CHAPTER 2

SOLUTION OF THE SPIN HAMILTONIAN WITH ORTHORHOMBIC HF AND g TENSORS FOR S = \frac{1}{2}.

ABSTRACT

Using perturbation method a theory is developed to analyse the EPR spectra characterized by \( H = g \cdot \vec{g} \cdot \vec{S} + A \cdot \vec{A} \) for \( S = \frac{1}{2} \). It is found that the perturbation is zero for isotropic \( g \) and \( A \). For axially symmetric \( g \) and \( A \), the perturbation is zero when \( H \) is along z-axis and for \( H \) along any other direction perturbation terms should be added which may be very small. For the general orientation of \( \vec{H} \) an expression for the line position of the allowed transition is given.

2.1 INTRODUCTION

In the first chapter general Hamiltonian for a paramagnetic ion is described. Our purpose is now to take the appropriate spin Hamiltonian for \( S = \frac{1}{2} \) ions (\( Cu^{2+}, VO^{2+} \) etc) and solve it for the energies of the magnetic dipole transitions. The detailed methods of solution are numerous because of different approximations used for a unique spin Hamiltonian. In the present chapter we give second order perturbation theory.

The EPR spectra of Vanadium ions in a number of oxide glasses have been studied. It is noted that spectra
yielded experimental $g$-values and hyperfine structure for $^{51}$V ($I = \frac{7}{2}$, 100% abundant) that are very similar to those of the vanadyl ion, $\text{VO}^{2+}$, which is known to occur in a number of organic and inorganic complexes. In vanadyl ion complexes the unpaired electron is in the $b_2$ vanadium orbital ($3d_{xy}$). On the application of a magnetic field this spin doublet splits into two and paramagnetic resonance absorption is observed between these two levels or in this case $S = \frac{1}{2}$.

Nuclear spin, $I$, of copper is $3/2$ for both $^{63}\text{Cu}$ (69% abundant) and $^{65}\text{Cu}$ (31% abundant). As discussed in section 1.8 the ground state of $\text{Cu}^{2+}$ is doubly degenerate in the spin $S = \frac{1}{2}$. Electron paramagnetic resonance absorption spectra is observed because of this doubly degenerate ground state.

2.2 SOLUTION OF THE SPIN HAMILTONIAN

The paramagnetic resonance spectra of $\text{VO}^{2+}$ or $\text{Cu}^{2+}$ ($S = \frac{1}{2}$ for both) can be described by a spin-Hamiltonian of the form$^{1,2}$:

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{A} \cdot I \quad (2.1)$$

where the symbols have their usual meaning as discussed in chapter 1. Additional terms including the nuclear Zeeman interaction and quadrupole coupling have been found to be
quite small and are usually neglected\textsuperscript{3,4}. In Eq. (2.1) we assume that the second term (the hyperfine interaction) is small in relation to the first term.

Further we assume that $\frac{\mathbf{g}}{g}$ and $\frac{\mathbf{A}}{A}$ have a common principal co-ordinate system. It is represented as \(xyz\). Under this assumption the electron spin is quantized\textsuperscript{5-7} along $\mathbf{H}.\mathbf{g}$ and the nuclear spin along $\mathbf{S}.\mathbf{A}$ (\(\mathbf{S} = \mathbf{H}.\mathbf{g}.\mathbf{A}\)). Here we use the notation and co-ordinate systems given by Pake and Estle\textsuperscript{5} as shown in Fig. 2.1. Co-ordinate system for the electron spin is $\mathbf{s}$ and is determined by taking the $\mathbf{s}$ axis to be along $\mathbf{H}.\mathbf{g}$ and $\gamma$ to be in the \(xy\) plane.

Similarly, the nuclear spin is described by the co-ordinate system $\mathbf{s}'$ in which $\mathbf{s}'$ is parallel to $\mathbf{H}.\mathbf{g}.\mathbf{A}$ and $\gamma'$ is in the \(xy\) plane. From this we get the following unit vectors:

\[
\mathbf{s} = \frac{\mathbf{H}.\mathbf{g}}{gH}, \quad \mathbf{s}' = \frac{\mathbf{H}.\mathbf{g}.\mathbf{A}}{gHK}
\]

\[
\mathbf{\eta} = \frac{\mathbf{s} \times \mathbf{z}}{|\mathbf{s} \times \mathbf{z}|}, \quad \mathbf{\eta}' = \frac{\mathbf{s}' \times \mathbf{z}}{|\mathbf{s}' \times \mathbf{z}|}, \quad (2.2)
\]

\[
\mathbf{\zeta} = \mathbf{\eta} \times \mathbf{s}, \quad \mathbf{\zeta}' = \mathbf{\eta}' \times \mathbf{s}'
\]

where $|\mathbf{H}.\mathbf{g}| = gH$ and $|\mathbf{H}.\mathbf{g}.\mathbf{A}| = gHK$

\[
\mathcal{H} = \beta \sum_{i} S_{i} \mathbf{s}_{i} gH + (\mathbf{s} S_{z} + \mathbf{\eta} S_{z} + \mathbf{s} S_{z}). \mathbf{A}. (\mathbf{\zeta} + \mathbf{\eta}' + \mathbf{s} I_{z} + \mathbf{s}' I_{z})
\]

\[
= g\beta H S_{z} + S_{z} \mathbf{s}. \mathbf{A}. (\mathbf{\zeta} + \mathbf{\eta}' + \mathbf{s} I_{z} + \mathbf{s}' I_{z})
\]
Figure 2.1. Co-ordinate systems used in the second order solutions of the eigenvalue problem arising from the Hamiltonian of Eq. (2.1). The Cartesian co-ordinate system $xyz$ is determined by the principal axes or symmetry axes of the paramagnet. The Cartesian co-ordinate system $x'y'z'$ is determined by taking the $z'$ axis to be along $H_g$ and $y'$ to be in the $xy$ plane. The co-ordinate system $\xi\eta\zeta$ is determined by choosing $\xi'$ to be parallel to $H_g A^*$ and requiring that $\eta'$ be in the $xy$ plane.
Using from relation (2.2)
\[ \hat{A} \cdot \hat{A} = K \hat{\xi} \]

\[ \mathcal{H}' = \beta \mathbf{H} \mathbf{S} + K \mathbf{S} \hat{\xi} + \hat{\eta} \mathbf{S} \hat{\eta} + \hat{\xi} \mathbf{S} \hat{\xi} \]

