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**CALCULATION OF FORBIDDEN-DOUBLET SEPARATIONS AND INTENSITY
OF ALLOWED AND FORBIDDEN-HYPERFINE TRANSITIONS IN THE EPR
SPECTRUM OF TRANSITION-METAL COMPLEXES**

Kingsley Okwuchukwu Mbaeie

**A Thesis
in
The Department
of
Physics**

**Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science at
Concordia University
Montreal, Quebec, Canada**

March, 1989

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ABSTRACT

CALCULATION OF FORBIDDEN-DOUBLET SEPARATIONS AND INTENSITY OF ALLOWED AND FORBIDDEN-HYPERFINE TRANSITIONS IN THE EPR SPECTRUM OF TRANSITION-METAL COMPLEXES

Kingsley Okwuchukwu Mbaebie

Three important problems concerning the positions and intensities of EPR lines have been investigated in this thesis. They are as follows:

(i) The details of a procedure using the third-order perturbation-energy expressions of the spin-Hamiltonian $\mathcal{H} = \beta_e S^T \cdot \tilde{g} \cdot H + S^T \cdot \tilde{D} \cdot S + S^T \cdot \tilde{A} \cdot I + I^T \cdot \tilde{P} \cdot I - \beta_n I^T \cdot \tilde{g}_n \cdot H$, wherein the axes of the various tensors \tilde{g} , \tilde{D} , \tilde{P} , and \tilde{g}_n are assumed to be non-coincident, to derive the expressions for the doublet separations of the hyperfine forbidden transitions: $\Delta M = \pm 1$; $\Delta m = \pm 1, \pm 2$ (M, m are the electronic and nuclear magnetic quantum numbers, respectively) in the EPR spectrum are described. These expressions are useful for estimating the nuclear quadrupole tensor, \tilde{P} , and the nuclear g -tensor, \tilde{g}_n , which cannot, otherwise, be determined, in first order of approximation, from the positions of the allowed transitions ($\Delta M = \pm 1, \Delta m = 0$). The expressions for the doublet separations, specifically applicable to Mn^{2+} ($S = I = \frac{5}{2}$; S and I are, respectively, the electronic and nuclear spins) have been listed for the transitions $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$: $\Delta m = \pm 1, \Delta m = \pm 2$; $M = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$: $\Delta m = \pm 1$ and $M = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$: $\Delta m = \pm 1$.

(ii) It is well known that forbidden hyperfine transitions of non-zero intensity are not observable for the external magnetic field orientation along the two-fold symmetry axis, when it is parallel to a crystal-field axis, of paramagnetic complexes, characterized by monoclinic site symmetry; but are observable for all orientations of the external magnetic field for complexes characterized by triclinic

symmetry. General expressions are given for the intensities of the forbidden hyperfine transitions ($\Delta M = \pm 1$, $\Delta m = \pm 1$), relative to those of the allowed hyperfine transitions ($\Delta M = \pm 1$, $\Delta m = 0$) for an arbitrary orientation of the external magnetic field. The three cases, where the monoclinic symmetry axis is parallel to a crystal-field axis have been specifically considered.

(iii) Expressions have been derived for the intensity of the fine structure ($S > \frac{1}{2}$, $I = 0$) and hyperfine ($S > \frac{1}{2}$, $I \neq 0$) transitions in the EPR spectra of paramagnetic complexes described by the spin-Hamiltonian $\mathcal{H} = \mathcal{H}_{ez} + \mathcal{H}_{zf} + \mathcal{H}_{hf} + \mathcal{H}_{nq} + \mathcal{H}_{nz}$, where the various terms represent, respectively, the electronic Zeeman, zero-field, hyperfine, nuclear quadrupole and nuclear Zeeman interactions. The particular case where the excitation field is oriented normally to the Zeeman field, and the various spin-Hamiltonian tensors are anisotropic, with non-coincident principal axes, is considered. It is assumed, following Bir [3], that $\mathcal{H}_{ez} \gg \mathcal{H}_{zf} \gg \mathcal{H}_{hf}$. The axis of quantization for the nuclear spin is chosen to be along the direction of the effective magnetic field at the nuclear site produced by the electrons in a given electronic state. The present results are compared with those published previously [3,15], taking into account the specific approximations made in the spin-Hamiltonian tensors considered therein.

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In closing, the following quotation from Abraham Lincoln (The Great Thoughts) seems most appropriate: "And, inasmuch [as] most good things are produced by labour, it follows that [all] such things of right

belong to those whose labour has produced them. But it has so happened in all the ages of the world, that some have laboured, and others have, without labour, enjoyed a large proportion of the fruits. This is wrong, and should not continue. To [secure] to each labourer the whole product of his labour, or as nearly as possible, is a most worthy object of any good government."

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If you once forfeit the confidence of your fellow citizens, you can never regain their respect and esteem. It is true that you may fool all the people some of the time; you can even fool some of the people all of the time; but you can't fool all of the people all of the time.

-- Abraham Lincoln (The great Thoughts)

CHAPTER I

INTRODUCTION

Paramagnetism occurs whenever a system of charges has a resultant angular momentum. If this momentum is of electronic origin, one speaks of electronic paramagnetism. Such paramagnetism can occur in various ways. (a) Atoms, molecules, and lattice defects possessing an odd number of electrons, as here the total spin of the system is not zero. Examples are: free sodium atoms; gaseous nitric oxide (NO); organic free radicals such as triphenylmethyl, $C(C_6H_5)_3$; F-centers in alkali halides. (b) Free atoms and ions with a partly filled inner shell of transition-metal elements, ions isoelectronic with transition elements, rare-earth and actinide elements. Examples are: Mn^{2+} , Gd^{3+} , U^{4+} . Paramagnetism is most commonly exhibited by many of these ions when incorporated into solids, although not always. (c) A few compounds with an even number of electrons, including molecular oxygen (O_2) and organic biradicals. Examples are: $(NH_4)_2 Zn(SO_4)_2 \cdot 6H_2O$, $(NH_3)Cr(SO_4)_2 \cdot 12H_2O$. (d) Metals. In all these cases, transitions between energy levels induced by an appropriate excitation magnetic field in the presence of an external Zeeman field can be observed, whose frequencies correspond to the energy-level separation. Substances consisting of ions of the various transition groups are paramagnetic materials. In general, a paramagnetic material is one which possesses no resultant magnetic moment in the absence of an external magnetic field, but acquires a magnetic moment in the direction of the applied magnetic field, whose magnitude is a function of the intensity of the field [1]. In this thesis, attention

will be confined exclusively to those substances which exhibit paramagnetism; the corresponding spectroscopy is referred to as the paramagnetic resonance spectroscopy. Also, attention is focussed mainly, on single-crystal host into which the paramagnetic ions are incorporated; for, more useful informations can be obtained from measurements on single crystals than on polycrystalline (powder) materials.

Paramagnetic resonance, whenever it can be measured, usually yields the most accurate description of the ground state (i.e., the lowest energy levels) and of the effect of the crystalline surroundings on the energy levels of the paramagnetic ion. One of the principal informations, that can be gained from electron paramagnetic resonance (EPR) spectra, is an estimate of the various parameters appearing in the spin-Hamiltonian. To better understand an EPR spectrum of a particular paramagnetic system, the EPR data need be recorded at several temperatures, at several frequencies of the excitation field and with the use of various microwave powers. At times, the EPR spectrum may be used to identify an unknown transition-metal ion, or lattice defect, or it may be used to distinguish several valence states of the same ion. The ESR spectrum frequently identifies the lattice site and symmetry of the paramagnetic species, particularly if single-crystal structure data are available.

When a magnetic field is applied to a paramagnetic ion, imbedded in a solid, splitting of its free-ion energy levels occurs, the energy levels being those due to the electronic Zeeman, crystal field, nuclear quadrupole, hyperfine and nuclear Zeeman terms, as considered in the present thesis. If a microwave field of appropriate frequency, ν , is

applied perpendicular to the direction of the external magnetic field H (this is the case considered in the present work), energy is absorbed by the system, and the photons, (microwave quanta) possessing energies equal to the differences in the energy levels, will induce transitions. Another important condition for transitions to be induced is that the probability for transition between the levels participating in resonance be non-zero. The energy absorbed as a function of the magnetic field is referred to as the paramagnetic resonance (EPR) spectrum of the material [12]. In principle, paramagnetic resonance can be observed even at low frequencies. However, it is in general, preferable for interpretation of data to operate at the highest possible magnetic field intensity, and thus, the highest-possible frequency available.

The angular variation of the EPR spectrum is, generally, studied by keeping the frequency of excitation field fixed and varying the external magnetic field in magnitude and direction with respect to a reference-axes system, fixed within the sample; these are usually taken to be the crystal or crystal-field, axes. Alternatively, one can vary the microwave frequency and keep the magnitude of the external magnetic field fixed (in the laboratory frame) and rotate the crystal itself. The former approach is typical of EPR experimental arrangement.

In EPR one generally observes the so called "allowed" ($\Delta M = \pm 1, \Delta m = 0$) and "forbidden" ($\Delta M = \pm 1, \Delta m = 0; \Delta M = \pm 1, \Delta m = \pm 1; \text{ or } \Delta M = \pm 1, \Delta m = 0$) transitions. (Here M and m denote respectively the electronic and nuclear magnetic quantum numbers). The forbidden hyperfine transitions in EPR are those apparently violating the selection rules of the so called "allowed" transitions. These are usually observed in transition-metal ions because of the non-orthogonality of the nuclear

part of the wave function due to perturbations, e.g., by the crystal-field, the hyperfine, the quadrupole, the radio-frequency, and the dynamic phonon interactions. The perturbed nuclear part of a wavefunction thus becomes a linear combination of the unperturbed wavefunctions, so that the apparently forbidden transitions become weakly "allowed". The selection rules for these weak hyperfine lines are $\Delta M = \pm 1$; $\Delta m = \pm 1, \pm 2, \dots$, etc. These are referred to, in the literature, as hyperfine forbidden transitions. The EPR spectra are experimentally observed as typical first derivatives of absorption of the microwaves by the samples as functions of the magnitudes of the external magnetic field (or Zeeman field) H , for a chosen orientation of H . This is because it is convenient for the spectrometer output to record the first derivative of the absorption line, rather than to record directly the absorption line itself. Occasionally, the second derivative of the absorption line, resembling the actual absorption more closely than the first derivative, which is easier to interpret, is recorded.

There have been published numerous calculations of the positions and intensities (absorptions) of EPR lines in a variety of hosts. However, in most of these systems the studies were confined to isotropic g (and / or A) tensors. In the cases studied where g and A anisotropy were considered, their principal axes were assumed coincident (Misra and Upreti [23]): In the present work no such restriction is made with regard to the anisotropy of the various spin-Hamiltonian tensors.

In this thesis, three important problems concerning the positions and intensities of EPR lines have been investigated in detail. They are:

- (i) A procedure to calculate the doublet separations of the hyperfine forbidden transitions to cover the case, where the various tensors,

appearing in the applicable spin Hamiltonian have non-coincident principal axes [8,9,30,39] is presented. The separations of the forbidden hyperfine doublets ($\Delta M = \pm 1$; $\Delta m = \pm 1, \pm 2$) in the various fine structure transitions for Mn^{2+} , for which the electron and nuclear spin values S and I are each $\frac{5}{2}$, have been previously reported [16,36]. These expressions for forbidden doublet separations derived by Mialhe [16] and by Upreti [36] are found to contain some important errors in them. Moreover, their expressions are not valid for the general case of non-coincident principal axes of the \tilde{g} , \tilde{D} , \tilde{A} , \tilde{P} , and \tilde{g}_n tensors; they assumed the principal axes of these tensors to be coincident. (ii) The possibility of observing forbidden hyperfine transitions for the orientations of the external magnetic field along the principal crystal field axes, for the monoclinic and triclinic site symmetries, has been previously discussed [5]. However, the spin Hamiltonian considered did not include all necessary terms needed for triclinic symmetry; in particular, the terms with the spin operator O_k^q (O_k^q are the equivalent operators of the crystalline field spin Hamiltonian as defined by Abragam and Bleaney [1]) with $q < 0$ were omitted. In addition, the spin-Hamiltonian for monoclinic symmetry was not at all correct; no account was taken of the specific orientation of the two-fold monoclinic symmetry axis, C_2 , with respect to the crystal-field axes. In the present work, the intensities of the forbidden hyperfine transitions ($\Delta M = \pm 1$, $\Delta m = \pm 1$), relative to the allowed transitions ($\Delta M = \pm 1$, $\Delta m = 0$) for an arbitrary orientation of H have been treated in detail; particular specialization of the relative-intensity expression for the orientation of H along the principal axes of the crystal field for the monoclinic site symmetry, using the correct spin-Hamiltonian has been made. (iii)

The method of Bir [3] has been used to derive explicit expressions of the intensity of fine structure ($S > \frac{1}{2}, I = 0$) and hyperfine ($S > \frac{1}{2}, I \neq 0$) transitions, with no restriction on either the orientation of the principal axes of the various spin-Hamiltonian tensors, or the direction of the excitation microwave field. Previously, a method to calculate the angular dependence of transition probabilities in electron paramagnetic resonance spectra has been given by Bir [3], wherein the direction of the external magnetic field \vec{H} was assumed to be normal to the direction of microwave radio-frequency excitation field. Furthermore, the principal axes of the various spin-Hamiltonian tensors were assumed to be coincident, with the \tilde{g} and \tilde{A} tensors isotropic.

CHAPTER II

SPIN HAMILTONIAN

II.1. General Hamiltonian

It is worthwhile to write a single Hamiltonian that encompasses all interactions. In doing so, we should remind ourselves of the significance of each term. Written below is the Hamiltonian describing a nucleus interacting with an electron in the presence of an applied magnetic field, \vec{H} . Define a vector potential $\vec{\lambda}$, associated with the field \vec{H} , and another, $\vec{\lambda}_n$, that associated with the field at the electron, due to the nuclear moment, $\vec{\mu}$ (normally, $\vec{\lambda}_n = \frac{\vec{\mu} \times \vec{r}}{r^3}$) [35].

Define the vector

$$\vec{\pi} = \frac{\hbar}{i} \vec{\nabla} + \frac{e}{c} \vec{\lambda} \quad (\text{II.1.1})$$

The energy of an atom, or a radical containing unpaired electrons and nuclei with non-zero spin, is written in terms of the following Hamiltonian:

$$\begin{aligned} \mathcal{H} = & -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_0 + V_{\text{cryst}} + \frac{e\hbar}{2m^2 c^2} \vec{S} \cdot [\vec{E} \times (\vec{p} + \frac{e}{c} \vec{\lambda})] \\ & + \frac{e}{2mc} (\vec{p} \cdot \vec{\lambda} + \vec{\lambda} \cdot \vec{p}) + \frac{e^2 \Lambda^2}{2mc^2} + \frac{e}{2mc} (\vec{\pi} \cdot \vec{\lambda}_n + \vec{\lambda}_n \cdot \vec{\pi}) + \hbar g_e \beta_e \vec{H} \cdot \vec{S} \\ & + \frac{\hbar^2 g_e \beta_e g_n \beta_n}{r^3} \left[\frac{3(\vec{r} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^2} - \vec{r} \cdot \vec{S} \right] + \frac{8}{3} \pi \hbar^2 g_e \beta_e g_n \beta_n \vec{r} \cdot \vec{S} \delta(\vec{r}) \\ & + \mathcal{H}_{\text{nq}} - \hbar g_n \beta_n \vec{H} \cdot \vec{I} \end{aligned} \quad (\text{II.1.2})$$

The coupling of nuclei with each other and the magnetic coupling of electrons with each other can be included, if so desired, in the expression of the general Hamiltonian of equation (II.1.2). The term, $-\frac{\hbar^2}{2m} \vec{\nabla}^2$, is the sum of the kinetic energy of the various electrons. V_0 is

the electron potential energy in the field of the nucleus and that of the other electrons. The potential energy of each electron relative to the nuclei is $-Z_n e^2/r_n$, and the interelectronic repulsion energy is

$$V_0 = \sum_{i, n_1} -Z_n e^2/r_{n_1} + \sum_{i > j} e^2/r_{ij}, \quad (\text{II.1.3})$$

where n_1 denotes the sum over nuclei and i, j denote the sum over the electrons. V_{cryst} represents the electron potential energy due to charges outside the atoms; one can say that it arises from the electrostatic action of the crystalline environments. In the point-charge approximation of the crystal field, ordinarily, only the nearest neighbour ligands are taken into account. It is essentially a Stark effect resulting from an electric potential of the type

$$V = \sum_{i, j} Q_j/r_{i, j}, \quad (\text{II.1.4})$$

where the summation is over the j charges on the host lattice and the i electrons. The fourth term in the Hamiltonian of equation (II.1.2), represents the electron spin-orbit coupling. An electron of momentum, \vec{P} , moving in an electric field, \vec{E} , experiences a coupling of its spin to the orbital motion, denoted by \mathcal{H}_{so} . This spin-orbit interaction can be written in the well-known form $\lambda \vec{L} \cdot \vec{S}$, where the parameter λ is the spin-orbit coupling constant, $\vec{L} = \vec{E} \times (\vec{P} + e/c \vec{A})$ and \vec{S} are the orbital and spin angular momenta vectors respectively. $\frac{e}{2mc} (\vec{P} \cdot \vec{A} + \vec{A} \cdot \vec{P}) + \frac{e^2}{2mc^2}$ represents the coupling of electron orbital motion with external field. $\frac{e}{2mc} (\vec{\pi} \cdot \vec{A}_n + \vec{A}_n \cdot \vec{\pi})$ is the coupling of nuclear moment with the orbital electron. $hg_e \beta_e \vec{H} \cdot \vec{S}$ is the electron spin Zeeman energy. In general, it is written as $\beta_e \vec{S} \cdot \tilde{g} \cdot \vec{H}$ and represents the interaction with, or coupling of the electron spin moment to, the external magnetic field,

β_e is the Bohr magneton, \tilde{g} is the electronic spectroscopic splitting g-tensor. The ninth term represents the coupling of the nuclear moment with the electron spin moment for non S-state ions. For the case of S-state ions this term is zero and must be replaced by the tenth term. The most general form of the hyperfine coupling is obtained by adding the coupling of the nuclear moment with the electron spin moment for non S-states to the coupling of the nuclear moment with the electron spin moment for S-states. The result gives

$$\mathcal{H}_{hf} = \vec{S}^T \cdot \tilde{A} \cdot \vec{I}, \quad (\text{II.1.6})$$

which is the interaction between the electronic and nuclear spins; here \tilde{A} is the hyperfine splitting tensor and the superscript T denotes the transpose. Following this term in equation (II.1.2) is the term expressing the coupling of the nuclear moment with the electron spin moment for S-state.

$$\mathcal{H}_{nq} = \frac{eQ}{6I(I+1)} \sum_{\alpha, \beta} V_{\alpha\beta} \left[-\frac{3}{2} (I_{\alpha} I_{\beta} + I_{\beta} I_{\alpha}) - \delta_{\alpha\beta} I^2 \right];$$

$$(\alpha, \beta) = (x, y, z) \quad (\text{II.1.5})$$

is the coupling of nuclear quadrupole moment to the field gradient due to the electron and external charges; here Q is the quadrupole moment of the nucleus, $V_{\alpha\beta}$ is the field gradient. \mathcal{H}_{nq} is most often written as $\vec{I}^T \cdot \tilde{Q} \cdot \vec{I}$, where \tilde{Q} is the quadrupole energy tensor. The nuclear Zeeman term,

$$\mathcal{H}_{nz} = -h g_n \beta_n \vec{H} \cdot \vec{I}, \quad (\text{II.1.7})$$

is due to the interaction of the external magnetic field, \vec{H} with the nuclear spin \vec{I} . It is usually given by $-\beta_n \vec{H}^T \cdot \tilde{g}_n \cdot \vec{I}$ where β_n is the nuclear Bohr magneton and \tilde{g}_n is the nuclear spectroscopic splitting

tensor. The coupling of the various nuclei with each other is given by the expression,

$$\mathcal{K}_{II} = \sum_{I > J} \vec{I}_I^T \cdot \vec{J}_{IJ} \cdot \vec{I}_J, \quad (\text{II.1.8})$$

where \vec{J}_{IJ} is the exchange-interaction tensor. The magnetic coupling of electrons with each other is, likewise, expressed as

$$\mathcal{K}_{ij} = \sum_{I > J} \vec{S}_i^T \cdot \vec{J}'_{ij} \cdot \vec{S}_j, \quad (\text{II.1.9})$$

The order of magnitude of these interactions can be estimated from the observed atomic spectra for the rare-earth [29]:

$$\mathcal{K}_{el} = \sum_i p_i^2 / 2m - \sum_{i, n_1} Z_n e^2 / r_{n_1} + \sum_{I > J} e^2 / r_{nq} \sim 10^5 \text{ cm}^{-1},$$

$$\mathcal{K}_{ss} = [D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2)] \sim 1 \text{ cm}^{-1},$$

$$\mathcal{K}_{ez} \sim 10^{-1} \text{ cm}^{-1}, \quad \mathcal{K}_{nz} \sim 10^{-3} \text{ cm}^{-1}, \quad \mathcal{K}_{ls} \sim 10^{-3} \text{ cm}^{-1},$$

$$\mathcal{K}_{II} \sim 10^{-1} \text{ cm}^{-1}, \quad \mathcal{K}_{nq} \sim 10^{-3} \text{ cm}^{-1}, \quad \mathcal{K}_{hf} \sim 10^{-3} \text{ cm}^{-1}$$

other terms, not listed above, are excluded in the estimate.

II.2. Spin-Hamiltonian

From the general Hamiltonian above, only those terms that are spin dependent are now extracted; the spin-independent terms are dropped, since they only shift the energy levels up or down equally and hence cancel out when the energy differences are taken into account in the resonance spectra (see below). The total spin Hamiltonian can thus be expressed as:

$$\mathcal{H} = \mathcal{K}_{ez} + \mathcal{K}_{hf} + \mathcal{K}_{ss} + \mathcal{K}_{nq} + \mathcal{K}_{nz} + \mathcal{K}_{II}, \quad (\text{II.2.1})$$

where the various terms \mathcal{K}_{ez} , \mathcal{K}_{hf} , \mathcal{K}_{ss} , \mathcal{K}_{nq} , \mathcal{K}_{nz} and \mathcal{K}_{II} represent,

respectively, the electronic Zeeman, the hyperfine, the electron spin-spin interaction, the quadrupole, the nuclear Zeeman, and the nuclear spin-spin interaction terms. Ordinarily, only three, or four of the above terms are present for most cases. Typical spin Hamiltonians for certain cases are:

$$\mathcal{H} = \mathcal{H}_{ez} + \mathcal{H}_{hf} + \mathcal{H}_{ss} \quad (\text{ESR, electron spin resonance}); \quad (\text{II.2.2})$$

$$\mathcal{H} = \mathcal{H}_{nz} + \mathcal{H}_{II} \quad (\text{NMR, nuclear magnetic resonance}); \quad (\text{II.2.3})$$

$$\mathcal{H} = \mathcal{H}_{nq} + \mathcal{H}_{nz} \quad (\text{NQR, nuclear quadrupole resonance}). \quad (\text{II.2.4})$$

II.3. Equivalent operators

The spin-Hamiltonian for an unpaired electron spin, \vec{S} , coupled to a nuclear spin, \vec{I} , can be, equivalently, written as

$$\mathcal{H} = \beta_e \vec{S}^T \cdot \tilde{g} \cdot \vec{H} + \vec{S}^T \cdot \tilde{A} \cdot \vec{I} - \beta_n \vec{H}^T \cdot \tilde{g}_n \cdot \vec{I} + \sum_{k,q} B_k^q O_k^q \quad (\text{II.3.1})$$

(k even, $\leq 2S$)

The first three terms have been defined in the general Hamiltonian and have their usual meanings. Particular combinations of angular momentum operators are referred to as equivalent operators O_k^q ; they have coefficients B_k^q . The integers k must be non-zero even numbers, $\leq 2S$ while q takes both positive and negative integers within the limits $-k \leq q \leq k$. The coefficients B_k^q assume definite values for specific interactions. The O_k^q operators, that are encountered in crystal-field theory have been tabulated by [2], along with their non-zero matrix elements taken between various electronic states. Another good source is the text by Abragam and Bleaney [1].

CHAPTER III

DOUBLET SEPARATIONS OF FORBIDDEN-HYPERFINE TRANSITIONS

IN THE EPR OF TRANSITION-METAL COMPLEXES

III.1. Introduction

The normally forbidden hyperfine (h.f.) EPR transitions ($\Delta m = 0$; where m is the nuclear magnetic quantum number), which are due to the non-orthogonality of the nuclear wavefunctions in the presence of perturbations, such as crystal field, h.f., and nuclear quadrupole interactions can often be observed [22,23]. The measurement of the intensities and positions of the h.f. forbidden transitions is important; for example, the evaluation of the components of the nuclear-quadrupole and the nuclear-g tensors, which cannot be estimated from the intensities and positions of the allowed transitions can be estimated from them [22,23]. (For allowed transitions $\Delta M = \pm 1$, $\Delta m = 0$; here M is the electronic magnetic quantum number.) Mialhe [16] has calculated the values of these parameters for Mn^{2+} (electronic spin $S = \frac{5}{2}$ and nuclear spin $I = \frac{5}{2}$), in the host lattice of α -alumina single crystal, from the positions of the h.f. forbidden transitions $\frac{1}{2}, m \leftrightarrow -\frac{1}{2}, m \pm 1$ and $\frac{3}{2}, m \leftrightarrow \frac{1}{2}, m \pm 1$. From a measurement of the separations of the h.f.-forbidden doublets corresponding to the $M = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$, and $M = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$ transitions, Upreti estimated the values of the nuclear quadrupole moment of Mn^{2+} in the host lattices of $Cd(CH_3COO)_2 \cdot 3H_2O$ [36] and $Zn(CH_3COO)_2 \cdot 2H_2O$ [37] single crystals. By redoing their calculations, it is found that the expressions for h.f. forbidden-doublet separations, derived by Upreti [36,37] and by Mialhe [16], contain some significant errors. Their expressions can not be applied to the general case of non-coincident principal axes of the \tilde{g} , \tilde{D} (zero-field), \tilde{A} (h.f.), \tilde{P}

(nuclear quadrupole) and \tilde{g}_n tensors.

