QUADRUPOLE ALLOWED TRANSITIONS

IN NITROGEN FOURTEEN

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A Thesis Describing Chemical Research in Ch 80

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Abstract

Quadrupole Allowed Transitions In Nitrogen Fourteen

The ^{14}N nucleus is not spherical but rather is ellipsoidal; hence, it has a quadrupole moment. The spin of ^{14}N is 1 so that the application of a magnetic field splits the doubly degenerate quadrupole levels, $m_I=\pm 1$.

Normally, transitions are allowed only if $|\Delta m|=1$. For this case transitions with $|\Delta m|=2$ are possible; that is, transitions from $m_I=1$ to $m_I=-1$ have nonzero probabilities since the $m_I=\pm 1$ states are coupled by the magnetic field to the $m_I=0$ state. This is what the experiment will attempt to observe. The analytical problems were solved in the following steps:

a) Quadrupole Hamiltonian with cylindrically symmetric field gradient

b) Quadrupole Hamiltonian with non-axial field gradient

c) Magnetic field alone

d) Magnetic field as a perturbation to the Hamiltonian in case a)

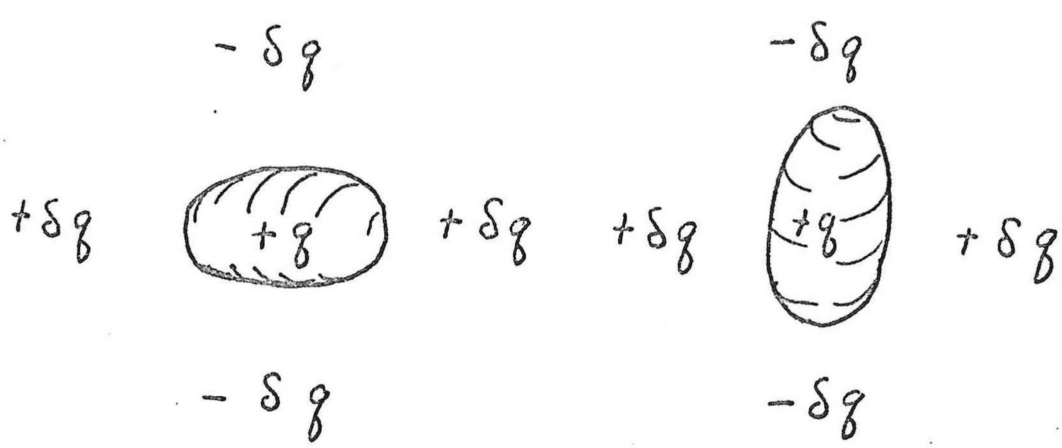
e) Magnetic field plus the Hamiltonian in case a)

f) Magnetic field plus the Hamiltonian in case b).

An energy correlation diagram and intensities for the quadrupole allowed transitions as a function of magnetic field strength varying between the limits of pure quadrupole field to pure magnetic field will be calculated by computer.

I. Introduction

The ^{14}N nucleus is not spherical but rather is ellipsoidal; hence, it has a quadrupole moment. Quantitatively, the quadrupole moment of a nucleus measures the departure from a spherical charge distribution. The nature of the electrostatic interaction can be understood by considering a simple model discussed by Slichter:



Here a nucleus with a prolate charge distribution, as ^{14}N has, is oriented in two directions in repect to an external field. The configuration on the right has the lower energy. This model also demonstrates that for a quadrupole interaction the nuclear spin must be greater than $\frac{1}{2}$ since $I=\frac{1}{2}$ corresponds to flipping the nucleus which leaves the energy unchanged. For $I=1$, $m_I=\pm1$ will be degenerate for an axially symmetric field gradient. However, the application of a constant magnetic field splits the degeneracy, coupling the $m_I=\pm1$ states to the $m_I=0$ state. The calculations are being done for ^{14}N, $I=1$, since the quadrupole resonance occurs at comparable frequencies to the magnetic resonance. Because of the coupling, transitions with $|\Delta m|=2$ can have nonzero probabilities. This paper deals with the theoretical calculation of these quadrupole allowed transitions.

II. Derivation of the Quadrupole Hamiltonian

There are different methods by which one may derive the expression for the quadrupole Hamiltonian. In general though, each makes a mathematical expansion of the integral for electrostatic energy; quantum mechanical analogs are then used for the nuclear charge distribution; and finally the Wigner-Eckart theorem relates spatial operators to nuclear spin operators. The latter step is necessary to reduce an N-body problem into a manageable form.

The electrostatic energy from a nuclear charge distribution $\rho(\vec{r})$ and a potential $V(\vec{r})$ due to the electron cloud about the nucleus is classically, $E = \int \rho(\vec{r})\, V(\vec{r})\, d\tau$. 1)

The potential can be expanded in a Taylor series,

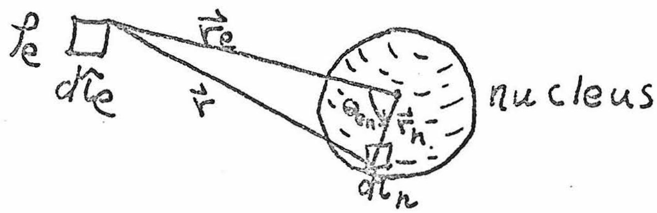
$$V(\vec{r}) = V(0) + \sum_i x_i \left.\frac{\partial V}{\partial x_i}\right)_{r=0} + \frac{1}{2} \sum_{i,j} x_i x_j \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_{r=0} \qquad 2)$$

which is substituted into 1):

$$E = \int \rho(\vec{r}) V(0)\, d\tau + \sum_i \int \rho(\vec{r})\, x_i \left.\frac{\partial V}{\partial x_i}\right)_{r=0} d\tau + \frac{1}{2} \sum_{i,j} \int \rho(\vec{r})\, x_i x_j \left.\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_{r=0} d\tau \qquad 3)$$

The first term is the electrostatic energy treating the nucleus as a point charge. The second term is the dipole interaction but can be shown in general to be zero.