Because \( \xi', \eta', \xi' \) are perpendicular to each other:

\[ \mathcal{H}' = \beta \mathbf{H} \mathbf{S} + K \mathbf{S} \hat{\xi}' + \hat{\eta} \hat{\xi}' \mathbf{S} \hat{\eta}' + \hat{\xi}' \mathbf{S} \hat{\xi}' + \hat{\eta} \hat{\xi}' \mathbf{S} \hat{\eta}' + \hat{\xi}' \mathbf{S} \hat{\xi}' \]

It is more convenient to work with the raising and lowering operators:

\[ S_+ = S_\xi + i S_\eta \]
\[ S_- = S_\xi - i S_\eta \]
\[ I_+ = I_\xi + i I_\eta \]
\[ I_- = I_\xi - i I_\eta \]

(2.4)

It should be noted here that \( S_\pm \) and \( I_\pm \) are referred to different co-ordinate systems, neither of these two co-ordinate systems is a principal axis system in general.

Thus we have

\[ \mathcal{H}' = \beta \mathbf{H} \mathbf{S} + K \mathbf{S} \hat{\xi}' + \hat{\eta} S_+ \mathbf{I}_\xi + \hat{\xi}' S_- \mathbf{I}_\xi + K_1 S_+ I_\xi + K_2 S_+ I_+ + K_3 S_\xi + I_\xi \]

(2.5)

where
where
\[
K_1 = \frac{1}{2} \left( \hat{x} \cdot \hat{A} \cdot \hat{2} - i \hat{A} \cdot \hat{\mathbf{2}} \right)
\]
\[
K_2 = \frac{1}{4} \left( \hat{x} \cdot \hat{A} \cdot \hat{2} - \hat{A} \cdot \hat{\mathbf{2}} - i \hat{A} \cdot \hat{\mathbf{2}} - i \hat{A} \cdot \hat{\mathbf{2}} \right)
\]
and
\[
K_3 = \frac{1}{4} \left( \hat{x} \cdot \hat{A} \cdot \hat{2} + \hat{A} \cdot \hat{\mathbf{2}} + i \hat{A} \cdot \hat{\mathbf{2}} + i \hat{A} \cdot \hat{\mathbf{2}} \right)
\]

Before analyzing the general case, we will write all vector and tensor components in terms of the principal axis coordinate system, \(x, y, z\) we have
\[
\mathbf{H} = H (1, m, n)
\]
and
\[
\mathbf{g} = \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix}
\]
where \(l, m,\) and \(n\) are the direction cosines of the magnetic field with respect to principal axis coordinate system. From these we can calculate the required unit vectors:
\[
\hat{\mathbf{2}} = \frac{\mathbf{H} \cdot \mathbf{g}}{g \mathbf{H}} = \frac{1}{g \mathbf{H}} \mathbf{H} (1, m, n) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix}
\]
\[
= \frac{1}{g} (lg_x \cdot mg_y \cdot ng_z)
\]
\[
| \hat{\mathbf{2}} | = \frac{1}{g} (l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2)^{1/2}
\]
\[
= 1
\]
or
\[
g = (l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2)^{1/2}
\]
and
\[ \gamma' = \frac{H \mathbf{g} \mathbf{A}}{gK} \]
\[ = \frac{H}{gHK} (1, m, n) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \]
\[ = \frac{1}{gK} (1, m, n) \begin{pmatrix} g_x A_x & 0 & 0 \\ 0 & g_y A_y & 0 \\ 0 & 0 & g_z A_z \end{pmatrix} \]
\[ = \frac{1}{gK} (1, m, n, m g_x A_x, m g_y A_y, m g_z A_z) \]

\[ |\mathbf{\hat{S}}'| = \frac{1}{gK^2} \left( l^2 g_x^2 A_x^2 + m^2 g_y^2 A_y^2 + n^2 g_z^2 A_z^2 \right) \]
\[ = 1 \]

or \( |\mathbf{\hat{S}}'| = \left( l^2 g_x^2 A_x^2 + m^2 g_y^2 A_y^2 + n^2 g_z^2 A_z^2 \right)^{-1/2} \]

\[ \mathbf{\hat{n}} = \frac{\mathbf{\hat{S}} \times \mathbf{z}}{|\mathbf{\hat{S}} \times \mathbf{z}|} = \frac{1}{g} \frac{\begin{pmatrix} l g_x, m g_y, n g_z \end{pmatrix} \times (0, 0, z)}{|\begin{pmatrix} l g_x, m g_y, n g_z \end{pmatrix} \times (0, 0, z)} \]
\[ = \frac{(m z g_y, -l z g_x, 0)}{|m z g_y, -l z g_x, 0|} \]
\[ = \frac{(m g_y, -l g_x, 0)}{(l^2 g_x^2 + m^2 g_y^2)^{1/2}} \]

Similarly
\[ \mathbf{\hat{n}}' = \frac{\mathbf{\hat{S}}' \times \mathbf{z}}{|\mathbf{\hat{S}}' \times \mathbf{z}|} = \frac{1}{gK} \frac{\begin{pmatrix} l g_x A_x, m g_y A_y, n g_z A_z \end{pmatrix}}{|\begin{pmatrix} l g_x A_x, m g_y A_y, n g_z A_z \end{pmatrix}|} \]
\[
\hat{\mathbf{S}} \times \hat{\mathbf{\eta}} = \frac{-1}{\varepsilon_K} \cdot \frac{(l g_x A_x, m g_y A_y, m g_z A_z) \times (m g_y, -l g_x, 0)}{(m^2 g_y^2 + l^2 g_x^2)^{1/2}}
\]

