Theory of ESR Spectrum of S=5/2 Ions with Large Fine Structure Constant

by

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Abstract

The analysis of the spin Hamiltonian $D[(S_z^2-\frac{1}{3}\boldsymbol{S}^2)+\lambda(S_x^2-S_y^2)]+g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}+\boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I}$ with $S=5/2$ is made for an arbitrary direction of an applied constant magnetic field $\boldsymbol{H}$. A deviation of λ from 1/3 and $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$ are treated as a perturbation. Then $\boldsymbol{S}\cdot\boldsymbol{A}\cdot\boldsymbol{I}$ is treated as a perturbation to them. From these calculations, the effective g-factor, the transition probability and the hyperfine splitting are evaluated. These results are useful for the analysis of the ESR signal with $g=4.29$ observed in amorphous materials doped with transition metal ions with $S=5/2$. The method of the extension of the present calculation to more general values of S is also presented.

1. Introduction

The ESR signal with $g=4.29$ is observed in almost all amorphous materials doped with transition metal ions with $S=5/2$.[1-6] This signal is known to be explained by the spin Hamiltonian

$$\mathscr{H}=g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}+D(S_z^2-\frac{1}{3}\boldsymbol{S}^2)+E(S_x^2-S_y^2), \tag{1}$$

for $S=5/2$, provided that $E/D\equiv\lambda=1/3$ and D is much larger than $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$. Here $g_o\simeq2$. For $\lambda=1/3$, Hamiltonian (1) without $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$ can be diagonalized analytically.

Dowsing[7] made a computer analysis of the Hamiltonian (1) for various values of λ. There is also a perturbation calculation of the Hamiltonian by Nicklin *et al.*[8,9] Both calculations were carried out only for the case that a direction of an applied constant magnetic field coincides with one of the principal axes of a crystal field.

In order to calculate a powder pattern, a line width and a concentration of the ESR center for the ESR spectrum in amorphous materials, we must consider a transition probability and an influence of a deviation of λ from 1/3 for the case of an arbitrary direction of a constant magnetic field. The analysis of the spin Hamiltonian (1) including a hyperfine interaction term should be necessary to obtain a hyperfine constant from the observed hyperfine structure in the signal with $g=4.29$. To our knowledge, there has not been such a calculation.

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In the present article, we made an analysis of the spin Hamiltonian (1) with a hyperfine interaction term for an arbitrary direction of a constant magnetic field. For an arbitrary direction of a constant magnetic field, it is difficult to obtain exact eigenvalues of the spin Hamiltonian (1) analytically. Assuming that D is much larger than $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$, a deviation of a fine structure term from $\lambda=1/3$ and a Zeeman term $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$ are treated as perturbations to

$$\mathscr{H}_0=D[(S_z^2-\frac{1}{3}\boldsymbol{S}^2)+\frac{1}{3}(S_x^2-S_y^2)]. \qquad (2)$$

Further a hyperfine interaction term is taken as a perturbation to a deviation term from $\lambda=1/3$ and $g_o\mu\boldsymbol{S}\cdot\boldsymbol{H}$.

2. Eigenvalues and Eigenfunctions of Nonperturbed Hamiltonian

Any value of $\lambda(=E/D)$ in (1) can be transformed into values between 0 and 1/3 by a suitable transformation of coordinate axes. So we assume λ to lie between 0 and 1/3.

A deviation of a fine structure term from $\lambda=1/3$ is given by the following form.

$$V=(\lambda-1/3)D[S_x^2-S_y^2]\equiv\delta D(S_x^2-S_y^2)=\delta D(S_+^2+S_-^2)/2 \quad (-1/3\leqq\delta\leqq 0). \qquad (3)$$

The eigenvalues E_i° and the eigenfunctions of $\mathscr{H}_o$ for $S=5/2$ can be shown to be as follows:

$$\left.\begin{array}{ll}
E_+^\circ=+\frac{4}{3}\sqrt{7}D & |+\alpha\rangle=C_{1+}|5/2\rangle+C_{2+}|1/2\rangle+C_{3+}|-3/2\rangle \\
 & |+\beta\rangle=C_{1+}|-5/2\rangle+C_{2+}|-1/2\rangle+C_{3+}|3/2\rangle \\
E_o^\circ=0 & |0\alpha\rangle=C_{10}|5/2\rangle+C_{20}|1/2\rangle+C_{30}|-3/2\rangle \\
 & |0\beta\rangle=C_{10}|-5/2\rangle+C_{20}|-1/2\rangle+C_{30}|3/2\rangle \\
E_-^\circ=-\frac{4}{3}\sqrt{7}D & |-\alpha\rangle=C_{1-}|5/2\rangle+C_{2-}|1/2\rangle+C_{3-}|-3/2\rangle \\
 & |-\beta\rangle=C_{1-}|-5/2\rangle+C_{2-}|-1/2\rangle+C_{3-}|3/2\rangle
\end{array}\right\} \qquad (4)$$

where $C_{1\pm}/C_{2\pm}=\pm\sqrt{10}\,(2\sqrt{7}\pm5)/6$, $C_{3\pm}/C_{2\pm}=\pm\sqrt{2}\,(2\sqrt{7}\mp1)/18$, $C_{10}/C_{20}=-1/\sqrt{10}$, $C_{30}/C_{20}=3/\sqrt{2}$, $C_{20}=\sqrt{5}/2\sqrt{7}$, $C_{2\pm}=(4\sqrt{14}\mp7\sqrt{2})/28$.

In the present article, we express the eigenfunctions of S_z for $S=5/2$ as $|m_s\rangle$ $(m_s=\pm5/2,\pm3/2,\pm1/2)$ and the eigenfunctions of Eq. (2) as $|l\alpha\rangle$, $|l\beta\rangle$. $|+\alpha\rangle$ and $|+\beta\rangle$ are two degenerate eigenfunctions (Kramers doublet) of the eigenvalue E_+°, $|0\alpha\rangle$ and $|0\beta\rangle$ are those of E_0°, and $|-\alpha\rangle$ and $|-\beta\rangle$ are those of E_-°. In the later calculation, m and n are also used instead of l. The matrix elements for S_+, S_-, S_z and V by $|l\alpha\rangle$ and $|l\beta\rangle$ are given in Appendix A.