That the dipole term is zero is more easily seen if a different expansion is employed as discussed by Ramsey. The coordinates of the electron cloud are separated from those of the nucleus. The potential energy is $\rho_e(\vec{r}_e)/r$, where r is the variable representing the distance between the electronic charge $\rho_e\, d\tau_e$ and the nuclear charge $\rho_n\, d\tau_n$:



The energy then becomes, $$E = \iint \frac{\rho_e(\vec{r}_e)\, \rho_n(\vec{r}_n)}{r}\, d\tau_e\, d\tau_n \qquad 4)$$

From vector algebra $\quad r = (r_e^2 + r_n^2 - 2 r_e r_n \cos\theta_{en})^{1/2}$

The factor 1/r can be expanded in a legendre polynomial series: $$1/r = 1/r_e\left(1 + \frac{r_n}{r_e} P_1(\cos\theta_{en}) + \frac{r_n^2}{r_e^2} P_2(\cos\theta_{en}) + \cdots\right) \qquad 5)$$

If one considers the dipole term in E,

$$E_d = \iint \frac{\rho_e(\vec{r}_e)}{r_e^2}\, r_n\, \rho_n(\vec{r}_n)\, P_1(\cos\theta_{en})\, d\tau_e\, d\tau_n \qquad 6)$$

The charge density $\rho_n(\vec{r}_n)$ and $P_1(\cos\theta_{en})$ are even functions but the length r_n is an odd function which implies the dipole term will vanish.

The third term in the Taylor series expansion 3) is the electrical quadrupole energy. Principal axes can be chosen so that all integrals involving $x_i x_j$ will be zero unless i=j. Then the quadrupole energy is given as,

$$E_Q = \tfrac{1}{2} \sum_i \int \rho(\vec{r})\, x_i^2 \left.\frac{\partial^2 V}{\partial x_i^2}\right)_{r=0} d\tau \qquad 7)$$

Since the potential V must satisfy Laplace's equation outside the nucleus, $\nabla^2 V=0$, E_Q can be rewritten,

$$E_Q = \tfrac{1}{6} \sum_i \int \rho(\vec{r})\, (3x_i^2 - r^2) \left.\frac{\partial^2 V}{\partial x_i^2}\right)_{r=0} d\tau \qquad 8)$$

Quantum mechanically, $\rho(\vec{r})$ the charge distribution in the nucleus is replaced by an operator $\hat{\rho}(\vec{r})$ which treats each proton as a point charge, $\hat{\rho}(\vec{r}) = \sum_p e\,\delta(\vec{r}-\vec{r}_p)$ 9)

This changes E_Q in 8) to an operator,

$$\hat{H}_Q = \tfrac{1}{6} \sum_i \int \sum_p e\,\delta(\vec{r}-\vec{r}_p)\,(3x_i^2 - r^2) \left.\frac{\partial^2 V}{\partial x_i^2}\right)_{r=0} d\tau \qquad 10)$$

$$\hat{H}_Q = \tfrac{1}{6} \sum_i \sum_p e \left.\frac{\partial^2 V}{\partial x_i^2}\right)_{r=0} (3x_{ip}^2 - r_p^2)$$

where r_p with Cartesian components x_{ip} is the distance from the pth proton to a point in space outside of the nucleus.

The electric quadrupole operator is defined as:

$$\hat{Q}_{ii} = e \sum_p (3x_{ip}^2 - r_p^2) \qquad 11)$$

Matrix elements for the quadrupole operator will be diagonal in I since the electrical quadrupole interaction arises from different spatial configurations corresponding to $m_I = I, I-1, \ldots, -I$. Since the operator $\hat{Q}_{ii}$ satisfies the same commutation rules with respect to the spin operator $\hat{I}$ as does $\vec{r}$, the Wigner-Eckart theorem states that its matrix elements will be proportional to the analogous matrix elements for $\hat{I}$:

$$\langle I\, m_I | e \sum_p (3x_{ip}^2 - r_p^2) | I\, m_I' \rangle = C \langle I\, m_I | 3\hat{I}_i^2 - \hat{I}^2 | I\, m_I' \rangle \qquad 12)$$

The right hand side integral is easily evaluated as $CI(2I-1)$ for $m_I=I$ and $I_i=I_z$. The left hand side integral defines the quadrupole moment Q:

$$eQ = \langle II | e \sum_p (3x_{ip}^2 - r_p^2) | I\, I \rangle \qquad 13)$$

Qualitatively one can see this definition does measure the nonsphericity of the nuclear charge distribution. If the nucleus is elongated along the z axis or prolate, then Q will be positive since $3x_{ip}^2 - r_p^2 = 3z_p^2 - r_p^2 > 0.$ Conversely, if the nuclear distribution is oblate $3z_p^2 - r_p^2 < 0$ then Q will be negative. For the intermediate case of a spherical charge distribution $3z_p^2 - r_p^2 = 0$ which causes the integral for Q to vanish.