\[
\hat{\mathbf{S}}' \times \hat{\mathbf{\eta}}' = \frac{-1}{\varepsilon_K} \cdot \frac{(l g_x A_x, m g_y A_y, m g_z A_z) \times (m g_y, -l g_x, 0)}{(m^2 g_y^2 + l^2 g_x^2)^{1/2}}
\]

\[
\frac{1}{\varepsilon_K} \cdot \frac{(l g_x A_x, m g_y A_y, m g_z A_z) \times (m g_y, -l g_x, 0)}{(m^2 g_y^2 + l^2 g_x^2)^{1/2}}
\]

\[
\frac{1}{\varepsilon_K} \cdot \frac{(l g_x A_x, m g_y A_y, m g_z A_z) \times (m g_y, -l g_x, 0)}{(m^2 g_y^2 + l^2 g_x^2)^{1/2}}
\]

\[
\frac{1}{\varepsilon_K} \cdot \frac{(l g_x A_x, m g_y A_y, m g_z A_z) \times (m g_y, -l g_x, 0)}{(m^2 g_y^2 + l^2 g_x^2)^{1/2}}
\]
\[ = \frac{1}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left(-nlig_{g_z} + mg_y A^2 + l_{g_x}^2 g_{g_z} + m_{g_y}^2 g_{g_z}\right) \]

\[ = \frac{1}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left(-nl_{g_x}^2 g_{g_z} A_x^2 - m_{g_y}^2 g_{g_z} A^2 + l_{g_x}^2 n_{g_z} A_z^2 - m_{g_y}^2 n_{g_z} A_z^2\right) \]

\[ = \frac{ng_z}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left[l_{g_x}^2 g_{g_z} (A_x^2 - A^2) + m_{g_y}^2 g_{g_z} (A_z^2 - A_y^2)\right] \quad (2.13) \]

\[ \hat{\eta} \cdot \hat{A} \cdot \hat{\zeta} = \frac{(mg_y, -lg_{g_x}, 0)}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left(A_x 0 0\right) \left(l_{g_x} A_x\right) \]

\[ = \frac{1}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left(l_{g_x} A_x^2\right) \left(mg_y A_y^2\right) \]

\[ = \frac{1}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \left(ml_{g_x} g_y A_x^2 - l_{g_x} g_y A_y^2\right) \]

\[ = \frac{l_{g_x} g_y \left(A_x^2 - A_y^2\right)}{gK\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}} \quad (2.14) \]
\[
\hat{A}_x \hat{A}_y \hat{A}_z = \frac{1}{g \sqrt{\left(l^2 g_x^2 + m^2 g_y^2\right)^{1/2}}} (-n l g_x g_z, -m n g_y g_z, \left[l^2 g_x^2 + m^2 g_y^2\right])
\]

\[
\begin{pmatrix}
A_x & 0 & 0 \\
0 & A_y & 0 \\
0 & 0 & A_z
\end{pmatrix} \frac{1}{g K \sqrt{\left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)^{1/2}}} \begin{pmatrix}
-n l g_x g_z A_x A_z \\
-m n g_y g_z A_x A_z \\
l^2 g_x A_x^2 + m^2 g_y A_y^2 A_z
\end{pmatrix}
\]

\[
= \frac{1}{g^2 K \left(l^2 g_x^2 + m^2 g_y^2 \right) \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)^{1/2}} \begin{pmatrix}
-n l g_x g_z A_x A_z \\
-m n g_y g_z A_x A_z \\
l^2 g_x A_x^2 + m^2 g_y A_y^2 A_z
\end{pmatrix}
\]

\[
= \frac{A_z \left[(n^2 l^2 g_x g_z^2 A_x^2 + m^2 n^2 g_y g_z A_y^2) + (l^2 g_x^2 + m^2 g_y^2) \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)\right]}{g^2 K \left[l^2 g_x^2 + m^2 g_y^2 \right) \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)^{1/2}}
\]

\[
= \frac{A_z \left[l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2 \right) \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)}{g^2 K \left(l^2 g_x^2 + m^2 g_y^2 \right) \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)^{1/2}} \left[l^2 g_x A_x^2 + m^2 g_y A_y^2\right]^{1/2}
\]

\[
= \frac{A_z \left[l^2 g_x^2 + m^2 g_y^2\right]}{K \left[l^2 g_x^2 + m^2 g_y^2\right]^{1/2}} \left(l^2 g_x A_x^2 + m^2 g_y A_y^2\right)^{1/2} \cdot (2.16)
\]
\[ \mathbf{\hat{\eta} . A . \hat{\eta}'} = \frac{1}{(l_{g_x}^2 + m_{g_y}^2)^{1/2}} \begin{pmatrix} m_{g_y} & -l_{g_x} & 0 \end{pmatrix} \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix} \]

\[ \begin{pmatrix} m_{g_y}A_xA_y \\ -l_{g_x}A_xA_y \\ 0 \end{pmatrix} \]

\[ \begin{pmatrix} m_{g_y}^2A_x^2 + l_{g_x}^2A_y^2 \\ \left[\left(l_{g_x}^2 + m_{g_y}^2\right) \left(l_{g_x}^2A_x^2 + m_{g_y}^2A_y^2\right)\right]^{1/2} \\ \frac{A_xA_y\left(l_{g_x}^2 + m_{g_y}^2\right)^{1/2}}{(l_{g_x}^2A_x^2 + m_{g_y}^2A_y^2)} \end{pmatrix} \]

\[ \mathbf{\hat{\eta} . A . \hat{\eta}'} = \frac{1}{(l_{g_x}^2 + m_{g_y}^2)^{1/2}} \begin{pmatrix} m_{g_y} & -l_{g_x} & 0 \end{pmatrix} \begin{pmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{pmatrix} \]
\[
X = \frac{1}{gK\left(1^2g_x^2A_x^2 + m^2g_y^2A_y^2\right)^{1/2}} \begin{pmatrix}
-nl\gamma_x g_z A_x A_z \\
-m\gamma_y g_z A_y A_z \\
l^2g_x^2A_x^2 + m^2g_y^2A_y^2
\end{pmatrix}
\]