3. Preturbation Energies

3.1 General form

We take a sum of V and a Zeeman term $\mathcal{H}_z$ for an arbitrary direction of an applied constant magnetic field as a perturbation $\mathcal{H}'$ to $\mathcal{H}_o$. We calculate perturbation energies to the second order.

The first order and the second order perturbation energies for a Kramers doublet (l) are, respectively,

$$E^{(1)}_{l\pm}=<l\alpha|\ V|\ l\alpha>\pm\Delta E^{1/2}_{zll} \tag{5}$$

and
$$E^{(2)}_{l\pm}=\sum_{m\neq l}\frac{1}{E^0_l-E^0_m}\left[<m\alpha|\ V|\ l\alpha>^2\pm 2<m\alpha|\ V|\ l\alpha>\frac{\Delta E_{zlml}}{\Delta E^{1/2}_{zll}}+\Delta E_{zlmm}\right]. \tag{6}$$

Here

$$\Delta E_{zlmn}=<m\alpha|\mathcal{H}_z|\ l\alpha><n\alpha|\mathcal{H}_z|\ l\alpha>+Re\left[<m\beta|\mathcal{H}_z|\ l\alpha><n\beta|\mathcal{H}_z|\ l\alpha>^*\right], \tag{7}$$

especially $\Delta E_{zll},\ \Delta E_{zlmm}>0$,

and
$$\mathcal{H}_z=g_o\mu H\left[S_z\cos\theta+\frac{1}{2}(S_+e^{-i\phi}+S_-e^{+i\phi})\sin\theta\right]\equiv g_o\mu HS_{\parallel}. \tag{8}$$

Here we suppose $g_o=2$. The polar angles θ and ϕ of a constant magnetic field with respect to coordinate axes x, y and z are shown in Fig.1. The matrix elements satisfy the following relations:

$$<m\alpha|\ V|\ n\alpha>=<n\alpha|\ V|\ m\alpha>=<m\beta|\ V|\ n\beta>$$
$$=<n\beta|\ V|\ m\beta>,\ <n\beta|\ V\ |\ m\alpha>=0, \tag{9}$$
$$<m\alpha|\mathcal{H}_z|\ n\beta>=<n\alpha|\mathcal{H}_z|\ m\beta>$$
$$=<m\beta|\mathcal{H}_z|\ n\alpha>^*=<n\beta|\mathcal{H}_z|\ m\alpha>^*,$$
$$<m\alpha|\mathcal{H}_z|\ n\alpha>=<n\alpha|\mathcal{H}_z|\ m\alpha>$$
$$=-<m\beta|\mathcal{H}_z|\ n\beta>=-<n\beta|\mathcal{H}_z|\ m\beta>. \tag{10}$$

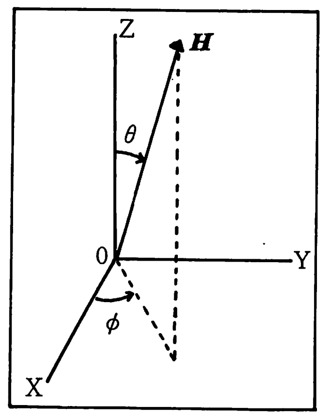

Fig.1. The polar angles θ and ϕ of a constant magnetic field with respect to coordinate axes x, y, and z.

We denote the zeroth order eigenfunctions of $\mathcal{H}'$ as $|\chi^\circ_{l+}>$ and $|\chi^\circ_{l-}>$ whose energies are $E^{(1)}_{l+}$ and $E^{(1)}_{l-}$, respectively. Then

$$|\ \chi^\circ_{l+}>=C^l_{+\alpha}|\ l\alpha>+C^l_{+\beta}|\ l\beta>$$
$$|\ \chi^\circ_{l-}>=C^l_{-\alpha}|\ l\alpha>+C^l_{-\beta}|\ l\beta>. \tag{11}$$

The coefficients satisfy the following relations:

$$|C^l_{+\alpha}|^2+|C^l_{+\beta}|^2=|C^l_{-\alpha}|^2+|C^l_{-\beta}|^2=1,\ C^l_{+\alpha}C^{l*}_{-\alpha}+C^l_{+\beta}C^{l*}_{-\beta}=0,$$ (the orthonormal condition)

$$(|C^l_{+\alpha}|^2-|C^l_{+\beta}|^2)=-(|C^l_{-\alpha}|^2-|C^l_{-\beta}|^2)=\langle l\alpha|\mathcal{H}_z|l\alpha\rangle^*/\Delta E^{1/2}_{zll},$$

and $$2C^l_{+\alpha}C^{l*}_{+\beta}=-2C^l_{-\alpha}C^{l*}_{-\beta}=\langle l\beta|\mathcal{H}_z|l\alpha\rangle^*/\Delta E^{1/2}_{zll}. \qquad (12)$$

In order to derive the perturbation energies (6), we need only these relations (12).

3.2 g-factor

If we concider a resonant condition of the ESR for a Kramers doublet whose eigenvalue for $\mathcal{H}_0$ is E°_l, an effective g-factor $g_{(l)}$ is defined by the following relation.

$$h\nu=[E^{(1)}_{l+}+E^{(2)}_{l+}]-[E^{(1)}_{l-}+E^{(2)}_{l-}]\equiv g_{(l)}\mu H\equiv(g^\circ_l+\Delta g_l)\mu H. \qquad (13)$$

Here ν is a microwave frequency.

$$\therefore\ g_{(l)}=g^\circ_l+\Delta g_l=[2\Delta E^{1/2}_{zll}+4\sum_{m\neq l}\frac{\langle m\alpha\dagger V|l\alpha\rangle}{E^0_l-E^0_m}\cdot\frac{\Delta E_{zlml}}{\Delta E^{1/2}_{zll}}]/\mu H. \qquad (14)$$

The first term gives a g-factor for the case $\lambda=1/3$, and the second term gives a g-shift caused by the deviation of λ from 1/3.

