	0.01
	0.5	0.65	0.13	···	0.06	0.02
	0.6	0.75	0.23	···	0.06	0.03
	0.7	0.85	0.36	···	0.06	0.04
	0.8	0.93	0.51	0.01	0.06	0.06
	0.9	1.01	0.69	0.02	0.05	0.07
	1.0	1.08	0.88	0.03	0.05	0.09
G	0.1	14.20	11.93	7.00	0.08	···
	0.2	12.35	11.78	7.01	0.27	···
	0.3	10.38	11.64	7.03	0.45	0.01
	0.4	8.76	11.55	7.04	0.57	0.02
	0.5	7.57	11.49	7.06	0.62	0.04
	0.6	6.72	11.43	7.08	0.61	0.07
	0.7	6.12	11.31	7.11	0.56	0.11
	0.8	5.69	11.12	7.13	0.50	0.16
	0.9	5.37	10.85	7.17	0.43	0.21
	1.0	5.12	10.50	7.21	0.35	0.27

$I=7/2$

Quantity	η	Transitions (1/2,3/2)	(3/2,5/2)	(5/2,7/2)	(1/2,5/2)	(3/2,7/2)
J	0.1	1.40	0.36	0.14	···	···
	0.2	2.36	0.72	0.28	0.01	···
	0.3	2.81	1.09	0.42	0.02	···
	0.4	2.95	1.48	0.56	0.03	···
	0.5	2.93	1.87	0.71	0.03	···
	0.6	2.85	2.27	0.85	0.03	0.01
	0.7	2.76	2.65	1.00	0.03	0.01
	0.8	2.66	2.99	1.15	0.02	0.02
	0.9	2.58	3.27	1.30	0.01	0.03
	1.0	2.50	3.50	1.45	···	0.04
$\bar{W}$	0.1	4.77	3.98	2.33	0.03	···
	0.2	4.26	3.93	2.34	0.10	···
	0.3	3.71	3.90	2.34	0.17	0.01
	0.4	3.27	3.89	2.35	0.22	0.02
	0.5	2.96	3.92	2.35	0.24	0.03
	0.6	2.74	3.96	2.36	0.24	0.04
	0.7	2.60	4.01	2.37	0.23	0.07
	0.8	2.52	4.05	2.38	0.21	0.09
	0.9	2.46	4.08	2.40	0.18	0.12
	1.0	2.42	4.08	2.42	0.15	0.15

$I=9/2$

Quantity	η	Transitions (1/2,3/2)	(3/2,5/2)	(5/2,7/2)	(7/2,9/2)	(1/2,5/2)	(3/2,7/2)
D	0.1	0.14	···	···	···	0.01	···
	0.2	0.40	0.03	···	···	0.04	0.01
	0.3	0.63	0.12	···	···	0.06	0.03
	0.4	0.80	0.29	···	···	0.07	0.06
	0.5	0.95	0.54	0.01	···	0.07	0.09
	0.6	1.08	0.83	0.04	···	0.06	0.12
	0.7	1.20	1.14	0.08	···	0.04	0.15
	0.8	1.30	1.43	0.15	···	0.03	0.17
	0.9	1.39	1.69	0.27	···	0.02	0.19
	1.0	1.47	1.92	0.43	···	0.02	0.19
G	0.1	21.05	20.71	16.00	9.01	0.32	···
	0.2	16.02	20.24	16.01	9.01	0.83	0.02
	0.3	12.37	19.89	16.00	9.05	1.08	0.08
	0.4	10.19	19.47	15.97	9.08	1.07	0.20
	0.5	8.90	18.76	15.92	9.13	0.92	0.37
	0.6	8.10	17.73	15.87	9.18	0.73	0.57
	0.7	7.56	16.49	15.85	9.25	0.56	0.76
	0.8	7.15	15.22	15.87	9.32	0.42	0.91
	0.9	6.83	14.05	15.94	9.40	0.31	1.00
	1.0	6.56	13.06	16.04	9.49	0.23	1.03
J	0.1	3.08	0.84	0.39	0.17	···	···
	0.2	4.34	1.72	0.78	0.31	0.02	···
	0.3	4.49	2.66	1.17	0.52	0.02	···
	0.4	4.14	3.61	1.57	0.69	0.01	0.01
	0.5	4.10	4.46	1.97	0.87	−0.01	0.03
	0.6	3.89	5.10	2.37	1.05	0.04	0.05
	0.7	3.70	5.50	2.80	1.23	0.05	0.08
	0.8	3.54	5.69	3.24	1.42	0.06	0.11
	0.9	3.40	5.73	3.70	1.61	0.06	0.12
	1.0	3.27	5.68	4.18	1.80	0.06	0.13
$\bar{W}$	0.1	7.11	6.90	5.33	3.00	0.12	···
	0.2	5.61	6.77	5.34	3.00	0.30	0.02
	0.3	4.54	6.71	5.33	3.02	0.40	0.05
	0.4	3.93	6.68	5.33	3.03	0.40	0.10
	0.5	3.60	6.61	5.32	3.04	0.35	0.18
	0.6	3.42	6.46	5.31	3.06	0.28	0.27
	0.7	3.32	6.25	5.34	3.08	0.22	0.35
	0.8	3.25	6.02	5.39	3.11	0.16	0.42
	0.9	3.20	5.81	5.49	3.13	0.12	0.46
	1.0	3.17	5.63	5.63	3.17	0.09	0.47