The quadrupole Hamiltonian thus becomes by the Wigner-Eckart theorem,

$$\hat{H}_Q = \frac{eQ}{6I(2I-1)} \sum_i \frac{\partial^2 V}{\partial x_i^2} (3\hat{I}_i^2 - \hat{I}^2) \qquad 14)$$

Defining the asymmetry factor η as the amount the field gradient deviates from being axially symmetric:

$$\eta = \left(\frac{\partial^2 V}{\partial x^2} - \frac{\partial^2 V}{\partial y^2}\right) \Big/ \frac{\partial^2 V}{\partial z^2} \quad , \quad \frac{\partial^2 V}{\partial z^2} = eq \qquad 15)$$

and applying Laplace's equation, one arrives at the quadrupole Hamiltonian:

$$\hat{H}_Q = \frac{e^2 q Q}{4I(2I-1)} \left\{ (3\hat{I}_z^2 - \hat{I}^2) + \eta(\hat{I}_x^2 - \hat{I}_y^2) \right\} \qquad 16)$$

The main part of the derivation followed that of Slichter; other supporting ideas from Ramsey, Cohen and Reif, Das and Hahn.

III. <u>Discussion of the Analytical Problems for I=1</u>

Since $\hat{I}_x$ and $\hat{I}_y$ are difficult to use in calculations, lowering and raising operators were introduced: $\hat{I}_x = \frac{1}{2}(\hat{I}_+ + \hat{I}_-)$, $\hat{I}_y = \frac{1}{2i}(\hat{I}_+ - \hat{I}_-)$. The resulting Hamiltonian is given by (denoted by $\hat{H}_Q^\eta$ when the nonsymmetry of the field gradient is taken into account and $\hat{H}_Q^a$ when the approximation of a symmetric field gradient is made):

$$\hat{H}_Q^\eta = A(3\hat{I}_z^2 - \hat{I}^2) + \eta A(\hat{I}_x^2 - \hat{I}_y^2)$$

$$\hat{H}_Q^\eta = A(3\hat{I}_z^2 - \hat{I}^2) + \frac{\eta A}{2}(\hat{I}_+^2 + \hat{I}_-^2) \qquad 1)$$

$$A = \frac{e^2 Q q}{4I(2I-1)}$$

The basis vectors used are $|-\rangle, |0\rangle, |+\rangle$ relative to a principal axis coordinate system with the quadrupole moment along the z axis. Only matrix elements diagonal in I are considered, thus this will not be shown in the integrals, but assumed. The analytical problems were solved by increasing the complexity of the Hamiltonian in each step.

The first problem, also shown in Das and Hahn, is that of the quadrupole Hamiltonian, $\hat{H}_Q^a = A(3\hat{I}_z^2 - \hat{I}^2)$, with an axially symmetric field gradient; i.e., the x and y axes are not unique, but arbitrary. The only nonzero matrix elements are diagonal in m_I:

$$\langle m_I | \hat{H}_Q^a | m_I' \rangle = A \langle m_I | 3\hat{I}_z^2 - \hat{I}^2 | m_I' \rangle = E_Q^a$$

$$E_Q^a = A\left\{3m_I^2 - I(I+1)\right\}\delta_{m_I m_I'} \qquad 2)$$

where E_Q^a are the eigenvalues.

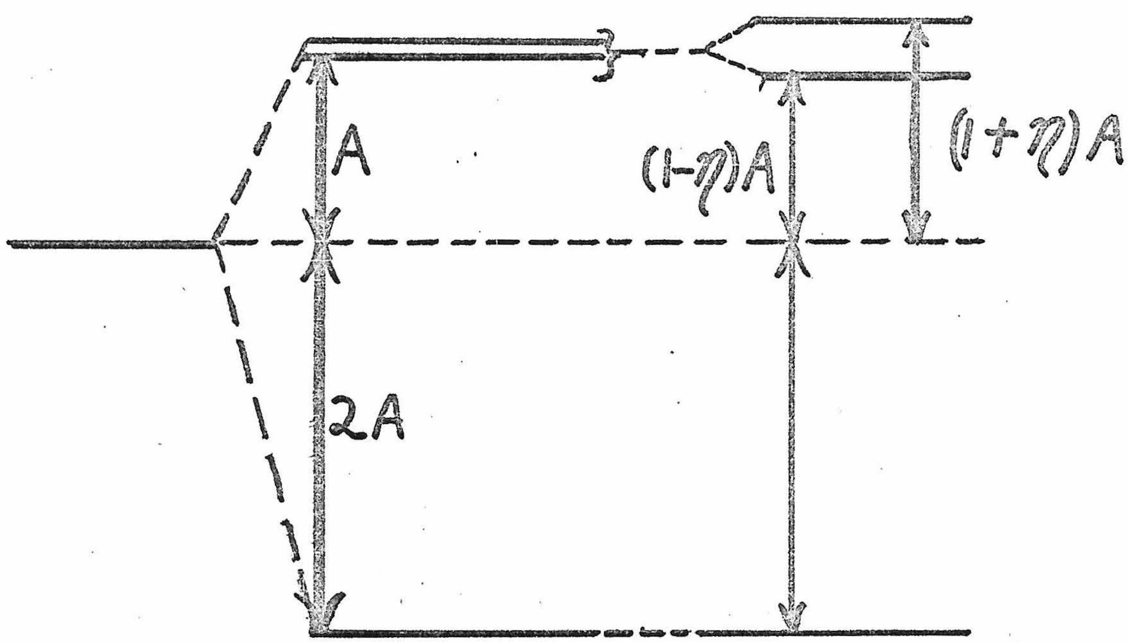
The solution of the second problem, that of the quadrupole Hamiltonian with a nonaxially symmetric field gradient is also given in Das and Hahn. The operator is given by 1). The matrix representation is the following: We note two things. First, the trace of the matrix is zero. This is true since the average value of $3X_i^2 - r^2$ summed over $X_i = x, y, z$ is zero.