By using Tables A1, A2 and A3, Eq.(14) can be calculated to be

$$g_{(l)}=g^\circ_l+8\delta[P^l_z\cos^2\theta+P^l_x\cos^2\phi\sin^2\theta+P^l_y\sin^2\phi\sin^2\theta]/g^\circ_l \qquad (15)$$

and $$g^0_l=[g^2_{zl}\cos^2\theta+g^2_{\perp l}\sin^2\theta]^{1/2} \text{ and } g_{\perp l}=[g^2_{xl}\cos^2\phi+g^2_{yl}\sin^2\phi]^{1/2}, \qquad (16)$$

where $$g_{zl}=4|\langle l\alpha|S_z|l\alpha\rangle|,\ g_{xl}=2|\langle l\beta|S_+|l\alpha\rangle+\langle l\beta|S_-|l\alpha\rangle|,$$

$$g_{yl}=2|\langle l\beta|S_+|l\alpha\rangle-\langle l\beta|S_-|l\alpha\rangle|, \qquad (17)$$

$$P^l_z=4\langle l\alpha|S_z|l\alpha\rangle\sigma^l_z,\ P^l_x=(\langle l\beta|S_+|l\alpha\rangle+\langle l\beta|S_-|l\alpha\rangle)(\sigma^l_++\sigma^l_-),$$

$$P^l_y=(\langle l\beta|S_+|l\alpha\rangle-\langle l\beta|S_-|l\alpha\rangle)(\sigma^l_+-\sigma^l_-), \qquad (18)$$

$$\sigma^l_z=\sum_{m\neq l}\frac{\langle m\alpha|V|l\alpha\rangle\langle m\alpha|S_z|l\alpha\rangle}{\delta\cdot(E^0_l-E^0_m)} \text{ and } \sigma^l_\pm=\sum_{m\neq l}\frac{\langle m\alpha|V|l\alpha\rangle\langle m\beta|S_\pm|l\alpha\rangle}{\delta\cdot(E^0_l-E^0_m)}. \qquad (19)$$

g_{il} $(i=x,y,z)$, P^l_j $(j=x,y,z)$, and σ^l_k $(k=z,+,-)$ are shown in Table 1,2 and 3, respectively.

From Table 1, g^0_0 is seen to be independent of θ, ϕ and $30/7\simeq4.29$. From Eq.(15) and Table 2, a solid angle average of Δg_0 can be shown to be 0. Accordingly, the g-factor of the middle Kramers doublet averaged over a solid angle varies little and is 4.29, even if λ deviates slightly from 1/3. The linear deviation of λ gives only the line width of the signal with $g=4.29$. The signal with $g_{(+)}$ or $g_{(-)}$ varies largely with θ, ϕ and the detection of those signal appears to be difficult for amorphous materials. Those results are useful for the analysis of the ESR spectrum for amorphous materials.

$g_{(-)}$ has the similar form as $g_{(+)}$ by the following transformations

$\sin\theta\sin\phi=\cos\theta', \sin\theta\cos\phi=\sin\theta'\cos\phi', \cos\theta=\sin\theta'\sin\phi'$ and $-\delta=\delta'$. (20)

An illustration of Eq.(20) is shown in Fig.2. Those transformations will be used in the next section.

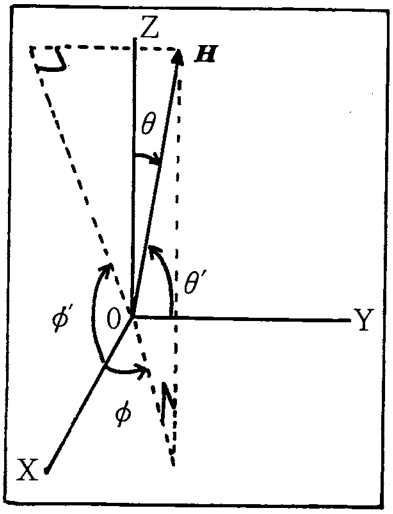

Fig.2. The relations between (θ,ϕ) and (θ',ϕ').

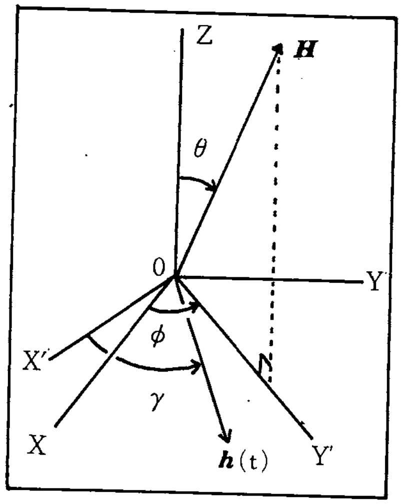

Fig.3. The relation between **H** and **h**(t). x'-y' plane is the same plane as x-y plane. A new coordinate axis y' coincides with a direction of a projection of **H** to x-y plane. γ is an angle between a new coordinate axis x' and **h**(t).

4. Transition Probabilities within Kramers Doublet

Denote a perturbation by an oscillating magnetic field $\boldsymbol{h}$(t), which is perpendicular to a constant magnetic field $\boldsymbol{H}$, as $\mathcal{H}''$. We express a projection of $\boldsymbol{S}$ to $\boldsymbol{h}$(t) as $S_\perp$. From Fig.3, $\mathcal{H}''$ is given by

$$\mathcal{H}''=g_0\mu\boldsymbol{h}(t)\cdot\boldsymbol{S}=g_0\mu h(t)S_\perp, \tag{21}$$

where
$$S_\perp=KS_+ + K^*S_- - K_0S_z, \tag{22}$$
$$K=\frac{1}{2}e^{-i\phi}(\sin\gamma\cos\theta+i\cos\gamma) \text{ and } K_0=\sin\gamma\sin\theta. \tag{23}$$

γ is shown in Fig.3. The similar relations as Eq.(10) hold also for $\mathcal{H}''$.

We calculate the transition probabilities between two states belonging to a same Kramers doublet. The matrix element of $\mathcal{H}''$ is

$$<\chi^0_{l-}\,|\,\mathcal{H}''\,|\,\chi^0_{l+}>=\frac{|<l\beta|\mathcal{H}_z|\,l\alpha>|^2<l\alpha|\mathcal{H}''\,|\,l\alpha>-<l\alpha|\mathcal{H}_z|\,l\alpha>ReZ_l-i\Delta E^{1/2}_{zlll}ImZ_l}{\Delta E^{1/2}_{zlll}\,|<l\beta|\mathcal{H}_z|\,l\alpha>|}, \tag{24}$$

where $Z_l=<l\beta\,|\,\mathcal{H}_z\,|\,l\alpha>^*<l\beta\,|\,\mathcal{H}''\,|\,l\alpha>$.