Orientation of the rf-field parallel to the x axis again appears to be favorable in the majority of cases. One cannot be certain without detailed numerical analysis.

For this simplest case the transition probabilities for the multiplet $|m|, |m'|$ become

$$W=\frac{\frac{1}{4}(G+2J)}{(1+|r|^2)(1+|s|^2)}M, \tag{11}$$

where

$$r=-\frac{\sin\theta[I_{m,-m}{}^{+}e^{i\phi}+I_{m,-m}{}^{-}e^{-i\phi}]}{2[|I_{mm}{}^{z}|\cos\theta+|\Delta E_m|]}. \tag{12}$$

In Eq. (11), s is the same quantity for the levels $\pm m'$ as r is for the levels $\pm m$. Further, M is a 2×2 matrix, the indices of which indicate the signs of m and m'. In Eq. (12), $|\Delta E_m|$ is the magnitude of the Zeeman shift (i.e., half the level separation) in units of $g\beta H_0$. We must distinguish two cases before writing M explicitly: in case I, $|m|$ and $|m'|$ belong to the same group; in case II, they do not. Noting that $M_{++}=M_{--}$ and $M_{+-}=M_{-+}$, we obtain

$$\begin{aligned} M_{++}{}^{\mathrm{I}}&=|r^*+s|^2, \quad M_{++}{}^{\mathrm{II}}=|1+r^*s|^2,\\ M_{+-}{}^{\mathrm{I}}&=|1-rs|^2, \quad M_{+-}{}^{\mathrm{II}}=|r-s|^2. \end{aligned} \tag{13}$$

The quantities needed to evaluate W through Eqs. (11), (12), and (13) may be found in Tables II, III, and IV.

As examples of the use of the matrix M, consider the multiplets $\pm7/2$, $\pm5/2$ and $\pm7/2, \pm3/2$. In the former case, 7/2 and 5/2 are in different groups and we must use M^{II}; in the latter case, 7/2 and 3/2 are in the same group and we must use M^{I}. Let $W=ZM$. Then

$$\begin{aligned} W_{7/2,5/2}&=W_{-7/2,-5/2}=Z_{7/2,5/2}M_{++}{}^{\mathrm{II}},\\ W_{-7/2,5/2}&=W_{7/2,-5/2}=Z_{7/2,5/2}M_{+-}{}^{\mathrm{II}},\\ W_{7/2,3/2}&=W_{-7/2,-3/2}=Z_{7/2,3/2}M_{++}{}^{\mathrm{I}},\\ W_{-7/2,3/2}&=W_{7/2,-3/2}=Z_{7/2,3/2}M_{+-}{}^{\mathrm{I}}. \end{aligned}$$

All "allowed" transitions are of type I; all observable "forbidden" transitions are of type II.

C. Large Quadrupole Coupling

There are cases when the quadrupole coupling is so large that the frequencies of the pure quadrupole spectrum lie beyond the reach of conventional nuclear resonance or induction equipment, say greater than 10^8 cps. Then, however, it becomes possible to observe in single crystals transitions between the levels $\pm m$ in a strong magnetic field, the frequencies of which are $2|\Delta E_m|$. Such measurements could yield a value for the magnetic moment, for η, and for the orientation of the principal aces. The mixing of the $\pm m$ states by $\mathbf{H}_0$ is sufficiently strong for intermediate and large values of η that all $I+\frac{1}{2}$ transitions $m\rightarrow-m$ should be observable. Depending on the values of m and η, it is sometimes favorable to have $\mathbf{H}'\|z$ and sometimes paral-

TABLE IV. Matrix elements of the angular momentum.

