SOLID STATE PHYSICS

SUPPLEMENT 1

NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

T. P. DAS
Saha Institute of Nuclear Physics, Calcutta, India

E. L. HAHN
Department of Physics, University of California, Berkeley, California

ACADEMIC PRESS INC., PUBLISHERS
NEW YORK • LONDON • 1958

ACADEMIC PRESS INC.
111 Fifth Avenue
New York 3, N. Y.

ACADEMIC PRESS INC.
(London) Ltd., Publishers
40 Pall Mall
London, S. W. 1

Library of Congress Catalog Card Number: 58-10410

PRINTED IN THE UNITED STATES OF AMERICA

Preface

Nuclear quadrupole resonance is one of the special branches of radiofrequency resonance physics that is being used more and more as an analytical tool for solid state studies and structural chemistry. A great deal of material on the analysis of compounds and crystals exists in the literature that considers the point of view of purely magnetic interactions. The nuclear electric quadrupole moment plays a minor role, or is absent, and the nuclear magnetic moment interactions are chiefly important. This review emphasizes the pure nuclear quadrupole interactions with crystalline and molecular electric fields, and magnetic interactions play a minor role. We have attempted to relate the theory, applications, and important examples of nuclear quadrupole studies and to present this information in a systematic fashion as a useful source of reference for the general investigator.

We wish to thank the U. S. Office of Naval Research and the U. S. National Security Agency for their support during the preparation of this review at Berkeley. One of the authors (T. P. D.) would like to express his indebtedness to Professor R. Bersohn of Cornell University for introducing him to the subject of nuclear quadrupole resonance, and to the U. S. Atomic Energy Commission for support of early work on this review while at Cornell. Several suggestions made by Professor Bersohn have been incorporated in the review. We are grateful to Professor M. Cohen and Professor F. Reif of The University of Chicago for valuable suggestions and correspondence, and to Dr. R. Livingston of the Oak Ridge National Laboratory and Dr. D. C. Douglass of Cornell University for informing us of several of their results prior to publication. We wish to thank Mrs. E. Thornhill for typing the entire text and for assistance in proofreading. We would also like to thank Mr. W. E. Blumberg, Mr. Marvin Weber, and Mr. E. G. Wikner, of the University of California, for helpful comments and criticism of the text.

T. P. DAS
E. L. HAHN

Calcutta, India
Berkeley, California
March, 1958

Contents

TABLES

Introduction

The fundamental analysis and description of nuclear electric quadrupole interactions have been given in a previous article[1] by Cohen and Reif. They discuss the quantum-mechanical Hamiltonian describing the interaction of the nuclear quadrupole moment with the surrounding charge distribution, and treat the case where the electric quadrupole interaction energy is a small perturbation upon the interaction between the magnetic dipole moment of the nucleus and a large applied magnetic field. We shall deal with the converse case where the quadrupole interaction energy, even in the absence of any applied magnetic field, is strong enough to give rise to resonance frequencies in the radio-frequency range.[2,3] The lines resulting from transitions between these quadrupole levels will be termed quadrupole spectra. Any additional perturbation caused by the magnetic interaction with a small applied magnetic field will produce Zeeman splittings of the quadrupole spectra. The aim of this review is to explain the features of the quadrupole spectra, and to show how they are interpreted in terms of the electron distributions that produce the necessary electric field gradients at nuclei. Furthermore, the spectra will provide information concerning positions of molecules and ions in the crystalline unit cell and their motional behavior. In many cases, the study of quadrupole spectra has revealed new information regarding these features of the solid state. The technique used in experiment is generally that of the field of nuclear magnetic resonance. We shall attempt to review most of the phenomena studied to date, and to outline the scope of the quadrupole resonance technique from the point of view of its usefulness for investigations on the nature of the solid state.

---

[1] M. H. Cohen and F. Reif, Nuclear quadrupole effects in nuclear magnetic resonance. *Solid State Phys.* **5**, 321 (1957).

[2] Zero field quadrupole resonance was first observed for Na^{23} in sodium halide molecules by the molecular beam technique [W. Nierenberg, N. F. Ramsey, and S. B. Brody, *Phys. Rev.* **70**, 773 (1946); W. Nierenberg and N. F. Ramsey, *ibid.* **72**, 1075 (1947)].