$$\underset{\sim}{H}_Q^\eta = \begin{pmatrix} A & 0 & \eta A \\ 0 & -2A & 0 \\ \eta A & 0 & A \end{pmatrix} \qquad 3)$$

Second, the asymmetry of the field gradient couples the $|-\rangle$ state to the $|+\rangle$ state, the $|0\rangle$ state remaining unmixed. The secular equation is, $(2A+\lambda)\{(\eta A)^2 - (A-\lambda)^2\} = 0$, 4) which yields the eigenvalues $\lambda = -2A, (1 \pm \eta)A$. See Fig. 1 for an energy level diagram for $\hat{H}_Q^a$ and the resulting splitting occurring when $\eta \neq 0$.

Next the problem of adding a Zeeman field at the angles θ and ϕ to the z axis was calculated. The Hamiltonian for a magnetic field $\vec{H}$ is $\hat{H}_Z = -\hbar\gamma\hat{I}\cdot\vec{H}$ where γ is the gyromagnetic ratio for the nucleus. Letting $\vec{H}$ be a constant field H_0 in space and defining $\Omega \equiv \gamma H_0$. The magnetic Hamiltonian is,

Quadrupole Levels for ^{14}N



$$\hat{H}_Q^0 = A(3\hat{I}_z^2 - \hat{I}^2) \qquad \hat{H}_Q^\eta = H_Q^0 + \eta A(\hat{I}_x^2 - \hat{I}_y^2)$$

Fig. 1

$$\hat{H}_z = -\hbar\Omega(\hat{I}_z \cos\theta + \hat{I}_x \sin\theta\cos\phi + \hat{I}_y \sin\theta \sin\phi).$$

Again using lowering and raising operators to express $\hat{I}_x$ and $\hat{I}_y$ the operator is found to be,

$$\hat{H}_z = -\hbar\Omega(\hat{I}_z \cos\theta + \tfrac{1}{2} e^{-i\phi}\sin\theta\, \hat{I}_+ + \tfrac{1}{2} e^{+i\phi}\sin\theta\, \hat{I}_-) \qquad 5)$$

See Fig. 2 for the spatial relation of the magnetic and quadrupole fields.

In order to obtain a better physical feeling for the interaction of the magnetic field with the quadrupole field, $\hat{H}_z$ was used as a perturbation to $\hat{H}^a_Q$. Schrödinger-Rayleigh perturbation theory gives the following differential equation for first order corrections in the wavefunctions:

$$(\hat{H}^a_Q - E^\circ)\psi' + (\hat{H}_z - E')\psi^\circ = 0 \qquad 6)$$

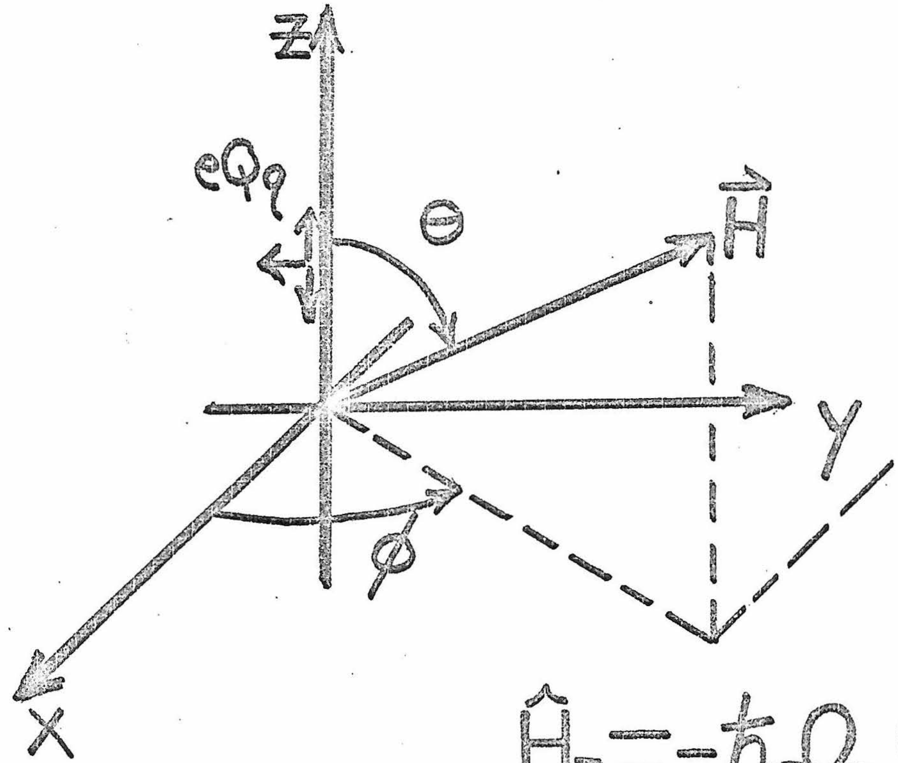
(numerals used as superscripts denote the order and 1, 0, -1 as subscripts denote the basis vector for which the correction is added). Second order energies were calculated according to $E^2 = \langle \psi^\circ | \hat{H}_z | \psi' \rangle$ 7)

