Tutorial theory 8th EFEPR-school

1 a. $S_-^{\dagger} = (S_x - i S_y)^{\dagger} = S_x^{\dagger} + i S_y^{\dagger} = S_x + i S_y = S_+$

(S_x and S_y Hermitian operators.)

b. $[S_z, S_+] = [S_z, S_x + i S_y]$
$= [S_z, S_x] + i[S_z, S_y] = i S_y + i(-S_x)$
$= S_x + i S_y = S_+$

c. $S_z \{S_+ |s\, m_s\rangle\} \underset{(b)}{=} (S_+ S_z + S_+)|s\, m_s\rangle = S_+ (S_z + 1)|s\, m_s\rangle$
$= S_+ (m_s + 1)|s\, m_s\rangle = (m_s+1)\{S_+ |s\, m_s\rangle\}$

$\rightarrow$ $\{S_+|s\,m_s\rangle\}$ is an eigenstate of S_z with eigenvalue (m_s+1)

$\rightarrow$ $\{S_+|s\,m_s\rangle\}$ must be proportional to $|s\; m_s+1\rangle$, which means that we can write $S_+|s\,m_s\rangle = \lambda_+ |s\; m_s+1\rangle$

d. $S_- S_+ = (S_x - i S_y)(S_x + i S_y) = S_x^2 + S_y^2 + i(S_x S_y - S_y S_x)$

$= S^2 - S_z^2 + i[S_x, S_y] = S^2 - S_z^2 - S_z.$

e. $\langle s\, m_s | S_- S_+ | s\, m_s\rangle = \langle S_-^{\dagger}\, s\, m_s | S_+ | s\, m_s\rangle$
$\underset{(a)}{=} \langle S_+\, s\, m_s | S_+ | s\, m_s\rangle \underset{(c)}{=} \lambda_+^* \lambda_+ \langle s\; m_s+1 | s\; m_s+1\rangle = |\lambda_+|^2$

$\langle s\, m_s | S_- S_+ | s\, m_s\rangle \underset{(d)}{=} \langle s\, m_s | S^2 - S_z^2 - S_z | s\, m_s\rangle$
$= [s(s+1) - m_s^2 - m_s]\langle s\, m_s | s\, m_s\rangle = [s(s+1) - m_s(m_s+1)]$ $\Rightarrow$

$\lambda^+ = \sqrt{s(s+1) - m_s(m_s+1)}\,.$

2 a. $\left.\begin{array}{l} s_1 = \frac{1}{2} \\ s_2 = \frac{1}{2} \end{array}\right\} \mathcal{S} = 1, 0$ (values of total spin quantum number according to Clebsch-Gordan)

$\rightarrow$ eigenstates $|1\ 1\rangle \quad |1\ 0\rangle \quad |1\ {-1}\rangle \quad |0\ 0\rangle$

b. individual spins 1 and 2:
eigenstates spin 1: $|\tfrac{1}{2}\ \tfrac{1}{2}\rangle_1 \equiv |\alpha_1\rangle \quad |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle_1 \equiv |\beta_1\rangle$
eigenstates spin 2: $|\tfrac{1}{2}\ \tfrac{1}{2}\rangle_2 \equiv |\alpha_2\rangle \quad |\tfrac{1}{2}\ {-\tfrac{1}{2}}\rangle_2 \equiv |\beta_2\rangle$

$$\mathcal{S}_z |\alpha_1\rangle|\alpha_2\rangle = (s_{1z} + s_{2z})|\alpha_1\rangle|\alpha_2\rangle$$
$$= s_{1z}|\alpha_1\rangle|\alpha_2\rangle + s_{2z}|\alpha_1\rangle|\alpha_2\rangle = \tfrac{1}{2}|\alpha_1\rangle|\alpha_2\rangle + \tfrac{1}{2}|\alpha_1\rangle|\alpha_2\rangle$$
$$= |\alpha_1\rangle|\alpha_2\rangle$$

So $|\alpha_1\rangle|\alpha_2\rangle$ is an eigenstate of $\mathcal{S}_z$ with eigenvalue 1,

i.e. $|1\ 1\rangle$: $\boxed{|1\ 1\rangle = |\alpha_1\rangle|\alpha_2\rangle}$

Equivalently: $\boxed{|1\ {-1}\rangle = |\beta_1\rangle|\beta_2\rangle}$

$\mathcal{S}_z|\alpha_1\rangle|\beta_2\rangle = \mathcal{S}_z|\beta_1\rangle|\alpha_2\rangle = 0$. In order to find the expressions for $|1\ 0\rangle$ and $|0\ 0\rangle$, we have to consider $\mathcal{S}^2$.