[3] The theory of nuclear quadrupole interactions in solids was first given by R. V. Pound [*Phys. Rev.* **79**, 685 (1950)]. The first successful pure quadrupole resonance experiment in solids was performed by H. G. Dehmelt and H. Krüger for Cl^{35} nuclei in transdichloroethylene [*Naturwiss.* **37**, 111 (1950); **38**, 921 (1951)].

The review is divided broadly into three parts. Part I will deal with the phenomenological theory for the frequencies of the quadrupole spectra, the nature of their Zeeman patterns, the line shapes and line widths, and the relaxation times. Some results will be mentioned occasionally in this part to illustrate the theory. Part II will deal with the required experimental apparatus for observing the different aspects of the quadrupole spectra. Part III will deal with interpretation of experimental results. Results obtained to date in imperfect and impure solids will also be discussed.

I. Theory

1. Frequencies and Intensities of Pure Quadrupole Spectra

a. Hamiltonian

As discussed in the article by Cohen and Reif,[1] the Hamiltonian for the interaction of the quadrupole moment of a nucleus with the field gradient at its position due to surrounding charges is given by the tensor-scalar product,

$$\mathcal{H}_Q = \mathbf{Q} \cdot \nabla E = \sum_m \mathbf{Q}_2{}^m (\nabla E)_2{}^{-m} \tag{1.1}$$

where **Q** is the tensor defining the quadrupole charge distribution in the nucleus. Its irreducible components in terms of coordinates x, y, z are given by

$$\begin{aligned} Q_2{}^0 &= \frac{eQ}{2I(2I-1)}\,(3I_z{}^2 - \mathbf{I}^2) \\ Q_2{}^{\pm 1} &= \frac{eQ}{2I(2I-1)}\,\frac{\sqrt{6}}{2}\,[I_z(I_x \pm iI_y) + (I_x \pm iI_y)I_z] \\ Q_2{}^{\pm 2} &= \frac{\sqrt{6}\,eQ}{4I(2I-1)}\,(I_x \pm iI_y)^2. \end{aligned} \tag{1.2}$$

The scalar quadrupole moment Q of the nucleus is defined by Casimir[4] as

$$eQ = \int \rho_i r_i{}^2 (3\cos^2\theta_{iI} - 1)\,d\tau_i \tag{1.3}$$

where ρ_i is the charge density in a small volume element $d\tau_i$ inside the nucleus at a distance r_i from the center, and θ_{iI} is the angle which the radius vector $\mathbf{r}_i$ makes with the nuclear spin axis. The field gradient at the nucleus is defined by the tensor $(\nabla E')$, having 9 components $-V_{ij}$ in Cartesian coordinates, where

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \qquad (x_i, x_j = x, y, z)$$

and V is the electrostatic potential at the nucleus due to the surround-

---

[4] H. B. G. Casimir, Interaction between atomic nuclei and electrons. *Teyler's Tweede Genootschap Haarlem* **11**, 36 (1936).

ing charges. If the Laplace equation gives

$$V_{xx} + V_{yy} + V_{zz} = 0$$

meaning that the electric field at the nucleus is produced entirely by charges wholly external to the nucleus, then $(\nabla E')$ is a symmetric traceless tensor.[1] Therefore we can represent the tensor by its five irreducible components as follows:

$$\begin{aligned} (\nabla E')_0 &= \tfrac{1}{2} V_{zz} \\ (\nabla E')_{\pm 1} &= -\frac{1}{\sqrt{6}} (V_{xz} \pm i V_{yz}) \\ (\nabla E')_{\pm 2} &= \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm 2i V_{xy}). \end{aligned} \tag{1.4}$$

If one transforms the tensor to a set of principal axes X, Y, Z, the resulting irreducible components in the new system are:

$$\begin{aligned} (\nabla E)_0 &= \tfrac{1}{2} V_{ZZ} = \tfrac{1}{2} eq \\ (\nabla E)_{\pm 1} &= 0 \\ (\nabla E)_{\pm 2} &= \frac{1}{2\sqrt{6}} (V_{XX} - V_{YY}) = \frac{1}{2\sqrt{6}} \eta eq. \end{aligned} \tag{1.5}$$

Conventionally e^2qQ is termed the quadrupole coupling constant for the nucleus in the particular environment under consideration. The asymmetry parameter for the field gradient tensor η is defined by the relation