It is the purpose of the present thesis to describe a procedure to calculate the doublet separations of the h.f. forbidden transitions for the general case, where the principal axes of the \tilde{g} , \tilde{g}_n , \tilde{D} , \tilde{A} and \tilde{P} tensors are non-coincident [8,9,25,26,30,39], using the eigenvalues calculated to third order in perturbation [8, 34]. Finally, this procedure will be applied to the explicit derivation of the expressions applicable to the case of Mn^{2+} ion for the transitions $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$, $\Delta m = \pm 1, \pm 2$; $M = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$, $\Delta m = \pm 1$; and $M = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$, $\Delta m = \pm 1$. (It should be noted that the derivation of the expressions for the doublet separations for $\Delta m = \pm 2$ has, here, been made only for the transition $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$, in conformity with that done in the previous publications [36,37]. It should be mentioned that the $\Delta m = \pm 2$ h.f. forbidden transitions are not of much interest, being characterized by much weaker intensities, in comparison with those of the $\Delta m = \pm 1$ h.f. forbidden transitions; thus they are often not clearly observed.

III.2. Spin Hamiltonian

The general spin Hamiltonian (S.H.), where the principal axes of the various tensors are non-coincident, can be expressed as [9]

$$\mathcal{H} = \mathcal{H}_{ez} + \mathcal{H}_{zf} + \mathcal{H}_{hf} + \mathcal{H}_{nq} + \mathcal{H}_{nz}; \quad (III.1)$$

where,

$$\mathcal{H}_{ez} = \beta_e \tilde{S}^T \cdot \tilde{g} \cdot \tilde{H};$$

$$\mathcal{H}_{zf} = \tilde{S}^T \cdot \tilde{D} \cdot \tilde{S};$$

$$\mathcal{H}_{hf} = \tilde{S}^T \cdot \tilde{A} \cdot \tilde{I};$$

$$\mathcal{H}_{nq} = \tilde{I}^T \cdot \tilde{P} \cdot \tilde{I}; \text{ and}$$

$$\mathcal{H}_{nz} = -\beta_n \tilde{I}^T \cdot \tilde{g}_n \cdot \tilde{H}.$$

In eq. (III.1), β_e and β_n are, respectively, the electronic and nuclear

Bohr magnetons, \vec{S} and \vec{I} are the electronic and nuclear spin vectors, \vec{H} is the external magnetic field vector, \tilde{g} , \tilde{D} , \tilde{A} , \tilde{P} and \tilde{g}_n are the usual S.H. tensors characterizing, respectively, the electronic-Zeeman, zero-field, hyperfine, nuclear quadrupole and nuclear-Zeeman interactions, and the superscript T denotes the transpose. Here, \tilde{g} , \tilde{A} , \tilde{D} , \tilde{P} and \tilde{g}_n are described as 3x3 matrices, e.g., with components $g_{\alpha\beta}$, $A_{\alpha\beta}$ ($\alpha, \beta = x, y, z$); while \vec{H} is described as a column vector, whose elements are H_x, H_y, H_z (x, y, z are the laboratory axes). (\vec{H}^T is then a row vector).

To find the eigenvalues of eq. (III.1), it is helpful if a transformation is made to different sets of axes for the electronic and nuclear spins [9]. The quantization axes for \vec{S} and \vec{I} are, here, chosen to be along the directions represented by the vectors $\vec{H}^T \cdot \tilde{g}$ and $\vec{H}^T \cdot \tilde{g} \cdot \tilde{A}$, respectively. For these quantization axes, the various terms of the spin-Hamiltonian given by equation (III.1) can be expressed [30]:

$$\mathcal{H}_{ez} = \beta_e g H S_{z_1}$$

$$\begin{aligned} \mathcal{H}_{zf} = & \frac{1}{2} (3S_{z_1}^2 - S(S+1)) (\vec{T}_3^T \cdot \tilde{D} \cdot \vec{T}_3) + \frac{1}{4} S_+^2 (\vec{T}_-^T \cdot \tilde{D} \cdot \vec{T}_-) + \frac{1}{4} S_-^2 (\vec{T}_+^T \cdot \tilde{D} \cdot \vec{T}_+) \\ & + \frac{1}{2} (S_+ S_{z_1} + S_{z_1} S_+) (\vec{T}_-^T \cdot \tilde{D} \cdot \vec{T}_3) + \frac{1}{2} (S_- S_{z_1} + S_{z_1} S_-) (\vec{T}_+^T \cdot \tilde{D} \cdot \vec{T}_3) \end{aligned}$$

$$\begin{aligned} \mathcal{H}_{hf} = & K S_{z_1} I_{z_2} + \frac{1}{2} S_+ I_{z_2} (\vec{T}_3^T \cdot \tilde{A} \cdot \vec{T}_-) + \frac{1}{2} S_- I_{z_2} (\vec{T}_3^T \cdot \tilde{A} \cdot \vec{T}_-) \\ & + \frac{1}{4} S_+ I_+ (\vec{T}_-^T \cdot \tilde{A} \cdot \vec{T}_-) + \frac{1}{4} S_- I_- (\vec{T}_+^T \cdot \tilde{A} \cdot \vec{T}_+) + \frac{1}{4} S_+ I_- (\vec{T}_+^T \cdot \tilde{A} \cdot \vec{T}_-) \\ & + \frac{1}{4} S_- I_+ (\vec{T}_-^T \cdot \tilde{A} \cdot \vec{T}_+) \end{aligned}$$

$$\mathcal{H}_{nq} = \frac{1}{2} (3I_{z_2}^2 - I(I+1)) (\vec{T}_3^T \cdot \tilde{P} \cdot \vec{T}_3) + \frac{1}{4} I_+^2 (\vec{T}_-^T \cdot \tilde{P} \cdot \vec{T}_-) + \frac{1}{4} I_-^2 (\vec{T}_+^T \cdot \tilde{P} \cdot \vec{T}_+)$$

$$+ \frac{1}{2} (I_{+} I_{z_2} + I_{z_2} I_{+}) (\vec{T}'_{-}{}^T \cdot \vec{P} \cdot \vec{T}'_{3}) + \frac{1}{2} (I_{-} I_{z_2} + I_{z_2} I_{-}) (\vec{T}'_{+}{}^T \cdot \vec{P} \cdot \vec{T}'_{3})$$

$$\kappa_{nz} = -\beta_n H \left[\frac{1}{2} (\vec{T}'_{-}{}^T \cdot \vec{g}_n \cdot \vec{\eta}) I_{+} + \frac{1}{2} (\vec{T}'_{+}{}^T \cdot \vec{g}_n \cdot \vec{\eta}) I_{-} + (\vec{T}'_{3}{}^T \cdot \vec{g}_n \cdot \vec{\eta}) I_{z_2} \right]$$

(III.1a)

In equation (III.1a), (x_1, y_1, z_1) and (x_2, y_2, z_2) represent two special coordinate systems introduced in order to obtain the most suitable form of the spin-Hamiltonian of equation (III.1). \vec{T} and \vec{T}' represent the real unitary matrices used to transform the laboratory (x, y, z) system in which the spin Hamiltonian of equation (1) is given into the (x_1, y_1, z_1) and (x_2, y_2, z_2) systems. For the sake of more concise notation \vec{T} and \vec{T}' matrices are considered as arrays of three orthonormal row vectors, namely

$$\vec{T} = \begin{bmatrix} \vec{T}_1 \\ \vec{T}_2 \\ \vec{T}_3 \end{bmatrix} \quad \text{and} \quad \vec{T}' = \begin{bmatrix} \vec{T}'_1 \\ \vec{T}'_2 \\ \vec{T}'_3 \end{bmatrix}, \quad \text{where} \quad \vec{T}_1 = (T_{11}, T_{12}, T_{13})$$

$$\vec{T}'_1 = (T'_{11}, T'_{12}, T'_{13})$$

$$i = (1, 2, 3); \quad \vec{T}_{\pm} = \vec{T}_1 \pm i \vec{T}_2, \quad \vec{T}'_{\pm} = \vec{T}'_1 \pm i \vec{T}'_2$$

$$S_{\pm} = S_{x_1} \pm i S_{y_1}, \quad I_{\pm} = I_{x_2} \pm i I_{y_2} \quad \text{(III.1b)}$$

The vectors defined by \vec{T}_1 and \vec{T}'_1 in equation (III.1b) are projectors, which facilitate the description of transformations. Here, \vec{T}_3 and \vec{T}'_3 vectors give the projections onto the z_1 and z_2 axes, and are equal to $\vec{g} \cdot \vec{\eta} / g$ and $\vec{A} \cdot \vec{g} \cdot \vec{\eta} / Kg$ respectively. $K, g, \vec{\eta}$ are defined in equation (III.3) below. Other projectors $\vec{T}_1, \vec{T}_2, \vec{T}'_1, \vec{T}'_2$ are parallel to the unfixed x_1, y_1, x_2, y_2 axes respectively. The calculation of the eigenvalues of the spin Hamiltonian, given by eq. (III.1), using the perturbation technique

to second-order approximation, and choosing the quantization axes as described above have been published by a number of researchers. (See [25] for a general review). As for the third-order perturbation calculations, they have been reported by Golding and Tennant [8], and by Weil [34], for the same choice of the quantization axes, as described above. (It is noted that [34] lists only the third-order h.f. terms). The energy expression corresponding to the S.H. given by eq. (III.1), calculated to third order in perturbation, is [8,34]:

$$\begin{aligned}
 E_{M,m} = & GM + \frac{3}{2}d_1(M^2 - \frac{x}{3}) + bb^*(8M^2 - 4x + 1)\frac{M}{2G} \\
 & + aa^*(2x - 2M^2 - 1)\frac{M}{8G} + Km - G_1\beta_n Hm \\
 & + \frac{\alpha_1\beta_n^2 H^2 m}{2M} - \frac{\alpha_5\beta_n H_1}{M}(3m^2 - y) + \frac{3}{2}P_1(m^2 - \frac{y}{3}) \\
 & + \alpha_6(8m^2 - 4y + 1)\frac{m}{2M} + \alpha_7(2y - 2m^2 - 1)\frac{m}{8M} \\
 & + \frac{1}{4G}[\alpha_2 M(y - m^2) - 2\alpha_3(x - M^2)m + 2\alpha_4 Mm^2 + 4\alpha_8(3M^2 - x)m] \\
 & + \frac{aa^*}{32G^2}[3d_1\{S_{01}^2 S_{12}^2(M+1) - S_{01}^2 S_{12}^2(M-1)\}] \\
 & + Km\{S_{01}^2 S_{12}^2 - S_{01}^2 S_{12}^2\} \\
 & + \frac{bb^*}{4G^2}[\frac{3}{2}d_1\{S_{01}^2(2M+1)^3 - S_{01}^2(2M-1)^3\}] \\
 & + Km\{S_{01}^2(2M+1)^2 - S_{01}^2(2M-1)^2\} \\
 & + \frac{FF^*}{16G^2}[\frac{3}{2}d_1\{S_{01}^2 I_{01}^2(2M+1) - S_{01}^2 I_{01}^2(2M-1)\}] \\
 & + K\{S_{01}^2 I_{01}^2(M+m+1) - S_{01}^2 I_{01}^2(M+m-1)\} \\
 & + \frac{BB^*}{16G^2}[\frac{3}{2}d_1\{S_{01}^2 I_{01}^2(2M+1) - S_{01}^2 I_{01}^2(2M-1)\}]
 \end{aligned}$$

$$\begin{aligned}
& - K \{ S_{01}^2 I_{01}^2 (M - m^* + 1) - S_{01}^2 I_{01}^2 (M - m - 1) \}] \\
& + \frac{(ab^* + a^* b^2)}{16G^2} [(2M + 1) S_{01}^2 (2x - 6M^2 - 6M - 3) \\
& - (2M - 1) S_{01}^2 (2x - 6M^2 + 6M - 3)] \\
& + \frac{(aF^* B_1 + a^* F B_1^*)}{16G^2} (y - m^2)(3M^2 - x). \quad (III.2)
\end{aligned}$$

In eq. (III.2),

$$aa^* = \text{Tr}(\tilde{D}^2) - 2d_2 + d_1^2 - 2d_{-1} \det(\tilde{D});$$

$$bb^* = d_2 - d_1^2;$$

$$FF^* = \text{Tr}(\tilde{A}^T \tilde{A}) - k^2 - \frac{2}{K} \det(\tilde{A});$$

$$B_1^* B_1 = \text{Tr}(\tilde{A}^T \tilde{A}) - k^2 + \frac{2}{K} \det(\tilde{A});$$

$$\alpha_1 = (g_n^2 - G_1^2)/K;$$

$$\alpha_2 = \text{Tr}(\tilde{A}^T \tilde{A}) - k^2;$$

$$\alpha_3 = [\det(\tilde{A})]/K;$$

$$\alpha_4 = (k^2 - K^2);$$

$$\alpha_5 = [q - G_1 P_1]/K;$$

$$\alpha_6 = [P_2 - P_1^2]/K;$$

$$\alpha_7 = [\text{Tr}(\tilde{P}^T \tilde{P}) - 2P_2 + P_1^2 - 2P_{-1} \det(\tilde{P})]/K;$$

$$\alpha_8 = K(e - d_1);$$

$$G = 2\beta_e H;$$

$$\hat{\eta} = \hat{H}/H;$$

$$g^2 = \hat{\eta}^T \cdot \tilde{g}^T \cdot \tilde{g} \cdot \hat{\eta};$$

$$g^2 d_n = \hat{\eta}^T \cdot \tilde{g}^T \cdot \tilde{D}^n \cdot \tilde{g} \cdot \hat{\eta} \quad (n = \pm 1, \pm 2);$$

$$g_n^2 = \hat{\eta}^T \cdot \tilde{g}_n^T \cdot \tilde{g}_n \cdot \hat{\eta};$$

$$g^2 K^2 = \hat{\eta}^T \cdot \tilde{g}^T \cdot \tilde{A}^T \cdot \tilde{A} \cdot \tilde{g} \cdot \hat{\eta};$$

$$g^2 K^2 k^2 = \hat{\eta}^T \cdot \tilde{g}^T \cdot \tilde{A}^T \cdot \tilde{A} \cdot \tilde{A}^T \cdot \tilde{A} \cdot \tilde{g} \cdot \hat{\eta};$$

$$gK G_1 = \hat{\eta}^T \cdot \frac{1}{2} (\tilde{g}^T \cdot \tilde{A}^T \cdot \tilde{g}_n + \tilde{g}_n^T \cdot \tilde{A} \cdot \tilde{g}) \cdot \hat{\eta};$$

$$g^2 K^2 P_n = \hat{\eta}^T \cdot \tilde{g}^T \cdot \tilde{A}^T \cdot \tilde{P}^n \cdot \tilde{A} \cdot \tilde{g} \cdot \hat{\eta} \quad (n = \pm 1, \pm 2);$$

$$gKq = \hat{\eta}^T \cdot \frac{1}{2} (\tilde{g}^T \cdot \tilde{A}^T \cdot \tilde{P} \cdot \tilde{g}_n + \tilde{g}_n^T \cdot \tilde{P} \cdot \tilde{A} \cdot \tilde{g}) \cdot \hat{\eta};$$

$$g^2 K^2 e = \hat{\eta}^T \cdot \tilde{g}^T \cdot \frac{1}{2} (\tilde{D} \cdot \tilde{A}^T \cdot \tilde{A} + \tilde{A}^T \cdot \tilde{A} \cdot \tilde{D}) \cdot \tilde{g} \cdot \hat{\eta};$$

$$S_{\alpha\beta}^2 = [x - (M + \alpha)(M + \beta)];$$

$$I_{\alpha\beta}^2 = [y - (m + \alpha)(m + \beta)] \quad (\alpha, \beta = 0, \pm 1, \pm 2, \dots);$$

$$x = S(S+1); \text{ and}$$

$$y = I(I+1) \quad \text{(III.3)}$$

In eqs. (III.2) and (III.3), $\bar{\alpha}$, $\bar{\beta}$ subscripts on S and I (e.g., $S_{\bar{\alpha}\bar{\beta}}$, $I_{\bar{\alpha}\bar{\beta}}$) are shorthand notations for the subscripts $(-\alpha)$ and $(-\beta)$ respectively. The star (*) denotes the complex conjugate, and the caret (^) denotes a unit vector.

To calculate the eigenvalues, the electronic Zeeman term of the S.H., given by eq. (III.1), has been assumed to be the dominant term.

The term in eq. (III.2) varying as $\frac{1}{M}$ has been derived on the assumption that the first-order h.f.-energy term, K_{Mm} , is much greater than the nuclear-Zeeman and nuclear-quadrupole terms. Thus, eq. (III.2) is not applicable to the case for which $M = 0$.

III.3 Procedure for the Calculation of Forbidden Doublet Separations

Typical EPR resonant transition, is induced between a pair of energy levels (characterized by the quantum number M, m and M', m' , with energies E_1 and E_2 respectively), when (i) the energy of the microwave quantum, $h\nu$, equals the difference in energy of the pair of levels participating in the resonance:

$$\Delta E = |E_1 - E_2| = h\nu, \quad (\text{III.4})$$

and (ii) the transition probability from the level M, m to the level M', m' due to the interaction of the electron magnetic moment with the microwave excitation field is non-zero [1]. (Here h is Planck's constant, and ν is the frequency of the microwave field.) The external magnetic field value, H_r , which satisfy the condition (III.4) is called the resonance field. Let H_{r1} and H_{r2} denote respectively the resonance fields at which the transitions corresponding to the forbidden doublet $M, m' \leftrightarrow M-1, m$ and $M, m \leftrightarrow M-1, m'$ ($m \neq m'$) occur. H_{r1} and H_{r2} are, then, the line positions corresponding to the forbidden doublet. The difference of the two resonance fields, $\Delta H = |H_{r1} - H_{r2}|$, is referred to as the forbidden-doublet separation. This separation can in general, be calculated by the method of successive approximations [14].

Using the eigenvalues, calculated to third order in perturbation, given in Section 2, it is, now, noted that any resonance field, H_r , obeys an equation of the form

$$H_r = H_0 \left[1 - a - \frac{b}{H_r} - \frac{c}{H_r^2} \right], \quad (III.5)$$

where $H_0 = hv/g\beta_e$; and a, b, c are constants. The solution of eq. (III.5), to third order, using the method of successive approximations, is

$$H_r^{(3)} = H_0 \left[1 - a - \frac{b}{H_0} - \frac{ab}{H_0^2} - \frac{c}{H_0^2} \right]. \quad (III.6)$$

Using equations (III.2), (III.4) and (III.6) one can easily, derive the general expressions for the doublet separations. The calculated general expressions (retaining only terms in H_0 , H_0^2 , H_0^{-1} , H_0^{-2} and also constant terms independent of these) turn out to be very long, and are, thus, given in Appendix A.

III.4. Doublet separations for Mn^{2+} ($S = I = \frac{5}{2}$)

The specific case of Mn^{2+} , considered by Upreti [36], will now be treated for illustration. The particular S. H. is as follows:

$$\begin{aligned} \mathcal{H} = & g\beta_e H S_{z_1} + \sigma \left(S_{z_1}^2 - \frac{1}{3} S(S+1) \right) + \rho S_+^2 \\ & + \rho^* S_- + \frac{\lambda}{2} (S_{z_1} S_+ + S_+ S_{z_1}) + \frac{\lambda^*}{2} (S_{z_1} S_- + S_- S_{z_1}) \\ & + A S_{z_1} I_{z_1} + \frac{A}{2} (S_+ I_- + S_- I_+) \\ & - g_n \beta_n H I_{z_1} + P \left(I_{z_1}^2 - \frac{1}{3} I(I+1) \right), \end{aligned} \quad (III.7)$$

where the external magnetic field \vec{H} is along the z_1 -axis. The quantities σ , ρ , and λ , appearing in eq. (III.7), are defined below by eq. (III.9). The \tilde{g} , \tilde{A} , and \tilde{g}_n tensors of the spin Hamiltonian are isotropic, while \tilde{D} and \tilde{P} tensors conform to orthorhombic symmetry.

The various doublet separations, presently calculated, are listed for the transitions $M \leftrightarrow M-1$ ($M = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$), $\Delta m = \pm 1$ and $M = \frac{1}{2}$

$\leftrightarrow -\frac{1}{2}, \Delta m = \pm 2$ as follows:

$M = \frac{1}{2} \leftrightarrow -\frac{1}{2}, \Delta m = \pm 1:$

$$\Delta H = 2\gamma H_0 + \frac{17 A^2}{2g^2\beta_e^2 H_0} + 2\gamma^3 H_0 - (m^2 + m - \frac{33}{4} \gamma A^2) \frac{1}{g^2\beta_e^2 H_0}$$

$$- \frac{32\gamma|\lambda|^2}{g^2\beta_e^2 H_0} - (2m+1) \left[\frac{2P}{g\beta_e} + \frac{\gamma A}{g\beta_e} - \frac{8A^2\sigma}{g^3\beta_e^3 H_0^2} + \frac{25A^3}{2g^3\beta_e^3 H_0^2} \right]$$

$$+ \frac{2\gamma^2 P}{g\beta_e} - (m^2 + m - \frac{33}{4} \frac{A^2 P}{g^3\beta_e^3 H_0^2} - \frac{32|\lambda|^2 P}{g^3\beta_e^3 H_0^2})$$

$M = \frac{1}{2} \leftrightarrow -\frac{1}{2}, \Delta m = \pm 2:$

$$\Delta H = 4\gamma H_0 + \frac{17A^2}{g^2\beta_e^2 H_0} + 16\gamma^3 H_0 - \frac{64\gamma|\lambda|^2}{g^2\beta_e^2 H_0} + \frac{128\gamma|\rho|^2}{g^2\beta_e^2 H_0}$$

$$- (2m^2 - \frac{31}{2} \frac{\gamma A^2}{g^2\beta_e^2 H_0} + \frac{6|\rho|^2 A}{g^3\beta_e^3 H_0^2} + \frac{m(4m^2 - 31)A^2 P}{g^3\beta_e^3 H_0^2})$$

$$- 2m \left[\frac{4P}{g\beta_e} + \frac{2\gamma A}{g\beta_e} + \frac{16\gamma^2 P}{g\beta_e} - \frac{64|\lambda|^2 P}{g^3\beta_e^3 H_0^2} \right]$$

$$+ \frac{25A^3}{g^3\beta_e^3 H_0^2} + \frac{128|\rho|^2 P}{g^3\beta_e^3 H_0^2} - \frac{16A^2\sigma}{g^3\beta_e^3 H_0^2}]$$