The transition probability is determined essentially by the matrix element of $S_\perp$ in Eq.(24), and we denote $|<\chi_{l-}^0|S_\perp|\chi_{l+}^0>|^2$ as $P_l(\theta,\phi,\gamma)$:

$$P_l(\theta,\phi,\gamma)=[g_{zl}^2 g_{\perp l}^2 \sin^2\gamma+\{g_{zl}^2(g_{xl}^2\sin^2\phi+g_{yl}^2\cos^2\phi)\cos^2\theta+g_{xl}^2 g_{yl}^2\sin^2\theta\}\cos^2\gamma$$
$$+\frac{1}{2}g_{zl}^2(g_{xl}^2-g_{yl}^2)\sin2\gamma\sin2\phi\cos\theta]/16[g_l^0]^2. \quad (25)$$

$P_0(\theta,\phi,\gamma)$ is independent of θ,ϕ and γ, and is $[g_0^0]^2/16=(15/14)^2$. We make an average of Eq.(25) over γ, and denote this average as $P_l(\theta,\phi)$. Then

$$P_l(\theta,\phi)=[g_{zl}^2(g_{xl}^2+g_{yl}^2)\cos^2\theta+(g_{zl}^2 g_{\perp l}^2+g_{xl}^2 g_{yl}^2)\sin^2\theta]/32[g_l^0]^2. \quad (26)$$

This result can be used to calculate a powder pattern of the ESR spectrum for amorphous materials.

$P_-(\theta,\phi)$ can be transformed to the similar form as $P_+(\theta,\phi)$ using Eq.(20), that is, $P_-(\theta,\phi)=P_+(\theta',\phi')$, so an average of $P_-(\theta,\phi)$ over a solid angle is equal to that of $P_+(\theta,\phi)$. First we make an average of $P_l(\theta,\phi)$ over ϕ, and then over θ graphically. We have $P_+=P_-\simeq0.38$ and $P_\pm/P_0\sim1/3$.

Using P_0, a concentration of the ESR center which contributes to the signal with $g=4.29$ can be evaluated.

5. Hyperfine Interaction

5.1 General form

We consider a new coordinate system (x',y',z') as shown in Fig.4, and denote components of nuclear spin operator $\boldsymbol{I}$ in a new coordinate system as (I'_x,I'_y,I'_z). Using these components (I'_x,I'_y,I'_z), an anisotropic hyperfine interaction $\mathcal{H}_h$ is

$$\mathcal{H}_h=A_xI_xS_x+A_yI_yS_y+A_zI_zS_z=(A_+N_++A_-N_-)S_++(A_-N_++A_+N_-)S_-+A_zN_zS_z, \quad (27)$$

where $A_\pm=(A_x\pm A_y)/2$, $N_\pm=\frac{1}{2}e^{\mp i\phi}\{I'_z\sin\theta\pm\frac{i}{2}[I'_+(1\mp\cos\theta)+I'_-(1\pm\cos\theta)]\}$,

$$N_z=[I'_z\cos\theta+\frac{i}{2}(I'_+-I'_-)\sin\theta]$$

and $I'_\pm=I'_x\pm iI'_y$. (28)

Nuclear spin operators I'_z and $I'_\pm$ satisfy the following relations:

$$I'_z|m_I>=m_I|m_I>$$

and $I'_\pm|m_I>=[(I\mp m_I)(I\pm m_I+1)]^{1/2}|m_I\pm1>$. (29)

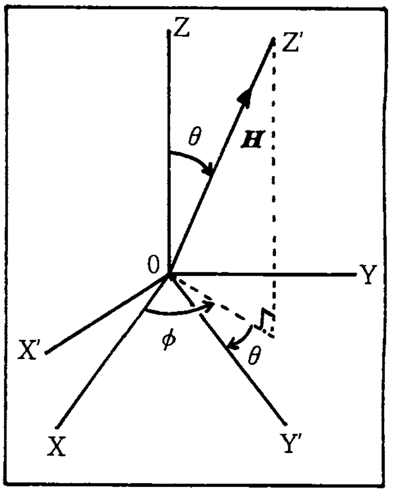

Fig.4. The relation between the coordinate system (x, y, z,) and the new coordinate system (x', y', z'). The coordinate axis z' coincides with a direction of **H**. A projection of the coordinate axis y' to x-y plane coincides with a direction of a projection of **H** to x-y plane.

The first opder perturbation energies can be obtained by diagonalizing matrices $[<m'_I\chi^0_{l+} \mid \mathcal{H}_h \mid \chi^0_{l+}\, m_I>]$ and $[<m'_I\chi^0_{l-} \mid \mathcal{H}_h \mid \chi^0_{l-}\, m_I>]$. We write the eigenvalues as $\varepsilon^{(1)}_{l\pm,m_I}$, then

$$\varepsilon^{(1)}_{l\pm,m_I} = \pm\frac{1}{2} m_I A^l_{eff}, \text{ where } A^l_{eff} = [A^2_z g^4_{zl} \cos^2\theta + (A^2_x g^4_{xl} \cos^2\phi + A^2_y g^4_{yl} \sin^2\phi)\sin^2\theta]^{1/2}/2g^0_l. \quad (30)$$

Our assumption is $\mathcal{H}_h \ll \mathcal{H}' \ll \mathcal{H}_0$, and $\mathcal{H}^2_h/\mathcal{H}_0$ and $\mathcal{H}_h(\mathcal{H}'/\mathcal{H}_0)$ are expected to be of the same order of magnitude, so there exist two types of the second order perturbation energies.