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}. \tag{1.6}$$

Throughout our discussions we shall assume that[5] the condition

$$|V_{XX}| < |V_{YY}| < |V_{ZZ}| \tag{1.7}$$

applies in the principal axis system. Therefore η can vary from 0 to 1, where $\eta = 0$ corresponds to axial symmetry around Z:

$$\begin{aligned} V_{XX} &= V_{YY} = -\tfrac{1}{2} eq \\ V_{ZZ} &= eq \end{aligned} \tag{1.8}$$

and $\eta = 1$ corresponds to the condition:

$$\begin{aligned} V_{XX} &= 0 \\ V_{YY} &= -V_{ZZ}. \end{aligned} \tag{1.9}$$

The components of the field gradient tensor in a laboratory system of

---

[5] C. Dean, *Phys. Rev.* **96**, 1053 (1954); Thesis, Harvard University (1952).

coordinates can be obtained from those in the principal axis system given by (1.5), if the Eulerian angles (α, β, γ) describing their relative orientations are known.[6] The field gradient tensor can be specified completely in terms of five quantities, namely q, η, α, β, and γ. Of course we cannot get q from the spectra unless the quadrupole moment Q of the nucleus is known. Therefore the statement should be amended to read: the features of the nuclear quadrupole interaction tensor are determined completely by the five quantities e^2qQ, η, α, β, and γ. In the following sections the theory for the determination of these quantities from the observed quadrupole spectra will be described.

b. Pure Quadrupole Spectra for Axially Symmetric Field Gradients

The features of pure quadrupole spectra and their Zeeman effects have been discussed by a number of authors.[1,2,5,7] The convention for the choice of XYZ axis is that given by (1.8). It is then found from (1.1), (1.2), and (1.5) that, if m and m' represent the magnetic quantum numbers for the nuclear spin in different states, then the matrix elements of $\mathcal{H}_Q$ are

$$<m|\mathcal{H}_Q|m'> = \frac{e^2qQ}{4I(2I-1)}[3m^2 - I(I+1)]\delta_{mm'} \qquad (1.10)$$

where $\delta_{mm'}$ is the Krönecker δ, i.e.

$$\begin{aligned} \delta_{mm'} &= 0 \qquad m \neq m' \\ &= 1 \qquad m = m'. \end{aligned} \qquad (1.11)$$

We choose a representation in which the eigenvalues of I_z are diagonal. Then the energy levels are given by

$$E_m = A[3m^2 - I(I+1)] \qquad (1.12)$$

where

$$A = \frac{e^2qQ}{4I(2I-1)}. \qquad (1.13)$$

This result holds for both half-integral and integral spins. The energy levels are thus doubly degenerate in m, since the two states $\psi_{\pm m}$ have the same energy. For half-integral spins there are $I + \frac{1}{2}$ energy levels all doubly degenerate, while for integral spins there are $I + 1$ energy levels where I of these are doubly degenerate, and only one of them with $m = 0$ is nondegenerate.

---

[6] R. Bersohn, *J. Chem. Phys.* **20**, 1505 (1952).

[7] R. Livingston, *Science* **118**, 61 (1953).

Transitions between the energy levels given by (1.12) are produced by the application of an oscillating magnetic field that interacts with the magnetic dipole moment of the nucleus, thereby producing a time-dependent perturbation. Electric fields are not used because the nucleus[8] does not have an electric dipole moment. Conceivably, transitions could be brought about by applying oscillating inhomogenous electric fields with which the quadruple moment of the nucleus would undergo a time-dependent interaction. But, in order to induce a sufficient number of transitions by this procedure, electric field gradients too large for generation in the laboratory would be required.