\[
= \frac{1}{gK\left[1^2g_x^2 + m^2g_y^2\right]\left(1^2g_x^2A_x^2 + m^2g_y^2A_y^2\right)^{1/2}}
\begin{pmatrix}
-nl\gamma_x g_z A_x A_z \\
-m\gamma_y g_z A_y A_z \\
l^2g_x^2A_x^2 + m^2g_y^2A_y^2
\end{pmatrix}
\]

\[
= -\frac{mnl\gamma_x g_y g_z A_x^2 A_z + mnl\gamma_x g_y g_z A_y^2 A_z}{gK\left[1^2g_x^2 + m^2g_y^2\right]\left(1^2g_x^2A_x^2 + m^2g_y^2A_y^2\right)^{1/2}}
\]

\[
= \frac{1mng_y g_z A_y (A_y^2 - A_x^2)}{gK\left[1^2g_x^2 + m^2g_y^2\right]\left(1^2g_x^2A_x^2 + m^2g_y^2A_y^2\right)^{1/2}}
\]

\[
\hat{\gamma}' = \frac{1}{g\left(1^2g_x^2 + m^2g_y^2\right)^{1/2}} \begin{pmatrix}
-nl\gamma_x g_z & -m\gamma_y g_z, & l^2g_x^2 + m^2g_y^2
\end{pmatrix}
\]

\[
\begin{pmatrix}
A_x & 0 & 0 \\
0 & A_y & 0 \\
0 & 0 & A_z
\end{pmatrix}
\]

\[
\begin{pmatrix}
A_x & 0 & 0 \\
0 & A_y & 0 \\
0 & 0 & A_z
\end{pmatrix} = \frac{1}{g\left(1^2g_x^2A_x^2 + m^2g_y^2A_y^2\right)^{1/2}} \begin{pmatrix}
-m\gamma_y A_y \\
-l\gamma_x A_x
\end{pmatrix}
\]
\[
\frac{1}{g \left[ (l^2g_x^2 + m^2g_y^2) \left( l^2g_x^2 + m^2g_y^2 \right) \right]^{1/2}}
\]

\[
(-n_l g_z, -mg_y g_z, \ l^2g_x^2 + m^2g_y^2) \quad \left( + mg_y A_x A_y \right) \\
\quad \left( - l g_x A_x A_y \right) \\
\quad 0
\]

\[
= -\frac{mn_l g_y g_z A_x A_y - mn_l g_y g_z A_x A_y}{g \left[ (l^2g_x^2 + m^2g_y^2) \left( l^2g_x^2 + m^2g_y^2 \right) \right]^{1/2}} = 0 \quad (2.18)
\]

Using Eqs. (2.13) to (2.18) in to Eqs. (2.6), we find

\[
K_1K_1^* = \frac{1}{4} \left[ \left( \frac{\hat{\eta} \cdot A \cdot \hat{\eta}^*}{2} \right)^2 + \left( \frac{\hat{\eta} \cdot A \cdot \hat{\eta}^*}{2} \right)^2 \right]
\]

\[
= \frac{1}{4} \left[ \frac{n^2 g_z^2}{g^4 K^2 (l^2g_x^2 + m^2g_y^2)} \left\{ l^2g_x^2(A_z^2 - A_x^2) + m^2g_y^2(A_z^2 - A_y^2) \right\}^2 \\
+ \frac{l^2m^2g_x^2g_y^2(A_x^2 - A_y^2)^2}{g^2 K^2 (l^2g_x^2 + m^2g_y^2)} \right]
\]

\[
= \frac{1}{4g^2 K^2 (l^2g_x^2 + m^2g_y^2)} \left[ \frac{n^2 g_z^2}{g^2} \left\{ A_z^2(l^2g_x^2 + m^2g_y^2) - \\
\left( l^2g_x^2 + m^2g_y^2 \right)^2 \right\} + l^2m^2g_x^2g_y^2 \left( A_x^4 + A_y^4 - 2A_x^2A_y^2 \right) \right]
\]
\[
\begin{align*}
&= \frac{1}{4g^2 K^2 (l^2 g_x^2 + m^2 g_y^2)} \left[ \frac{n^2 g_z^2}{g^2} \left\{ A_z^2 (g^2 - n^2 g_z^2) - (g^2 K^2 - n^2 g_z A_z^2) \right\} \right]^2 \\
&\quad + l^2 m^2 g_x g_y A_x^4 + l^2 m^2 g_x g_y A_y^4 - l^2 g_x^2 A_x^2 (g^2 K^2 - l^2 g_x A_x - n^2 g_z A_z^2) \\
&\quad - n^2 g_y A_y (g^2 K^2 - m^2 g_y A_y - n^2 g_z A_z^2) \\
&= \frac{1}{4g^2 K^2 (l^2 g_x^2 + m^2 g_y^2)} \left[ \frac{n^2 g_z^2}{g^2} \left\{ (A_z^2 - K^2) g^2 \right\} \right]^2 \\
&\quad + l^2 g_x^2 (l^2 g_x^2 + m^2 g_y^2) + m^2 g_x A_y^4 (l^2 g_x + m^2 g_y^2) \\
&\quad - (g^2 K^2 - n^2 g_z A_z^2) (l^2 g_x A_x^2 + m^2 g_y A_y^2) \\
&= \frac{1}{4g^2 K^2 (l^2 g_x^2 + m^2 g_y^2)} \left[ n^2 g_z^2 A_z^2 g^2 + n^2 g_z^2 g^2 K^2 - 2n^2 g_z^2 A_z^2 g K^2 \\
&\quad + (l^2 g_x A_x^4 + m^2 g_y A_y^4) (l^2 g_x^2 + m^2 g_y^2) - g^4 K^2 - n^4 g_z A_z^4 + 2n^2 g_z A_z^2 g^2 K^2 \\
&\quad = \frac{1}{4g^2 K^2} (l^2 g_x A_x^4 + m^2 g_y A_y^4 + n^2 g_z A_z^4 - 2A_z K^2) + (2.19)
\end{align*}
\]
\[ K_2^* K_2 = \frac{1}{16} \left[ \left( \frac{\hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} - \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 + \left( \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} + \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 \right] \]  