The second order perturbation energies of the first type are obtained as follows by a usual second order perturbation formula.

$$\varepsilon^{(2)}_{l+,m_I} = \sum_{m'_I} \frac{|<m'_I\chi^0_{l-} \mid \mathcal{H}_h \mid \chi^0_{l+} m_I>|^2}{g^0_l \mu H^l_0} = \frac{m^2_I |\eta^l_z|^2 + C_{+m_I} |\eta^l_+|^2 + C_{-m_I} |\eta^l_-|^2}{g^0_l \mu H^l_0} \quad (31)$$

$$\varepsilon^{(2)}_{l-,m_I} = \sum_{m'_I} \frac{|<m'_I\chi^0_{l+} \mid \mathcal{H}_h \mid \chi^0_{l-} m_I>|^2}{-g^0_l \mu H^l_0} = \frac{m^2_I |\xi^l_z|^2 + C_{+m_I} |\xi^l_+|^2 + C_{-m_I} |\xi^l_-|^2}{-g^0_l \mu H^l_0} \quad (32)$$

Here $<\chi^\circ_{l-} \mid \mathcal{H}_h \mid \chi^\circ_{l+}> = \eta^l_z I'_z + \eta^l_+ I'_+ + \eta^l_- I'_-$, $<\chi^\circ_{l+} \mid \mathcal{H}_h \mid \chi^\circ_{l-}> = \xi^l_z I'_z + \xi^l_+ I'_+ + \xi^l_- I'_-$,

$H^l_o = h\nu/g^\circ_l \mu$,

$$\xi^l_z = \eta^{l*}_z, \xi^l_\pm = \eta^{l*}_\mp, \; C_{\pm m_I} = (I \mp m_I)(I \pm m_I + 1), \text{ and } \eta^l_z = 0, \text{ if } A_z = A_x = A_y. \quad (33)$$

The second order perturbation energy of the second type can be obtained by the following way. Using a perturbation formula for a degenerate case, the first order perturbed state for electron spin denoted by $\mid \chi^{(1)}_{l\pm}>$ is given by

$$\mid \chi^{(1)}_{l\pm}> = \mid \chi^0_{l\pm}> + \sum_{\substack{m \neq l \\ r=\alpha,\beta}} \left[\frac{<\chi^0_{l\mp} \mid \mathcal{H}' \mid mr> \cdot <mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^{(1)}_{l\pm} - E^{(1)}_{l\mp})(E^0_l - E^0_m)} \mid \chi^0_{l\mp}> + \frac{<mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^0_l - E^0_m)} \mid mr> \right]$$

$$\equiv \mid \chi^0_{l\pm}> + \mid \chi'_{l\pm}>, \quad (34)$$

where $\sum_{r=\alpha,\beta} <\chi^0_{l\mp} \mid \mathcal{H}' \mid mr><mr \mid \mathcal{H}' \mid \chi^0_{l\pm}> = \sum_{r=\alpha,\beta} <\chi^0_{l\mp} \mid \mathcal{H}_z \mid mr><mr \mid V \mid \chi^0_{l\pm}>$

$$+ <\chi^0_{l\mp} \mid V \mid mr><mr \mid \mathcal{H}_z \mid \chi^0_{l\pm}>. \quad (35)$$

Using Eq.(34), the second order perturbation energy of the second type is shown to have a following form:

$$\varepsilon^{(2)'}_{l\pm,m_I} = <m_I \mid [<\chi^0_{l\pm} \mid \mathcal{H}_h \mid \chi'_{l\pm}> + (\text{conjugate complex})] \mid m_I>$$

$$= <m_I \mid \sum_{\substack{m \neq l \\ r=\alpha,\beta}} \left[\frac{<\chi^0_{l\pm} \mid \mathcal{H}_h \mid \chi^0_{l\mp}><\chi^0_{l\mp} \mid \mathcal{H}' \mid mr><mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^{(1)}_{l\pm} - E^{(1)}_{l\mp})(E^0_l - E^0_m)} + \right.$$

$$\frac{<\chi^0_{l\pm} \mid \mathcal{H}_h \mid mr><mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^0_l - E^0_m)}$$

$$+(\text{conjugate complex})] \mid m_I> \equiv m_I(\Delta R^l_\pm + R^l_\pm), \tag{36}$$

where

$$m_I \Delta R^l_\pm = <m_I \mid \sum_{\substack{m \neq l \\ r=\alpha,\beta}} [\frac{<\chi^0_{l\pm} \mid \mathcal{H}_h \mid \chi^0_{l\mp}><\chi^0_{l\mp} \mid \mathcal{H}' \mid mr><mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^{(1)}_{l\pm} - E^{(1)}_{l\mp})(E^0_l - E^0_m)}$$

$$+(\text{conjugate complex})] \mid m_I>, \tag{37}$$

and

$$m_I R^l_\pm = <m_I \mid \sum_{\substack{m \neq l \\ r=\alpha,\beta}} [\frac{<\chi^0_{l\pm} \mid \mathcal{H}_h \mid mr><mr \mid \mathcal{H}' \mid \chi^0_{l\pm}>}{(E^0_l - E^0_m)} + (\text{conjugate complex})] \mid m_I>. \tag{38}$$

A resonant condition of the ESR for a Kramers doublet (l) in the presence of a hyperfine interaction is:

$$h\nu = g_{(l)}\mu H^l_{m_I} + (E^{hfs}_{l+,m_I} - E^{hfs}_{l-,m_I}) = g_{(l)}\mu H^l_{m_I-1} + (E^{hfs}_{l+,m_I-1} - E^{hfs}_{l-,m_I-1}), \tag{39}$$

where $E^{hfs}_{l\pm,m_I} = \varepsilon^{(1)}_{l\pm,m_I} + \varepsilon^{(2)}_{l\pm,m_I} + \varepsilon^{(2)\prime}_{l\pm,m_I}$ and $H^l_{m_I}$ is the applied constant magnetic field satisfying the resonant condition with a nuclear quantum number m_I. From Eq.(39), the hyperfine splitting $\Delta H^l_{m_I}$ is obtained as follows:

$$\Delta H^l_{m_I} = H^l_{m_I-1} - H^l_{m_I} = [(E^{hfs}_{l+,m_I} - E^{hfs}_{l-,m_I}) - (E^{hfs}_{l+,m_I-1} - E^{hfs}_{l-,m_I-1})]/g_{(l)}\mu, \tag{40}$$