$$\mathcal{S}^2 = (s_1 + s_2)^2 = s_1^2 + s_2^2 + 2\, s_1 . s_2$$
$$s_1 . s_2 = s_{1x}s_{2x} + s_{1y}s_{2y} + s_{1z}s_{2z}$$

$$\left.\begin{array}{l} s_x = \dfrac{s_+ + s_-}{2} \\[2ex] s_y = \dfrac{s_+ - s_-}{2i} \end{array}\right\} \quad \begin{array}{l} s_{1x}s_{2x} = \frac{1}{4}(s_{1+} + s_{1-})(s_{2+} + s_{2-}) \\ s_{1y}s_{2y} = -\frac{1}{4}(s_{1+} - s_{1-})(s_{2+} - s_{2-}) \\ \hline s_{1x}s_{2x} + s_{1y}s_{2y} = \frac{1}{2}(s_{1+}s_{2-} + s_{1-}s_{2+}) \end{array}$$

$$S'^2 |\alpha_1\rangle|\beta_2\rangle = \tfrac{3}{4}|\alpha_1\rangle|\beta_2\rangle + \tfrac{3}{4}|\alpha_1\rangle|\beta_2\rangle + (s_{1+}s_{2-} + s_{1-}s_{2+})|\alpha_1\rangle|\beta_2\rangle$$
$$+ 2 s_{1z}s_{2z}|\alpha_1\rangle|\beta_2\rangle = \tfrac{3}{2}|\alpha_1\rangle|\beta_2\rangle + s_{1-}s_{2+}|\alpha_1\rangle|\beta_2\rangle - \tfrac{1}{2}|\alpha_1\rangle|\beta_2\rangle$$
$$= |\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle$$

Equivalently: $S'^2|\beta_1\rangle|\alpha_2\rangle = |\alpha_1\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle$

Consider $|\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle$

$$S'^2\left\{|\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle\right\} = 2\left\{|\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle\right\}$$

$\rightarrow$ $\{|\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle\}$ eigenstate of S'^2 with eigenvalue 2 $[=1(1+1)]$

$\rightarrow$ after normalization: $\boxed{|1\ 0\rangle = \frac{1}{\sqrt{2}}\left\{|\alpha_1\rangle|\beta_2\rangle + |\beta_1\rangle|\alpha_2\rangle\right\}}$

Consider $|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle$

$$S'^2\left\{|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle\right\} = 0$$

$\rightarrow$ $\{|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle\}$ eigenstate of S'^2 with eigenvalue 0 $[=0(0+1)]$

$\rightarrow$ after normalization: $\boxed{|0\ 0\rangle = \frac{1}{\sqrt{2}}\left\{|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle\right\}}$

c. Weak coupling $|J| \ll (|g_1 - g_2|)\beta_e B$

Start from the basis of eigenstates of s_1^2, s_{1z}, s_2^2 and s_{2z}:

$|\alpha_1\rangle|\alpha_2\rangle \qquad |\alpha_1\rangle|\beta_2\rangle \qquad |\beta_1\rangle|\alpha_2\rangle \qquad |\beta_1\rangle|\beta_2\rangle$

In this basis the matrix representation of H becomes:

	$\|\alpha_1\rangle\|\alpha_2\rangle$	$\|\alpha_1\rangle\|\beta_2\rangle$	$\|\beta_1\rangle\|\alpha_2\rangle$	$\|\beta_1\rangle\|\beta_2\rangle$
$\langle\alpha_1\|\langle\alpha_2\|$	$\frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$	0	0	0
$\langle\alpha_1\|\langle\beta_2\|$	0	$\frac{1}{2}\beta_e B(g_1-g_2)-\frac{1}{4}J$	$\frac{1}{2}J$	0
$\langle\beta_1\|\langle\alpha_2\|$	0	$\frac{1}{2}J$	$-\frac{1}{2}\beta_e B(g_1-g_2)-\frac{1}{4}J$	0
$\langle\beta_1\|\langle\beta_2\|$	0	0	0	$-\frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$

The energies follow after diagonalization of the central 2×2 matrix:

$$\varepsilon_1 = \frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$$

$$\varepsilon_2 \approx \frac{1}{2}\beta_e B(g_1-g_2)-\frac{1}{4}J$$

$$\varepsilon_3 \approx -\frac{1}{2}\beta_e B(g_1-g_2)-\frac{1}{4}J$$

$$\varepsilon_4 = -\frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$$

Strong coupling $|J| \gg (|g_1-g_2|)\beta_e B$.