(2.20)

\[ K_3^* K_3 = \frac{1}{16} \left[ \left( \frac{\hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} + \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 + \left( \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} - \frac{1}{3} \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 \right] \]  

(2.21)

\[ K_2^* K_2 - K_3^* K_3 = \frac{1}{4} \left[ \left( \frac{\hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} - \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right) \left( \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right) + \left( \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right) \left( \frac{\hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} - \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right) \right] \]  

(2.22)

\[ \begin{align*}
&= \frac{1}{4} \left[ - \frac{A_z (1^{2}g^{2}2^{2} + m^{2}2^{2})^{1/2}}{k(1^{2}g^{2}2^{2} + m^{2}2^{2})^{1/2}} \cdot \frac{A_x A_y (1^{2}g^{2}2^{2} + m^{2}2^{2})^{1/2}}{(1^{2}g^{2}2^{2} + m^{2}2^{2})^{1/2}} \\
&+ \frac{1 m n g_x g_y g_z A_z (A^2_y - A^2_x)}{g_k \left[ (1^{2}g^{2}2^{2} + m^{2}2^{2}) (1^{2}g^{2}x^2 + m^{2}g^2y^2)^{1/2} \right] x 0} \right] \\
&= - \frac{A_x A_y A_z}{4K} \\
&= (2.23)
\end{align*} \]

From Eqs. (2.20) and (2.21) we have

\[ \begin{align*}
K_2^* K_2 + K_3^* K_3 &= \frac{1}{8} \left[ \left( \frac{\hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} - \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 + \left( \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} + \mathbf{A} \cdot \hat{\mathbf{r}} \cdot \mathbf{A} \cdot \hat{\mathbf{r}} \right)^2 \right] \\
&= \frac{1}{8} \left[ \frac{A_z^2 (1^{2}g^{2}x^2 + m^{2}g^2y^2)^2}{k^2 (1^{2}g^{2}x^2 + m^{2}g^2y^2)} + \frac{A_x A_y^2 (1^{2}g^{2}x^2 + m^{2}g^2y^2)^2}{(1^{2}g^{2}x^2 + m^{2}g^2y^2)} \\
&+ \frac{1 m^2g^2x^2g_y^2g_z^2(A^2_y - A^2_x)}{g^2 K^2 (1^{2}g^{2}x^2 + m^{2}g^2y^2)^2 (1^{2}g^2x^2 + m^{2}g^2y^2)^2} \right] \\
&= \frac{8g^2 K^2 (1^{2}g^{2}x^2 + m^{2}g^2y^2)(1^{2}g^2x^2 + m^{2}g^2y^2)}{1^{2}g^{2}x^2 + m^{2}g^2y^2} \\
&= (2.24)
\end{align*} \]
where

\[ S = g^2 A_x^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2) + g^2 A_y^2 A_y^2 (l^2 g_x^2 + m^2 g_y^2)^2 \]

\[ + l^2 m^2 n^2 g_x g_y g_z A_x^2 A_y^2 (A_y^4 + A_x^4 - 2A_x^2 A_y^2) \]

\[ = g^2 A_x^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2)^2 + A_y^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y + n^2 g_z A_z^2) \]

\[ + l^2 m^2 n^2 g_x g_y g_z A_x^2 A_y^2 (A_y^4 + A_x^4 - 2A_x^2 A_y^2) \]

\[ = g^2 A_x^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2)^2 + A_y^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y + n^2 g_z A_z^2) \]

\[ + l^2 m^2 n^2 g_x g_y g_z A_x^2 A_y^2 (A_y^4 + A_x^4 - 2A_x^2 A_y^2) \]

\[ = \left[ g^2 A_x^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2) + A_y^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2)^2 \right] \]

\[ + A_x A_y (l^2 g_x^2 + m^2 g_y^2)^2 + n^2 A_y^2 A_x^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y + n^2 g_z A_z^2) \]

\[ = (l^2 g_x A_x^2 + m^2 g_y A_y^2) \left[ g^2 A_x^2 (l^2 g_x A_x^2 + m^2 g_y A_y^2) + A_y^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y)^2 \right] \]

\[ + A_y A_y (l^2 g_x^2 + m^2 g_y^2)^2 + n^2 A_y^2 A_x^2 A_y^2 (l^2 g_x A_x^2 + m^2 g_y A_y + n^2 g_z A_z^2) \]

\[ = (l^2 g_x A_x^2 + m^2 g_y A_y^2) \left[ A_x A_y (l^2 g_x^2 + m^2 g_y^2)^2 + A_x A_y (l^2 g_x A_x^2 + m^2 g_y A_y)^2 \right] \]

\[ + A_y A_y (l^2 g_x^2 + m^2 g_y^2)^2 + A_y A_y (l^2 g_x A_x^2 + m^2 g_y A_y)^2 + A_y A_y (l^2 g_x A_x^2 + m^2 g_y A_y)(m^2 g_y g_z + n^2 g_x g_z) \]
When the isotropic part of the hf interaction is large, the anisotropy in $A$ is small, we can write

$$A_x \simeq A_y \simeq A_z = a$$

and $K_1 K_1^*$ from Eq. (2.19) can be written as:

$$K_1 K_1^* = \frac{a^2}{4g^2 K_2^2} (l^2 g_x^2 A_x^2 + m^2 g_y^2 A_y^2 + n^2 g_z^2 A_z^2 - g^2 K^2)$$

or $K_1 K_1^* = 0$ (2.25)

This postulation is not serious for the centres with $a \geq 1000 G$ (g=2).