Quantity	η	$I=5/2$ $m=1/2$	3/2	5/2	$I=7/2$ $m=1/2$	3/2	5/2	7/2
$I_{mm}{}^{z}$	0.1	0.49	1.49	2.50	0.47	1.47	2.50	3.50
	0.2	0.46	1.46	2.50	0.39	1.39	2.49	3.50
	0.3	0.43	1.42	2.49	0.32	1.30	2.47	3.50
	0.4	0.38	1.37	2.49	0.25	1.20	2.45	3.49
	0.5	0.34	1.32	2.48	0.19	1.12	2.42	3.49
	0.6	0.29	1.27	2.48	0.14	1.03	2.37	3.48
	0.7	0.25	1.22	2.47	0.11	0.95	2.32	3.48
	0.8	0.21	1.17	2.45	0.08	0.87	2.25	3.47
	0.9	0.18	1.12	2.44	0.06	0.78	2.18	3.46
	1.0	0.15	1.07	2.42	0.04	0.70	2.10	3.45
$I_{m-m}{}^{+}$	0.1	2.99	0.40	···	3.96	0.96	0.02	···
	0.2	2.96	0.77	0.01	3.88	1.75	0.09	···
	0.3	2.92	1.09	0.03	3.78	2.30	0.20	···
	0.4	2.87	1.37	0.06	3.70	2.66	0.34	0.01
	0.5	2.82	1.59	0.09	3.63	2.88	0.52	0.01
	0.6	2.78	1.77	0.13	3.59	3.00	0.73	0.02
	0.7	2.73	1.91	0.18	3.55	3.07	0.96	0.04
	0.8	2.69	2.01	0.24	3.53	3.08	1.19	0.05
	0.9	2.66	2.09	0.30	3.52	3.07	1.42	0.08
	1.0	2.63	2.14	0.37	3.51	3.03	1.63	0.11
$I_{m-m}{}^{-}$	0.1	−0.40	0.01	···	−0.96	0.01	···	···
	0.2	0.77	0.02	···	1.75	0.04	···	···
	0.3	1.09	0.05	···	2.31	0.02	0.01	···
	0.4	1.37	0.07	···	2.69	−0.04	0.02	···
	0.5	1.60	0.09	0.01	2.94	0.16	0.04	···
	0.6	1.78	0.09	0.01	3.10	0.32	0.07	···
	0.7	1.93	0.09	0.02	3.21	0.51	0.11	···
	0.8	2.04	0.07	0.03	3.29	0.73	0.15	0.01
	0.9	2.13	0.04	0.05	3.34	0.95	0.19	0.01
	1.0	2.21	···	0.06	3.38	1.16	0.24	0.02

Quantity	η	$I=9/2$ $m=1/2$	3/2	5/2	7/2	9/2
$I_{m,m}{}^{z}$	0.1	0.43	1.43	2.49	3.50	4.50
	0.2	0.31	1.28	2.47	3.49	4.50
	0.3	0.20	1.14	2.42	3.48	4.50
	0.4	0.13	1.01	2.35	3.47	4.49
	0.5	0.09	0.87	2.25	3.45	4.49
	0.6	0.06	0.74	2.13	3.43	4.48
	0.7	0.04	0.62	1.99	3.39	4.48
	0.8	0.03	0.50	1.86	3.36	4.47
	0.9	0.02	0.40	1.72	3.31	4.46
	1.0	0.01	0.31	1.59	3.24	4.45
$I_{m,-m}{}^{+}$	0.1	4.90	1.83	0.08	···	···
	0.2	4.73	3.00	0.30	0.01	···
	0.3	4.61	3.60	0.66	0.02	···
	0.4	4.53	3.86	1.10	0.05	···
	0.5	4.49	3.95	1.58	0.10	···
	0.6	4.47	3.94	2.04	0.17	···
	0.7	4.47	3.89	2.45	0.27	0.01
	0.8	4.47	3.82	2.77	0.40	0.01
	0.9	4.47	3.75	3.02	0.56	0.02
	1.0	4.47	3.68	3.18	0.75	0.03
$I_{m,-m}{}^{-}$	0.1	−1.84	−0.02	···	···	···
	0.2	3.02	0.04	0.01	···	···
	0.3	3.65	0.26	0.03	···	···
	0.4	3.98	0.64	0.07	···	···
	0.5	4.17	1.08	0.12	0.01	···
	0.6	4.28	1.54	0.16	0.02	···
	0.7	4.34	1.96	0.18	0.03	···
	0.8	4.39	2.31	0.17	0.05	···
	0.9	4.42	2.59	0.11	0.09	···
	1.0	4.44	2.81	···	0.13	···

lel to x or y.