The results of perturbing $\hat{H}^a_Q$ by a small constant magnetic field, H_0, are given in the following table and the energy levels graphically displayed in Fig. 3:

<u>$\hat{H}_z$ Perturbing $\hat{H}^a_Q$</u>

ψ°	$\|+\rangle$	$\|-\rangle$	$\|0\rangle$
ψ'	$\frac{-\hbar\Omega \sin\theta\, e^{i\phi}}{3\sqrt{2}\,A}\|0\rangle$	$\frac{-\hbar\Omega \sin\theta\, e^{-i\phi}}{3\sqrt{2}\,A}\|0\rangle$	$\frac{\hbar\Omega}{3\sqrt{2}A}(e^{-i\phi}\|+\rangle + e^{i\phi}\|-\rangle)$
E°	A	A	$-2A$

Magnetic and Quadrupole Fields



$$\hat{H}_Z = -\hbar\gamma\hat{I}\cdot\vec{H}$$

$$\Omega = \gamma H_0$$

$$\hat{H}_Z = -\hbar\Omega\left(\cos\theta\,\hat{I}_z + \frac{e^{-i\phi}}{2}\sin\theta\,\hat{I}_+ + \frac{e^{+i\phi}}{2}\sin\theta\,\hat{I}_-\right)$$

Fig.2

$\hat{H}_Z$ as a Perturbation to $\hat{H}_Q^a$

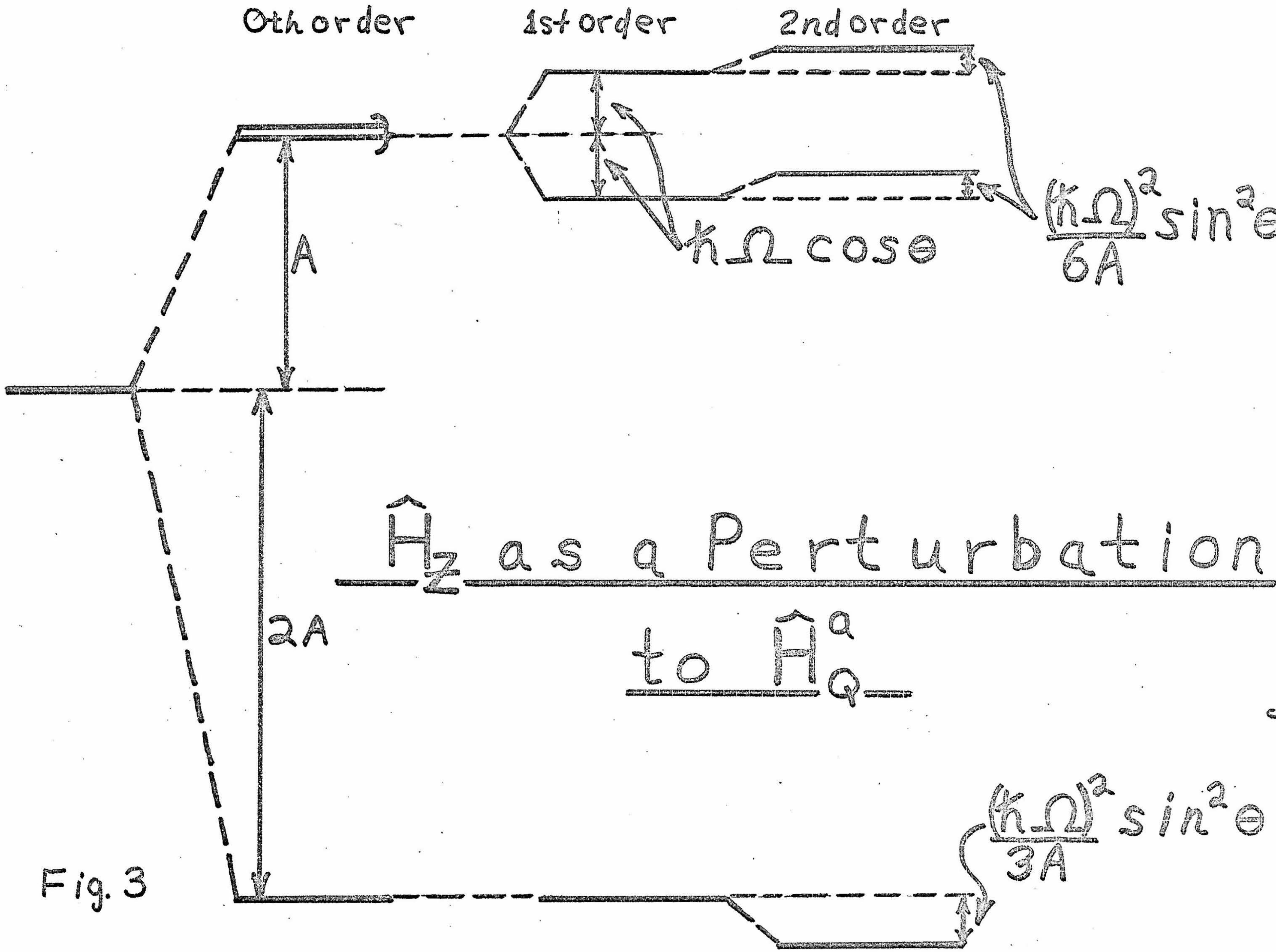


Fig. 3

E^1	$-\hbar\Omega\cos\theta$	$+\hbar\Omega\cos\theta$	0
E^2	$\frac{(\hbar\Omega)^2}{6A}\sin^2\theta$	$\frac{(\hbar\Omega)^2}{6A}\sin^2\theta$	$\frac{-(\hbar\Omega)^2}{3A}\sin^2\theta$

The first order energies are proportional to the first power of the magnetic field, likewise the second order correction to the second power of the magnetic field, as would be expected from perturbation theory. Also there is no ϕ dependence because as mentioned before the x and y axes are arbitrary for $\hat{H}^a_Q$. The degeneracy of the $|+\rangle, |-\rangle$ levels is lifted in first order by equal amounts of coupling from the $|0\rangle$ level. Also as expected from perturbation theory the sum of the energy shifts to each order is zero.

The magnetic Hamiltonian problem was then solved exactly in the quadrupole basis states. In this representation the Hamiltonian matrix was found to be.

$$\underset{\sim}{H_z} = \hbar\Omega \begin{pmatrix} \cos\theta & -\frac{e^{i\phi}}{\sqrt{2}}\sin\theta & 0 \\ -\frac{e^{-i\phi}}{\sqrt{2}}\sin\theta & 0 & -\frac{e^{i\phi}}{\sqrt{2}}\sin\theta \\ 0 & -\frac{e^{-i\phi}}{\sqrt{2}}\sin\theta & -\cos\theta \end{pmatrix} \qquad 8)$$

The secular equation reduced to, $\lambda\left(1-(\hbar\Omega\lambda)^2\right)$, 9)