From Eqs.(30),(31),(32),(37) and (38), $\Delta H^l_{m_I}$ is

$$\Delta H^l_{m_I} = \{A^l_{eff} + [(R^l_+ - R^l_-) + (\Delta R^l_+ - \Delta R^l_-)] - \frac{4(m_I - \frac{1}{2})}{g^0_l \mu H^l_0}[\mid \eta^l_+ \mid^2 + \mid \eta^l_- \mid^2 - \mid \eta^l_z \mid^2]\} / g_{(l)}\mu \tag{41}$$

where $A^l_{eff} = [A^2_z g^4_{zl} \cos^2\theta + (A^2_x g^4_{xl} \cos^2\phi + A^2_y g^4_{yl} \sin^2\phi) \sin^2\theta]^{1/2} / 2g^0_l$, (42)

$$(R^l_+ - R^l_-) = 4\delta(A_z P^l_z \cos^2\theta + A_x P^l_x \cos^2\phi \sin^2\theta + A_y P^l_y \sin^2\phi \sin^2\theta)/g^0_l, \tag{43}$$

$$(\Delta R^l_+ - \Delta R^l_-) = 4\delta[(Q^l_x \cos^2\phi + Q^l_y \sin^2\phi) F_l(\theta,\phi) \sin\theta\cos\theta - (g^0_l)^2 C_l f_l(\theta,\phi) \sin^2\theta \sin 2\phi] / [g^0_l]^3, \tag{44}$$

$$(\mid \eta^l_+ \mid^2 + \mid \eta^l_- \mid^2 - \mid \eta^l_z \mid^2) = \{g^2_{zl}[(A_z g^2_{\perp l} \sin^2\theta + A_x g^2_{xl} \cos^2\phi \cos^2\theta + A_y g^2_{yl} \sin^2\phi \cos^2\theta)^2$$

$$+ (A_x g^2_{xl} - A_y g^2_{yl})^2 \sin^2\phi \cos^2\phi \cos^2\theta] + (g^0_l)^2 g^2_{xl} g^2_{yl} (A^2_x \sin^2\phi + A^2_y \cos^2\phi)$$

$$- g^4_{\perp l}[3(g^0_l)^2 f_l(\theta,\phi)^2 + 2g^2_{zl} F_l(\theta,\phi)^2]\} / 32(g^0_l)^2 g^2_{\perp l}, \tag{45}$$

$Q^l_j = (P^l_z g^2_{jl} - P^l_j g^2_{zl})$ $(j=x,y)$,

$C_l = (<l\beta \mid S_- \mid l\alpha> \sigma^l_+ - <l\beta \mid S_+ \mid l\alpha> \sigma^l_-)(<l\beta \mid S_+ \mid l\alpha>^2 - <l\beta \mid S_- \mid l\alpha>^2)/4$ (46)

$$F_l(\theta,\phi) = [(A_z - A_x) g^2_{xl} \cos^2\phi + (A_z - A_y) g^2_{yl} \sin^2\phi] \sin 2\theta / 2g^2_{\perp l}, \tag{47}$$

and $$f_l(\theta,\phi)=(A_x-A_y)\sin\theta\sin2\phi\cdot 2(<l\beta|S_+|l\alpha>^2-<l\beta|S_-|l\alpha>^2)/g_{1l}^2. \quad (48)$$

Numerical values for C_l are given in Table 4.

$F_l(\theta,\phi)$ and $f_l(\theta,\phi)$ vanish when $A_x=A_y=A_z$ or a direction of a constant magnetic field coincides with a principal axis of a crystal field.

5.2 Special cases

Equation (41) has very complicated form, so we consider several special cases. We express A_α as $g_0\mu\Delta H_\alpha(\alpha=x,y,z)$ in the followings.

a) When a direction of an applied constant magnetic field coincides with a direction of a principal axis (α) of a crystal field,

$$\Delta H^l_{m_I(\alpha)}=\Delta H_\alpha-\frac{(m_I-\frac{1}{2})}{(1+\frac{\Delta g_{\alpha l}}{g_{\alpha l}})}\cdot\frac{[\Delta H_\beta^2(g_{\beta l})^2+\Delta H_\gamma^2(g_{\gamma l})^2]}{2(g_{\alpha l})^2} \quad (\alpha,\beta,\gamma=x,y,z)\ (\beta,\gamma\neq\alpha). \quad (49)$$

b) When $g_x=g_y=g_z=g_0^0=30/7$,

$$\Delta H^0_{m_I}=\{A^0_{eff}+[(R^0_+-R^0_-)+(\Delta R^0_+-\Delta R^0_-)] -\frac{4(m_I-\frac{1}{2})}{g_0^0\mu H_0^0}[|\eta^0_+|^2+|\eta^0_-|^2-|\eta^0_z|^2]\}/g_{(r)}\mu, \quad (50)$$

where $$A^0_{eff}=g_0^0[A_z^2\cos^2\theta+(A_x^2\cos^2\phi+A_y^2\sin^2\phi)\sin^2\theta]^{1/2}/2, \quad (51)$$

$$(R^0_+-R^0_-)=4\delta P^0_y(-A_z\cos^2\theta+A_y\sin^2\phi\sin^2\theta)/g_0^0, \quad (52)$$

$$(\Delta R^0_+-\Delta R^0_-)=-4\delta[P^0_y(1+\sin^2\phi)F_0(\theta,\phi)\sin\theta\cos\theta+C_0f_0(\theta,\phi)\sin^2\theta\sin2\phi]/g_0^0, \quad (53)$$

$$(|\eta^0_+|^2+|\eta^0_-|^2-|\eta^0_z|^2)=(g_0^0)^2[(A_z\sin^2\theta+A_x\cos^2\phi\cos^2\theta+A_y\sin^2\phi\cos^2\theta)^2 +(A_x^2\sin^2\phi+A_y^2\cos^2\phi)+(A_x-A_y)^2\sin^2\phi\cos^2\phi\cos^2\theta-(3f_0(\theta,\phi)^2+2F_0(\theta,\phi)^2)]/32, \quad (54)$$

$$F_0(\theta,\phi)=[A_z-A_x\cos^2\phi-A_y\sin^2\phi]\sin2\theta/2, \quad (55)$$

and $$f_0(\theta,\phi)=(A_x-A_y)\sin\theta\sin2\phi/2. \quad (56)$$

c) When $A_x=A_y=A_z=g_0\mu\Delta H_h$ (an isotropic hyperfine interaction),

$$\Delta H_{m_I}=\Delta H_h(1+\frac{\zeta_l(\theta,\phi)}{1+\frac{\Delta g_l}{g_l^0}})-\frac{(m_I-\frac{1}{2})\Delta H_h^2}{(1+\frac{\Delta g_l}{g_l^0})H_0^l}\cdot\frac{16P_l(\theta,\phi)}{(g_l^0)^2}. \quad (57)$$

Here $\zeta_l(\theta,\phi)=[G_l(\theta,\phi)-(g_l^0)^2]/(g_l^0)^2$, where $G_l(\theta,\phi)=[g_{zl}^4\cos^2\theta+(g_{xl}^4\cos^2\phi+g_{yl}^4\sin^2\phi)\sin^2\theta]^{1/2}$.