The time-dependent Hamiltonian representing the interaction of the nucleus with the applied radio-frequency magnetic field is given by

$$\mathcal{H}'(t) = -\gamma\hbar[H_X(t)I_X + H_Y(t)I_Y + H_Z(t)I_Z] \tag{1.14}$$

where γ is the magnetogyric ratio for the nucleus, and $H_X(t)$, $H_Y(t)$, $H_Z(t)$ are the components of the linearly polarized radio-frequency magnetic field $2H_1 \cos \omega t$. Since the matrix elements of the spin angular momentum of the nuclei are given by

$$\begin{aligned} <m|I_Z|m'> &= m\delta_{mm'} \\ <m|I_X \pm iI_Y|m'> &= [(I \pm m)(I \mp m + 1)]^{\frac{1}{2}}\delta_{m\mp 1,m'} \end{aligned} \tag{1.15}$$

only transitions $\Delta m = \pm 1$ can be induced by the X and Y components of the rf field; the Z component produces $\Delta m = 0$ transitions. The $\Delta m = 0$ transitions do not interest us here, since they do not involve any change in energy. The transition probabilities for the $\Delta m = \pm 1$ transitions, according to Eqs. (1.14) and (1.15), involve the component of the rf field perpendicular to the axis of symmetry of the field gradient. By the conventional time-dependent perturbation theory it can be shown, as in the case of magnetic resonance,[9] that maximum probability for the transition between two levels m and $m + 1$ results when the rf field frequency ω satisfies the Bohr condition $\omega = \omega_m$, where

$$\omega = \frac{E_{m+1} - E_m}{\hbar}. \tag{1.16}$$

Using (1.12),

$$\omega_m = \frac{3A}{\hbar}(2|m| + 1). \tag{1.17}$$

There will be $I - \frac{1}{2}$ distinct transition frequencies for half-integral

---

[8] N. F. Ramsey, "Nuclear Moments," p. 8. McGraw-Hill, New York, 1953.

[9] G. E. Pake, Nuclear magnetic resonance. *Solid State Phys.* **2**, 24 (1956).

spins and I of them for integral spins. The quantity A, and therefore e^2qQ, can be obtained very accurately by measuring the resonance frequencies, if assignment of the various m values pertaining to the observed frequencies can be made. The measurement of A is thus possible when two or more of the $I - \frac{1}{2}$ frequencies are observed so that the two m values that satisfy the relation

$$\frac{\omega_1}{\omega_2} = \frac{2|m_1| + 1}{2|m_2| + 1} \tag{1.18}$$

can be uniquely determined. For spin $I = \frac{3}{2}$ (for example, Cl^{35} and Br^{79}) and $I = 1$ (N^{14}), the problem of assignment does not arise, because there is only one resonance frequency in each case. For spin $I = \frac{1}{2}$,[6] no nuclear quadrupole moment is found, and the question of quadrupole resonance frequencies does not arise.

The orientation of the axis of symmetry of the field gradient tensor could be found by studying the dependence of the intensity of the quadrupole resonance lines upon the orientation of the rf field with respect to axes fixed in the crystal in which the nuclei are contained. We note (1) that the intensity vanishes when the rf field is along the symmetry axis; and (2) the intensity becomes a maximum when the field is applied in a plane perpendicular to the symmetry axis. However, intensity measurements are neither very convenient nor precise. They are apt to be rather complicated when several lattice sites exist in the unit cell. These sites may have different directions for the axes of symmetry (Cl^{35} resonance in $NaClO_3$ for example, to be discussed in Section 6b). In practice, the Zeeman splittings in a weak constant magnetic field (to be described in Section 1c) are used to locate the symmetry axis. Nevertheless the directional dependence of the intensity may be used as a check on the result obtained from the Zeeman study.

c. *Zeeman Splitting of the Quadrupole Spectra. Case of Axially Symmetric Field Gradient*

When a constant magnetic field H_0 is applied at an angle θ with respect to the symmetry axis, the net Hamiltonian is given by $\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_M$, where $\mathcal{H}_Q$ is given by (1.10), and

$$\mathcal{H}_M = -\hbar\Omega(I_z \cos\theta + I_x \sin\theta\cos\phi + I_y \sin\theta\sin\phi). \tag{1.19}$$

The azimuthal angle for H_0 is given by ϕ for a particular choice of X and Y axis of the principal system, and $\Omega = \gamma H_0$. The resulting Zeeman pattern is independent of ϕ. The magnetic field is considered to be weak, i.e., $\hbar\Omega \ll e^2qQ$. We shall consider the cases of half-integral and integral spins separately.