$M = \frac{3}{2} \leftrightarrow \frac{1}{2}, \Delta m = \pm 1:$

$$\begin{aligned}
\Delta H = & -\frac{2A}{g\beta_e} + 2\gamma H_0 - \frac{8|\lambda'|^2}{3g\beta_e}(12m^2 + 12m - 13) \\
& + \frac{16|\rho'|^2}{3g\beta_e}(6m^2 + 6m - \frac{29}{2}) - \frac{4\gamma\sigma}{g\beta_e} + (2m + \frac{17}{2})\frac{A^2}{g^2\beta_e^2 H_0} \\
& - \frac{2\gamma^2 A}{g\beta_e} + 2\gamma^3 H_0 + \frac{12|\rho|^2 A}{g^3\beta_e^3 H_0^2} - \frac{12|\lambda|^2 A^4}{g^3\beta_e^3 H_0^2} + \frac{(14m + 9)A^2\sigma}{g^3\beta_e^3 H_0^2} \\
& - (22m + 5)\frac{A^3}{g^3\beta_e^3 H_0^2} + (2m^3 - m^2 - \frac{39}{2}m - \frac{37}{4})\frac{A^2 P}{g^3\beta_e^3 H_0^2} \\
& - (m^2 - m - \frac{41}{8})\frac{\gamma A^2}{g^2\beta_e^2 H_0} + \frac{40\gamma|\rho|^2}{g^2\beta_e^2 H_0} - \frac{8\gamma|\lambda|^2}{g^2\beta_e^2 H_0} \\
& - (2m+1)\left[\frac{2P}{g\beta_e} + \frac{\gamma A}{g\beta_e} + \frac{2\gamma^2 P}{g\beta_e} - \frac{8|\lambda|^2 P}{g^3\beta_e^3 H_0^2} + \frac{40|\rho|^2 P}{g^3\beta_e^3 H_0^2}\right]
\end{aligned}$$

$$M = \frac{5}{2} \leftrightarrow \frac{3}{2}, \Delta m = \pm 1:$$

$$\Delta H = -\frac{4A}{g\beta_e} + 2\gamma H_0 - \frac{16|\lambda'|^2}{15g\beta_e}(12m^2 + 12m - 13)$$

$$+ \frac{32|\rho'|^2}{15g\beta_e}(6m^2 + 6m - \frac{29}{2}) - \frac{8\gamma\sigma}{g\beta_e} + (4m + \frac{13}{2})\frac{A^2}{g^2\beta_e^2 H_0}$$

$$- \frac{4\gamma^2 A}{g\beta_e} + 2\gamma^3 H_0 + 120\frac{|\rho|^2 A}{g^3\beta_e^3 H_0^2} - 120\frac{|\lambda|^2 A}{g^3\beta_e^3 H_0^2} + 8(m+1)\frac{A^2\sigma}{g^3\beta_e^3 H_0^2}$$

$$\begin{aligned}
& - (13m + \frac{1}{2}) \frac{\Lambda^3}{g^3 \beta_e^3 H_0^2} + (2m^3 - 5m^2 - \frac{47}{2}m - \frac{41}{4}) \frac{\Lambda^2 P}{g^3 \beta_e^3 H_0^2} \\
& - (m^2 - 3m - \frac{41}{4}) \frac{\gamma \Lambda^2}{g^2 \beta_e^2 H_0} + 64 \frac{\gamma |\lambda|^2}{g^2 \beta_e^2 H_0} - 32 \frac{\gamma |p|^2}{g^2 \beta_e^2 H_0} \\
& - (2m + 1) \left[\frac{2P}{g \beta_e} + \frac{\gamma \Lambda}{g \beta_e} + \frac{2\gamma^2 P}{g \beta_e} + 64 \frac{|\lambda|^2 P}{g^3 \beta_e^3 H_0^2} - 32 \frac{|p|^2 P}{g^3 \beta_e^3 H_0^2} \right]
\end{aligned}$$

$$M = -\frac{1}{2} \leftrightarrow -\frac{3}{2}, \Delta m = \pm 1:$$

$$\begin{aligned}
\Delta H = & \frac{2\Lambda}{g \beta_e} + 2\gamma H_0 + \frac{8|\lambda'|^2}{3g \beta_e} (12m^2 + 12m - 13) \\
& - \frac{16|\rho'|^2}{3g \beta_e} (6m^2 + 6m - \frac{29}{2}) \\
& + \frac{4\gamma \sigma}{g \beta_e} - (2m - \frac{13}{2}) \frac{\Lambda^2}{g^2 \beta_e^2 H_0} + 2 \frac{\gamma^2 \Lambda}{g \beta_e} + 2\gamma^3 H_0 - 12 \frac{|p|^2 \Lambda}{g^3 \beta_e^3 H_0^2} \\
& + 12 \frac{|\lambda|^2 \Lambda}{g^3 \beta_e^3 H_0^2} + (14m + 5) \frac{\Lambda^2 \sigma}{g^3 \beta_e^3 H_0^2} + \frac{40\gamma |p|^2}{g^2 \beta_e^2 H_0} - (22m + 17) \frac{\Lambda^3}{g^3 \beta_e^3 H_0^2} \\
& + (2m^3 + 7m^2 - \frac{23m}{2} - \frac{29}{4}) \frac{\Lambda^2 P}{g^3 \beta_e^3 H_0^2} - (m^2 + 3m - \frac{29}{4}) \frac{\gamma \Lambda^2}{g^2 \beta_e^2 H_0} \\
& - \frac{8\gamma |\lambda|^2}{g^2 \beta_e^2 H_0} - (2m + 1) \left[\frac{2P}{g \beta_e} + \frac{\gamma \Lambda}{g \beta_e} + \frac{2\gamma^2 P}{g \beta_e} - \frac{8|\lambda|^2 P}{g^3 \beta_e^3 H_0^2} + \frac{40|p|^2 P}{g^3 \beta_e^3 H_0^2} \right]
\end{aligned}$$

$$M = -\frac{3}{2} \leftrightarrow -\frac{5}{2}, \Delta m = \pm 1:$$

$$\begin{aligned}
\Delta H = & \frac{4A}{g\beta_e} + 2\gamma H_0 + \frac{16|\lambda'|^2}{15g\beta_e} (12m^2 + 12m - 13) \\
& - \frac{32|\rho'|^2}{15g\beta_e} (6m^2 + 6m - \frac{29}{2}) + \frac{8\gamma\sigma}{g\beta_e} - (4m - \frac{5}{2}) \frac{A^2}{g^2\beta_e^2 H_0^2} \\
& + \frac{4\gamma^2 A}{g\beta_e} + 2\gamma^3 H_0 - \frac{120|\rho|^2 A}{g^3\beta_e^3 H_0^2} + \frac{120|\lambda|^2 A}{g^3\beta_e^3 H_0^2} + \frac{8mA^2\sigma}{g^3\beta_e^3 H_0^2} \\
& - (13m^3 + \frac{25}{2}) \frac{A^3}{g^3\beta_e^3 H_0^2} + (2m^3 + 11m^2 - \frac{15}{2} - \frac{25}{4}) \frac{A^2 P}{g^3\beta_e^3 H_0^2} \\
& - (m^2 + 5m - \frac{25}{4}) \frac{\gamma A^2}{g^2\beta_e^2 H_0^2} - \frac{32\gamma|\rho|^2}{g^2\beta_e^2 H_0^2} + \frac{64\gamma|\lambda|^2}{g^2\beta_e^2 H_0^2} \\
& - (2m + 1) \left[\frac{2P}{g\beta_e} + \frac{\gamma A}{g\beta_e} + \frac{2\gamma^2 P}{g\beta_e} + \frac{64|\lambda|^2 P}{g^3\beta_e^3 H_0^2} - \frac{32|\rho|^2 P}{g^3\beta_e^3 H_0^2} \right]
\end{aligned}$$

(III.8)

In the expressions, given by eqs. (III.7) and (III.8) above

$$\sigma = \frac{1}{2} [D(3\cos^2\theta - 1) + 3E\sin^2\theta\cos 2\phi];$$

$$\rho = \frac{1}{4} [D\sin^2\theta + E\cos 2\phi(1 + \cos^2\theta) + i 2E \cos\theta\sin 2\phi];$$

$$\lambda = \sin\theta [(D - E\cos 2\phi)\cos\theta + i E\sin 2\phi];$$

$$\rho' = \frac{1}{4A} [Q'\sin^2\theta + Q''\cos 2\phi(1 + \cos^2\theta) + i 2Q'' \cos\theta\sin 2\phi];$$

$$\lambda' = \frac{\sin\theta}{A^{1/2}} [\cos\theta(Q' - Q''\cos 2\phi) + i Q''\sin 2\phi];$$

$$P = \frac{1}{2} [Q'(3\cos^2\theta - 1) + 3Q''\sin^2\theta\cos 2\phi];$$

$$H_0 = \frac{h\nu}{g\beta_e};$$

$$\gamma = g_n\beta_n / (g\beta_e); \text{ and}$$

$(\theta, \phi) =$ Euler angles defining the orientation of \vec{H} with respect to

the principal axis of \tilde{D} .

(III.9)

5 Discussion

In this present thesis the axis of quantization for the nuclear spin (I) has been chosen to be along the vector $\tilde{H}^T \cdot \tilde{g} \cdot \tilde{A}$ for the calculation of h.f. forbidden doublet separations; this is in conformity with that used traditionally, e.g., by Abragam and Bleaney [1], Orton [27], Iwasaki [9], Weil [39], Rockenbauer and Simon [30], Golding and Tennant [8], and Low [12]. However, Upreti [36] used the axis of quantization for I to be along the effective magnetic field, \tilde{H}^e , which is different for different electronic states in accordance with that used by Bir [3]; i.e., $\tilde{H}_\beta^e; M, M' = \sum_\alpha (g_n \beta_n)^{-1} A_{\alpha\beta} \langle M | S_\alpha | M' \rangle$; $\alpha, \beta = x, y, z$. Bir's approach [3] is valid for the situation where the h.f. interaction ($\tilde{S}^T \cdot \tilde{A} \cdot I$) is much smaller than the crystal field and electronic-Zeeman interactions. In the typical X-band EPR situation the h.f. interaction term, being sufficiently large, is not small compared with the crystal-field and electronic-Zeeman terms and cannot be neglected. In this case, it is appropriate to choose the direction of $\tilde{H}^T \cdot \tilde{g} \cdot \tilde{A}$ as the quantization axis for I, the same as that utilized in this thesis. It is noted that Mialhe [16] chose the direction $\tilde{H}^T \cdot \tilde{g}$ as the axis of quantization for both the electron and nuclear spins.

The presently-derived expressions do not quite complement those of Upreti [36,37]. The main reasons for this discrepancy are as follows. (1) Upreti used the same expressions i.e., $H_{r1} = H_{r2}$, to approximate the resonant fields in the denominators of both the transitions $M, m \leftrightarrow M-1, m'$ and $M, m' \leftrightarrow M-1, m$. This approximation is not correct, since different transitions do occur at different resonance fields ($H_{r1} \neq H_{r2}$). (11) The correct coefficient of E appearing in the real part of ρ

in the expression for the Hamiltonian, considered by Upreti [36], should read $\cos 2\phi(1 + \cos^2\theta)$, as given by eq. (III.9) above. (iii) The quantization axis used presently for I is different from that used by Upreti [36]. This choice of quantization axis is also responsible for the coefficient of $\lambda^2\rho$ in the present thesis being different from that of Upreti [36]. Upreti [36] employed the method, proposed by Bir [3], to calculate the eigenvalues to third order. Using these eigenvalues, he calculated the doublet separations; all the various terms given in [36] are found to be correct, as verified by redoing his calculations entirely independently, except for (i) the coefficient of the $A^2\sigma$ term given by Upreti [36] for the $-\frac{5}{2} \leftrightarrow -\frac{3}{2}$, $\Delta m = \pm 1$ transition should be $8m$ instead of $18m$; (ii) the coefficients of the A^3 terms given by Upreti [36] for the various transitions are all wrong; the correct expressions should be the same as those given by eq. (III.8) of the present thesis and (iii) certain terms are completely missing, because Upreti did not take into account some important second and third-order terms in the application of the method of successive approximations. These missing terms are listed below for the various doublets:

$$M = \frac{1}{2} \leftrightarrow -\frac{1}{2}, \Delta m = \pm 1:$$

$$2 \gamma^3 H_0 - (2m + 1) \left[\frac{2\gamma^2 P}{\gamma_0} - (m^2 + m - \frac{33}{4}) \frac{A^2 P}{\gamma_0^3 H_0^2} \right]$$

$$M = \frac{1}{2} \leftrightarrow -\frac{1}{2}, \Delta m = \pm 2:$$

$$16 \gamma^3 H_0 - 32 \frac{\gamma^2 P}{\gamma_0} + m(4m^2 - 31) \frac{A^2 P}{\gamma_0^3 H_0^2}$$

$$M = \frac{3}{2} \leftrightarrow \frac{1}{2}, \Delta m = \pm 1:$$

$$-\frac{\gamma}{\gamma_0} [4\sigma + (2m+1)A] - \frac{2\gamma^2}{\gamma_0} [A + (2m+1)P] + 2\gamma^3 H_0 +$$

$$+ (2m^3 - m^2 - \frac{39}{2}m - \frac{37}{4}) \frac{A^2 P}{\gamma_0^3 H_0^2}$$

$$M = \frac{5}{2} \leftrightarrow \frac{3}{2}, \Delta m = \pm 1:$$

$$-\frac{\gamma}{\gamma_0} [8\sigma + (2m+1)A] - \frac{2\gamma^2}{\gamma_0} [2A + (2m+1)P] + 2\gamma^3 H_0 +$$

$$+ (2m^3 - 5m^2 - \frac{47}{2}m - \frac{41}{4}) \frac{A^2 P}{\gamma_0^3 H_0^2}$$

$$M = -\frac{1}{2} \leftrightarrow -\frac{3}{2}, \Delta m = \pm 1:$$

$$\frac{\gamma}{\gamma_0} [4\sigma - (2m+1)A] + \frac{2\gamma^2}{\gamma_0} [A - (2m+1)P] + 2\gamma^3 H_0$$

$$+ (2m^3 + 7m^2 - \frac{23}{2}m - \frac{29}{4}) \frac{A^2 P}{\gamma_0^3 H_0^2}$$

$$M = -\frac{3}{2} \leftrightarrow -\frac{5}{2}, \Delta m = \pm 1:$$

$$\frac{\gamma}{\gamma_0} [8\sigma - (2m+1)A] + \frac{2\gamma^2}{\gamma_0} [2A - (2m+1)P] + 2\gamma^3 H_0$$

$$+ (2m^3 + 11m^2 - \frac{15}{2}m - \frac{25}{4}) \frac{A^2 P}{\gamma_0^3 H_0^2} \quad \text{(III. 10)}$$

Here, $\gamma_0 = g\beta_e$ and $\gamma = (g_n \beta_n / g\beta_e)$.

Mialhe's calculation of doublet separations [16] considered a spin

Hamiltonian with isotropic \tilde{g} and \tilde{g}_n tensors while \tilde{D} , \tilde{A} , \tilde{P} tensors conform to uniaxial symmetry, along with fourth-order terms in electronic spin, appropriate to trigonally-distorted cubic symmetry. However, all the contributions coming from the second-order terms in the eigenvalues were not taken into account. After an independent calculation, the corrected Malhe's expression (eq. (III.8) of [16]), except for the $C(\theta, \phi)$ term, is listed below:

$$\begin{aligned} \Delta_{\frac{1}{2}, \frac{3}{2}} - \Delta_{\frac{1}{2}, \frac{5}{2}} &= \frac{8Q'}{g\beta_e} [(3\cos^2\theta - 1) - \frac{6(A-B)}{B} \sin^2\theta \cos^2\theta] \\ &- \frac{32DB}{(g\beta_e)^3 H_0^2} (3\cos^2\theta - 1)(A\sin^2\theta + B\cos^2\theta) + \frac{100B^2A}{(g\beta_e)^3 H_0^2} \\ &+ \frac{18Q'}{(g\beta_e)^3 H_0^2} [B^2(3\cos^2\theta - 1) - B(A - B)(9\cos^4\theta - 10\cos^2\theta + 1)] \\ &+ \frac{32D}{(g\beta_e)^3 H_0^2} [B(A - B)(5\cos^4\theta - 6\cos^2\theta + 1)]. \quad (\text{III.11}) \end{aligned}$$

In eq. (III.11), $\Delta_{M,m} = H_{\Gamma}(M, m \leftrightarrow M-1, m+1) - H_{\Gamma}(M, m+1 \leftrightarrow M-1, m)$. Here, no attempt was made to check the correctness of the $C(\theta, \phi)$ term of [16] which arises out of the fourth-order terms in electron spin operators in the S.H. Finally, in this thesis, these fourth-order terms are not taken into account in the S.H., given by eq. (III.1).

III.6. Numerical Fitting

As shown in section III.4, forbidden hyperfine transitions occur in pairs, and the magnitude of the splitting of these pairs of lines depends on the orientation of the external magnetic field, H , as well as

the spin-Hamiltonian parameters. In this section the measured doublet separations, reported by Upreti [36], will be used to estimate the parameters Q' and Q'' ; these are, respectively, the axial and rhombic components of the quadrupole-coupling constants of the Mn^{2+} nucleus. In order to calculate theoretically the forbidden-doublet separations one needs to know the parameters A, D, E , as well as the klystron frequency, ν . A , is the isotropic hyperfine coupling constant, while D and E are the zero-field coupling constants. These parameters have been listed by Upreti [36]. However, there is no mention of the klystron frequency, ν . The klystron frequency, ν , along with other spin-Hamiltonian parameters can be estimated by the use of a least-square fitting procedure with the "chi-squared" (χ^2) value for EPR data defined [40] as $\chi^2 = \sum_i (\Delta H_{cal}^i - \Delta H_{expt}^i)^2$, where ΔH_{cal}^i are the calculated hyperfine doublet separations and ΔH_{expt}^i are the experimental (observed) doublet separations. The index i covers all the data points used simultaneously in the fitting. To commence with the least square fitting, Upreti's expressions for the doublet separations of the forbidden hyperfine transitions $M = 1/2 \leftrightarrow -1/2$, ($\Delta m = \pm 1$) were used to fit the observed doublet separations to estimate the microwave frequency, ν , the isotropic hyperfine coupling constants A , the zero-field coupling constants D and E , using the reported values of Q' and Q'' by Upreti [36]. The best-fit values of the spin-Hamiltonian parameters ($A = -86.417G$, $D = 340.986G$, $E = -34.001G$), along with the microwave frequency ($\nu = 9.461GHz$), so estimated, were then used in the expressions for the doublet separations of the forbidden hyperfine transitions $M = +1/2 \leftrightarrow -1/2$, $M = +3/2 \leftrightarrow +1/2$, $M = -1/2 \leftrightarrow -3/2$; $\Delta m = \pm 1$ and $M = +1/2 \leftrightarrow -1/2$; $\Delta m = \pm 2$, obtained presentedly (see equation (III.8)) and assuming $g_n \beta_n / g \beta_e$ equal to

0.37×10^{-3} as given in NMR Tables [40], to determine the best-fit values of Q' and Q'' . These are found to be: $Q' = 0.402G$, $Q'' = 0.614G$. The doublet separations of the forbidden-hyperfine transitions $M = +5/2 \leftrightarrow +3/2$, $M = -3/2 \leftrightarrow -5/2$; $\Delta m = \pm 1$ were not included in the fitting, since these experimental values are rather imprecise as revealed by a comparison of the calculated values of Upreti [36] using $Q' = 0.28G$, $Q'' = 0.67G$, estimated by him. Comparing the present best-fit values of Q' , Q'' with those reported by Upreti [36], significant difference in these two sets of values are found. Q' presently estimated is larger by 43.6% than that reported by Upreti, whereas Q'' estimated presently is smaller by 8.4%. As for the χ^2 values, $\chi^2 = 26G^2$ for 20 lines (included in Tables 1-3, 6 using) the presently derived expression, whereas $\chi^2 = 652G^2$ using the expression given by Upreti [36]. These values of χ^2 is improved by a factor of 25 using the present expressions. The observed [36] and calculated doublet separations (equation III.8) for the transitions $M = +1/2 \leftrightarrow -1/2$, $M = +3/2 \leftrightarrow +1/2$, $M = -1/2 \leftrightarrow -3/2$, $M = +5/2 \leftrightarrow 3/2$, $M = -3/2 \leftrightarrow -5/2$; $\Delta m = \pm 1$ are listed in Table 1-5 respectively, while those for the transitions $M = +1/2 \leftrightarrow -1/2$; $\Delta m = \pm 2$ are given in Table 6. Tables 1-6 also include the calculated values of the various forbidden doublets using Upreti's expressions along with his reported Q' , Q'' values. The agreement between the observed [36] and the calculated values is fairly good, except for the transition $M = +5/2 \leftrightarrow +3/2$; $\Delta m = \pm 1$ (Table 5). The relatively large differences between the observed [36] and calculated doublet separations for this group may be due to a large angle θ ($= 20^\circ$). For large angles, conventional perturbation theory is known to be unsatisfactory, because of considerable deviation of the direction of the nuclear magnetic moment

from that of H [13].

TABLE 1

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 1$ IN THE $M = +1/2 \leftrightarrow -1/2$ TRANSITION AT $\theta = 8^\circ$, $\phi = 0^\circ$. $Q' = 0.402G$, $Q'' = 0.614G$ (present); $Q' = 0.28G$, $Q'' = 0.67G$ (Upreti)

$$\Delta H = H_{1/2, m+1 \leftrightarrow -1/2, m} - H_{1/2, m \leftrightarrow -1/2, m+1}$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (present)
-5/2	13.72	13.55	14.50
-3/2	17.01	17.57	18.05
-1/2	21.30	21.59	21.59
+1/2	25.32	25.61	25.14
+3/2	29.54	29.63	28.68

TABLE 2

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 1$ IN THE $M = +3/2 \leftrightarrow +1/2$ TRANSITION AT $\theta = 10^\circ$, $\phi = 0^\circ$. For the Q' , Q'' values see the caption of Table 1

$$\Delta H = H_{3/2, m+1 \leftrightarrow +1/2, m} - H_{3/2, m \leftrightarrow +1/2, m+1}$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (Present)
-5/2	189.35	179.34	188.76
-3/2	191.72	186.61	190.59
-1/2	192.12	194.00	192.49
+1/2	193.04	201.50	194.45
+3/2	195.14	209.12	196.49

TABLE 3

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 1$ IN THE $M = -1/2 \leftrightarrow -3/2$ TRANSITION AT $\theta = 10^\circ$, $\phi = 0^\circ$. For the Q' , Q'' values see the caption of Table 1

$$\Delta H = H_{-1/2, m+1} \leftrightarrow -3/2, m - H_{-1/2, m} \leftrightarrow -3/2, m+1$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (Present)
-5/2	150.52	156.04	150.08
-3/2	152.87	157.42	151.69
-1/2	154.17	158.92	153.37
+1/2	156.22	160.54	155.13
+3/2	158.29	162.28	156.95

TABLE 4

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 1$ IN THE $M = +5/2 \leftrightarrow +3/2$ TRANSITION AT $\theta = 20^\circ$, $\phi = 0^\circ$. For the Q' , Q'' values see the caption of Table 1

$$\Delta H = H_{5/2, m+1} \leftrightarrow 3/2, m - H_{5/2, m} \leftrightarrow 3/2, m+1$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (Present)
-5/2	332.73	341.23	333.06
-3/2	346.04	349.82	340.27
-1/2	352.25	358.63	347.51
+1/2	359.85	367.67	354.76
+3/2	369.45	376.96	362.04

TABLE 5

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 1$ IN THE $M = -3/2 \leftrightarrow -5/2$ TRANSITION AT $\theta = 20^\circ$, $\phi = 0^\circ$. For Q' , Q'' values see the caption of Table 1

$$\Delta H = H_{-3/2, m+1} \leftrightarrow -5/2, m - H_{-3/2, m} \leftrightarrow -5/2, m+1$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (Present)
-5/2	318.25	315.77	312.45
-3/2	321.12	324.49	317.55
-1/2	326.23	333.46	322.68
+1/2	331.54	342.66	327.84
+3/2	335.87	352.09	333.02

TABLE 6

OBSERVED AND CALCULATED DOUBLET SEPERATIONS (IN GAUSS) OF FORBIDDEN TRANSITIONS $\Delta m = \pm 2$ IN THE $M = +1/2 \leftrightarrow -1/2$ TRANSITION AT $\theta = 8^\circ$, $\phi = 0^\circ$. For Q' , Q'' see the caption of Table 1

$$\Delta H = H_{1/2, m+1} \leftrightarrow -1/2, m-1 - H_{1/2, m-1} \leftrightarrow -1/2, m+1$$

m	Expt. (Upreti)	Theor. (Upreti)	Theor. (Present)
-3/2	31.95	31.33	32.70
-1/2	39.24	39.23	39.69
+1/2	46.12	47.13	46.67
+3/2	53.89	55.03	53.65

CHAPTER IV

OBSERVABILITY OF FORBIDDEN HYPERFINE TRANSITIONS ALONG THE PRINCIPAL AXES IN THE EPR OF LOW-SYMMETRY COMPLEXES

IV.1. Introduction

Forbidden hyperfine transitions can be observed when the orientations of the external magnetic field \vec{H} is along the principal axes of the crystal-field when the symmetry of the crystal-field is higher than monoclinic [22,23]. Pandey and Upreti [28] have discussed the possibility of observing forbidden hyperfine transitions for the orientation of the externally applied magnetic field along the principal axes of the crystal-field for monoclinic and triclinic site symmetries. However, the spin Hamiltonian they considered did not include all the necessary terms required for the triclinic symmetry; the terms with spin operators O_k^q with $q < 0$ were not considered. The specific orientation of the two-fold monoclinic symmetry axis, C_2 with respect to the crystal-field axes was not taken into account; that changes the form of the monoclinic spin Hamiltonian.

Misra and Rudowicz [24] recently, discussed the form of the spin Hamiltonian appropriate to monoclinic symmetry (for three cases $C_2 \parallel X, Y, Z$; where $X, Y,$ and Z are the three principal axes of the crystal-field). The calculation of the intensities of forbidden hyperfine transitions for \vec{H} along the principal axes of the crystal-field taking into account the correct monoclinic spin-Hamiltonian (for three cases $C_2 \parallel X, Y, Z$) and for triclinic symmetry is presented in this thesis.

IV.2. Spin-Hamiltonian

A. Triclinic symmetry

The spin-Hamiltonian for triclinic symmetry, in the notation of Abragam and Bleaney [1], is

$$\mathcal{H} = \mathcal{H}_{ez} + \mathcal{H}_{zf} + \mathcal{H}_{hf} + \mathcal{H}_{nq} \quad (\text{A.1})$$

In equation (A.1), \mathcal{H}_{ez} , \mathcal{H}_{zf} , \mathcal{H}_{hf} , and \mathcal{H}_{nq} are, respectively, the electronic Zeeman term, the zero-field term, the hyperfine term and the nuclear quadrupole term. They are expressed as follows;

$$\mathcal{H}_{ez} = \beta_e \vec{S}^T \cdot \tilde{g} \cdot \vec{H}; \quad (\text{A.2})$$

$$\mathcal{H}_{zf} = \sum_k \sum_{q=-k}^{+k} \{B_k^q\} \{O_k^q\}; \quad (k \text{ even, } \leq 2S) \quad (\text{A.3})$$

$$\mathcal{H}_{hf} = \vec{S}^T \cdot \tilde{A} \cdot \vec{I}; \quad (\text{A.4})$$

$$\mathcal{H}_{nq} = \vec{I}^T \cdot \tilde{P} \cdot \vec{I} \quad (\text{A.5})$$

In equations (A.2) - (A.5), \tilde{g} , \tilde{A} , \tilde{P} , and B_k^q are the usual spin Hamiltonian parameters that can be determined from experimental data (EPR line positions and intensities), and O_k^q are the extended Stevens operators, as defined, for example, by Rudowicz [32]. Curly brackets indicate that the parameters and the operators are expressed in an original coordinate system. Recently, the subject of spin operators was reviewed and clarified [33]. The relation between the conventional Stevens operators (O_l^m) and the O_k^q operators of equation (A.3), as well as their transformation under rotations is given in [32].