Using (2.7), (2.8) and (2.19) one finds that

$$(K_1 K_1^*)_x = (K_1 K_1^*)_y = (K_1 K_1^*)_z = 0$$ (2.26)
where the subscript defines the orientation of $\mathbf{H}$ along the axis of the principal coordinate system of $g^*$ and $\mathbf{A}$. Similarly, using Eqs. (2.7), (2.8), (2.23) and (2.24) we get

$$(K_zK_2^*)_x = \frac{1}{16}(A_z-A_y)^2, \quad (K_zK_3^*)_x = \frac{1}{16}(A_z+A_y)^2 \quad \text{when } A_x > 0,$$

or

$$(K_zK_2^*)_y = \frac{1}{16}(A_z+A_x)^2, \quad (K_zK_3^*)_y = \frac{1}{16}(A_z-A_x)^2 \quad \text{when } A_y < 0,$$

and

$$(K_zK_2^*)_z = \frac{1}{16}(A_y-A_x)^2, \quad (K_zK_3^*)_z = \frac{1}{16}(A_y+A_x)^2 \quad \text{when } A_z > 0,$$

or

$$(K_zK_2^*)_z = \frac{1}{16}(A_y+A_x)^2, \quad (K_zK_3^*)_z = \frac{1}{16}(A_y-A_x)^2 \quad \text{when } A_z < 0,$$

If $\mathbf{g}$ and $\mathbf{A}$ are axially symmetric, we write

$$A_x = A_y = A_{\perp}$$
$$A_z = A_{\parallel}$$
$$g_x = g_y = g_{\perp}$$
$$g_z = g_{\parallel},$$

(2.27)
then from Eqs. (2.23) and (2.24),

\[ K_2 K_2^* = \frac{A_{\perp}^2 (A_{\parallel}^2 + K^2)}{16K^2} - \frac{A_{\perp}^2 A_{\parallel}}{8K} \]

and

\[ K_3 K_3^* = \frac{A_{\perp}^2 (A_{\parallel}^2 + K^2)}{16K^2} + \frac{A_{\perp}^2 A_{\parallel}}{8K} \]

\[ = \frac{A_{\perp}^2 (A_{\parallel}^2 + K^2)}{16K^2} \quad (2.29) \]

and

\[ = \frac{A_{\perp}^2 (A_{\parallel}^2 + K^2)}{16K^2} \quad (2.30) \]

We use the perturbation theory to solve the equation for Hamiltonian (2.5). The basis spin functions, \( \phi_i = |S_z, I_z\rangle \), for Cu^{2+} (Spin \( S = \frac{1}{2} \) and nuclear spin \( I = \frac{3}{2} \)) are

\[ \phi_1 = |\frac{1}{2}, -\frac{3}{2}\rangle \quad \phi_5 = |\frac{1}{2}, -\frac{1}{2}\rangle \]

\[ \phi_2 = |\frac{1}{2}, \frac{3}{2}\rangle \quad \phi_6 = |\frac{1}{2}, -\frac{3}{2}\rangle \quad (2.31) \]

\[ \phi_3 = |\frac{1}{2}, \frac{3}{2}\rangle \quad \phi_7 = |\frac{1}{2}, -\frac{1}{2}\rangle \]

\[ \phi_4 = |\frac{1}{2}, -\frac{1}{2}\rangle \quad \phi_8 = |\frac{1}{2}, \frac{1}{2}\rangle \]

Where the subscripts differentiate electronic and nuclear spin function. The matrix for \( \mathcal{H} \) given in Eq. (2.5) is:
\[
\begin{pmatrix}
\frac{\Delta}{2} - \frac{3}{4}K & 0 & 0 & 0 & 0 & 0 & -\frac{3}{2}K_1 & \sqrt[3]{3K_3} & 0 \\
0 & \frac{\Delta}{2} - \frac{3}{4}K & \frac{3}{2}K_1 & 0 & 0 & 0 & 0 & \sqrt[3]{3K_3}^* \\
0 & \frac{3}{2}K_1 & \frac{\Delta + 3}{2}K & \sqrt[3]{3K_2} & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt[3]{3K_2} & -\frac{\Delta}{2} - \frac{1}{4}K & 2K_3^* & 0 & 0 & \frac{1}{2}K_1^* \\
0 & 0 & 0 & 2K_3 & \frac{\Delta}{2} - \frac{K}{4} & \sqrt[3]{3K_2} & -\frac{1}{2}K_1 & 0 \\
-\frac{3}{2}K_1^* & 0 & 0 & 0 & \sqrt[3]{3K_2}^* & -\frac{\Delta + 3}{2}K & 0 & 0 \\
\sqrt[3]{3K_3}^* & 0 & 0 & 0 & -\frac{1}{2}K_1^* & 0 & -\frac{\Delta}{2} + \frac{K}{4} & 2K_2^* \\
0 & \sqrt[3]{3K_3} & 0 & \frac{1}{2}K_1 & 0 & 0 & 2K_2 & \frac{\Delta}{2} + \frac{K}{4}
\end{pmatrix}
\]

where
\[
\Delta = g\beta H
\]

Along any axis \(K_1 = 0\) and taking \(K_3\) to be negligibly small the zeroth order solutions for eigenvalues and eigenfunctions are:

\[
E_1^0 = \frac{\Delta}{2} - \frac{3}{4}K \\
\psi_1^0 = \phi_1
\]

\[
E_2^0 = -\frac{\Delta}{2} - \frac{3}{4}K \\
\psi_2^0 = \phi_2
\]

\[
E_3^0 = \frac{K}{4} + \frac{1}{2}\left[(\Delta + K)^2 + 12K_2K_2^*\right]^{1/2} \\
\psi_3^0 = c_3\phi_3 + c_4\phi_4
\]

\[
E_4^0 = \frac{K}{4} - \frac{1}{2}\left[(\Delta + K)^2 + 12K_2K_2^*\right]^{1/2} \\
\psi_4^0 = d_3\phi_3 + d_4\phi_4
\]
\[ E_5^0 = \frac{K}{4} + \frac{1}{2} \left[ (\Delta - K)^2 + 12K_2K_2^* \right]^{1/2} \]
\[ \psi_5^0 = C_5 \phi_5 + C_6 \phi_6 \]
\[ E_6^0 = \frac{K}{4} - \frac{1}{2} \left[ (\Delta - K)^2 + 12K_2K_2^* \right]^{1/2} \]
\[ \psi_6^0 = d_5 \phi_5 + d_6 \phi_6 \cdot \]
\[ E_7^0 = \frac{K}{4} + \frac{1}{2} \left[ (\Delta^2 + 16K_2K_2^*) \right]^{1/2} \]
\[ \psi_7^0 = C_7 \phi_7 + C_8 \phi_8 \cdot \]
\[ E_8^0 = \frac{K}{4} - \frac{1}{2} \left[ (\Delta^2 + 16K_2K_2^*) \right]^{1/2} \]
\[ \psi_8^0 = d_7 \phi_7 + d_8 \phi_8 \cdot \]