$\zeta_l(\theta,\phi)$ vanishes when a direction of an applied constant magnetic field coincides with a principal axis of a crystal field or g-factor is istropic ($l=0$). The appearance of a correction term $\zeta_l(\theta,\phi)$ in Eq.(57) is caused by the anisotropy of g-tensor.

d) When $A_x=A_y=A_z=g_0\mu\Delta H_h$ and $g_x=g_y=g_z=30/7$, from Eq.(57),

$$\Delta H^0_{m_I}=\Delta H_h-(m_I-\frac{1}{2})(\Delta H_h^2/H_0^0). \quad (58)$$

Here $\Delta g_0/g_0^0$ is neglected in Eq.(57), because a solid angle average of Δg_0 is 0. Equation (58) agrees with the wellknown formula for a free ion. This result means that a slight deviation of λ from 1/3 has no influence on a hyperfine splitting. From Eq.(50), a slight anisotropy of hyperfine structure constants is found to give a line width of the signal with $g=4.29$, even if g-tensor is isotropic and λ is 1/3.

6. Conclusion

Being used the eigenvalues and the eigenfunctions of the spin Hamiltonian $D[(S_z^2-\frac{1}{3}\boldsymbol{S}^2)+\frac{1}{3}(S_x^2-S_y^2)]$ for $S=5/2$, $(\lambda-\frac{1}{3})D(S_x^2-S_y^2)$ and $g_0\mu\boldsymbol{S}\cdot\boldsymbol{H}$ are treated as perturbations to it for an arbitrary direction of an applied constant magnetic field. Further an anisotropic hyperfine interaction is treated as a perturbation to $(\lambda-\frac{1}{3})D(S_x^2-S_y^2)$ and $g_0\mu\boldsymbol{S}\cdot\boldsymbol{H}$.

From these calculations, the following results are obtained.

(1) The effective g-factor of the ESR signal due to a transition in the middle Kramers doublet is 4.29 for $\lambda=1/3$ and the angular average of it varies little with a small deviation from $\lambda=1/3$. The first order deviation from $\lambda=1/3$ has an influence on only the line width for amorphous materials.

(2) The transition probability in the middle Kramers doublet is calculated. Being used this, a concentration of the ESR center can be evaluated.

(3) A hyperfine splitting of the signal with $g=4.29$ is given by the same formula as wellknown formula for a free ion, if the hyperfine interaction is isotropic.

Finally we should notice that the results obtained in the present article for $S=5/2$, that is, Eqs.(6), (15) and (25), can be used for more general values, $S=N-\frac{1}{2}$ $(N=2,4,5\cdots)$. A proof of this generalization is given in Appendix B.

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Appendix A. Tables of the matrix elements of $S_z, S_\pm$ and V

• Table A1 (The matrix elements of $V/\delta D=(S_+^2+S_-^2)/2$)

	$\vert +\alpha\rangle$	$\vert 0\alpha\rangle$	$\vert -\alpha\rangle$
$\langle +\alpha \vert$	$(7\sqrt{7}-10)/7$	$9\sqrt{5}/7\sqrt{2}$	18/7
$\langle 0\alpha \vert$	$9\sqrt{5}/7\sqrt{2}$	20/7	$9\sqrt{5}/7\sqrt{2}$
$\langle -\alpha \vert$	18/7	$9\sqrt{5}/7\sqrt{2}$	$-(7\sqrt{7}+10)/7$

The other matrix elements $\langle m\beta \vert V \vert n\beta\rangle$ and $\langle m\beta \vert V \vert n\alpha\rangle$ can be obtained using Eq.(9).

• Table A2 (The matrix elements of S_z)

	$\mid +\alpha$	$\mid 0\alpha>$	$\mid -\alpha>$
$<+\alpha\mid$	$(9+3\sqrt{7})/7$	$-\sqrt{10}(\sqrt{7}-1)/14$	$-3/14$
$<0\alpha\mid$	$-\sqrt{10}(\sqrt{7}-1)/14$	$-15/14$	$\sqrt{10}(\sqrt{7}+1)/14$
$<-\alpha\mid$	$-3/14$	$\sqrt{10}(\sqrt{7}+1)/14$	$(9-3\sqrt{7})/7$

The other matrix elements $<m\beta\mid S_z\mid n\beta>$ and $<m\beta\mid S_z\mid n\alpha>$ can be obtained using the following relations;
$<m\alpha\mid S_z\mid n\alpha> =-<m\beta\mid S_z\mid n\beta>$,
$<m\alpha\mid S_z\mid n\beta> =<m\beta\mid S_z\mid n\alpha>=0$.

• Table A3 (the matrix elements of S_+)

	$\mid +\alpha>$	$\mid +\beta>$	$\mid 0\alpha>$	$\mid 0\beta>$	$\mid -\alpha>$	$\mid -\beta>$
$<+\alpha\mid$	0	$(21-6\sqrt{7})/14$	0	$\sqrt{10}(7+\sqrt{7})/14$	0	$-1/2$
$<+\beta\mid$	$(6\sqrt{7}-15)/14$	0	$\sqrt{10}(5-\sqrt{7})/14$	0	$-1/14$	0
$<0\alpha\mid$	0	$\sqrt{10}(7+\sqrt{7})/14$	0	0	0	$\sqrt{10}(7-\sqrt{7})/14$
$<0\beta\mid$	$\sqrt{10}(5-\sqrt{7})/14$	0	15/7	0	$\sqrt{10}(5+\sqrt{7})/14$	0
$<-\alpha\mid$	0	$-1/2$	0	$\sqrt{10}(7-\sqrt{7})/14$	0	$(21+6\sqrt{7})/14$
$<-\beta\mid$	$-1/14$	0	$\sqrt{10}(5+\sqrt{7})/14$	0	$-(6\sqrt{7}+15)/14$	0

The matrix of S_- is given by the transpose of the matrix of S_+. (a proof is given in Appendix B.)