B. Monoclinic symmetry

The cases where the monoclinic symmetry axis, C_2 is parallel to one of the crystal-field axes X, Y, Z have been considered, in detail by Misra and Rudowicz [33]. The explicit forms of the zero-field Hamiltonian, \mathcal{H}_{zf} , for these three possible choices, including terms upto sixth order, are

[33]:

$$\mathcal{H}_{zf} = \mathcal{H}_{ortho} + \mathcal{H}_{mono} \quad (B.1)$$

where,

$$\mathcal{H}_{ortho} = \sum_{k=0,2} \langle B_2^k \rangle \langle O_2^k \rangle + \sum_{k=0,2,4} \langle B_4^k \rangle \langle O_4^k \rangle + \sum_{k=0,2,4,6} \langle B_6^k \rangle \langle O_6^k \rangle \quad (B.2)$$

and for: $C_2 \parallel Z$,

$$\begin{aligned} \mathcal{H}_{mono} = & \langle B_2^{-2} \rangle \langle O_2^{-2} \rangle + \langle B_4^{-2} \rangle \langle O_4^{-2} \rangle + \langle B_4^{-4} \rangle \langle O_4^{-4} \rangle \\ & + \langle B_6^{-2} \rangle \langle O_6^{-2} \rangle + \langle B_6^{-4} \rangle \langle O_6^{-4} \rangle + \langle B_6^{-6} \rangle \langle O_6^{-6} \rangle \end{aligned} \quad (B.3)$$

$C_2 \parallel Y$,

$$\begin{aligned} \mathcal{H}_{mono} = & \langle B_2^1 \rangle \langle O_2^1 \rangle + \langle B_4^1 \rangle \langle O_4^1 \rangle + \langle B_4^3 \rangle \langle O_4^3 \rangle \\ & + \langle B_6^1 \rangle \langle O_6^1 \rangle + \langle B_6^3 \rangle \langle O_6^3 \rangle + \langle B_6^5 \rangle \langle O_6^5 \rangle \end{aligned} \quad (B.4)$$

$C_2 \parallel X$,

$$\begin{aligned} \mathcal{H}_{mono} = & \langle B_2^{-1} \rangle \langle O_2^{-1} \rangle + \langle B_4^{-1} \rangle \langle O_4^{-1} \rangle + \langle B_4^{-3} \rangle \langle O_4^{-3} \rangle \\ & + \langle B_6^{-1} \rangle \langle O_6^{-1} \rangle + \langle B_6^{-3} \rangle \langle O_6^{-3} \rangle + \langle B_6^{-5} \rangle \langle O_6^{-5} \rangle \end{aligned} \quad (B.5)$$

IV.3. Intensities of forbidden transitions relative to the allowed transitions

A. Derivation of intensity formulas

Consider a paramagnetic ion, with electronic and nuclear spins S and I respectively. Assume the spin Hamiltonian for such a paramagnetic ion in a triclinic symmetry crystalline field is,

$$\begin{aligned}
\mathcal{H} = & \beta_e g \vec{S}^T \cdot \vec{H} + A \vec{S}^T \cdot \vec{I} + \sum_{q=-2}^{+2} \langle B_2^q \rangle \langle O_2^q \rangle + \sum_{q=-4}^{+4} \langle B_4^q \rangle \langle O_4^q \rangle \\
& + \sum_{q=-6}^{+6} \langle B_6^q \rangle \langle O_6^q \rangle \quad (C.1)
\end{aligned}$$

Assume for simplicity that g and A tensors are isotropic. The electronic Zeeman is chosen to be the dominant term, the hyperfine term being small or large compared to the electronic Zeeman term depends on the circumstances. In this thesis, the situation whereby the hyperfine term is small compared to the Zeeman term should be considered. In order to calculate the intensity of the forbidden, relative to the allowed transitions, the normalised eigenfunctions of the spin Hamiltonian of equation (C.1) should be calculated by the use of perturbation theory. In the EPR situation, usually the electronic Zeeman term is chosen to be very much greater than the remaining terms in the spin Hamiltonian. Now, choose the quantization axis for the electronic spin such that the electronic Zeeman term is diagonal. Let the direction of the external magnetic field vector, \vec{H} with respect to the crystal-field axes (X, Y, Z) be described by the spherical coordinates θ and ϕ . Since one assumes that the spectroscopic splitting factor, \tilde{g} , is isotropic, then the Zeeman term can always be chosen diagonal in any coordinate system, in particular the one for which the Z -axis is rotated relative to the reference coordinate system by angles θ and ϕ [12]. The result obtained on transforming the hyperfine interaction operators is given in [12]:

$$A S_z I_z + \frac{1}{2} A (S_+ I_- + S_- I_+) \longrightarrow A S_z I_{z_1} + \frac{1}{2} A (S_+ I_- + S_- I_+).$$

The subscript, 1 designates the Zeeman diagonal coordinate system. The transformations of all O_k^q operators and their associated coefficients in the transformed coordinate system, denoted by the square bracket $[B_k^q]$

have been listed by Rudowicz [32]. In the Zeeman diagonal coordinate system, the spin Hamiltonian of equation (C.1) takes the form:

$$\begin{aligned} \mathcal{H} = & \beta_e g H S_{z_1} + A S_{z_1} I_{z_1} + \frac{1}{2} A (S_+ I_- + S_- I_+) \\ & + \sum_{q=-2}^{+2} [B_2^q][O_2^q] + \sum_{q=-4}^{+4} [B_4^q][O_4^q] + \sum_{q=-6}^{+6} [B_6^q][O_6^q] \end{aligned} \quad (C.2)$$

The unperturbed Hamiltonian \mathcal{H}_0 is now chosen as

$$\begin{aligned} \mathcal{H}_0 = & \beta_e g H S_{z_1} + A S_{z_1} I_{z_1} + [B_2^0][O_2^0] \\ & + [B_4^0][O_4^0] + [B_6^0][O_6^0], \end{aligned} \quad (C.3)$$

whose eigenstates are $|M, m\rangle^0$.

$$\begin{aligned} \mathcal{H}' = & \frac{1}{2} A (S_+ I_- + S_- I_+) + \sum_{q=-2}^{+2} [B_2^q][O_2^q] + \\ & \sum_{q=-4}^{+4} [B_4^q][O_4^q] + \sum_{q=-6}^{+6} [B_6^q][O_6^q] \end{aligned} \quad (C.4)$$

is then chosen as perturbation. The prime over the summation sign in equation (C.4) indicates that the terms with $q=0$ are not included. The $[B_k^q]$ are the coefficients of the $[O_k^q]$ operators, which are expressed in the transformed system. $[B_k^q]$ can be obtained from $\{B_k^q\}$, the coefficients in the original system using the transformations listed by Rudowicz [31]. Wavefunctions $|M, m\rangle^0$ are perturbed by the off-diagonal matrix elements of the spin-Hamiltonian of equation (C.1); the perturbed wavefunctions are denoted as $|M, m\rangle^{(n)}$, where n is the order of perturbation and takes values of 1, 2, 3, ..., etc. $n=0$ corresponds to

the zero order wavefunctions. The off-diagonal operator \mathcal{H} is expressed as

$$\mathcal{H} = \mathcal{H}_{11} + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \mathcal{H}_4 + \mathcal{H}_5 + \mathcal{H}_6 \quad (\text{C.5})$$

$$\text{where, } \mathcal{H}_{11} = \frac{1}{2} A (S_{+} I_{-} + S_{-} I_{+}) \quad (\text{C.6})$$

$$\begin{aligned} \mathcal{H}_1 = & [B_2^1][O_2^1] + [B_2^{-1}][O_2^{-1}] + [B_4^1][O_4^1] + [B_4^{-1}][O_4^{-1}] + [B_6^1][O_6^1] \\ & + [B_6^{-1}][O_6^{-1}] \end{aligned} \quad (\text{C.7})$$

$$\begin{aligned} \mathcal{H}_2 = & [B_2^2][O_2^2] + [B_2^{-2}][O_2^{-2}] + [B_4^2][O_4^2] + [B_4^{-2}][O_4^{-2}] \\ & + [B_6^2][O_6^2] + [B_6^{-2}][O_6^{-2}] \end{aligned} \quad (\text{C.8})$$

$$\mathcal{H}_3 = [B_4^3][O_4^3] + [B_4^{-3}][O_4^{-3}] + [B_6^3][O_6^3] + [B_6^{-3}][O_6^{-3}] \quad (\text{C.9})$$

$$\mathcal{H}_4 = [B_4^4][O_4^4] + [B_4^{-4}][O_4^{-4}] + [B_6^4][O_6^4] + [B_6^{-4}][O_6^{-4}] \quad (\text{C.10})$$

$$\mathcal{H}_5 = [B_6^5][O_6^5] + [B_6^{-5}][O_6^{-5}] \quad (\text{C.11})$$

$$\mathcal{H}_6 = [B_6^6][O_6^6] + [B_6^{-6}][O_6^{-6}] \quad (\text{C.12})$$

Only those states admixed into $|M, m\rangle^{(n)}$ for which the denominator is of order $(\beta_e gH)$ will here be considered. Furthermore, for the forbidden transitions $\Delta M = \pm 1$; $\Delta m = \pm 1$, one only need consider admixtures of states which produce $\Delta M = \pm 1$, $\Delta m = \pm 1$. It is therefore, necessary to go to second order in perturbation where these admixtures are obtained. For this, one requires the matrix elements $\langle M | \mathcal{H} | M \pm 1 \rangle^0$, which are independent of m ; thus, one needs only those parts of the crystal-field operators which

shifts the M values by ± 1 . Since the crystal-field operators are composed of second, O_2^q , fourth, O_4^q , and sixth, O_6^q , order spin operators (definitions of the O_k^q operators are given in [32]), one looks for the coefficients of the parts of the spin-Hamiltonian which have the form of $O_k^{\pm 1}$, where $k = 2, 4$, and 6 . The crystal-field operators $O_2^{\pm 1}$, $O_4^{\pm 1}$ and $O_6^{\pm 1}$ along with the hyperfine interaction, $\vec{S} \cdot \vec{A} \cdot \vec{I}$, mix the hyperfine states. The second order perturbed eigenfunctions are [5];

$$|M, m\rangle = |M, m\rangle^0 + \sum_{N, n} a'_{M \pm N, m \pm n} |M, m\rangle^0, \quad (C.13)$$

where N, n are non-zero integers, the a 's are the second order admixture coefficients of the states participating in resonance; they are proportional to

$$\frac{{}^0\langle M', m' | \mathcal{H}' | M, m \rangle^0}{(E_{M, m}^0 - E_{M', m'}^0)} + \sum_{M'', m'' \neq M, m} \frac{{}^0\langle M'', m'' | \mathcal{H}' | M, m \rangle^0 {}^0\langle M', m' | \mathcal{H}' | M'', m'' \rangle^0}{(E_{M, m}^0 - E_{M', m'}^0)(E_{M, m}^0 - E_{M'', m''}^0)}$$

The prime over the summation sign in equation (C.13) indicates that the term with $N = n = 0$ has been omitted. In evaluating the matrix elements of $[O_k^q]$, the relations

$${}^0\langle M' | O_k^{-q} | M \rangle^0 = \pm {}^0\langle M' | O_k^q | M \rangle^0 \quad (C.14)$$

$$\begin{aligned} \text{and } {}^0\langle M | O_k^q | M - q \rangle^0 &= (-1)^{q+k} {}^0\langle -M | O_k^q | -M + q \rangle^0 \\ &= {}^0\langle M - q | O_k^q | M \rangle^0 \end{aligned} \quad (C.15)$$

have been used [2,38]. In equation (C.14), the upper and lower signs apply to $M' < M$ and $M' > M$ respectively. Specifically, since one only needs the operators $O_k^{\pm 1}$, where $k = 2, 4, 6$, the only states in the second order perturbed wavefunction, $|M, m\rangle$ which one needs to consider are the

° following:

$$|M, m\rangle = |M, m\rangle^0 + \alpha(M, m)|M, m+1\rangle^0 + \beta(M, m)|M, m-1\rangle^0 + \gamma_1(M, m)|M+1, m-1\rangle^0 + \gamma_2(M, m)|M-1, m+1\rangle^0, \quad (C. 16)$$

where

$$\begin{aligned} \alpha(M, m) = & -\frac{S_{0\bar{1}} I_{0\bar{1}}}{2MG} \left[{}^0\langle M, m+1 | [B_2^1][O_2^1] + [B_4^1][O_4^1] \right. \\ & + [B_6^1][O_6^1] |M-1, m+1\rangle^0 - {}^0\langle M, m+1 | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] \\ & \left. + [B_6^{-1}][O_6^1] |M-1, m+1\rangle^0 \right] + \frac{S_{0\bar{1}} I_{0\bar{1}}}{2MG} \left[{}^0\langle M+1, m | [B_2^1][O_2^1] + [B_4^1][O_4^1] \right. \\ & + [B_6^1][O_6^1] |M, m\rangle^0 - {}^0\langle M+1, m | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] \\ & \left. + [B_6^{-1}][O_6^1] |M, m\rangle^0 \right], \quad (C. 17) \end{aligned}$$

$$\begin{aligned} \beta(M, m) = & -\frac{S_{0\bar{1}} I_{0\bar{1}}}{2MG} \left[{}^0\langle M, m-1 | [B_2^1][O_2^1] + [B_4^1][O_4^1] \right. \\ & + [B_6^1][O_6^1] |M+1, m-1\rangle^0 + {}^0\langle M, m-1 | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] \\ & \left. + [B_6^{-1}][O_6^1] |M+1, m-1\rangle^0 \right] + \frac{S_{0\bar{1}} I_{0\bar{1}}}{2MG} \left[{}^0\langle M-1, m | [B_2^1][O_2^1] + [B_4^1][O_4^1] \right. \\ & + [B_6^1][O_6^1] |M, m\rangle^0 + {}^0\langle M-1, m | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] \\ & \left. + [B_6^{-1}][O_6^1] |M, m\rangle^0 \right], \quad (C. 18) \end{aligned}$$

$$\gamma_1(M, m) = \frac{A S_{0\bar{1}} I_{0\bar{1}}}{2G}, \quad (C. 19)$$

$$\gamma_2(M, m) = \frac{A S_{0\bar{1}} I_{0\bar{1}}}{2G}, \quad (C. 20)$$

In the EPR experimental set-up the applied microwave field h_0 , can be

arranged to lie in the xy (or x_1y_1) plane, with H in the z or z_1 -axis. The spin Hamiltonian for the microwave field can be taken as

$$\mathcal{H}'' = \beta_e g (h_{0x_1} S_{x_1} + h_{0y_1} S_{y_1} + h_{0z_1} S_{z_1}) \quad (C.21)$$

Here, h_{0x_1} , h_{0y_1} , h_{0z_1} are the components of the amplitude of the microwave (r.f.) field with respect to the (x_1, y_1, z_1) coordinate system. The general expression of the intensity of the hyperfine forbidden (I_f) transitions $M-1, m \pm 1 \leftrightarrow M, m$ relative to the corresponding allowed (I_a) transitions $M-1, m \leftrightarrow M, m$ applicable to any orientation of the external magnetic field \vec{H} , with the excitation (r.f) field being along the x_1 -axis, choosing the z_1 -axis along the external magnetic field, \vec{H} is given by [3]

$$I_f/I_a = |\omega_{M-1, m \pm 1}|^2; \quad (C.22)$$

where,

$$\omega_{M-1, m \pm 1} = \langle M-1, m \pm 1 | S_{x_1} | M, m \rangle / \langle M-1, m | S_{x_1} | M, m \rangle \quad (C.23)$$

In equation (C.23), S_{x_1} is the x-component of the electronic spin. (Here the choice of the direction of the external magnetic field relative to the excitation field, i.e. at 90° is a typical EPR experimental set-up. For instance, the excitation (microwave) field could be in the vertical direction, which does not vary, while the external magnetic field is rotated in the horizontal plane.) Direct evaluation of the matrix element of the numerator of equation (C.23), using equations (C.13), (C.14) and (C.15) and retaining only terms in G^{-1} , and approximating the denominator of equation (C.23) as ${}^0\langle M-1, m | S_{x_1} | M, m \rangle^0$, yields

$$\omega_{M-1, m \pm 1} = \begin{cases} \alpha(M, m) + \beta^*(M-1, m+1), & \text{for } |M-1, m+1\rangle \leftrightarrow |M, m\rangle \\ & \text{transitions} \quad (C.24) \\ \alpha^*(M-1, m-1) + \beta(M, m), & \text{for } |M-1, m-1\rangle \leftrightarrow |M, m\rangle \\ & \text{transitions} \quad (C.25) \end{cases}$$

where,

$$\begin{aligned} \alpha(M-1, m-1) = & -\frac{S_{12}^{-1} I_{01}}{2(M-1)G} \left[{}^0\langle M-1, m | [B_2^1][O_2^1] + [B_4^1][O_4^1] \right. \\ & + [B_6^1][O_6^1] | M-2, m \rangle^0 \\ & \left. - {}^0\langle M-1, m | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] + [B_6^{-1}][O_6^1] | M-2, m \rangle^0 \right] \\ & + \frac{S_{01}^{-1} I_{01}}{2(M-1)G} \left[{}^0\langle M, m-1 | [B_2^1][O_2^1] + [B_4^1][O_4^1] + [B_6^1][O_6^1] | M-1, m-1 \rangle^0 \right. \\ & \left. - {}^0\langle M, m-1 | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] + [B_6^{-1}][O_6^1] | M-1, m-1 \rangle^0 \right] \end{aligned} \quad (C.26a)$$

$$\begin{aligned} \beta(M-1, m+1) = & -\frac{S_{01}^{-1} I_{01}}{2(M-1)G} \left[{}^0\langle M-1, m | [B_2^1][O_2^1] \right. \\ & + [B_4^1][O_4^1] + [B_6^1][O_6^1] | M, m \rangle^0 \\ & \left. + {}^0\langle M-1, m | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] + [B_6^{-1}][O_6^1] | M, m \rangle^0 \right] \\ & + \frac{S_{12}^{-1} I_{01}}{2(M-1)G} \left[{}^0\langle M-2, m+1 | [B_2^1][O_2^1] + [B_4^1][O_4^1] + [B_6^1][O_6^1] | M-1, m+1 \rangle^0 \right. \\ & \left. + {}^0\langle M-2, m+1 | [B_2^{-1}][O_2^1] + [B_4^{-1}][O_4^1] + [B_6^{-1}][O_6^1] | M-1, m+1 \rangle^0 \right] \end{aligned} \quad (C.26b)$$

From equations (C.24) and (C.25) it is seen that the intensities of the two lines corresponding to the two forbidden doublets $M-1, m \pm 1 \leftrightarrow M, m$ are equal to each other. In equation (C.26), the operators O_k^{-1} ($k=2,4,6$) no longer appear since their matrix elements have been related to those

of the corresponding O_k^1 , via equation (C.14). It is noted from equations (C.22) to (C.26) that the operators $O_k^{\pm 1}$ ($k =$ all even values $\leq 2S$) are responsible for the non-zero intensity of the forbidden transitions. This means that whenever their coefficients, $[B_k^{\pm 1}]$, are non-zero, transitions with non-zero intensity are expected. One now treats separately the two symmetry cases considered:

a. Triclinic Symmetry. In the case of triclinic symmetry the coefficients $[B_k^{\pm 1}]$, $k = 2, 4, 6$ are not zero for any orientation of the external magnetic field \vec{H} , as seen from equation (A.3). Thus, forbidden transitions are, then observed for the orientation of \vec{H} including along the crystal-field axes.

b. Monoclinic Symmetry. The transformation relations, needed to calculate I_f/I_a , between the coefficients $[B_k^q]$ and $\{B_k^q\}$ are listed in Table I [31], as derived using the matrix elements given by Al'tshuler and Kozyrev [2]. It can be seen from Table I, for the case of monoclinic symmetry, that all the coefficients $[B_k^{\pm 1}]$, $k = 2, 4, 6$ are zero only for $\vec{H} \parallel Z$ ($C_2 \parallel Z$), $\vec{H} \parallel Y$ ($C_2 \parallel Y$) and $\vec{H} \parallel X$ ($C_2 \parallel X$), i.e. for the external applied magnetic field along the monoclinic symmetry axis. For these cases then, the forbidden transitions are not at all observed. For the other directions of \vec{H} , one or more of these coefficients are non-zero, e.g. for $\vec{H} \parallel X$ ($C_2 \parallel Z$), the coefficients $[B_2^{-1}]$, $[B_4^{-1}]$, $[B_6^{-1}]$ are non-zero; forbidden transitions with non-zero intensity are therefore observed for these orientation of \vec{H} .

IV.4. Illustrative example

Consider the specific case of $S = 5/2$ and I, M, m are arbitrary (this is applicable to Mn^{2+} , for which $S = I = 5/2$.) For this case, the intensity of the forbidden transitions $M-1, m \pm 1 \leftrightarrow M, m$ relative to the

allowed transitions $M-1, m \leftrightarrow M, m$ for an arbitrary orientation of the external magnetic field, is using equations (C.22) to (C.27):

Transition $\mp 1/2, m \pm 1 \leftrightarrow \pm 1/2, m$:

$$\frac{I_f}{I_a} = \frac{64I_{0, \pm 1}^2}{G^2} \left[([B_2^1] - 15[B_4^1])^2 + ([B_2^{-1}] - 15[B_4^{-1}])^2 \right] \quad (\text{IV.4.1})$$

Transition $\pm 1/2, m \pm 1 \leftrightarrow \pm 3/2, m$:

$$\frac{I_f}{I_a} = \frac{I_{0, \pm 1}^2}{9G^2} \left[(11[B_2^1] - 270[B_4^1])^2 + (11[B_2^{-1}] - 270[B_4^{-1}])^2 \right] \quad (\text{IV.4.2})$$

Transition $\pm 3/2, m \pm 1 \leftrightarrow \pm 5/2, m$:

$$\frac{I_f}{I_a} = \frac{I_{0, \pm 1}^2}{9G^2} \left[(4[B_2^1] + 108[B_4^1])^2 + (4[B_2^{-1}] + 108[B_4^{-1}])^2 \right] \quad (\text{IV.4.3})$$

In equation (IV.4.3), the coefficients $[B_k^q]$ denote the coefficients in the transformed coordinate system, i.e. for the choice of Z-axis along the external magnetic field. The relative intensities I_f/I_a , as calculated using equations (IV.4.1) to (IV.4.3) and Table I, are listed in Table II. From Table II it is clear that for complexes, characterized by monoclinic symmetry, forbidden EPR hyperfine transitions should be observed for the orientation of \vec{H} not only along the directions off the principal axes, but also along some of the principal axes. For example, when $C_2 \parallel Y$ ($\vec{H} \parallel Z$) the relative intensity is $64I_{0, \pm 1}^2 [(B_2^1) - 15(B_4^1)]^2 / G^2$ for the $\mp 1/2, m \pm 1 \leftrightarrow \pm 1/2, m$ transitions. Furthermore, it is seen that one can obtain the values of the combinations $[(B_2^1) - 15(B_4^1)]$ and $[(B_2^{-1}) - 15(B_4^{-1})]$ from the observed intensities of the forbidden transitions ($\mp 1/2, m \pm 1 \leftrightarrow \pm 1/2, m$) relative to the allowed transitions ($\mp 1/2, m \leftrightarrow \pm 1/2, m$), for $\vec{H} \parallel Z$ and, $C_2 \parallel Y$ and $C_2 \parallel X$ respectively.

Table I

Expressions for the transformed coefficients $[B_k^{\pm 1}]$ in terms of the coefficients $\{B_k^{\pm q}\}$, expressed in the original axis system. For reference, the form of the monoclinic spin-Hamiltonian is described as follows:

$$C_2 \parallel \hat{Z}: \mathcal{H}_{\text{mono}} = \{B_2^{-2}\}\{O_2^{-2}\} + \{B_4^{-2}\}\{O_4^{-2}\} + \{B_4^{-4}\}\{O_4^{-4}\} \\ + \{B_6^{-2}\}\{O_6^{-2}\} + \{B_6^{-4}\}\{O_6^{-4}\} + \{B_6^{-6}\}\{O_6^{-6}\};$$

$$C_2 \parallel \hat{Y}: \mathcal{H}_{\text{mono}} = \{B_2^1\}\{O_2^1\} + \{B_4^1\}\{O_4^1\} + \{B_4^3\}\{O_4^3\} + \{B_6^1\}\{O_6^1\} \\ + \{B_6^3\}\{O_6^3\} + \{B_6^5\}\{O_6^5\};$$

$$C_2 \parallel \hat{X}: \mathcal{H}_{\text{mono}} = \{B_2^{-1}\}\{O_2^{-1}\} + \{B_4^{-1}\}\{O_4^{-1}\} + \{B_4^{-3}\}\{O_4^{-3}\} \\ + \{B_6^{-1}\}\{O_6^{-1}\} + \{B_6^{-3}\}\{O_6^{-3}\} + \{B_6^{-5}\}\{O_6^{-5}\}.$$

	$\hat{H} \parallel \hat{X}$	$\hat{H} \parallel \hat{Y}$	$\hat{H} \parallel \hat{Z}$
$[B_2^1]$	$-(B_2^1)$	$-(B_2^{-1})$	$\{B_2^1\}$
$[B_2^{-1}]$	$2(B_2^{-2})$	$-2(B_2^{-2})$	$\{B_2^{-1}\}$
$[B_4^1]$	$\frac{1}{4}(3(B_4^1) - (B_4^3))$	$\frac{1}{4}(3(B_4^{-1}) + (B_4^{-3}))$	$\{B_4^1\}$
$[B_4^{-1}]$	$-\frac{1}{2}((B_4^{-2}) - 2(B_4^{-4}))$	$\frac{1}{2}((B_4^{-2}) + 2(B_4^{-4}))$	$\{B_4^{-1}\}$
$[B_6^1]$	$-\frac{1}{8}(5(B_6^1) - 3(B_6^3) + (B_6^5))$	$-\frac{1}{8}(5(B_6^{-1}) + 3(B_6^{-3}) + 3(B_6^{-5}))$	$\{B_6^1\}$
$[B_6^{-1}]$	$\frac{1}{4}((B_6^{-2}) - 2(B_6^{-4}) + 3(B_6^{-6}))$	$-\frac{1}{4}((B_6^{-2}) + 2(B_6^{-4}) + 3(B_6^{-6}))$	$\{B_6^{-1}\}$

Table II

The ratio, I_f/I_a , of intensities of the forbidden ($M-1, m \pm 1 \leftrightarrow M, m$) to allowed ($M-1, m \leftrightarrow M, m$) transitions, as calculated for H along the various crystal-field axes for monoclinic symmetry. Here $v_{1,j}^2 = [I(I+1)-(m+1)(m+j)]$ and $G = g\beta H$.