(*1*) *Half-integral spins.* In the absence of H_0 there are $I + \frac{1}{2}$ doubly degenerate energy levels E_m. The Zeeman field removes this degeneracy, and for $m > \frac{1}{2}$ there are two energy levels,

$$E_{\pm m} = A[3m^2 - I(I + 1)] \mp m\hbar\Omega \cos\theta, \tag{1.20}$$

corresponding to the states ψ_{+m} and ψ_{-m}, respectively. Actually there is some mixing between the adjacent states ψ_m and ψ_{m-1} due to the I_x and I_y terms in (1.19). However, this mixing is only of the first order in Ω/A and may be neglected. The case of the $\psi_{\pm\frac{1}{2}}$ states is somewhat special. They are of the same energy in the absence of the field, but give finite off-diagonal elements $<\frac{1}{2}|\mathcal{H}_M| - \frac{1}{2}>$ for $\mathcal{H}_M$. Therefore, the prescription of the degenerate perturbation theory[10] has to be used, and the Hamiltonian $\mathcal{H}_M$ must be diagonalized for these states. This leads to zero-order mixing of the states $\psi_{+\frac{1}{2}}$ and $\psi_{-\frac{1}{2}}$ to form new states ψ_+ and ψ_- with energies given by

$$E_\pm = A\left[\frac{3}{4} - I(I + 1)\right] \mp \frac{f}{2}\hbar\Omega\cos\theta \tag{1.21}$$

where

$$f = [1 + (I + \tfrac{1}{2})^2 \tan^2\theta]^{\frac{1}{2}}$$

and

$$\begin{aligned} \psi_+ &= \psi_{+\frac{1}{2}} \sin\alpha + \psi_{-\frac{1}{2}} \cos\alpha \\ \psi_- &= \psi_{-\frac{1}{2}} \sin\alpha - \psi_{+\frac{1}{2}} \cos\alpha \\ \tan\alpha &= [(f + 1)/(f - 1)]^{\frac{1}{2}}. \end{aligned} \tag{1.22}$$

The arrangement of the energy levels is shown schematically in Fig. 1. When the rf field [described by the Hamiltonian $\mathcal{H}'(t)$ in (1.14)] is applied, transitions occur between the different energy levels. As pointed out in Section 1b, the $\Delta m = 0$ transitions are of no interest, since they involve no change of energy for levels with $m > \frac{1}{2}$. For the mixed states $\psi_\pm$ a transition corresponds to the smaller arrow in Fig. 1 and involves a frequency much smaller than the quadrupole resonance frequency. For most nuclei of interest, with Zeeman fields of the order of 100 gauss, these transitions correspond to frequencies only of the order of a hundred kilocycles or less and shall not be considered. With $m > \frac{1}{2}$, the $\Delta m = \pm 1$ transitions between the $\pm m$ and $\pm(m + 1)$ levels lead to two frequencies $\omega_m{}^+$ and $\omega_m{}^-$, which replace the single

---

[10] L. I. Schiff, "Quantum Mechanics," Chapter 7. McGraw-Hill, New York, 1955.

pure quadrupole frequency ω_m in (1.16). The new frequencies are

$$\omega_m^{\pm} = \frac{3A}{\hbar}(2|m| + 1) \pm \Omega \cos \theta. \qquad (1.23)$$