\text{(2.34)}

In terms of these eigenfunctions the allowed transitions (\(\Delta M = \pm 1\) and \(\Delta m = 0\)) are termed as

\[ T_1 = \psi_2^0 \leftrightarrow \psi_3^0 \]
\[ T_2 = \psi_2^0 \leftrightarrow \psi_4^0 \]
\[ T_3 = \psi_3^0 \leftrightarrow \psi_7^0 \]
\[ T_4 = \psi_3^0 \leftrightarrow \psi_8^0 \]
\[ T_5 = \psi_4^0 \leftrightarrow \psi_7^0 \]
\[ T_6 = \psi_4^0 \leftrightarrow \psi_8^0 \]
\[ T_7 = \psi_5^0 \leftrightarrow \psi_7^0 \]
\[ T_8 = \psi_5^0 \leftrightarrow \psi_8^0 \]
\[ T_9 = \psi_6^0 \leftrightarrow \psi_7^0 \]
\[ T_{10} = \psi_6^0 \leftrightarrow \psi_8^0 \]
\[ T_{11} = \Psi_1^0 \leftrightarrow \Psi_5^0 \]
\[ T_{12} = \Psi_1^0 \leftrightarrow \Psi_6^0 \]

\[ m_{-3/2} \quad (\text{or} \ m = -\frac{3}{2}) \]

where \( m_{3/2}, m_{1/2}, m_{-1/2}, m_{-3/2} \) denote transitions \( m \leftrightarrow m \)
or \( \frac{3}{2} \leftrightarrow \frac{3}{2}, \ \frac{1}{2} \leftrightarrow \frac{1}{2}, \ -\frac{1}{2} \leftrightarrow -\frac{1}{2} \) and \( -\frac{3}{2} \leftrightarrow -\frac{3}{2} \), respectively.

The resonance field of allowed transition is obtained by equating \( h\nu \) to the respective energy difference, we obtain

(i) for \( m_{3/2} \) transition

\[ \Delta = \frac{(h\nu)^2 + \frac{3}{4}K^2 - 2K\nu - 3K^*K^2}{(h\nu - K)^2} \]  

(ii) for \( m_{1/2} \) transition

\[ \Delta = -\frac{K}{2} \left[ 1 + \frac{4K^*K}{4(h\nu)^2 - K^2} \right] + h\nu \sqrt{1 - \frac{16K^*K}{4(h\nu)^2 - K^2} \left[ \frac{7}{2} - \frac{K^2K^*}{4(h\nu)^2 - K^2} \right]} \]

(iii) for \( m_{-1/2} \) transition

\[ \Delta = \frac{K}{2} \left[ 1 + \frac{4K^*K}{4(h\nu)^2 - K^2} \right] + h\nu \sqrt{1 - \frac{16K^*K}{4(h\nu)^2 - K^2} \left[ \frac{7}{2} - \frac{K^2K^*}{4(h\nu)^2 - K^2} \right]} \]
(iv) for $m_{-3/2}$ transition

$$
\Delta = \frac{(h\nu)^2 + \frac{3}{4}K^2 + 2K\nu - 3K_2K^*}{(h\nu + \frac{K}{2})} \quad (2.38)
$$

These four relations for the resonance field of allowed transition can be written in the following general form:

$$
\Delta = -Km(1+R) + \sqrt{1-4R} \left[ I(I+1) - m^2(1+R) \right] \quad (2.39)
$$

where

$$
R = \frac{4K_2K^*}{4(h\nu)^2 - K^2}
$$

Similar form for $\Delta$ is obtained for transitions in $V_0^{2+}$ having $S = \frac{1}{2}$, $I = \frac{7}{2}$. Now we will discuss the solution for the following two cases:

(i) $\vec{g}$ and $\vec{A}$ are isotropic: $\vec{g}$ and $\vec{A}$ are reduced to scalar quantities written as:

$$
\begin{align*}
\varepsilon_x &= \varepsilon_y = \varepsilon_z = \varepsilon \\
A_x &= A_y = A_z = a
\end{align*}
$$

(2.40)

If $a$ is negative then from Eqs. (2.19), (2.23) and (2.24)

$$
\begin{align*}
K_1K_1^* &= K_2K_3^* = 0 \\
K_2K_2^* &= \frac{a^2}{4}
\end{align*}
$$

(2.41)
In this case expression for $\Delta$ is exact with

$$R = \frac{4K_2K_2^*}{4(h\nu)^2-K_2^2} = \frac{a^2}{4(h\nu)^2-a^2} \quad (2.42)$$

If $\vec{g}$ and positive $\vec{A}$ are isotropic then from Eqs. (2.19), (2.23) and (2.24)

$$K_1K_1^* = K_2K_2^* = 0$$

$$K_3K_3^* = \frac{a^2}{4} \quad (2.43)$$

In this case also the Eq. can be solved exactly and we get the resonance field of each allowed transition written as:

$$\Delta = -Km(1+R') + h\nu \sqrt{1-4R'[I(I+1)-m^2(1+R')] - R'} \quad (2.44)$$

where

$$R' = \frac{4K_2K_3^*}{4(h\nu)^2-K_2^2} = \frac{a^2}{4(h\nu)^2-a^2} = R \quad (2.45)$$

(ii) $\vec{g}$ and $\vec{A}$ tensors are axially symmetric: $\vec{A}$ is negative then according to Eqs. (2.26), (2.29) and (2.30)

$$K_1K_1^* = K_3K_3^* = 0$$

$$K_2K_2^* = \frac{A_1^2}{4} \quad (2.46)$$

for $\theta = 0$ (magnetic field along $z$-axis), and

$$K_1K_1^* = 0, K_3K_3^* = \frac{(A_\| - A_\perp)^2}{16}, K_2K_2^* = \frac{(A_\| + A_\perp)^2}{16} \quad (2.47)$$
for $\theta = 90^\circ$ (magnetic field perpendicular to z-axis). In this case the expression obtained for $\Delta$ in Eq. (2.39) is exact for $\mathbf{H}$ along z-axis and $K_2K_2^*$ is small for $\mathbf{H}$ perpendicular to z-axis.