Forbidden Doublets $\mp \frac{1}{2}, m \pm 1 \leftrightarrow \pm \frac{1}{2}, m$			
	H \parallel \hat{Z}	H \parallel \hat{Y}	H \parallel \hat{X}
$C_2 \parallel \hat{Z}$	0	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (2\langle B_2^{-2} \rangle_+)$ $\left(\frac{15}{2} (\langle B_4^{-2} \rangle + 2\langle B_4^{-4} \rangle) \right)^2$	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (2\langle B_2^{-2} \rangle_+)$ $\left(\frac{15}{2} (\langle B_4^{-3} \rangle - 2\langle B_4^{-4} \rangle) \right)^2$
$C_2 \parallel \hat{Y}$	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (\langle B_2^1 \rangle_-)$ $\left(15\langle B_4^1 \rangle \right)^2$	0	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (\langle B_2^1 \rangle_+)$ $\left(\frac{15}{4} (3\langle B_4^1 \rangle - \langle B_4^3 \rangle) \right)^2$
$C_2 \parallel \hat{X}$	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (\langle B_2^{-1} \rangle_-)$ $\left(15\langle B_4^{-1} \rangle \right)^2$	$\frac{64I^2}{G^2} \frac{1}{v_{0,\pm 1}} (\langle B_2^{-1} \rangle_+)$ $\left(\frac{15}{4} (3\langle B_4^{-1} \rangle + \langle B_4^{-3} \rangle) \right)^2$	0

Forbidden Doublets $\pm \frac{1}{2}, m \pm 1 \leftrightarrow \pm \frac{3}{2}, m$			
	H \parallel \hat{Z}	H \parallel \hat{Y}	H \parallel \hat{X}
$C_2 \parallel \hat{Z}$	0	$(I_{0,\pm 1}^2 / 9G^2) (22\langle B_2^{-2} \rangle_+)$ $\left(135 (\langle B_4^{-2} \rangle + 2\langle B_4^{-4} \rangle) \right)^2$	$(I_{0,\pm 1}^2 / 9G^2) (22\langle B_2^{-2} \rangle_+)$ $\left(135 (\langle B_4^{-2} \rangle - 2\langle B_4^{-4} \rangle) \right)^2$
$C_2 \parallel \hat{Y}$	$(I_{0,\pm 1}^2 / 9G^2) (11\langle B_2^1 \rangle_+)$	0	$(I_{0,\pm 1}^2 / 9G^2) (11\langle B_2^1 \rangle_+)$

$$-270\{B_4^1\}^2$$

$$\frac{135}{2}(3\{B_4^1\}-\{B_4^3\})^2$$

$$C_2 \parallel \hat{X} \quad \frac{(I_{0,\pm 1}^2/9G^2)(11\{B_2^{-1}\})}{(-270\{B_4^{-1}\})^2} \quad \frac{(I_{0,\pm 1}^2/9G^2)(11\{B_2^{-1}\})}{(\frac{135}{2}(3\{B_4^{-1}\}+\{B_4^{-3}\}))^2} \quad 0$$

Forbidden Doublets $\pm\frac{3}{2}, m \pm 1 \leftrightarrow \pm\frac{5}{2}, m$

H \parallel \hat{Z}

H \parallel \hat{Y}

H \parallel \hat{X}

$$C_2 \parallel \hat{Z} \quad 0 \quad \frac{(I_{0,\pm 1}^2/9G^2)(8\{B_2^{-2}\})}{54(\{B_4^{-2}\}+2\{B_4^{-4}\})^2} \quad \frac{(I_{0,\pm 1}^2/9G^2)(8\{B_2^{-2}\})}{54(\{B_4^{-2}\}-2\{B_4^{-4}\})^2}$$

$$C_2 \parallel \hat{Y} \quad \frac{(I_{0,\pm 1}^2/9G^2)(4\{B_2^1\})}{+108\{B_4^1\}} \quad 0 \quad \frac{(I_{0,\pm 1}^2/9G^2)(4\{B_2^1\})}{27(3\{B_4^1\}-\{B_4^3\})^2}$$

$$C_2 \parallel \hat{X} \quad \frac{(I_{0,\pm 1}^2/9G^2)(4\{B_2^{-1}\})}{+108\{B_4^{-1}\})^2} \quad \frac{(I_{0,\pm 1}^2/9G^2)(4\{B_2^{-1}\})}{27(3\{B_4^{-1}\}+\{B_4^{-3}\})^2} \quad 0$$

CHAPTER V

INTENSITY OF ALLOWED AND HYPERFINE-FORBIDDEN TRANSITIONS IN THE EPR OF TRANSITION-METAL COMPLEXES

V.1. Introduction

In the electron paramagnetic resonance arrangement, where the static magnetic field \vec{H} , is normal to the microwave excitation field \vec{H}_0 , the selection rules for the allowed transitions are $\Delta M = \pm 1$, $\Delta m = 0$. However, these selection rules are often violated, due to perturbations such as crystal-field and/or hyperfine interactions; this leads to the observation of hyperfine forbidden transitions, for which $\Delta M = \pm 1$, $\Delta m \neq 0$; $\Delta M \neq 1$, $\Delta m = 0$. Bleaney and Rubin [5] ascribed the non-zero intensities of these so called hyperfine forbidden lines to the off-diagonal terms coming from the crystal-field and hyperfine interactions in the spin Hamiltonian.

The intensities of the allowed and forbidden hyperfine lines of ions in sufficiently strong crystalline fields exhibit strong angular variations when the orientation of the externally applied magnetic field is varied. It was shown by Bir[3] that the strong angular dependence of the line intensities is a result of the presence of a hyperfine field, as well as a crystal field. If hyperfine interaction is present, the nuclear spin is not acted upon by the external magnetic field alone, but also by the effective field associated with the hyperfine interaction with the electron spin. For X-band EPR this effective field is much greater than the external magnetic field, so that it is really the direction of the effective magnetic field, instead of the external magnetic field, that determines the nuclear spin quantization axis. Bir

[3] has given a comprehensive theory, explaining the intensity variations of the allowed and forbidden hyperfine lines for the case of small hyperfine interactions compared with crystal-field and Zeeman interactions — when a separation can be made between the electronic and nuclear states. He derived explicit expressions for the transition probabilities of the allowed and forbidden lines as functions of the spin-Hamiltonian parameters for the case of isotropic coincident tensors in the spin Hamiltonian. This method considers the effective-field direction as the nuclear spin axis of quantization, and ascribes the strong angular dependence of line intensity to the angular dependence of the scalar product of nuclear spin functions, and has been shown to give results in good agreement with experimental measurements [4,6,36].

The purpose of the present thesis is to obtain explicit expressions for EPR line intensities, using the method of Bir [3], with no restrictions on the anisotropy (or coincidences) of the principal axes of the various spin-Hamiltonian tensors. It should be mentioned here that the assumption of isotropic spin-Hamiltonian parameters as used by Bir [3] has only limited applicability. The present results will be compared with those of Upreti [36], Bir [3] and, Mialhe and Erbeia [15,17].

V.2. Theory

The spin Hamiltonian of a paramagnetic ion in a solid in the presence of an external magnetic field (\vec{H}) is of the form

$$\mathcal{H} = \mathcal{H}_{ez} + \mathcal{H}_{zf} + \mathcal{H}_{hf} + \mathcal{H}_{nq} + \mathcal{H}_{nz}, \quad (\text{V.1})$$

where all terms have been previously defined (chapter III, equation III.1). Here, one considers the case where the ground state of the paramagnetic ion is an orbital singlet. The result obtained can be

extended to the degenerate ground state case. For a non-degenerate ground state of the ion [12], the spin Hamiltonian takes the simple form of equation (V.1) above.

In order to calculate the line intensity, the normalized eigenfunctions of the spin-Hamiltonian given by equation (V.1) need be found either by a numerical diagonalization of the spin-Hamiltonian matrix, or by use of perturbation-theory approximation. In the present work, perturbation-theory approach will be utilized. Perturbation theory provides reasonably good results for the S-state ions [3] for the eigenvalues $E_{M,m}$ and eigenfunctions $|M,m\rangle$ of the spin-Hamiltonian, given by equation (V.1). In diagonalizing this spin Hamiltonian one should define axes of quantization for the electron and nuclear spins such that large off-diagonal matrix elements vanish. To this end, the approach of Bir [3], along with the transformation technique of Rockenbauer and Simon [30], is used here.

Consider a perturbed wavefunction of the form

$$|M,m\rangle^{(n)} = |M\rangle^{(n)} \cdot |M(m)\rangle^{(n)}, \quad (V.2)$$

where, $|M(m)\rangle^{(n)}$ represent nuclear spin functions associated with the electronic state designated by M and $|M\rangle^{(n)}$ is the perturbed wavefunction which diagonalizes the purely electronic part of the spin Hamiltonian \mathcal{H}_e , given by equation (V.1)

$$\mathcal{H}_e = \beta_e \vec{S}^T \cdot \vec{g} \cdot \vec{H} + \vec{S}^T \cdot \vec{D} \cdot \vec{S}. \quad (V.3)$$

The perturbed eigenfunction $|M\rangle^{(n)}$ is a linear combination of the zero-order eigenfunctions, $|M,m\rangle^{(0)}$, of the unperturbed Hamiltonian, \mathcal{H}_0 . The hyperfine interaction term, $\vec{S}^T \cdot \vec{A} \cdot \vec{I}$, can be written as the interaction between the effective magnetic field, $\vec{H}^{e;M,M}$, and the nuclear spin, \vec{I} , where the quantity $\vec{H}^{e;M,M}$ is defined by [3]

$$H_{\alpha}^{e;M,M} = 1/(g_n \beta_n) \sum_{\beta} A_{\alpha\beta}^{(n)} \langle M | S_{\alpha} | M \rangle^{(n)}, \quad (\alpha, \beta) = (x, y, z) \quad (V.4)$$

The effective hyperfine interaction, $g_n \beta_n (\tilde{H}^{e;M,M})^T \cdot \vec{I}$, for \tilde{A} not being too small, is much greater than the nuclear Zeeman term, $g_n \beta_n (\vec{H}^T \cdot \vec{I})$. Also, in general, the hyperfine interaction constant \tilde{A} is much greater than the quadrupole energy tensor \tilde{P} . Under these approximations, the operator

$$\mathcal{H}'_n = \vec{I}^T \cdot \tilde{P} \cdot \vec{I} + g_n \beta_n (\tilde{H}^{e;M,M})^T \cdot \vec{I} - g_n \beta_n \vec{H}^T \cdot \vec{I}, \quad (V.5)$$

is predominantly determined by the effective magnetic field, $\tilde{H}^{e;M,M}$:

$$\mathcal{H}'_n \approx g_n \beta_n (\tilde{H}^{e;M,M})^T \cdot \vec{I}. \quad (V.6)$$

Consequently, the nuclear axis of quantization is chosen along the effective magnetic field $\tilde{H}^{e;M,M}$.

Using equation (V.3), and choosing the electronic axis of quantization to be parallel to $\tilde{g} \cdot \vec{H}$, the spin-Hamiltonian given by equation (V.3), can be transformed [30]:

$$\begin{aligned} \mathcal{H}'_e = & \beta_e g H S_z + 3/2 (S_{z_1}^2 - 1/3 S(S+1)) (\vec{T}_3^T \cdot \tilde{D} \cdot \vec{T}_3) + 1/4 S_+^2 (\vec{T}_-^T \cdot \tilde{D} \cdot \vec{T}_-) \\ & + 1/4 S_-^2 (\vec{T}_+^T \cdot \tilde{D} \cdot \vec{T}_+) + 1/2 (S_+ S_{z_1} + S_{z_1} S_+) (\vec{T}_-^T \cdot \tilde{D} \cdot \vec{T}_3) \\ & + 1/2 (S_- S_{z_1} + S_{z_1} S_-) (\vec{T}_+^T \cdot \tilde{D} \cdot \vec{T}_3) \end{aligned} \quad (V.7)$$

Here, \vec{T}_+ , \vec{T}_- , \vec{T}_3 are as defined previously (see equation (III.1b)). Choose now $\mathcal{H}_0 = \beta_e g H S_z$ to be the unperturbed Hamiltonian, whose eigenfunctions are denoted by $|M\rangle^{(0)}$, and the remaining part of \mathcal{H}'_e as the perturbation. The normalized eigenfunction, which diagonalizes the spin Hamiltonian, given by equation (V.3), can be obtained from second-order perturbation theory as [7]:

$$\begin{aligned}
|M\rangle = & a_M |M\rangle^{(0)} + a_{M+1} |M+1\rangle^{(0)} + a_{M-1} |M-1\rangle^{(0)} + a_{M+2} |M+2\rangle^{(0)} \\
& + a_{M-2} |M-2\rangle^{(0)} + a_{M+3} |M+3\rangle^{(0)} + a_{M-3} |M-3\rangle^{(0)} + a_{M+4} |M+4\rangle^{(0)} \\
& + a_{M-4} |M-4\rangle^{(0)} \quad (V.8)
\end{aligned}$$

where the admixing coefficients, a_i , of the states participating in resonance are given by:

$$a_M = 1 - \left[\frac{bb^*}{8\beta_e^2 g^2 H^2} \{S_{01}^2 (2M+1)^2 + S_{0\bar{1}}^2 (2M-1)^2\} + \right.$$

$$\left. \frac{(aa^*/16) (S_{01}^2 S_{12}^2 + S_{0\bar{1}}^2 S_{\bar{1}2}^2)}{8\beta_e^2 g^2 H^2} \right]$$

$$a_{M+1} = - \frac{b(2M+1)S_{01}^*}{2\beta_e g H} + \frac{b^*(1/4)a S_{01}}{4\beta_e^2 g^2 H^2} \left[(2M+3)S_{12}^2 - 2(2M-1)S_{0\bar{1}}^2 \right] +$$

$$+ \frac{b(3/2)d_1 (2M+1)^2 S_{01}}{2\beta_e^2 g^2 H^2}$$

$$a_{M-1} = \frac{b^*(2M-1)S_{0\bar{1}}}{2\beta_e g H} + \frac{b(1/4)a^* S_{0\bar{1}}}{4\beta_e^2 g^2 H^2} \left[(2M-3)S_{\bar{1}2}^2 - 2(2M+1)S_{01}^2 \right] +$$

$$- \frac{b^*(3/2)d_1 (2M-1)^2 S_{0\bar{1}}}{2\beta_e^2 g^2 H^2}$$

$$a_{M+2} = - \frac{(1/4)a S_{01} S_{12}}{2\beta_e g H} + \frac{b^2 (2M+1)(2M+3) S_{01} S_{12}}{8\beta_e^2 g^2 H^2} +$$

$$\frac{(3/2)d_1 (1/4)a (M+1) S_{01} S_{12}}{\beta_e^2 g^2 H^2}$$

$$\begin{aligned}
a_{M-2} &= \frac{(1/4)a^* S_{01} S_{12}}{2\beta_e g H} + \frac{(b^*)^2 (2M-1)(2M-3) S_{01} S_{12}}{8\beta_e^2 g^2 H^2} \\
&\quad - \frac{(3/2)d_1 (1/4)a^* (M-1) S_{01} S_{12}}{\beta_e^2 g^2 H^2} \\
a_{M+3} &= \frac{b(1/4)a (6M+7) S_{01} S_{12} S_{23}}{12\beta_e^2 g^2 H^2} \\
a_{M-3} &= \frac{(b^*) (1/4)a^* (6M-7) S_{01} S_{12} S_{23}}{12\beta_e^2 g^2 H^2} \\
a_{M+4} &= \frac{(1/16)a^2 S_{01} S_{12} S_{23} S_{34}}{8\beta_e^2 g^2 H^2} \\
a_{M-4} &= \frac{(1/16)(a^*)^2 S_{01} S_{12} S_{23} S_{34}}{8\beta_e^2 g^2 H^2} \tag{V.8a}
\end{aligned}$$

The quantities $a, b, d_1, S_{\alpha\beta}$ and $I_{\alpha\beta}$ in equation (V.8a) above have been previously defined (equation III.3). Having chosen the quantization axis for the electronic spin, \vec{S} to be along $\vec{g}\cdot\vec{H}$ which is parallel to Oz_1 , shown in (figure V.1), and the direction of \vec{H} making angles (θ, ϕ) with respect to the (x, y, z) system (figure V.2), the average value of the hyperfine term in the electronic state M , after the application of a coordinate transformation, \vec{T} , already defined in chapter III, can be written as:

$$\langle M | \vec{S}^T \cdot \vec{A} \cdot \vec{T} | M \rangle = g_n \beta_n \left[H_x^{e; M, M} I_x + H_y^{e; M, M} I_y + H_z^{e; M, M} I_z \right] \tag{V.8b}$$

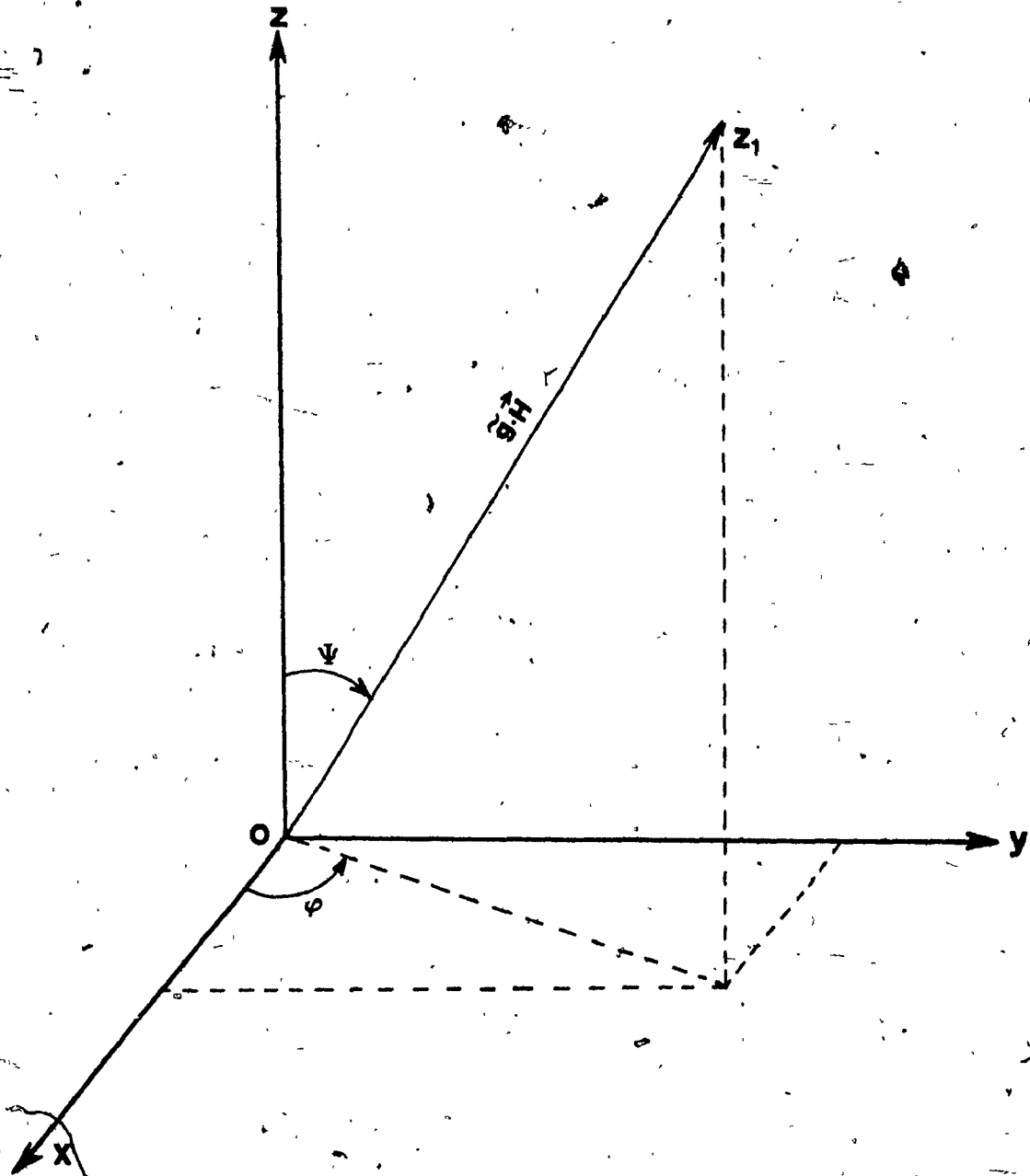


Fig.V.1. The angles ψ and ϕ which the effective magnetic field $\tilde{g}.\vec{H}$ directed along Oz_1 makes with respect to the (x, y, z) coordinate system.

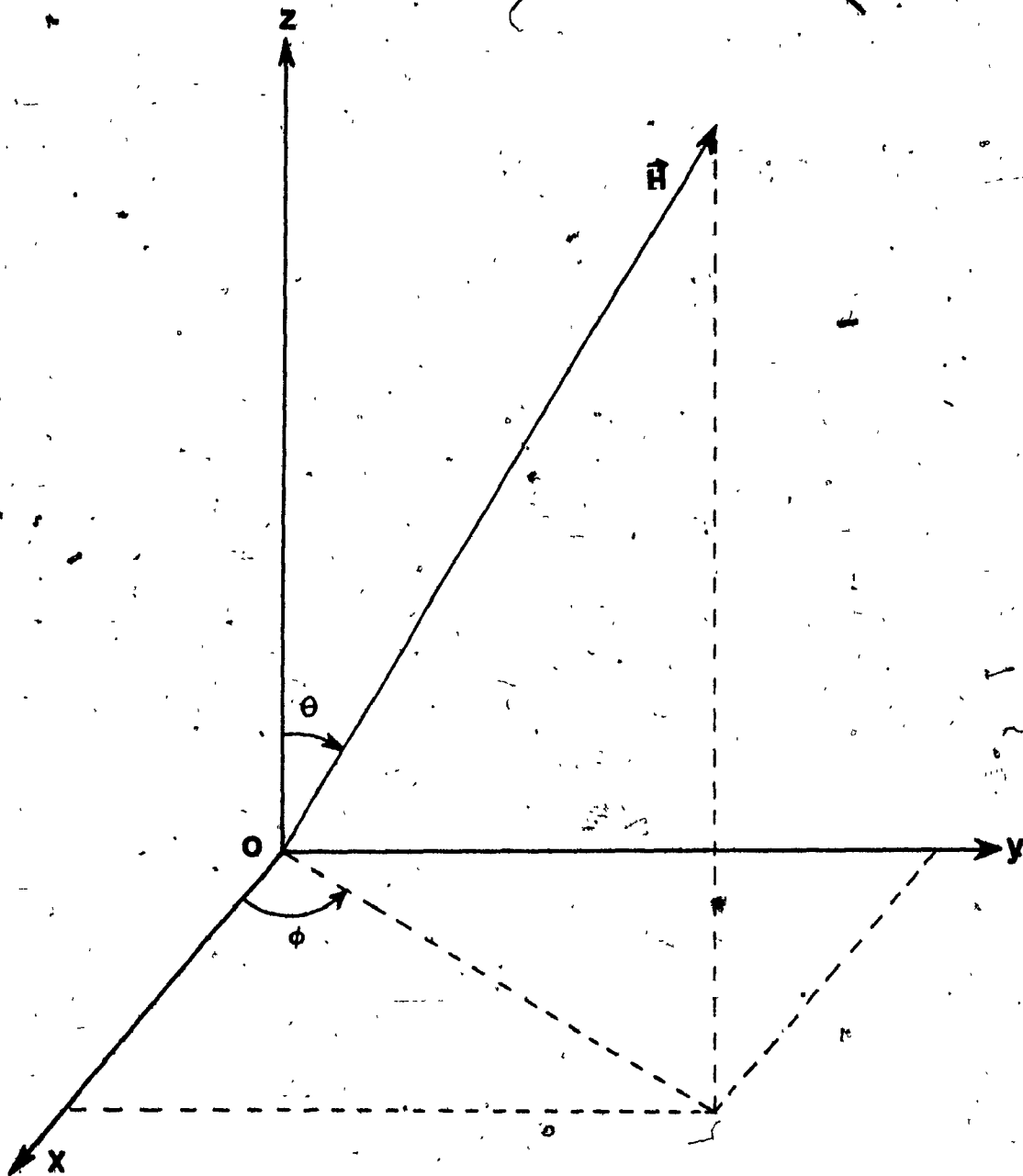


Fig.V.2. Arbitrary orientation of \vec{H} with respect to the (x, y, z) coordinate system, in spherical coordinates showing the polar (θ) and azimuthal (ϕ) angles.