with eigenvalues $\lambda = 0, \pm\hbar\Omega$. These energies correspond to the spin aligned perpendicular, against, and with the field. However, basis states with quantization along the magnetic field were not used so that the eigenvectors are linear combinations of the quadrupole basis states. The following normalized eigenfunctions were found:

Energy	Eigenfunction
0	$\frac{e^{i\phi}}{\sqrt{2}}\sin\theta\,|-\rangle + \cos\theta\,|-\rangle - \frac{e^{-i\phi}}{\sqrt{2}}\sin\theta\,|+\rangle$
$\hbar\Omega$	$\frac{e^{i\phi}(\cos\theta+1)}{(\cos^4\theta+3)^{1/2}}|-\rangle + \frac{\cos^2\theta-1}{\sin\theta}\left(\frac{2}{\cos^4\theta+3}\right)^{1/2}|0\rangle - \frac{e^{-i\phi}(\cos\theta-1)}{(\cos^4\theta+3)^{1/2}}|+\rangle$
$-\hbar\Omega$	$\frac{e^{i\phi}(\cos\theta-1)}{(\cos^4\theta+3)^{1/2}}|-\rangle + \frac{\cos^2\theta-1}{\sin\theta}\left(\frac{2}{\cos^4\theta+3}\right)^{1/2}|0\rangle - \frac{e^{-i\phi}(\cos\theta+1)}{(\cos^4\theta+3)^{1/2}}$

Inspection of the table reveals much mathematical symmetry as would be expected.

The mathematical exact solution for the quadrupole field having an axially symmetric field gradient interacting with a constant magnetic field was then solved. The matrix representation is the following:

$$\underset{\sim}{H}_Q^a + \underset{\sim}{H}_z = \begin{pmatrix} \hbar\Omega\cos\theta + A & -\hbar\Omega e^{i\phi}\sin\theta/\sqrt{3} & 0 \\ -\hbar\Omega e^{-i\phi}\sin\theta/\sqrt{2} & -2A & -\hbar\Omega e^{i\phi}\sin\theta/\sqrt{2} \\ 0 & -\hbar\Omega e^{-i\phi}\sin\theta/\sqrt{2} & -\hbar\Omega\cos\theta + A \end{pmatrix} \quad 10)$$

The secular equation was found to contain the natural parameter $A/\hbar\Omega = B$ in the following manner:

$$(\lambda/\hbar\Omega)^3 - (\lambda/\hbar\Omega)(1+3B^2) - (B\cos 2\theta + B\cos^2\theta - 2B^3) = 0 \quad 11)$$

Since the eigenvalues are real and in general different, the trigonometric form of the solution to a cubic equation can be used:

$$\lambda_{-1,0,+1} = \frac{2\hbar\Omega}{\sqrt{3}}\left(1 + \frac{3A^2}{(\hbar\Omega)^2}\right)^{1/2}\cos\left(\frac{\Phi(\theta)}{3} + 0_{(-1)} + 2\pi/3_{\,(0)} + \frac{4\pi}{3}_{(+1)}\right) \quad 12)$$

where

$$\cos\Phi(\theta) = \sqrt{27}\,(B\cos 2\theta + B\cos^2\theta - 2B^3)/2(1+3B^2)^{3/2}$$