$$W_z=\frac{4|r|^2}{[1+|r|^2]^2}A, \tag{14}$$

$$W_x=\frac{|1-r^2|^2}{[1+|r|^2]^2}(B+2C), \tag{15}$$

$$W_y=\frac{|1+r^2|^2}{[1+|r|^2]^2}(B-2C). \tag{16}$$

Again the intensity formulas for arbitrary orientation of $\mathbf{H}'$ are extremely complicated. Unless some knowledge of the orientation of the principal axes is available, say from symmetry considerations, the above intensity formulas will not be of use until after analysis of the orientation dependence of the frequencies.

IV. ACCURACY OF PERTURBATION THEORY

A. Zeeman Splitting

We take as the unperturbed Hamiltonian the pure quadrupole energy; the perturbation energy is $-g\beta\mathbf{I}\cdot\mathbf{H}_0$. Let $E_m^{(n)}$ be the nth order term in the perturbation theoretic expansion of the energy levels. It can be shown that

$$E_{-m}^{(n)}=(-1)^nE_m^{(n)}, \tag{17}$$

by induction on the general form of the nth order term. The proof rests on the behavior with respect to change of sign of m of the matrix elements of the Hamiltonian in the representation diagonalizing it to first order. A demonstration of Eq. (17) will not be given here; the corresponding theorem for the strong field case will be discussed more fully in Sec. B.

For accurate determination of the first order Zeeman parameters one needs as wide a range of field strengths as possible. At first glance it would appear that the magnetic field strength can be increased only until the second order effect is of the order of the experimental error. However, Eq. (17) shows that the second order term cancels out of $\nu_{m,m'}-\nu_{-m,-m'}$, and hence first order calculation of the separation between a symmetric pair in a multiplet gives second order accuracy. The working range of field strength extends until third order terms are of the order of the experimental error when first order calculations are used.

B. Strong-Field Case

Let R signify reflection of the coordinate system in the $x-y$ plane. Then in the expressions 4(a), 4(b), and 4(c) for the matrix elements of $\mathcal{H}$, $H_0^z\rightarrow-H_0^z$, $F_{\pm1}\rightarrow-F_{\pm1}$ upon application of R. Inspection of the matrix elements shows that

$$\mathcal{H}_{-m-m'}(\mathbf{H}_0,F_\mu)=\mathcal{H}_{mm'}(R\mathbf{H}_0,RF_\mu). \tag{18}$$

Therefore

$$E_{-m}(\mathbf{H}_0,F_\mu)=E_m(R\mathbf{H}_0,RF_\mu). \tag{19}$$

In the strong-field case, we take $\mathbf{H}_0\|z$ and $-g\beta I^zH_0$ as the unperturbed Hamiltonian. The latter is nondegenerate and hence perturbation theory yields an expansion in powers of F_μ and inverse powers of H_0 for the energy. The dependence on F_μ of a typical term might be

$$(F_0)^a(F_{-1})^b(F_{+1})^c(F_{-2})^d(F_{+2})^e, \tag{20}$$

with the condition that[18]

$$b-c+2d-2e=0. \tag{21}$$

Therefore $b-c$ must be even and the sign change in each term caused by R is determined by the sign change of $H_0^z=\pm H_0$. We conclude, therefore, that

$$E_{-m}^{(n)}=(-1)^{n-1}E_m^{(n)}. \tag{22}$$

Thus the third order calculations of Bersohn[3] give fourth order accuracy when the results of theory and experiment for $\nu_{m,m'}-\nu_{-m,-m'}$ are compared. This increased accuracy becomes important for quadrupole interactions of the order of that observed for Nb^{93} in $KNbO_3$ where $|e^2qQ/h|=23.1$ Mc/sec.[15] In most ferroelectrics and antiferroelectrics one could expect to encounter similarly large couplings.

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[18] Equations (20) and (21) become especially clear when one uses the perturbation techniques described in reference 13.