$H_{x,y,z}^{e;M,M}$ being components of the effective field, and are expressed below:

$$H_x^{e;M,M} = 1/(g_n \beta_n) \left[(\vec{\lambda}_1 \cdot \vec{T}_1^T) \langle M | S_{x_1} | M \rangle + (\vec{\lambda}_1 \cdot \vec{T}_2^T) \langle M | S_{y_1} | M \rangle + (\vec{\lambda}_1 \cdot \vec{T}_3^T) \langle M | S_{z_1} | M \rangle \right]$$

$$H_y^{e;M,M} = 1/(g_n \beta_n) \left[(\vec{\lambda}_2 \cdot \vec{T}_1^T) \langle M | S_{x_1} | M \rangle + (\vec{\lambda}_2 \cdot \vec{T}_2^T) \langle M | S_{y_1} | M \rangle + (\vec{\lambda}_2 \cdot \vec{T}_3^T) \langle M | S_{z_1} | M \rangle \right]$$

$$H_z^{e;M,M} = 1/(g_n \beta_n) \left[(\vec{\lambda}_3 \cdot \vec{T}_1^T) \langle M | S_{x_1} | M \rangle + (\vec{\lambda}_3 \cdot \vec{T}_2^T) \langle M | S_{y_1} | M \rangle + (\vec{\lambda}_3 \cdot \vec{T}_3^T) \langle M | S_{z_1} | M \rangle \right]. \quad (V.8c)$$

Here, the row vectors $\vec{\lambda}_1, \vec{\lambda}_2$ and $\vec{\lambda}_3$ of the 3×3 matrix $\vec{\lambda}$ are defined in a similar way as the transformation matrices \vec{T} and \vec{T}' , introduced in chapter III:

$$\vec{\lambda}_1 = \vec{\lambda} \cdot \hat{x} \quad (V.8e)$$

$$\vec{\lambda}_2 = \vec{\lambda} \cdot \hat{y} \quad (V.8f)$$

$$\vec{\lambda}_3 = \vec{\lambda} \cdot \hat{z} \quad (V.8g)$$

The direction Oz_2 of the effective field, $H^{e;M,M}$ (which is taken to be along the nuclear spin axis of quantization) makes angles θ_1 and ϕ_1 with respect to the (x,y,z) axes, as shown in figure V.3. They can be expressed in terms of the spherical angles θ and ϕ , which are determined from experiment. θ_1 and ϕ_1 here do not depend upon $\tilde{g}_{\alpha\beta}$ and $\tilde{\lambda}_{\alpha\beta}$, but rather upon their special bilinear combinations, which are, in fact, the elements of the $\tilde{g} \cdot \tilde{g}^T$ and $\tilde{\lambda} \cdot \tilde{\lambda}^T$ tensors; they are given by:

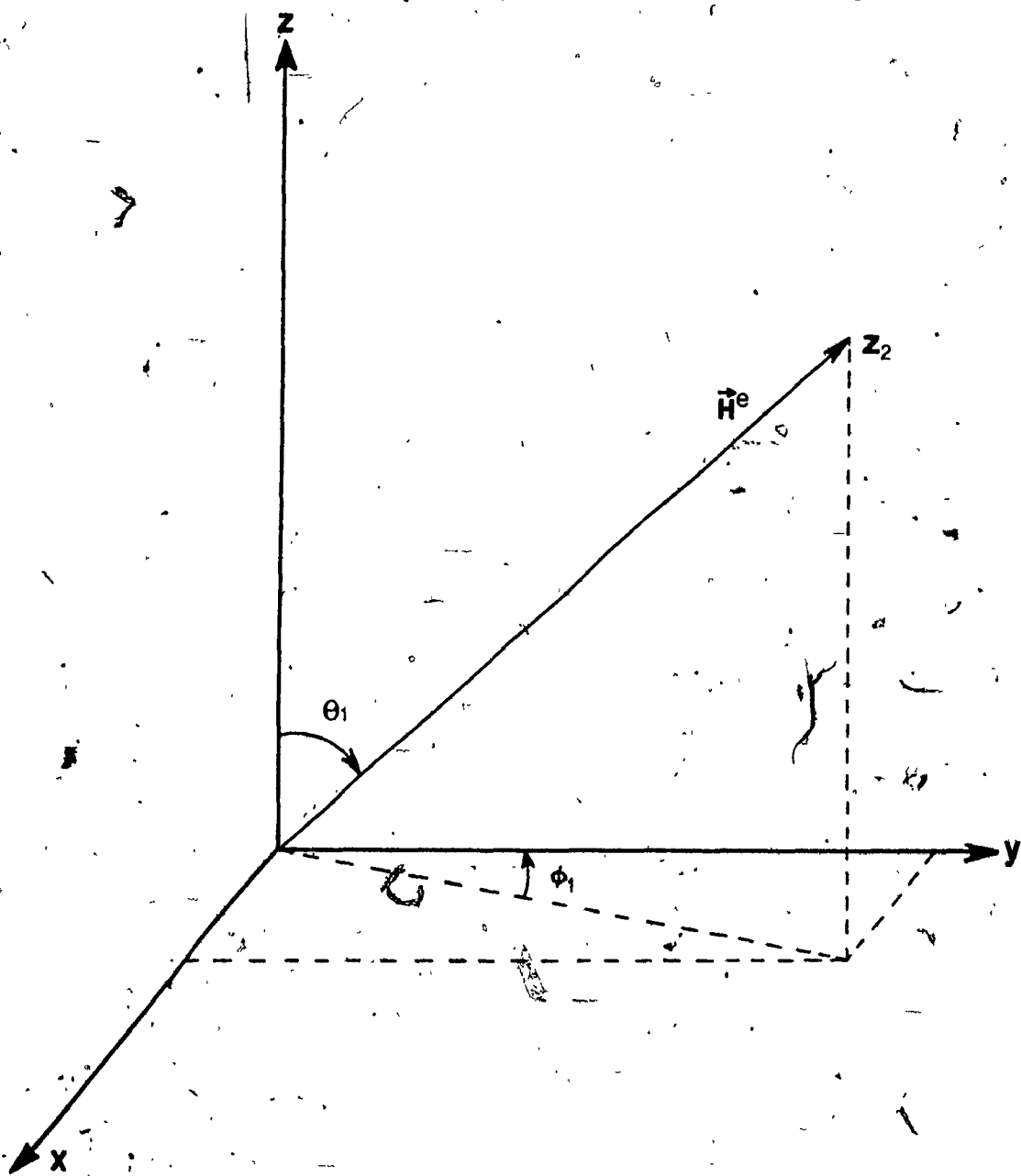


Fig.V.3. The angles θ_1 and ϕ_1 which the effective field, \vec{H}^e directed along Oz_2 , makes with respect to the (x, y, z) coordinate system.

$$\cos\theta_1 = \frac{(H_z^{e;M,M})}{\sqrt{(H_x^{e;M,M})^2 + (H_y^{e;M,M})^2}}; \quad \tan\phi_1 = \frac{(H_x^{e;M,M})}{(H_y^{e;M,M})}$$

The angles (θ_1, ϕ_1) have been calculated by Mialhe [15] for axial symmetry and coincident principal axes of the various spin/Hamiltonian tensors. In the present work, θ_1 and ϕ_1 are expressed for the general case of non-coincident principal axes. The effective magnetic field, $\vec{H}^{e;M,M}$, hence the axis of nuclear spin quantisation, can thus be determined from equation (V.4). The hyperfine interaction term $\vec{S}^T \cdot \vec{A} \cdot \vec{I}$ is then written, in the notation of Rockenbauer and Simon [30], as:

$$\begin{aligned} \vec{S}^T \cdot \vec{A} \cdot \vec{I} = & [(\vec{T}_1^T \cdot \vec{A} \cdot \vec{T}'_1)S_{x_1} + (\vec{T}_2^T \cdot \vec{A} \cdot \vec{T}'_1)S_{y_1} + (\vec{T}_3^T \cdot \vec{A} \cdot \vec{T}'_1)S_{z_1}]I_{x_2} \\ & + [(\vec{T}_1^T \cdot \vec{A} \cdot \vec{T}'_2)S_{x_1} + (\vec{T}_2^T \cdot \vec{A} \cdot \vec{T}'_2)S_{y_1} + (\vec{T}_3^T \cdot \vec{A} \cdot \vec{T}'_2)S_{z_1}]I_{y_2} \\ & + [(\vec{T}_1^T \cdot \vec{A} \cdot \vec{T}'_3)S_{x_1} + (\vec{T}_2^T \cdot \vec{A} \cdot \vec{T}'_3)S_{y_1} + (\vec{T}_3^T \cdot \vec{A} \cdot \vec{T}'_3)S_{z_1}]I_{z_2} \end{aligned} \quad (V.9)$$

In equation (V.9), T'_3 equals $\vec{H}^{e;M,M} / |\vec{H}^{e;M,M}|$. \vec{T}'_1 and \vec{T}'_2 are parallel to the undefined x_2, y_2 , axes respectively. (All one needs to know is that value of $\vec{S}^T \cdot \vec{A} \cdot \vec{I}$ in the electronic state M leads to the determination of the x_2, y_2, z_2 , components of the effective magnetic field, $\vec{H}^{e;M,M}$, experienced by the nucleus. These are expressed as follows:

$$\begin{aligned} H_{x_2}^{e;M,M} &= 1/g_n \beta_n [Z_1 \langle M | S_{x_1} | M \rangle + Z_2 \langle M | S_{y_1} | M \rangle + Z_3 \langle M | S_{z_1} | M \rangle], \\ H_{y_2}^{e;M,M} &= 1/g_n \beta_n [Z_4 \langle M | S_{x_1} | M \rangle + Z_5 \langle M | S_{y_1} | M \rangle + Z_6 \langle M | S_{z_1} | M \rangle], \end{aligned}$$

$$H_{z_2}^{e; M, M} = 1/g_n \beta_n [Z_7 \langle M | S_{x_1} | M \rangle + Z_8 \langle M | S_{y_1} | M \rangle + Z_9 \langle M | S_{z_1} | M \rangle],$$

(V. 10)

where,

$$Z_1 = (\vec{T}_1^T \cdot \tilde{A} \cdot \vec{T}'_1),$$

$$Z_2 = (\vec{T}_2^T \cdot \tilde{A} \cdot \vec{T}'_1),$$

$$Z_3 = (\vec{T}_3^T \cdot \tilde{A} \cdot \vec{T}'_1),$$

$$Z_4 = (\vec{T}_1^T \cdot \tilde{A} \cdot \vec{T}'_2),$$

$$Z_5 = (\vec{T}_2^T \cdot \tilde{A} \cdot \vec{T}'_2),$$

$$Z_6 = (\vec{T}_3^T \cdot \tilde{A} \cdot \vec{T}'_2),$$

$$Z_7 = (\vec{T}_1^T \cdot \tilde{A} \cdot \vec{T}'_3),$$

$$Z_8 = (\vec{T}_2^T \cdot \tilde{A} \cdot \vec{T}'_3),$$

$$Z_9 = (\vec{T}_3^T \cdot \tilde{A} \cdot \vec{T}'_3),$$

$$\langle M | S_{x_1} | M \rangle = \frac{[3M^2 - S(S+1)] \operatorname{Re}(b)}{\beta_e g H}$$

$$+ \frac{M [4S(S+1) - 8M^2 - 1] (3/2) d_1 \operatorname{Re}(b)}{\beta_e^2 g^2 H^2}$$

$$+ \frac{4M [-3S(S+1) + 5M^2 + 1] \operatorname{Re}(b(1/4)a)}{\beta_e^2 g^2 H^2}$$

$$\langle M | S_{y_1} | M \rangle = - \frac{[3M^2 - S(S+1)] \text{Im}(b)}{\beta_e g^2 H}$$

$$- \frac{M[4S(S+1) - 8M^2 - 1](3/2)d_1 \text{Im}(b)}{\beta_e^2 g^2 H^2}$$

$$+ \frac{4M[-3S(S+1) + 5M^2 + 1] \text{Im}(b(1/4)a^*)}{\beta_e^2 g^2 H^2}$$

$$\langle M | S_{z_1} | M \rangle = M \left[1 + \frac{bb^* [4S(S+1) - 8M^2 - 1]}{2\beta_e^2 g^2 H^2} \right]$$

$$+ \left[\frac{(1/8)aa^* [-2S(S+1) + 2M^2 + 1]}{\beta_e^2 g^2 H^2} \right]$$

During a magnetic resonance transition, the effective magnetic field experienced by the nucleus does not remain constant. This is because the initial (M) and final (M') electronic states participating in resonance are different. The transition probability is therefore expected to be a function of $\vec{H}^{e; M, M}$ and $\vec{H}^{e; M', M'}$.

V.3. Transition Probability

The interaction of electromagnetic radiation with a paramagnetic ion, embedded in a system, can lead to transitions between the energy levels of the ion when the resonance condition is satisfied. The probability of a transition from the initial state $|M, m\rangle^{(n)}$ to the final state $|M', m'\rangle^{(n)}$ due to the action of a linearly polarized microwave excitation field under the resonance condition, $h\nu = E_{M', m'} - E_{M, m}$ is given by [29]:

$$\omega_{M', m'; M, m} = K_1 |W_{M', m'; M, m}|^2, \quad (V.11)$$

where,

$$W_{M', m'; M, m} = {}^{(n)}\langle M', m' | W | M, m \rangle^{(n)}. \quad (V.11a)$$

Here, W is the perturbation operator (see equation (V.13) below) which represents the effect of the applied electromagnetic field. K_1 is a proportionality constant.

An outline of the steps in computing the transition probabilities is given below. The paramagnetic transitions are initiated by an excitation field

$$\vec{K}(t) = \vec{h}_0 \cos(\omega t), \quad (V.12)$$

where h_0 is the amplitude of the excitation field and ω , the angular frequency of oscillation. The perturbation operator is given by

$$W = - \vec{\mu} \cdot \vec{K}(t). \quad (V.13)$$

In equation (V.13), $\vec{\mu}$ is the electron magnetic moment vector of the ion. In quantum mechanical formalism, $\vec{\mu}$ should be replaced by the appropriate operator, given by

$$\vec{\mu} = - \beta_e \vec{S} \cdot \vec{g}. \quad (V.14)$$

Substituting equations (V.12) and (V.14) into equation (V.13) gives

$$W = \beta_e \cos(\omega t) \vec{S}^T \cdot \vec{g} \cdot \vec{h}_0. \quad (V.15)$$

Substituting equation (V.15) into equation (V.11a), and using equation (V.2) the transition probability given by equation (V.11) yields

$$\begin{aligned} |W_{M, m; M', m'}|^2 &= \beta_e^2 \cos^2(\omega t) \left| {}^{(n)}\langle M | \vec{S}^T \cdot \vec{g} \cdot \vec{h}_0 | M' \rangle^{(n)} \right|^2 \\ &\times \left| {}^{(n)}\langle M(m) | M'(m') \rangle^{(n)} \right|^2 \end{aligned} \quad (V.15a)$$

The functions $|M(m)\rangle^{(n)}$ and $|M'(m')\rangle^{(n)}$ are eigenfunctions of the nuclear

spin z-projection operator with different directions for the quantization axis (z_M axis), so they may be expressed as a linear combination of one another by means of the rotation matrix $D_{m',m}^{(I)}(\beta)$ of the irreducible-group representation [3] with weight I

$$|M'(m')\rangle^{(n)} = \sum_m D_{m',m}^{(I)}(\beta) |M(m)\rangle^{(n)}, \quad (V.15b)$$

where β is the rotation which relates the two eigenfunctions in equation (V.15b). Using equation (V.15b) and the orthogonality relations of the rotation matrix, $|\langle M(m) | M'(m') \rangle^{(n)}|^2$ can be expressed in terms of the square of the modulus of the rotation matrix element for the irreducible-group representation

$$\begin{aligned} |\langle M(m) | M'(m') \rangle^{(n)}|^2 &= |D_{m',m}^{(I)}(\beta)|^2 \\ &= |P_{m',m}^{(I)}(\mu_{M,M'})|^2 \end{aligned} \quad (V.15c)$$

Finally, the transition probability from the state $|M,m\rangle^{(n)}$ to the state $|M',m'\rangle^{(n)}$, is [3];

$$|W_{M,m;M',m'}|^2 = |\omega_{e;M,M'}|^2 |P_{m,m'}^{(I)}(\mu_{M,M'})|^2, \quad (V.16)$$

where,

$$|\omega_{e;M,M'}|^2 = \beta_e^2 h_0^2 \cos^2(\omega t) |\langle M | \vec{S}^T \cdot \vec{g} \cdot \vec{\eta}' | M' \rangle^{(n)}|^2 \quad (V.17)$$

is the electron transition probability, and $|P_{m,m'}^{(I)}(\mu_{M,M'})|^2$, the nuclear transition probability. $\vec{\eta}' = \frac{\vec{R}_0}{|\vec{R}_0|}$, is a unit vector in the direction of polarization of the excitation field. $P_{m,m'}^{(I)}(\mu_{M,M'})$ are known functions

[3]

$$\begin{aligned}
 P_{m,m'}^{(I)}(\mu_{M,M'}) &= \frac{(-1)^{I-m}}{(I-m)!} \times \frac{1^{m'-m}}{2^I} \left[\frac{(I-m)!(I+m')!}{(I+m)!(I-m')!} \right]^{1/2} \\
 &\times (1-\mu_{M,M'})^{-\binom{m'-m}{2}} (1+\mu_{M,M'})^{-\binom{m+m'}{2}} \\
 &\times \frac{d^{I-m'}}{d\mu^{I-m'}} \left[(1-\mu_{M,M'})^{I-m} (1+\mu_{M,M'})^{I+m} \right]
 \end{aligned}
 \tag{V.17a}$$

$\mu_{M,M'}$ in equation (V.16) is defined as the cosine of the angle between by the effective electron fields in the initial and final electron states, designated by M and M', respectively;

$$\mu_{M,M'} = \cos(\vec{H}^{e;M,M}, \vec{H}^{e;M',M'}) \tag{V.18}$$

Explicit evaluation of $\mu_{M,M'}$, using equation (V.10), yields

$$\begin{aligned}
 \mu_{M,M'} &= \frac{MM'}{|MM'|} \left[1 - \frac{9}{2\beta_e^2 g^2 H_0^2} (M-M')^2 \left[1 + \frac{S(S+1)}{3MM'} \right]^2 \times \right. \\
 &\left. \left\{ (F_1 - F_4^2) \{\text{Re}(b)\}^2 + (F_2 - F_5^2) \{\text{Im}(b)\}^2 - 2(F_3 - F_4 F_5) \text{Re}(b) \text{Im}(b) \right\} \right],
 \end{aligned}
 \tag{V.19}$$

where,

$$F_1 = \frac{(\vec{T}_1 \cdot \vec{A} \cdot \vec{T}_1)}{(\vec{T}_3 \cdot \vec{A} \cdot \vec{T}_3)}$$

$$F_2 = \frac{(\vec{T}_2^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_2)}{(\vec{T}_3^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}$$

$$F_3 = \frac{(\vec{T}_1^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_2)}{(\vec{T}_3^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}$$

$$F_4 = \frac{(\vec{T}_1^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}{(\vec{T}_3^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}$$

$$F_5 = \frac{(\vec{T}_2^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}{(\vec{T}_3^T \cdot \tilde{\Lambda}^T \cdot \tilde{\Lambda} \cdot \vec{T}_3)}$$

Note that equation (V.19) is only applicable to states with $M \neq 0$. It is thus possible, using equation (V.19) and the values of $P_{m,m'}^{(I)}$ ($\mu_{MM'}$) from equation (V.17a), to evaluate the nuclear transition probabilities, given by equation (V.15c). In order to calculate the electron transition probability, $|\omega_{e;M,M'}|^2$, applying the transformation introduced earlier (see equation (V.8)) and re-writing $\vec{S}^T \cdot \tilde{g} \cdot \vec{\eta}'$ as:

$$\vec{S}^T \cdot \tilde{g} \cdot \vec{\eta}' = \frac{1}{2}(\vec{T}_-^T \cdot \tilde{g} \cdot \vec{\eta}')S_+ + \frac{1}{2}(\vec{T}_+^T \cdot \tilde{g} \cdot \vec{\eta}')S_- + (\vec{T}_3^T \cdot \tilde{g} \cdot \vec{\eta}')S_{z_1} \quad (V.20)$$

For the transitions $M+n, m' \leftrightarrow M, m$ the electron transition probability, matrix element, $\omega_{e;M+n,M}$ (where $n = 0, \pm 1, \pm 2, \pm 3, \dots$, etc) can be expressed as follows:

$$\omega_{e;M+n,M} = \beta_e h \omega \cos(\omega t) (\vec{T}_-^T \cdot \tilde{g} \cdot \vec{\eta}') \left[\langle M+n | S_+ | M \rangle + \frac{(\vec{T}_+^T \cdot \tilde{g} \cdot \vec{\eta}')^2}{|\vec{T}_-^T \cdot \tilde{g} \cdot \vec{\eta}'|^2} \times \right. \\ \left. \langle M+n | S_- | M \rangle + \frac{2(\vec{T}_3^T \cdot \tilde{g} \cdot \vec{\eta}')(\vec{T}_+^T \cdot \tilde{g} \cdot \vec{\eta}')}{|\vec{T}_-^T \cdot \tilde{g} \cdot \vec{\eta}'|^2} \langle M+n | S_{z_1} | M \rangle \right] \quad (V.21)$$

where,

$$|\hat{T}_+^T \cdot \tilde{g} \cdot \hat{\eta}'|^2 = |\hat{T}_-^T \cdot \tilde{g} \cdot \hat{\eta}'|^2 = (\hat{\eta}'^T \cdot \tilde{g}^T \cdot \tilde{g} \cdot \hat{\eta}') - 1/g^2 (\hat{\eta}'^T \cdot \tilde{g}^T \cdot \tilde{g} \cdot \hat{\eta}'),$$

and

$$\hat{T}_3^T \cdot \tilde{g} \cdot \hat{\eta}' = \hat{\eta}'^T \cdot \tilde{g}^T \cdot \tilde{g} \cdot \hat{\eta}' \quad (\text{V.21a})$$

The matrix elements of S_+ , S_- , and S_z in equation (V.21) are lengthy; they are given in Appendix B. Abragam and Bleahey [1] have shown that the maximum intensity is attained when the direction of the excitation microwave field, \vec{h}_0 , is normal to the external Zeeman field, \vec{H} . To compute the intensity in this specific case, it is found convenient to choose a new coordinate system (x_3, y_3, z_3) with z_3 parallel to \vec{H} . The transformation matrix \tilde{T}'' transforms the (x, y, z) system to the new (x_3, y_3, z_3) system. In this new coordinate system, the vector \vec{h}_0 makes an angle ϕ_0 with the x_3 axis in the $x_3 y_3$ plane. The components of \vec{h}_0 along the (x_3, y_3, z_3) axes are then $h_0(\cos\phi_0, \sin\phi_0, 0)$. The transformation by \tilde{T}'' of the direction cosines $\hat{\eta}$ and $\hat{\eta}'$ of \vec{H} and \vec{h}_0 respectively, are:

$$\begin{aligned} \hat{\eta} &= (\tilde{T}'')^T \cdot \hat{\eta}^{(3)}, \text{ and} \\ \hat{\eta}' &= (\tilde{T}'')^T \cdot \hat{\eta}'^{(3)}, \end{aligned} \quad (\text{V.22})$$

where,

$$\hat{\eta}^{(3)} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}; \quad \hat{\eta}'^{(3)} = \begin{bmatrix} \cos\phi_0 \\ \sin\phi_0 \\ 0 \end{bmatrix}$$

For the specific case where the Zeeman field, \vec{H} , is normal to the excitation microwave field, \vec{h}_0 equation (V.21a) can be expressed in the (x_3, y_3, z_3) system by use of the transformation matrix \tilde{T}'' as:

$$\begin{aligned}
|\vec{T}_-^T \cdot \vec{g} \cdot \vec{\eta}'|^2 &= |\vec{T}_+^T \cdot \vec{g} \cdot \vec{\eta}'|^2 = \cos^2 \phi_0 (\vec{T}_1^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_1^{\prime}) + \\
&+ \sin^2 \phi_0 (\vec{T}_2^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_2^{\prime}) + \sin(2\phi_0) (\vec{T}_1^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_2^{\prime}) \\
&- 1/g^2 [\cos \phi_0 (\vec{T}_3^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_1^{\prime}) + \sin \phi_0 (\vec{T}_3^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_2^{\prime})]^2
\end{aligned}$$

and

$$\vec{T}_3^T \cdot \vec{g} \cdot \vec{\eta}' = \cos \phi_0 (\vec{T}_3^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_1^{\prime}) + \sin \phi_0 (\vec{T}_3^{\prime T} \cdot \vec{g} \cdot \vec{g} \cdot \vec{T}_2^{\prime})$$

(V.23)

The determination of the transformation matrices \vec{T} and \vec{T}'' is not unique; however, in practice, one can always derive appropriate transformations [7, 10, 11, 17], which lead to the correct results [3, 15]; the ones used here are listed in Appendix B. For the hyperfine transitions $M, m \leftrightarrow M-1, m\pm 1$ and the $\vec{g} \cdot \vec{g}^T$ and $\vec{A} \cdot \vec{A}^T$ being isotropic, the general results for the electron transition probability matrix element and the transition probability given by equations (V.21) and (V.16) respectively, reduce to that of Bir [3]; as well, for $\vec{g} \cdot \vec{g}^T$ being isotropic, while $\vec{A} \cdot \vec{A}^T$, \vec{D} , \vec{P} tensors conforming to uniaxial symmetry, the intensity expression reduces to that of Mialhe and Erbeia [15].