The subscripts indicating the three different levels were assigned by considering the limiting pure quadrupole and pure magnetic cases. The levels are linear combinations of the 3 states $|-\rangle, |0\rangle, |+\rangle$ but since energy is a continuous function of magnetic field the levels can be labelled according to the quadrupole limit. The quadrupole field limit corresponds to $\Phi(\Theta) = \pi$ whereas the magnetic field limit to $\Phi(\Theta) = \pi/2$. The eigenfunctions $\psi_{-1}, \psi_0, \psi_{+1}$ have the form $\psi = a_1|-\rangle + a_2|0\rangle + a_3|+\rangle$ where,

$$a_1 = \frac{e^{i\phi}\sin\theta \quad a_2}{\sqrt{2}\,(\cos\theta + B - \lambda/\hbar\Omega)} \qquad 13)$$

$$a_2 = a_2$$

$$a_3 = \frac{-e^{-i\phi}\sin\theta \quad a_2}{\sqrt{2}\,(\cos\theta - B + \lambda/\hbar\Omega)}$$

Fig 4 shows qualitatively (calculations by slide rule were done only for three values of magnetic field because of the complexity of the equations) how the levels vary with magnetic field when the magnetic field is perpendicular to the quadrupole field. It is interesting to note that the ψ_{+1} level has a dip between zero magnetic field and the point where $\hbar\Omega = A$.

The final problem calculating energy eigenvalues and eigenvectors is to include the effect of a non-axially symmetric field gradient. The Hamiltonian operator is then $\hat{H}_Q^\eta + \hat{H}_Z$ with the matrix representation:

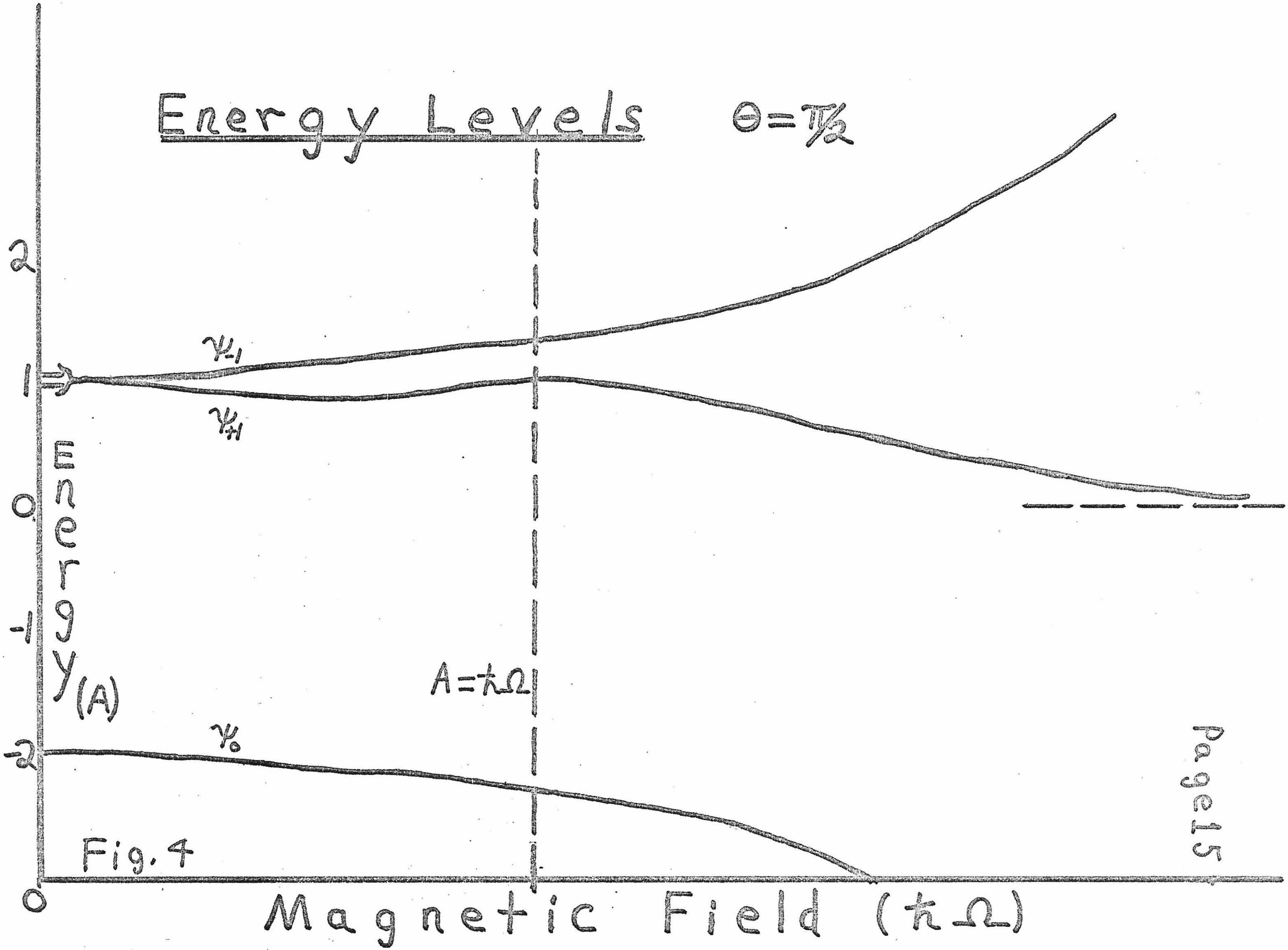

Energy Levels $\Theta=\pi/2$
2
1
0
-1
-2
Energy (A)
ψ_{-1}
ψ_{+1}
ψ_0
$A=\hbar\Omega$
0
Magnetic Field ($\hbar\Omega$)