When $\mathbf{g}$ and $\mathbf{A}$ tensors are axially symmetric and $A$ is positive then from Eqs. (2.26), (2.29) and (2.30):

\[ K_1K_1^* = K_2K_2^* = 0 \]
\[ K_3K_3^* = \frac{A_i^2}{4} \quad (2.48) \]

for $\theta = 0^\circ$ and

\[ K_1K_1^* = 0 , \quad K_2K_2^* = \frac{(A_{ii} - A_{I})^2}{16} \]
\[ K_3K_3^* = \frac{(A_{ii} + A_{I})^2}{16} \quad (2.49) \]

for $\theta = 90^\circ$. In this case we solve the equation for spin Hamiltonian (2.5) by assuming $K_2K_2^*$ as the perturbation term. It is found that the resonance field for allowed transition is given by:

\[ \Delta = -Km(1+R_1) + h\nu \sqrt{1-4R_1[I(I+1) - m^2(1+R_1)]} \quad (2.50) \]

where

\[ R_1 = \frac{4K_2K_3^*}{4(h\nu)^2 - K^2} \]
\[ = \frac{A_i^2}{4(h\nu)^2 - K^2} = R, \text{ for } \theta = 0 \quad (2.51) \]
Eqs. (2.46) and (2.48) show that the value of $\Delta$ as given in (2.39) or (2.50) is exact for $\vec{H}$ along the $z$-axis whereas for $\vec{H}$ along the $x$-axis or the $y$-axis $K_2K_2^*$ for positive $A$ and $K_3K_3^*$ for negative $A$ are non-zero. Their values are given in (2.27). Further for $\vec{H}$ along any other direction $K_1K_1^*$ is not equal to zero, although these terms are very small as compared to the term which we have taken into account. The contribution of these terms can be taken in (2.39) by using second-order perturbation theory. The final expression obtained for the resonance field of each allowed transition is:

$$\Delta = -Km(1+R)+\hbar\sqrt{1-4R[I(I+1)-m^2(1+R)]}$$

$$- \frac{A_2^2(A_{ll} - K)^2}{8K_2^2\hbar} \left[I(I+1)-m^2\right]$$

$$- \frac{1}{2} n^2 (1-n^2) \frac{g_u^2 g_1^2}{g^4} \frac{(A_{ll}^2 - A_1^2)^2}{K^2\hbar^2} m^2 \quad (2.53)$$

The third term on the right-hand side is due to $K_2K_2^*$ (positive $A$) or $K_3K_3^*$ (negative $A$) and the fourth term is due to $K_1K_1^*$.
In the present theory we have seen that when the $\mathbf{g}$- and $\mathbf{A}$-tensors are isotropic, the resonance field is the exact solution and it is given by (2.39) or (2.44). When $\mathbf{g}$ and $\mathbf{A}$ are axially symmetric (2.39) is the exact solution for $\mathbf{H}$ along z-axis. However, for $\mathbf{H}$ along any other direction, small perturbation terms should be added in (2.39) and the value of $A$ up to second-order perturbation theory is given by (2.53). If in (2.53) we take $R \ll 1$ and neglect $A_I$ as compared to $2(h\nu)$ in the denominator, we get (2.53) in the following form:

$$\Delta = h\nu - K_m - \frac{1}{4} \frac{A_{II}^2 (A_{II}^2 + K^2)}{K^2 h\nu} \left[ I(I+1) - m^2 \right]$$

$$- \frac{1}{2} n^2(1-n^2) \frac{g_{II}^2 g_{II}^2 (A_{II}^2 - A_I^2)}{g^4 K^2 h\nu} m^2$$  \hspace{1cm} (2.54)

Here we have also neglected $R$ in the coefficient of $K_m$ in (2.53). Eq. (2.54) is the same as given by Bleaney et al.\(^9\) and Pake and Estle\(^5\). Thus we conclude that (2.53) is exact for $\mathbf{H}$ along the z-axis and for $\mathbf{H}$ along any other direction (2.53) is a better approximation than (2.54).

For analysing EPR of Cu\(^{2+}\) or VO\(^{2+}\) ($S = \frac{1}{2}$) in glasses where we get the spectrum for the parallel and perpendicular component of the axial $\mathbf{g}$ and $\mathbf{A}$ tensor, the theory developed here is more suitable\(^7\). Solutions (2.53) of the spin
Hamiltonian for the parallel and perpendicular components may be written as:

\[
H_{\parallel}(m) = -mA_{\parallel}(1+R) + H_{\parallel}(0) \sqrt{1-4R[I(I+1)-m^2(1+R)]}
\]

\[
H_{\perp}(m) = -mA_{\perp}(1+R_1) + H_{\perp}(0) \sqrt{1-4R_1[I(I+1)-m^2(1+R_1)]}
\]

\[
- \frac{(A_{\parallel} - A_{\perp})^2}{8H_{\perp}(0)} \left[ I(I+1) - m^2 \right]
\]

where

\[
R = \frac{A_{\perp}^2}{4H_{\parallel}^2(0) - A_{\parallel}^2}
\]

\[
R_1 = \frac{(A_{\parallel} + A_{\perp})^2}{4[H_{\perp}(0) - A_{\perp}^2]}
\]

\[
H_{\parallel}(0) = \hbar \nu / g_{\parallel} \beta
\]

and

\[
H_{\perp}(0) = \hbar \nu / g_{\perp} \beta
\]

These relations will be used to determine spin-Hamiltonian parameters, for Cu$^{2+}$ and VO$^{2+}$ doped in glasses.
REFERENCES


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