Appendix B. A proof of the generalization to the case $2S+1=2N$ ($N=2,3,4\cdots$)

In order to show that the general form for $S=5/2$ obtained in the present article can be used for the general case of $S=N-\frac{1}{2}$ ($N=2,4,\cdots$), it is sufficient only to prove that Eqs.(9) and (10) hold for the general case, that is, $S=N-\frac{1}{2}$ ($N=2,3,4,\cdots$), provided that we can calculate eigenvales of $\mathcal{H}_0$. We can easily calculate the eigenvales of $\mathcal{H}_0$ for $S=3/2$ and $7/2$, and they are $\pm 2D/\sqrt{3}$ and $\pm 2D\sqrt{21\pm 4\sqrt{21}}/\sqrt{3}$, respectively.

Denote eigenfunctions of $\mathcal{H}_0$ corresponding to Eq.(4) as follows.

$$\mid m\alpha> =C_{1m}\mid S>+C_{2m}\mid S-2>+\cdots\cdots+C_{(N-1)m}\mid -S+3>+C_{Nm}\mid -S+1> \quad \text{(A.1)}$$

$$\mid m\beta> =C_{1m}\mid -S>+C_{2m}\mid -S+2>+\cdots+C_{(N-1)m}\mid S-3>+C_{Nm}\mid S-1>$$

1) Clearly, $<n\beta\mid S_z\mid m\alpha>=0, <m\alpha\mid S_z\mid n\alpha>=<n\alpha\mid S_z\mid m\alpha>=-<m\beta\mid S_z\mid n\beta>$
$=-<n\beta\mid S_z\mid m\beta>$. (A.2)

2) We denote $<m_s+1\mid S_+\mid m_s>=[(S-m_s)(S+m_s+1)]^{1/2}$ as $d(m_s)$. Then we have $<m_s-1\mid S_-\mid m_s>=d(-m_s)$ and $d(-m_s-1)=d(m_s)$. Using those relations, we can show

$$<n\beta\mid S_+\mid m\alpha>=<m\beta\mid S_+\mid n\alpha>=<n\alpha\mid S_-\mid m\beta>=<m\alpha\mid S_-\mid n\beta>, \quad \text{(A.3)}$$

and

$$<n\alpha\mid S_+\mid m\beta>=<m\alpha\mid S_+\mid n\beta>=<n\beta\mid S_-\mid m\alpha>=<m\beta\mid S_-\mid n\alpha> \quad \text{(A.4)}$$

3) Clearly, $<n\beta|(S_+^2+S_-^2)|m\alpha>=0$. We denote $<m_s+2|S_+^2|m_s>$ and $<m_s-2|S_-^2|m_s>$ as $f_+(m_s)$ and $f_-(m_s)$ respectively. Then we have $f_+(m_s)=d(m_s)d(m_s+1)$, $f_-(m_s)=d(-m_s)d(-m_s+1)$ and $f_-(m_s+2)=f_+(m_s)$. Using these relations, we can show

$$<n\alpha|(S_+^2+S_-^2)|m\alpha>=<m\alpha|(S_+^2+S_-^2)|n\alpha>=<n\beta|(S_+^2+S_-^2)|m\beta>=<m\beta|(S_+^2+S_-^2)|n\beta>. \quad (A.5)$$

We can easily show that Eqs.(9) and (10) hold for the general case, that is, $S=N-\frac{1}{2}$ ($N=2,3,4,\cdot\cdot\cdot$), using Eqs.(A.2), (A.3), (A.4) and (A.5). Thus we can make the similar tables as Tables A1, A2, A3, 1, 2 and 3 for $S=N-\frac{1}{2}$ ($N=2,4,\cdot\cdot\cdot\cdot$).

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Table 1. g_{il}

$l \backslash i$	x	y	z
+	$6/7 \simeq 0.86$	$12(3-\sqrt{7})/7 \simeq 0.61$	$12(3+\sqrt{7})/7$
0	$30/7 \simeq 4.29$	$30/7$	$30/7$
−	$6/7$	$12(3+\sqrt{7})/7 \simeq 9.68$	$12(3-\sqrt{7})/7$

Table 2. P_i^l

$l \backslash j$	x	y	z
+	$1053/686\sqrt{7} \simeq 0.58$	$-81(29-13\sqrt{7})/686\sqrt{7} \simeq 0.24$	$-81(29+13\sqrt{7})/686\sqrt{7} \simeq -2.83$
0	0	$2025/686 \simeq 2.95$	$-2025/686 \simeq -2.95$
−	$-1053/686\sqrt{7} \simeq -0.58$	$81(29+13\sqrt{7})/686\sqrt{7} \simeq 2.83$	$81(29-13\sqrt{7})/686\sqrt{7} \simeq -0.24$

Table 3. σ_k^l

$l \backslash k$	z	+	−
+	$-27(5\sqrt{7}-2)/392\sqrt{7}$	$27(24-5\sqrt{7})/392\sqrt{7}$	$27(28+5\sqrt{7})/392\sqrt{7}$
0	$135/196$	$135/196$	$-135/196$
−	$-27(5\sqrt{7}+2)/392\sqrt{7}$	$-27(24+5\sqrt{7})/392\sqrt{7}$	$-27(28-5\sqrt{7})/392\sqrt{7}$

Table 4. C_l

l	+	0	−
C_l	$\frac{81(154-57\sqrt{7})}{2744\sqrt{7}} \simeq 0.036$	$\frac{2025}{1372} \simeq 1.48$	$-\frac{81(154+57\sqrt{7})}{2744\sqrt{7}} \simeq -3.40$

Note added in proof:

Eguation (36) was found not to hold when either of the hyperfine interaction or the effective g-tensor is anisotropic. Accordingly, Eqs. (49)-(57) do not hold.