Fig. 4

$$\underset{\sim}{H_Q^\eta} + \underset{\sim}{H_z} = \begin{pmatrix} \hbar\Omega\cos\theta + A & -\hbar\Omega e^{i\phi}\sin\theta/\sqrt{2} & \eta A \\ -\hbar\Omega e^{-i\phi}\sin\theta/\sqrt{2} & -2A & -\hbar\Omega e^{i\phi}\sin\theta/\sqrt{2} \\ \eta A & -\hbar\Omega e^{-i\phi}\sin\theta/\sqrt{2} & -\hbar\Omega\cos\theta + A \end{pmatrix} \quad 14)$$

The resulting secular equation is,

$$0 = \left(\frac{\lambda}{\hbar\Omega}\right)^3 - \frac{\lambda}{\hbar\Omega}\left\{1 + (3+\eta^2)B^2\right\} - \left\{B\cos 2\theta + B\cos^2\theta - 2(1-\eta^2)B^3 + \eta B\sin^2\theta\cos 2\phi\right\} \quad 15)$$

Again using the solution to a general cubic equation,

the eigenvalues were found to be:

$$\lambda_{-1,0,+1} = \frac{2\hbar\Omega}{\sqrt{3}}\left(1 + (3+\eta^2)\frac{A^2}{(\hbar\Omega)^2}\right)^{1/2}\cos\left(\frac{\Phi(\theta,\phi)}{3} + 0_{(-1)}, + \frac{2\pi}{3}_{(0)}, + \frac{4\pi}{3}_{(+1)}\right)$$

where 16)

$$\cos\Phi(\theta,\phi) = \frac{\sqrt{27}\left\{B\cos 2\theta + B\cos^2\theta - 2(1-\eta^2)B^3 + \eta B\sin^2\theta\cos 2\phi\right\}}{2\left\{1 + (3+\eta^2)B^2\right\}^{3/2}}$$

Note that for $\eta = 0$ 16) reduces to 12). When η is included the quadrupole limit corresponds to $\cos\Phi = \frac{-\sqrt{27}\,(1-\eta^2)}{(3+\eta^2)^{3/2}}$ and the magnetic field limit to $\Phi = \pi/2$ as before. The eigenvectors, which will be necessary in the calculation of expected intensities, were found to be the following:

$$a_1 = \frac{\eta B e^{-i\phi}\sin\theta + (\cos\theta - B + \lambda')\, e^{i\phi}\sin\theta}{\sqrt{2}\left\{(\eta B)^2 + \cos^2\theta - (B-\lambda')^2\right\}}\, a_2$$

17)

$$a_2 = a_2 \qquad\qquad \lambda' = \lambda/\hbar\Omega$$

$$a_3 = \frac{\eta B e^{i\phi}\sin\theta - (\cos\theta + B - \lambda')e^{-i\phi}\sin\theta}{\sqrt{2}\left\{(\eta B)^2 + \cos^2\theta - (B-\lambda')^2\right\}}$$

where $\psi = a_1|-\rangle + a_2|0\rangle + a_3|+\rangle$.

The transition frequencies as a function of θ and ϕ and $B = A/\hbar\Omega$ are calculated from the energy eigenvalues given in 16):

$$\omega(1\to -1) = 2\Omega\left\{1 + (3+\eta^2)B^2\right\}^{1/2}\sin\left(\Phi/3 + 2\pi/3\right) \quad 18)$$

$$\omega(0\to -1) = \omega(0\to 1) = 2\Omega\left\{1 + (3+\eta^2)B^2\right\}^{1/2}\sin\left(\Phi/3 + \pi/3\right)$$

Formally the wavefunctions corresponding to the energy levels sketched in Fig. 4 can be written as:

$$\psi_{-1} = a_1^- |-\rangle + a_2^- |0\rangle + a_3^- |+\rangle$$

$$\psi_{+1} = a_1^+ |-\rangle + a_2^+ |0\rangle + a_3^+ |+\rangle \qquad 19)$$

$$\psi_0 = a_1^0 |-\rangle + a_2^0 |0\rangle + a_3^0 |+\rangle$$

The intensity for the $\omega(1\rightarrow -1)$ transition will have terms proportional to $|a_1^+ a_2^-|^2$, $|a_2^+ a_3^-|^2$, $|a_2^+ a_1^-|^2$, $|a_3^+ a_2^-|^2$ which by 17) will be proportional to $|a_2^+ a_1^-|^2$. Both the intensity and the frequency $\omega(1\rightarrow -1)$ are dependent on θ and ϕ which will broaden the spectral line for a powder spectrum. Computer calculations of intensities and frequencies as functions of $\theta, \phi,$ and the magnetic field are to be done. After accurate theoretical computations for these functions are tabulated, the optimum values of parameters will be chosen to perform an experiment verifying the predictions. The optimum values will depend mostly on expected intensities and resolution of the frequencies. For the magnetic field the optimum position will be near $A = \hbar\Omega$ since for that choice the interaction of the quadrupole field and the magnetic field should be greatest.

IV. Acknowledgments:

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