CHAPTER VI

CONCLUDING REMARKS

The present thesis deals with the following three calculations:

(i) A general procedure has been described to calculate the separations of the forbidden h.f. doublets ($M, m' \leftrightarrow M-1, m$; $M, m \leftrightarrow M-1, m'$) for the case of the general spin Hamiltonian, consisting of \tilde{g} , \tilde{A} , \tilde{D} , \tilde{P} and \tilde{g}_n tensors, whose principal axes are non-coincident. Using these expressions, and the experimentally determined forbidden-doublet separations, the values of the components of the nuclear quadrupole tensor, \tilde{P} , as well as those of the nuclear g-tensor, \tilde{g}_n , can be estimated, since the forbidden doublet separations clearly depend on them, as exhibited by eq. (III.8).

Specific expressions for Mn^{2+} ($S = I = 5/2$) have, here, been listed for the spin Hamiltonian for which the \tilde{A} , \tilde{g} , and \tilde{g}_n tensors are isotropic, while the \tilde{D} and \tilde{P} tensors are diagonal, but anisotropic. The h.f. forbidden-doublet separations can be used in a least-squares fitting (LSF) procedure to evaluate the components of the \tilde{P} and \tilde{g}_n tensors using the experimentally-measured doublet separations. The general details of the LSF procedure, as applied particularly to the case of EPR data analysis, have been described by Misra [18, 20, 21, 25, 26].

Finally, the correct expressions for the doublet separations to be expected for Mn^{2+} , using the approaches followed by Mialhe [16], and by Upreti [36], can be obtained by taking into account the corrections and/or omissions for the two cases, as pointed out in this thesis.

(ii) The correct spin Hamiltonians applicable to low-symmetry (monoclinic and triclinic) paramagnetic complexes has been taken into account in this thesis. The ratio I_f/I_a , of the intensities of the

forbidden to the allowed transitions, are found to be non-zero for all orientations of the external magnetic field in the case of triclinic symmetry. As for monoclinic symmetry, the intensity of the forbidden transitions is calculated to be zero when the Zeeman field is along the monoclinic symmetry axis, i.e., for $\vec{H} \parallel \vec{Z}$ ($C_2 \parallel \vec{Z}$), $\vec{H} \parallel \vec{Y}$ ($C_2 \parallel \vec{Y}$) and $\vec{H} \parallel \vec{X}$ ($C_2 \parallel \vec{X}$). However, forbidden transitions are calculated to have non-zero intensity for orientations of H parallel to the other crystal-field axes, i.e., for $\vec{H} \parallel \vec{X}$, \vec{Y} ($C_2 \parallel \vec{Z}$); $\vec{H} \parallel \vec{Y}$, \vec{Z} ($C_2 \parallel \vec{X}$) and $\vec{H} \parallel \vec{X}$, \vec{Z} ($C_2 \parallel \vec{Y}$). From the I_f/I_a values, it is possible to estimate the values of certain combinations of the parameters $\{B_k^q\}$, as discussed in sec. IV.4. The results reported in this thesis differ from those of Pandey and Upreti [28] in two respects. First, the present calculations included all the necessary O_k^q operators in the spin Hamiltonian, including those with $q < 0$, unlike that in Ref. [28]. Also, the present calculation takes into consideration the three possible orientations of the monoclinic symmetry axis, C_2 (i.e. parallel to X, Y, and Z, crystal-field axes). Pandey and Upreti [28] did not, at all, incorporate this very important fact into their calculations.

(iii) The general method developed by Bir [3] is used in obtaining expressions for the intensity variation of the allowed and the forbidden hyperfine transitions for the case of anisotropic (non-coincident) spin-Hamiltonian tensors. It is noted that there are important second-order admixtures arising from cross products of the terms in \vec{D} and \vec{A} , because the spin Hamiltonian consists of products such as $(S_z S_{\pm})(S_{\mp} I_{\pm})$ and others formed by the permutation of the components of \vec{S} and \vec{I} . The magnitude of the effective electron field, $H^{e;MM}$ experienced by the nucleus is calculated for the general case of

non-coincident spin-Hamiltonian tensors. The components of the effective electron field, $\vec{H}^{e,MM}$ obtained in the present work reduce to the results of Bir [3] and, Mialhe and Erbeia [31] if the same coordinate-transformation matrix \tilde{T} [15] is used for both the electron (\vec{S}) and nuclear (\vec{I}) spins vectors. This is because the hyperfine operator, $\vec{S}^T \cdot \tilde{A} \cdot \vec{I}$, is expressed in terms of spin operators $\vec{S}^{(1)}$ and $\vec{I}^{(1)}$, which are both quantized along the direction of \vec{H} for isotropic \tilde{g} tensor. (The superscript 1 designates the coordinate system in which the spin vectors are given). It should be mentioned that Bir [3] has only considered the simplest case, i.e., that of isotropic \tilde{g} and \tilde{A} tensors, and an axial D tensor (the P tensor was not considered in view of the approximations made), while Mialhe and Erbeia [15,17] considered the case of isotropic \tilde{g} , and axially symmetric \tilde{A} , \tilde{D} and \tilde{P} tensors. For the particular case, where the external magnetic field, \vec{H} is normal to the excitation (r.f) field, \vec{h}_0 , which has been considered presently, the derived expressions are found to be in good agreement with those of Bir [3], and Mialhe and Erbeia [15, 17], within the frame-work of their assumptions. It is found that a factor of $\frac{MM'}{|MM'|}$ is missing in the expression for $\mu_{MM'}$, given by Bir.

It is hoped that the results presented in this thesis would help the interpretation and understanding of EPR data of single crystals.

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APPENDIX A

The general expressions of the doublet separations of forbidden hyperfine transitions ($\Delta M = \pm 1$; $\Delta m = \pm 1, \pm 2$) are listed as follows.

$\Delta M = \pm 1, \Delta m = \pm 1$:

$$\begin{aligned} \Delta H &= H_{M, m+1 \leftarrow M-1, m} - H_{M, m \leftarrow M-1, m+1} \\ &= 2G_1 \beta_n H_o / (\beta_e g) - 3d_1 G_1 \beta_n (2M-1) / (\beta_e^2 g^2) - KG_1 \beta_n (2m+1) / (\beta_e^2 g^2) - \\ &KG_1^2 \beta_n^2 (2M-1) / (\beta_e^3 g^3) - 3P_1 G_1^2 \beta_n^2 (2m+1) / (\beta_e^3 g^3) + 2G_1^3 \beta_n^3 H_o / (\beta_e^3 g^3) - \\ &3d_1 G_1^3 \beta_n^3 (2M-1) / (\beta_e^4 g^4) - KG_1^3 \beta_n^3 (2m+1) / (\beta_e^4 g^4) - K(2M-1) / (\beta_e g) - \\ &3P_1 (2m+1) / (\beta_e g) - \alpha_1 \beta_n^2 [(M+m-1)H_1^2 + (M+m)H_2^2] / (2M(M-1)\beta_e g) - \\ &\alpha_5 \beta_n [(3(m+1)^2 - 3M(2m+1) - I(I+1))H_1 - \\ &\{3m^2 + 3M(2m+1) - I(I+1)\}H_2] / (M(M-1)\beta_e g) - \\ &\alpha_8 (2M-1) [24m(m+1) + 9 - 4I(I+1)] / (2M(M-1)\beta_e g) + \\ &\alpha_7 (2M-1) [6m(m+1) + 3 - 2I(I+1)] / (8M(M-1)\beta_e g) - \\ &bb^* [24M(M-1) + 9 - 4S(S+1)] [K(2M-1) / (2\beta_e^3 g^3 H_o^2) + \\ &3P_1 (2m+1) / (2\beta_e^3 g^3 H_o^2) - G_1 \beta_n / (\beta_e^3 g^3 H_o) - KG_1 \beta_n (2m+1) / (2\beta_e^4 g^4 H_o^2) - \\ &3d_1 G_1 \beta_n (2M-1) / (2\beta_e^4 g^4 H_o^2)] - \\ &- aa^* [2S(S+1) - 6M(M-1) - 3] [K(2M-1) / (8\beta_e^3 g^3 H_o^2) + \\ &3P_1 (2m+1) / (8\beta_e^3 g^3 H_o^2) - G_1 \beta_n / (4\beta_e^3 g^3 H_o) - 3d_1 G_1 \beta_n (2M-1) / (8\beta_e^4 g^4 H_o^2) \\ &- KG_1 \beta_n (2m+1) / (8\beta_e^4 g^4 H_o^2)] - \end{aligned}$$

$$\alpha_2 [-(2M-1)(2m+1)/(4\beta_e^2 g^2 H_o^2)] - 3d_1 (2M-1)^2 (2m+1)/(8\beta_e^3 g^3 H_o^2) +$$

$$K(2M-1)\{I(I+1)-(3m^2+3m+1)\}/(4\beta_e^3 g^3 H_o^2) +$$

$$3P_1 (2m+1)\{2I(I+1)-2m^2-2m-1\}/(8\beta_e^3 g^3 H_o^2) -$$

$$G_1 \beta_n \{2I(I+1)-2m^2-2m-1\}/(4\beta_e^3 g^3 H_o^2) -$$

$$3d_1 G_1 \beta_n (2M-1)\{2I(I+1)-2m^2-2m-1\}/(8\beta_e^4 g^4 H_o^2) -$$

$$KG_1 \beta_n (2m+1)\{I(I+1)-1-2M(M-1)-m(m+1)\}/(4\beta_e^4 g^4 H_o^2) +$$

$$\alpha_3 [\{2S(S+1)-(2M^2-2M+1)\}/(2\beta_e^2 g^2 H_o^2) +$$

$$3d_1 (2M-1)\{2S(S+1)-(2M^2-2M+1)\}/(4\beta_e^3 g^3 H_o^2) +$$

$$K(2m+1)\{S(S+1)-(3M^2-3M+1)\}/(2\beta_e^3 g^3 H_o^2) -$$

$$3P_1 (2m+1)^2 (2M-1)/(2\beta_e^3 g^3 H_o^2) + G_1 \beta_n (2M-1)(2m+1)/(2\beta_e^3 g^3 H_o^2) +$$

$$3d_1 G_1 \beta_n (2M-1)^2 (2m+1)/(4\beta_e^4 g^4 H_o^2) -$$

$$KG_1 \beta_n (2M-1)\{S(S+1)-1-M(M-1)-2m(m+1)\}/(2\beta_e^4 g^4 H_o^2) -$$

$$3P_1 G_1 \beta_n (2m+1)\{2S(S+1)-(2M^2-2M+1)\}/(4\beta_e^4 g^4 H_o^2) -$$

$$\alpha_4 [(2M-1)(2m+1)/(2\beta_e^2 g^2 H_o^2) + 3d_1 (2M-1)^2 (2m+1)/(4\beta_e^3 g^3 H_o^2) +$$

$$K(2M-1)(3m^2+3m+1)/(2\beta_e^3 g^3 H_o^2) + 3P_1 (2m+1)(2m^2+2m+1)/(4\beta_e^3 g^3 H_o^2) +$$

$$G_1 \beta_n (2m^2+2m+1)/(2\beta_e^3 g^3 H_o^2) - 3d_1 G_1 \beta_n (2M-1)(2m^2+2m+1)/(4\beta_e^4 g^4 H_o^2) -$$

$$KG_1 \beta_n (2m+1)\{2M^2-2M+m^2+m+1\}/(2\beta_e^4 g^4 H_o^2) -$$

$$3P_1 G_1 \beta_n (2M-1)(2m+1)^2/(2\beta_e^4 g^4 H_o^2) -$$

$$\alpha_g \{ (3(2M^2 - 2M + 1) - 2S(S+1)) / (\beta_{eg}^2 H_0^2) \} +$$

$$3d_1 (2M-1) (6M^2 - 6M + 3 - 2S(S+1)) / (2\beta_{eg}^3 H_0^3) +$$

$$K(2m+1) \{-S(S+1) + 9M^2 - 9M + 3\} / (\beta_{eg}^3 H_0^3) +$$

$$3(3/2P_1) (2M-1) (2m+1)^2 / (\beta_{eg}^3 H_0^3) -$$

$$3G_1 \beta_n (2M-1) (2m+1) / (\beta_{eg}^3 H_0^3) -$$

$$3G_1 \beta_n (3/2d_1) (2M-1)^2 (2m+1) / (\beta_{eg}^4 H_0^4) -$$

$$G_1 \beta_n K(2M-1) \{6m^2 + 6m + 3M^2 - 3M + 3 - S(S+1)\} / (\beta_{eg}^4 H_0^4) -$$

$$G_1 \beta_n (3/2P_1) (2m+1) \{6M^2 - 6M + 3 - 2S(S+1)\} / (\beta_{eg}^4 H_0^4) +$$

$$3d_1 (aa^*) G \beta_n (2M-1) \{-3S(S+1) + 5M(M+1) + 6\} / (2\beta_{eg}^4 H_0^4) -$$

$$K(aa^*) (2M-1) \{-2S(S+1) + 2M^2 - 2M + 3\} / (8\beta_{eg}^3 H_0^3) +$$

$$KG_1 \beta_n (aa^*) (2m+1) \{-2S(S+1) + 6M^2 - 6M + 3\} / (4\beta_{eg}^4 H_0^4) -$$

$$KG_1^2 \beta_n^2 (aa^*) (2M-1) \{-2S(S+1) + 2M^2 - 2M + 3\} / (8\beta_{eg}^5 H_0^5) +$$

$$6d_1 G_1 \beta_n (bb^*) (2M-1) \{6S(S+1) - 20M^2 + 20M - 27/2\} / (\beta_{eg}^4 H_0^4) -$$

$$K(bb^*) (2M-1) \{4S(S+1) - 8M^2 + 8M - 9\} / (2\beta_{eg}^4 H_0^4) +$$

$$KG_1 \beta_n (bb^*) (2m+1) \{4S(S+1) - 24M^2 + 24M - 8\} / (\beta_{eg}^4 H_0^4) -$$

$$KG_1^2 \beta_n^2 (bb^*) (2M-1) \{4S(S+1) - 8M^2 + 8M - 9\} / (2\beta_{eg}^5 H_0^5) -$$

$$3d_1 (FF^*) / 32 [\{-4S(S+1) + 4M^2 - 4M - 2M - 1\} +$$

$$\{12M^2 - 12M + 6 - 4S(S+1)\} (2m+1)] / (\beta_{eg}^3 H_0^3) -$$

$$2G_1 \beta_n \{ [2-4S(S+1)](2m+1) - 12I(I+1)(2M-1) + 24M^2 m$$

$$+ 12M^2 + 24Mm - 12m - 12m^2 - 2 \} / (\beta_e^4 g^4 H_o^2) +$$

$$G_1^2 \beta_n^2 \{ [2-4S(S+1)](2M-1) - 4S(S+1)(2m+1) +$$

$$8m^3 + 24M^2 m + 4m - 24Mm^2 + 2 \} / (\beta_e^5 g^5 H_o^2) -$$

$$K(F F^*) / 16 \{ 2S(S+1)(-8m-2M-3) - 2I(I+1)(2M-1) +$$

$$4M^3 + 24M^2 m + 6M^2 + 12Mm^2 + 2M + 6m - 6m^2 - 12Mm \} / (\beta_e^3 g^3 H_o^2) -$$

$$2G_1 \beta_n \{ 2S(S+1)(-2m-1) - 2I(I+1)(8M+2m-3) + 12M^2 m +$$

$$6M^2 + 24Mm^2 + 6M + 2m - 6m^2 + 4m^3 + 12Mm \} / (\beta_e^4 g^4 H_o^2) +$$

$$G_1^2 \beta_n^2 \{ 2S(S+1)(-8m-2M-3) - 2I(I+1)(2M-1) + 4M^3 +$$

$$24M^2 m + 6M^2 + 12Mm^2 + 2M + 6m - 6m^2 - 12Mm \} / (\beta_e^5 g^5 H_o^2) -$$

$$3d_1 (B_1 B_1^*) / 32 \{ [2(S+1)(4M-4m-4) - 8M^3 + 24M^2 - 24Mm -$$

$$28M + 12m + 24M^2 m + 12] \} / (\beta_e^3 g^3 H_o^2) -$$

$$2G_1 \beta_n \{ 2S(S+1)(4m+2) + 2I(I+1)(-12M+6) -$$

$$12M^2 + 48Mm + 24M - 24m + 24Mm - 12m^2 - 24M^2 m - 12 \} / (\beta_e^4 g^4 H_o^2) +$$

$$G_1^2 \beta_n^2 \{ 2S(S+1)(4M-4m-4) - 8M^3 + 24M^2 - 24Mm - 28M + 12m +$$

$$24M^2 m + 12 \} / (\beta_e^5 g^5 H_o^2) +$$

$$K(B_1 B_1^*) / 16 \{ 2S(S+1)(2M-8m-5) + 2I(I+1) - 4M^3 + 24M^2 m - 12Mm^2 - 26M +$$

$$18M^2 + 18m + 6m^2 - 36Mm + 12 \} / (\beta_e^3 g^3 H_o^2) -$$

$$2G_1 \beta_n \{2S(S+1)(2m+1) + 2I(I+1)(-8M+2m+5) - 12M^2 m + 24Mm^2 + 18M - 6M^2 - 26m$$

$$-18m^2 - 4m^3 + 36Mm - 12\} / (\beta_e^4 g^4 H_o^2) +$$

$$G_1^2 \beta_n^2 \{2S(S+1)(2M-8m-5) + 2I(I+1)(2M-1) - 4M^3 + 24M^2 m - 12Mm^2 - 26M + 18M^2$$

$$+ 18m + 6m^2 - 36Mm + 12\} / (\beta_e^5 g^5 H_o^2) +$$

$$G_1 \beta_n [ab^{*2} + a^* b^2] \{ (30 - 48S(S+1))(2M-1) + 240M^3 - 360M^2$$

$$+ 240M - 6Q \} / (4\beta_e^4 g^4 H_o^2)$$

$$- [aF^* B_1 + a^* F B_1^*] / 16 \{ 2S(S+1)(2m+1) - 12M^2 m - 6M^2 + 12Mm + 6M$$

$$- 6m - 3 \} / (\beta_e^3 g^3 H_o^2)$$

$$- 2G_1 \beta_n \{ 6I(I+1)(2M-1) - 12Mm^2 + 6m^2 - 12Mm - 6M + 6m + 3 \} / (\beta_e^4 g^4 H_o^2) +$$

$$G_1^2 \beta_n^2 \{ 2S(S+1)(2m+1) - 12M^2 m - 6M^2 + 12Mm + 6M - 6m - 3 \} / (\beta_e^5 g^5 H_o^2)]$$

$\Delta M = \pm 1, \Delta m = \pm 2:$

$$\Delta H = H_{M, m+1 \leftrightarrow M-1, m-1} - H_{M, m-1 \leftrightarrow M-1, m+1}$$

$$= -2K(2M-1) / (\beta_e g) - 12mP_1 / (\beta_e g) + 4G_1 \beta_n H_o / (\beta_e g) -$$

$$6d_1 G_1 \beta_n (2M-1) / (\beta_e^2 g^2) - 4KG_1 \beta_n m / (\beta_e^2 g^2) - 8KG_1^2 \beta_n^2 (2M-1) / (\beta_e^3 g^3) -$$

$$16KG_1^3 \beta_n^3 m / (\beta_e^4 g^4) + 16G_1^3 \beta_n^3 H_o / (\beta_e^3 g^3) - 48G_1^2 \beta_n^2 P_1 m / (\beta_e^3 g^3) -$$

$$24d_1 G_1^3 \beta_n^3 (2M-1) / (\beta_e^4 g^4) -$$

$$\alpha_1 \beta_n^2 / 2M(M-1) (\beta_e g) [4G_1 \beta_n (2M-1) \{ -4K(2M-1) H_o / (\beta_e g) -$$

$$24P_1 m H_o / (\beta_e g) + 6d_1 K(2M-1)^2 / (\beta_e^2 g^2) + 24KP_1 m^2 / (\beta_e^2 g^2) +$$

$$\begin{aligned}
& \cdot 36d_1 P_1 m(2M-1)/(\beta_e^2 g^2) + 4K^2(2M-1)m/(\beta_e^2 g^2) + \\
& (-1+12G_1^2 \beta_n^2 / \beta_e^2 g^2)(2M-1)\{2H_0^2 - 6d_1 H_0(2M-1)/(\beta_e g) - 4KH_0 m/(\beta_e g) + \\
& 6d_1 Km(2M-1)/(\beta_e^2 g^2) + 24KP_1 m(2M-1)/(\beta_e^2 g^2) + 9d_1^2(2M-1)^2/(2\beta_e^2 g^2) \\
& + 2K^2[(2M-1)^2 + m^2]/(\beta_e^2 g^2) + 72P_1^2 m^2/(\beta_e^2 g^2)\} - 4G_1 \beta_n m/(\beta_e g)\{2H_0^2 - \\
& 6d_1 H_0(2M-1)/(\beta_e g) - 4KH_0 m/(\beta_e g) + 6d_1 Km(2M-1)/(\beta_e^2 g^2) + \\
& 48KP_1 m(2M-1)/(\beta_e^2 g^2) + 9d_1^2(2M-1)^2/(2\beta_e^2 g^2) + \\
& 2K^2[(2M-1)^2 + m^2]/(\beta_e^2 g^2) + 72P_1^2 m^2/(\beta_e^2 g^2)\} - \\
& (1+12G_1^2 \beta_n^2 / \beta_e^2 g^2)m\{-4KH_0(2M-1)/(\beta_e g) - 24P_1 H_0 m/(\beta_e g) + \\
& 6d_1 K(2M-1)^2/(\beta_e^2 g^2) + 24KP_1 m^2/(\beta_e^2 g^2) + 36d_1 P_1 m(2M-1)/(\beta_e^2 g^2) + \\
& 4K^2 m(2M-1)/(\beta_e^2 g^2)\} + \alpha_g \beta_n / \beta_e g M(M-1)\{6m(2M-1)\{2H_0^2 - \\
& 3d_1(2M-1)/(\beta_e g) - 2Km/(\beta_e g) - 4KG_1 \beta_n(2M-1)/(\beta_e^2 g^2) - \\
& 8KG_1^2 \beta_n m/(\beta_e^3 g^3) + 8G_1^2 \beta_n H_0/(\beta_e^2 g^2) - 24P_1 G_1 \beta_n m/(\beta_e^2 g^2) - \\
& 12d_1 G_1^2 \beta_n^2(2M-1)/(\beta_e^3 g^3)\} - [-I(I+1)+3(m^2+1)]\{-2K(2M-1)/(\beta_e g) - \\
& 12P_1 m/(\beta_e g) - 4G_1 \beta_n H_0/(\beta_e g) - 6d_1 G_1 \beta_n(2M-1)/(\beta_e^2 g^2) - \\
& 4KG_1 \beta_n m/(\beta_e^2 g^2) - 8KG_1^2 \beta_n^2(2M-1)/(\beta_e^3 g^3) - 48P_1 G_1^2 \beta_n m/(\beta_e^3 g^3)\} - \\
& \alpha_g(2M-1)\{8(3m^2+1)-4I(I+1)+1\}/\beta_e g M(M-1) + \\
& \alpha_7(2M-1)\{2(3m^2+1)-2I(I+1)\}/4\beta_e g M(M-1) - \\
& bb^* \{8(3M^2-3M+1)-4S(S+1)+1\}[K(2M-1)/(\beta_e^3 g^3 H_0^2) + 6P_1 m/(\beta_e^3 g^3 H_0^2)] -
\end{aligned}$$