These are symmetric about ω_m, and each of them may be shown to have

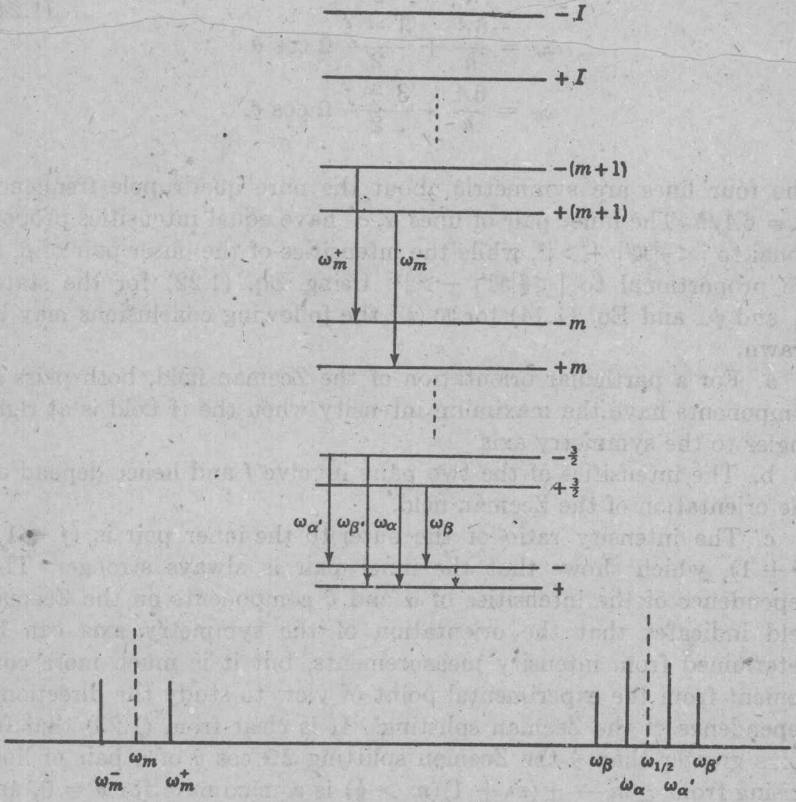

FIG. 1. Arrangement of energy levels for half-integral spins for axially symmetric quadrupole interaction in the presence of a Zeeman field. The order of the energy levels has been chosen so as to correspond to a positive γ. The heights shown for the different spectral lines have no bearing to their actual intensities, except for the $\alpha\alpha'\beta\beta'$ pattern where the $\beta\beta'$ lines are drawn smaller than the $\alpha\alpha'$ lines to show that they are in general weaker.

half the intensity of the original line. Their intensities involve the matrix elements $|\langle m|\mathcal{H}'(t)|m + 1\rangle|^2$, and are seen to be independent of the orientation of the Zeeman field.

The $\Delta m = \pm 1$ transitions between mixed states $\psi_\pm$ given by (1.22) and the states $\psi_{\pm\frac{3}{2}}$ give four lines, as shown in Fig. 1, with frequencies

$$\begin{aligned}
\omega_{\alpha} &= \frac{6A}{\hbar} - \frac{3-f}{2}\,\Omega\cos\theta \\
\omega_{\beta} &= \frac{6A}{\hbar} - \frac{3+f}{2}\,\Omega\cos\theta \\
\omega_{\alpha'} &= \frac{6A}{\hbar} + \frac{3-f}{2}\,\Omega\cos\theta \\
\omega_{\beta'} &= \frac{6A}{\hbar} + \frac{3+f}{2}\,\Omega\cos\theta.
\end{aligned} \tag{1.24}$$

The four lines are symmetric about the pure quadrupole frequency $\omega_{\frac{3}{2}} = 6A/\hbar$. The inner pair of lines α, α' have equal intensities proportional to $|<\frac{3}{2}|\mathcal{H}'|+>|^2$, while the intensities of the outer pair of β, β' are proportional to $|<\frac{3}{2}|\mathcal{H}'|->|^2$. Using Eq. (1.22) for the states ψ_+ and ψ_- and Eq. (1.14) for $\mathcal{H}'(t)$, the following conclusions may be drawn.

a. For a particular orientation of the Zeeman field, both pairs of components have the maximum intensity when the rf field is at right angles to the symmetry axis.

b. The intensities of the two pairs involve f and hence depend on the orientation of the Zeeman field.

c. The intensity ratio of the outer to the inner pair is $(f-1)/(f+1)$, which shows that the inner pair is always stronger. This dependence of the intensities of α and β components on the Zeeman field indicates that the orientation of the symmetry axis can be determined from intensity measurements, but it is much more convenient from the experimental point of view to study the directional dependence of the Zeeman splittings. It is clear from (1.23) that for spins greater than $\frac{3}{2}$ the Zeeman splitting $2\Omega\cos\theta$ of a pair of lines arising from $\pm m \to \pm(m+1)(m > \frac{1}{2})$ is a maximum for $\theta = 0$, and zero for $\theta = 90°$. The splitting is independent of the azimuthal direction of the Zeeman field H_0 in the principal axis system and is constant for orientations of H_0 lying on the surface of a cone with its axis coinciding with the symmetry axis. The splitting is zero when the cone collapses into a plane perpendicular to the symmetry axis. Therefore the symmetry axis may be located by making stereoscopic plots of the Zeeman splitting. The orientational dependence of the splitting of the $\alpha\alpha'$ and $\beta\beta'$ lines is somewhat more complicated. We shall now consider the splittings for some special orientations of the Zeeman field. Henceforth the term *locus of constant* (or zero) *splitting*