$$\begin{aligned}
& 2G_1\beta_n/(\beta_e^3g^3H_o^2) - 3d_1G_1\beta_n(2M-1)/(\beta_e^4g^4H_o^2) - 2KG_1\beta_n m/(\beta_e^4g^4H_o^2) + \\
& \alpha_2^* [2(3M^2-3M+1)-2S(S+1)+1][K(2M-1)/(4\beta_e^3g^3H_o^2) + 3P_1m/(2\beta_e^3g^3H_o^2) \\
& - G_1\beta_n/(2\beta_e^3g^3H_o^2) - 3d_1G_1\beta_n(2M-1)/(4\beta_e^4g^4H_o^2) - KG_1\beta_n m/(2\beta_e^4g^4H_o^2)] - \\
& \alpha_2/(4\beta_e^2g^2)[\{I(I+1)-m^2-1\}(2K(2M-1)/(\beta_e gH_o^2) + 12P_1m/(\beta_e gH_o^2) - \\
& 4G_1\beta_n/(\beta_e gH_o) - 6d_1G_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 4KG_1\beta_n m/(\beta_e^2g^2H_o^2)) - \\
& 2(2M-1)m(2/H_o + 3d_1(2M-1)/(\beta_e gH_o^2) + 2Km/(\beta_e gH_o^2) - \\
& 4KG_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 24P_1G_1\beta_n m/(\beta_e^2g^2H_o^2))] + \\
& \alpha_3/(2\beta_e^2g^2)[\{2S(S+1)-(2M^2-2M+1)\}(2/H_o + 3d_1(2M-1)/(\beta_e gH_o^2) + \\
& 2Km/(\beta_e gH_o^2) - 4KG_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 24P_1G_1\beta_n m/(\beta_e^2g^2H_o^2)) - \\
& m(2M-1)\{2K(2M-1)/(\beta_e gH_o^2) + 12P_1m/(\beta_e gH_o^2) - 4G_1\beta_n/(\beta_e gH_o) - \\
& 6P_1G_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 4KG_1\beta_n m/(\beta_e^2g^2H_o^2)}] - \\
& \alpha_4/(\beta_e^2g^2)[2(2M-1)m(2/H_o + 3d_1(2M-1)/(\beta_e gH_o^2) + 2Km/(\beta_e gH_o^2) - \\
& 4KG_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 24P_1G_1\beta_n m/(\beta_e^2g^2H_o^2)) + \\
& (m^2+1)\{2K(2M-1)/(\beta_e gH_o^2) + 12P_1m/(\beta_e gH_o^2) - 4G_1\beta_n/(\beta_e gH_o) - \\
& 6d_1G_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 4KG_1\beta_n m/(\beta_e^2g^2H_o^2)}] - \\
& \alpha_8/(\beta_e^2g^2)[3(2M-1)m(2K(2M-1)/(\beta_e gH_o^2) + 12P_1m/(\beta_e gH_o^2) - \\
& 4G_1\beta_n/(\beta_e gH_o) - 6d_1G_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 4KG_1\beta_n m/(\beta_e^2g^2H_o^2)) + \\
& [3(2M-2M+1)-2S(S+1)](2/H_o + 3d_1(2M-1)/(\beta_e gH_o^2) + 2Km/(\beta_e gH_o^2)) -
\end{aligned}$$

$$\begin{aligned}
& 4KG_1\beta_n(2M-1)/(\beta_e^2g^2H_o^2) - 24P_1G_1\beta_n/(\beta_e^2g^2H_o^2)] - \\
& 3(aa^*)d_1G_1\beta_n(2M-1)\{12S(S+1)-10(2M^2-2M+1)-14\}/(4\beta_e^4g^4H_o^2) - \\
& K(aa^*)/(8\beta_e^3g^3)[\{[1-2S(S+1)](2M-1)-2(M^2-M+1)\}\{2/H_o^2 + \\
& 8G_1^2\beta_n^2/(\beta_e^2g^2H_o^2)\} - 8G_1\beta_n/(\beta_e gH_o^2)\{[1-2S(S+1)]m + 2m(3M^2-3M+1)\}] \\
& + 6d_1(bb^*)G\beta_n(2M-1)[12S(S+1)-20(2M^2-2M+1)-7]/(\beta_e^4g^4H_o^2) - \\
& K(bb^*)/(2\beta_e^3g^3)[\{4S(S+1)-1\}(2M-1) - 8(2M-1)(M^2-M+1)]\{2/H_o^2 + \\
& 8G_1^2\beta_n^2/(\beta_e^2g^2H_o^2)\} - 8G_1\beta_n/(\beta_e gH_o^2)[\{4S(S+1)-1\}m-8m(3M^2-3M+1)] - \\
& 3d_1(FF^*)/(32\beta_e^3g^3)[\{2-4S(S+1)\}(2M-1)-8mS(S+1)+ \\
& 4(M^2-M+1)(2M-1)+6m[(2M-1)^2+1]\}\{2/H_o^2 + 8G_1^2\beta_n^2/(\beta_e^2g^2H_o^2)\} - \\
& 8G_1\beta_n/(\beta_e gH_o^2)\{[2-4S(S+1)]m - 6(2M-1)[I(I+1)-m^2-1] + \\
& 4m(3M^2-3M+1)\}] - \\
& K(FF^*)/(16\beta_e^3g^3)[\{2S(S+1)[-8m-(2M-1)]+(2M-1)[-2I(I+1)+ \\
& (M^2-M+1)+2(3m^2+1)+2]+6[(2M-1)^2+1]\}\{2/H_o^2 + 8G_1^2\beta_n^2/(\beta_e^2g^2H_o^2)\} - \\
& 8G_1\beta_n\{2m[-S(S+1)+(3M^2-3M+1)+(m^2+4)] - \\
& 2I(I+1)[2(2M-1)+m]+6(2M-1)(m^2+1)\}/(\beta_e gH_o^2)] - \\
& 3d_1(B_1B_1)/(32\beta_e^3g^3)[\{2S(S+1)[2(2M-1)-4m]-4(2M-1)(M^2-M+1)+ \\
& 6m[(2M-1)^2+1]-2(2M-1)\}\{2/H_o^2 + 8G_1^2\beta_n^2/(\beta_e^2g^2H_o^2)\} - \\
& 8G_1\beta_n\{4mS(S+1)-6I(I+1)(2M-1)-4m(3M^2-3M+1)+6(2M-1)(m^2+1)-
\end{aligned}$$

$$2m)/(\beta_e g H_0^2)] +$$

$$K(B_1 B_1^*)/(16\beta_e^3 g^3)[(2S(S+1))((2M-1)-8m)+$$

$$(2M-1)[2I(I+1)-(M^2-M+1)-2(3m^2+1)-2]+6m[(2M-1)^2+1]](2/H_0^2+)$$

$$8G_1^2 \beta_n^2 / (\beta_e^2 g^2 H_0^2) \} -$$

$$8G_1 \beta_n \{2S(S+1)m+2I(I+1)[m-2(2M-1)]-$$

$$2m(3M^2-3M+1)+6(2M-1)(m^2+1)-2m(m^2+3)-2m)/(\beta_e g H_0^2)] +$$

$$G_1 \beta_n [ab^{*2} + a^* b^2](2M-1)[\{30-48S(S+1)\}+60(2M^2-2M+1)]/(2\beta_e^4 g^4 H_0^2)-$$

$$[aF^* B_1 + a^* F B_1^*]/(16\beta_e^3 g^3)[\{4mS(S+1)-3m[(2M-1)^2+1]\}(2/H_0^2 +$$

$$8G_1^2 \beta_n^2 / (\beta_e^2 g^2 H_0^2) \} - 24G_1 \beta_n (2M-1)\{I(I+1)-(m^2+1)\}/(\beta_e g H_0^2)]$$

where

$$a = \vec{T}_-^T \cdot \vec{D} \cdot \vec{T}_-$$

$$b = \vec{T}_-^T \cdot \vec{D} \cdot \vec{T}_3$$

$$F = \vec{T}_-^T \cdot \vec{A} \cdot \vec{T}_-$$

$$B_1 = \vec{T}_-^T \cdot \vec{A} \cdot \vec{T}_+$$

$$aa^* = \text{Tr}(\vec{D}^2) - 2d_2 + d_1^2 - 2d_{-1} \det(\vec{D});$$

$$bb^* = d_2 - d_1^2;$$

$$FF^* = \text{Tr}(\vec{A}^T \cdot \vec{A}) - k^2 - \frac{2}{K} \det(\vec{A});$$

$$B_1 B_1^* = \text{Tr}(\vec{A}^T \cdot \vec{A}) - k^2 + \frac{2}{K} \det(\vec{A});$$

$$\alpha_1 = (g_n^2 - G_1^2)/K;$$

$$\alpha_2 = \text{Tr}(\tilde{\Lambda}^T \tilde{\Lambda}) - k^2;$$

$$\alpha_3 = [\det(\tilde{\Lambda})]/K;$$

$$\alpha_4 = (k^2 - K^2);$$

$$\alpha_5 = [q - G_1 \dot{P}_1]/K;$$

$$\alpha_6 = [P_2 - P_1^2]/K;$$

$$\alpha_7 = [\text{Tr}(\tilde{P}^T \tilde{P}) - 2P_2 + P_1^2 - 2P_{-1} \det(\tilde{P})]/K;$$

$$\alpha_8 = K(e - d_1);$$

$$g^2 = \hat{\eta}^T \tilde{g}^T \tilde{g} \hat{\eta};$$

$$g^2 d_n = \hat{\eta}^T \tilde{g}^T \tilde{D}^n \tilde{g} \hat{\eta} \quad (n = \pm 1, \pm 2);$$

$$g_n^2 = \hat{\eta}^T \tilde{g}_n^T \tilde{g}_n \hat{\eta};$$

$$g^2 K^2 = \hat{\eta}^T \tilde{g}^T \tilde{A}^T \tilde{A} \tilde{g} \hat{\eta};$$

$$g^2 K^2 k^2 = \hat{\eta}^T \tilde{g}^T \tilde{A}^T \tilde{A} \tilde{A}^T \tilde{A} \tilde{g} \hat{\eta};$$

$$g K G_1 = \hat{\eta}^T \frac{1}{2} (\tilde{g}^T \tilde{A}^T \tilde{g}_n + \tilde{g}_n^T \tilde{A} \tilde{g}) \hat{\eta};$$

$$g^2 K^2 P_n = \hat{\eta}^T \tilde{g}^T \tilde{A}^T \tilde{P}^n \tilde{A} \tilde{g} \hat{\eta} \quad (n = \pm 1, \pm 2);$$

$$g K q = \hat{\eta}^T \frac{1}{2} (\tilde{g}^T \tilde{A}^T \tilde{P} \tilde{g}_n + \tilde{g}_n^T \tilde{P} \tilde{A} \tilde{g}) \hat{\eta};$$

$$\hat{\eta} = H/H;$$

$$g^2 K^2 e = \hat{\eta}^T \tilde{g}^T \frac{1}{2} (\tilde{D} \tilde{A}^T \tilde{A} + \tilde{A}^T \tilde{A} \tilde{D}) \tilde{g} \hat{\eta};$$

$$S_{\alpha\beta}^2 = [x - (M + \alpha)(M + \beta)];$$

$$I_{\alpha\beta}^2 = [y - (m + \alpha)(m + \beta)] \quad (\alpha, \beta = 0, \pm 1, \pm 2, \dots);$$

x = S(S+1); and

y = I(I+1)

APPENDIX B

The matrix elements of S_+ , S_- , and S_z between the perturbed electronic states $|M+n\rangle$ and $|M\rangle$, required for calculating the transition probability in section 3 of chapter 5, are - listed as follows.

$$\begin{aligned}
 \langle M+n|S_+|M\rangle = & S_{01} \left[a_{M+1} a'_{M+n} \delta_{M+1, M+n} + a_{M+1} a'_{M+n+1} \delta_{M+1, M+n+1} \right. \\
 & + a_{M+1} a'_{M+n-1} \delta_{M+1, M+n-1} + a_{M+1} a'_{M+n+2} \delta_{M+1, M+n+2} \\
 & + a_{M+1} a'_{M+n-2} \delta_{M+1, M+n-2} + a_{M+1} a'_{M+n+3} \delta_{M+1, M+n+3} \\
 & + a_{M+1} a'_{M+n-3} \delta_{M+1, M+n-3} + a_{M+1} a'_{M+n+4} \delta_{M+1, M+n+4} \\
 & \left. + a_{M+1} a'_{M+n-4} \delta_{M+1, M+n-4} \right] \\
 & + S_{12} \left[a_{M+1} a'_{M+n} \delta_{M+2, M+n} + a_{M+1} a'_{M+n+1} \delta_{M+2, M+n+1} \right. \\
 & + a_{M+1} a'_{M+n-1} \delta_{M+2, M+n-1} + a_{M+1} a'_{M+n+2} \delta_{M+2, M+n+2} \\
 & \left. + a_{M+1} a'_{M+n-2} \delta_{M+2, M+n-2} \right] \\
 & + S_{0\bar{1}} \left[a_{M-1} a'_{M+n} \delta_{M, M+n} + a_{M-1} a'_{M+n+1} \delta_{M, M+n+1} \right. \\
 & + a_{M-1} a'_{M+n-1} \delta_{M, M+n-1} + a_{M-1} a'_{M+n+2} \delta_{M, M+n+2} \\
 & \left. + a_{M-1} a'_{M+n-2} \delta_{M, M+n-2} \right] \\
 & + S_{23} \left[a_{M+2} a'_{M+n} \delta_{M+3, M+n} + a_{M+2} a'_{M+n+1} \delta_{M+3, M+n+1} \right. \\
 & \left. + a_{M+2} a'_{M+n-1} \delta_{M+3, M+n-1} + a_{M+2} a'_{M+n+2} \delta_{M+3, M+n+2} \right]
 \end{aligned}$$

$$\begin{aligned}
& + a_{M+2} a_{M+n-2} \delta_{M+3, M+n-2} \\
& + S_{12}^{-1} \left[a_{M-2} a_{M+n} \delta_{M-1, M+n} + a_{M-2} a_{M+n+1} \delta_{M-1, M+n+1} \right. \\
& + a_{M-2} a_{M+n-1} \delta_{M-1, M+n-1} + a_{M-2} a_{M+n+2} \delta_{M-1, M+n+2} \\
& \left. + a_{M-2} a_{M+n-2} \delta_{M-1, M+n-2} \right] \\
& + S_{34}^{-1} a_{M+3} a_{M+n} \delta_{M+4, M+n} + S_{23}^{-1} a_{M-3} a_{M+n} \delta_{M-2, M+n} \\
& + S_{45}^{-1} a_{M+4} a_{M+n} \delta_{M+5, M+n} + S_{34}^{-1} a_{M-4} a_{M+n} \delta_{M-3, M+n} \\
\langle M+n | S_- | M \rangle & = S_{01}^{-1} \left[a_M a_{M+n} \delta_{M-1, M+n} + a_M a_{M+n+1} \delta_{M-1, M+n+1} \right. \\
& + a_M a_{M+n-1} \delta_{M-1, M+n-1} + a_M a_{M+n+2} \delta_{M-1, M+n+2} \\
& + a_M a_{M+n-2} \delta_{M-1, M+n-2} + a_M a_{M+n+3} \delta_{M-1, M+n+3} \\
& + a_M a_{M+n-3} \delta_{M-1, M+n-3} + a_M a_{M+n+4} \delta_{M-1, M+n+4} \\
& \left. + a_M a_{M+n-4} \delta_{M-1, M+n-4} \right] \\
& + S_{01} \left[a_{M+1} a_{M+n} \delta_{M, M+n} + a_{M+1} a_{M+n+1} \delta_{M, M+n+1} \right. \\
& + a_{M+1} a_{M+n-1} \delta_{M, M+n-1} + a_{M+1} a_{M+n+2} \delta_{M, M+n+2} \\
& \left. + a_{M+1} a_{M+n-2} \delta_{M, M+n-2} \right] \\
& + S_{12}^{-1} \left[a_{M-1} a_{M+n} \delta_{M-2, M+n} + a_{M-1} a_{M+n+1} \delta_{M-2, M+n+1} \right. \\
& + a_{M-1} a_{M+n-1} \delta_{M-2, M+n-1} + a_{M-1} a_{M+n+2} \delta_{M-2, M+n+2} \\
& \left. + a_{M-1} a_{M+n-2} \delta_{M-2, M+n-2} \right]
\end{aligned}$$

$$\begin{aligned}
& + S_{12} \left[a_{M+2} a_{M+n} \delta_{M+1, M+n} + a_{M+2} a_{M+n+1} \delta_{M+1, M+n+1} \right. \\
& + a_{M+2} a_{M+n-1} \delta_{M+1, M+n-1} + a_{M+2} a_{M+n+2} \delta_{M+1, M+n+2} \\
& \left. + a_{M+2} a_{M+n-2} \delta_{M+1, M+n-2} \right] \\
& + S_{23} \left[a_{M-2} a_{M+n} \delta_{M-3, M+n} + a_{M-2} a_{M+n+1} \delta_{M-3, M+n+1} \right. \\
& + a_{M-2} a_{M+n-1} \delta_{M-3, M+n-1} + a_{M-2} a_{M+n+2} \delta_{M-3, M+n+2} \\
& \left. + a_{M-2} a_{M+n-2} \delta_{M-3, M+n-2} \right] \\
& + S_{23} a_{M+3} a_{M+n} \delta_{M+2, M+n} + S_{34} a_{M-3} a_{M+n} \delta_{M-4, M+n} \\
& + S_{34} a_{M+4} a_{M+n} \delta_{M+3, M+n} + S_{45} a_{M-4} a_{M+n} \delta_{M-5, M+n}
\end{aligned}$$

$$\begin{aligned}
\langle M+n | S_{z_1} | M \rangle = & M \left[a_M a_{M+n} \delta_{M, M+n} + a_M a_{M+n+1} \delta_{M, M+n+1} \right. \\
& + a_M a_{M+n-1} \delta_{M, M+n-1} + a_M a_{M+n+2} \delta_{M, M+n+2} \\
& + a_M a_{M+n-2} \delta_{M, M+n-2} + a_M a_{M+n+3} \delta_{M, M+n+3} \\
& + a_M a_{M+n-3} \delta_{M, M+n-3} + a_M a_{M+n+4} \delta_{M, M+n+4} \\
& \left. + a_M a_{M+n-4} \delta_{M, M+n-4} \right] \\
& + (M+1) \left[a_{M+1} a_{M+n} \delta_{M+1, M+n} + a_{M+1} a_{M+n+1} \delta_{M+1, M+n+1} \right. \\
& + a_{M+1} a_{M+n-1} \delta_{M+1, M+n-1} + a_{M+1} a_{M+n+2} \delta_{M+1, M+n+2} \\
& \left. + a_{M+1} a_{M+n-2} \delta_{M+1, M+n-2} \right] \\
& + (M-1) \left[a_{M-1} a_{M+n} \delta_{M-1, M+n} + a_{M-1} a_{M+n+1} \delta_{M-1, M+n+1} \right.
\end{aligned}$$

$$\begin{aligned}
& + a_{M-1}^* a_{M+n-1}^* \delta_{M-1, M+n-1} + a_{M-1}^* a_{M+n+2}^* \delta_{M-1, M+n+2} \\
& + a_{M-1}^* a_{M+n-2}^* \delta_{M-1, M+n-2} \\
& + (M+2) \left[a_{M+2}^* a_{M+n}^* \delta_{M+2, M+n} + a_{M+2}^* a_{M+n+1}^* \delta_{M+2, M+n+1} \right. \\
& + a_{M+2}^* a_{M+n-1}^* \delta_{M+2, M+n-1} + a_{M+2}^* a_{M+n+2}^* \delta_{M+2, M+n+2} \\
& \left. + a_{M+2}^* a_{M+n-2}^* \delta_{M+2, M+n-2} \right] \\
& + (M-2) \left[a_{M-2}^* a_{M+n}^* \delta_{M-2, M+n} + a_{M-2}^* a_{M+n+1}^* \delta_{M-2, M+n+1} \right. \\
& + a_{M-2}^* a_{M+n-1}^* \delta_{M-2, M+n-1} + a_{M-2}^* a_{M+n+2}^* \delta_{M-2, M+n+2} \\
& \left. + a_{M-2}^* a_{M+n-2}^* \delta_{M-2, M+n-2} \right] \\
& + (M+3) a_{M+3}^* a_{M+n}^* \delta_{M+3, M+n} + (M-3) a_{M-3}^* a_{M+n}^* \delta_{M-3, M+n} \\
& + (M+4) a_{M+4}^* a_{M+n}^* \delta_{M+4, M+n} + (M-4) a_{M-4}^* a_{M+n}^* \delta_{M-4, M+n}
\end{aligned}$$

where,

$$\begin{aligned}
a_{M+n}^* &= 1 - \{ b b^* [S_{n, n+1}^2 (2M+2n+1)^2 \\
& + S_{n, n-1}^2 (2M+2n-1)^2] / (8 \beta_e^2 g^2 H^2) \\
& + a a^* [S_{n, n+1}^2 S_{n+1, n+2}^2 \\
& + S_{n, n-1}^2 S_{n-1, n-2}^2] / (128 \beta_e^2 g^2 H^2) \} \\
a_{M+n+1}^* &= - b S_{n, n+1} (2M+2n+1) / (2 \beta_e g H) \\
& + a b^* S_{n, n+1} \{ (2M+2n+3) S_{n+1, n+2}^2 \\
& - 2(2M+2n-1) S_{n, n-1}^2 \} / (16 \beta_e^2 g^2 H^2) \\
& + 3 d_1 b S_{n, n+1} (2M+2n+1)^2 / (4 \beta_e^2 g^2 H^2)
\end{aligned}$$

$$a'_{M+n-1} = b^* S_{n,n-1} (2M+2n-1) / (2\beta_e g H)$$

$$+ a^* b S_{n,n-1} \{ (2M+2n-3) S_{n-1,n-2}^2$$

$$- 2(2M+2n+1) S_{n,n+1}^2 \} / (16\beta_e^2 g^2 H^2)$$

$$- 3d_1 b^* S_{n,n-1} (2M+2n-1)^2 / (2\beta_e^2 g^2 H^2)$$

$$a'_{M+n+2} = - a S_{n+1,n+2} S_{n,n+1} / (8\beta_e g H)$$

$$+ b^2 S_{n,n+1} S_{n+1,n+2} (2M+2n+1)(2M+2n+3) / (8\beta_e^2 g^2 H^2)$$

$$+ 3d_1 a S_{n,n+1} S_{n+1,n+2} (M+n+1) / (8\beta_e^2 g^2 H^2)$$

$$a'_{M+n-2} = a^* S_{n,n-1} S_{n-1,n-2} / (8\beta_e g H)$$

$$+ b^2 S_{n,n-1} S_{n-1,n-2} (2M+2n-1)(2M+2n-3) / (8\beta_e^2 g^2 H^2)$$

$$- 3d_1 a^* S_{n,n-1} S_{n-1,n-2} / (8\beta_e^2 g^2 H^2)$$

$$a'_{M+n+3} = ab S_{n,n+1} S_{n+1,n+2} S_{n+2,n+3} (6M+6n+7) / (48\beta_e^2 g^2 H^2)$$

$$a'_{M+n-3} = a^* b^* S_{n,n-1} S_{n-1,n-2} S_{n-2,n-3} (6M+6n-7) / (48\beta_e^2 g^2 H^2)$$

$$a'_{M+n+4} = a^2 S_{n,n+1} S_{n+1,n+2} S_{n+2,n+3} S_{n+3,n+4} / (128\beta_e^2 g^2 H^2)$$

$$a'_{M+n-4} = a^{*2} S_{n,n-1} S_{n-1,n-2} S_{n-2,n-3} S_{n-3,n-4} / (128\beta_e^2 g^2 H^2)$$

$$\left. \begin{aligned} S_{n+n_1, n+n_2}^2 &= [S(S+1) - (M+n+n_1)(M+n+n_2)] \\ I_{n+n_1, n+n_2}^2 &= [I(I+1) - (m+n+n_1)(m+n+n_2)] \end{aligned} \right] ; n, n_1, n_2 = 0, \pm 1, \pm 2, \dots, \text{etc}$$

Note that $n = 0$ corresponds to the unprimed admixing coefficients.

a'_{M+i} ($i = 0, 1, 2, 3, 4$), in the above expressions for the matrix elements of S_+ , S_- , and S_z . The quantity H appearing in the

denominators of the above expressions, can be approximated by using the expression, $1/H^2 = 1/H_0^2 + 3d_1(2M+n)/(2\beta_e g H_0^2) + \dots$. Finally, the transformation matrices \tilde{T} , \tilde{T}' and \tilde{T}'' , required in equations (5.7) and (5.9) of section 2, and (5.22) of section 3 in chapter 5 are given as follows:

$$\tilde{T} = \begin{bmatrix} -k_1 k_3 / g(k_1^2 + k_2^2)^{1/2} & -k_2 k_3 / g(k_1^2 + k_2^2)^{1/2} & 1/g(k_1^2 + k_2^2)^{1/2} \\ k_2 / (k_1^2 + k_2^2)^{1/2} & -k_1 / (k_1^2 + k_2^2)^{1/2} & 0 \\ k_1 / g & k_2 / g & k_3 / g \end{bmatrix}$$

In the matrix for \tilde{T} ,

$$k_n = \sum_m \eta_m g_{mn}; \quad (m, n) = (1, 2, 3),$$

where η_m are the direction cosines of the external magnetic field with respect to the (x, y, z) coordinate system. (A necessary condition for the transformation matrix \tilde{T} is that $k_1^2 + k_2^2 \neq 0$).

$$\tilde{T}' = \begin{bmatrix} \cos\phi_1 & \sin\phi_1 \cos\theta_1 & \sin\phi_1 \sin\theta_1 \\ -\sin\phi_1 & \cos\phi_1 \cos\theta_1 & \cos\phi_1 \sin\theta_1 \\ 0 & -\sin\theta_1 & \cos\theta_1 \end{bmatrix}$$

In the matrix for \tilde{T}' , (θ_1, ϕ_1) have been defined and expressed in chapter

V.

$$\tilde{T}'' = \begin{bmatrix} -\cos\theta \cos\phi & -\cos\theta \sin\phi & \sin\theta \\ \sin\phi & -\cos\phi & 0 \\ \sin\theta \cos\phi & \sin\theta \sin\phi & \cos\theta \end{bmatrix}$$

It should be noted, here, that the general orthonormal transformations \tilde{T} , \tilde{T}' and \tilde{T}'' should satisfy the conditions,

$$\left. \begin{aligned} \sum_{j=1}^3 u_{pj} u_{qj} &= \delta_{pq} \\ \sum_{j=1}^3 u_{jp} u_{jq} &= \delta_{pq} \end{aligned} \right\} ; \delta_{pq} = 1, \text{ for } p = q \text{ and} \\ &= 0, \text{ for } p \neq q$$