Start from the basis of eigenstates of S^2 and S_z:
$|1\,1\rangle \quad |1\,0\rangle \quad |1\,-1\rangle \quad |0\,0\rangle$

In this basis the matrix representation of H becomes:

	$\vert 1\,1\rangle$	$\vert 1\,0\rangle$	$\vert 0\,0\rangle$	$\vert 1\,{-1}\rangle$
$\langle 1\,1\vert$	$\frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$	0	0	0
$\langle 1\,0\vert$	0	$\frac{1}{4}J$	$\frac{1}{2}\beta_e B(g_1-g_2)$	0
$\langle 0\,0\vert$	0	$\frac{1}{2}\beta_e B(g_1-g_2)$	$-\frac{3}{4}J$	0
$\langle 1\,{-1}\vert$	0	0	0	$-\frac{1}{2}\beta_e B(g_1+g_2)+\frac{1}{4}J$

The energies follow after diagonalization of the central $2*2$ matrix:

$$\varepsilon_1 = \frac{1}{2}\beta_e B\,(g_1+g_2) + \frac{1}{4}J$$

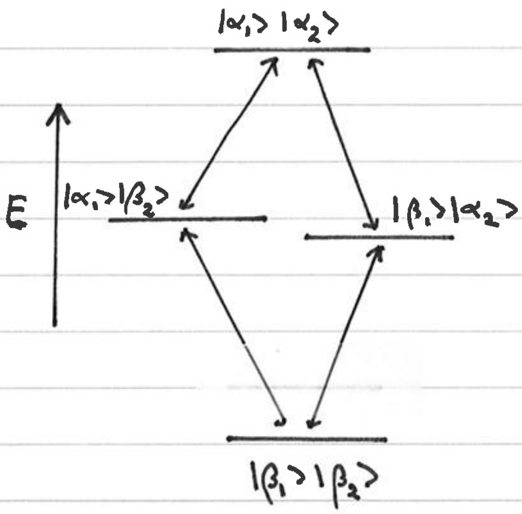
$$\varepsilon_2 \approx \frac{1}{4}J$$

$$\varepsilon_3 \approx -\frac{3}{4}J$$

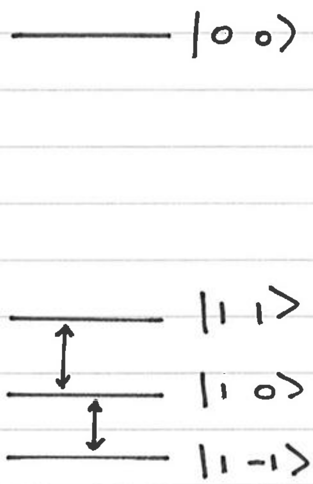
$$\varepsilon_4 = -\frac{1}{2}\beta_e B\,(g_1+g_2) + \frac{1}{4}J$$

d. For $J<0$ and $g_1 \approx g_2$

weak coupling



strong coupling



3 a. Make use of the Pauli matrices.

$$s_x s_y = \frac{1}{4}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0&-i\\i&0\end{pmatrix} = \frac{i}{4}\begin{pmatrix}1&0\\0&-1\end{pmatrix} = \frac{i}{2}s_z \quad \text{(and cyclic)}$$

$$s_x^2 = \frac{1}{4}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}0&1\\1&0\end{pmatrix} = \frac{1}{4}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \frac{1}{4}\mathbb{1}$$

b. $$S_j^2 = (s_{1j}+s_{2j})^2 = s_{1j}^2 + s_{2j}^2 + 2s_{1j}s_{2j} \underset{(a)}{=} \frac{1}{2}\mathbb{1} + 2s_{1j}s_{2j}$$

$$S_j S_k = (s_{1j}+s_{2j})(s_{1k}+s_{2k}) = s_{1j}s_{1k} + s_{1j}s_{2k} + s_{1k}s_{2j} + s_{2j}s_{2k}$$

$$S_k S_j = s_{1k}s_{1j} + s_{1j}s_{2k} + s_{1k}s_{2j} + s_{2k}s_{2j} \underset{(a)}{=} -s_{1j}s_{1k} + s_{1j}s_{2k} + s_{1k}s_{2j} - s_{2j}s_{2k}$$

$$S_j S_k + S_k S_j = 2(s_{1j}s_{2k} + s_{1k}s_{2j})$$

c. $$H \sim \left\{\frac{s_1\cdot s_2}{r^3} - \frac{3(s_1\cdot r)(s_2\cdot r)}{r^5}\right\}$$

$$= \left\{s_{1x}s_{2x}\left(\frac{r^2-3x^2}{r^5}\right) + \cdots + \cdots - (s_{1x}s_{2y}+s_{1y}s_{2x})\frac{3xy}{r^5} + \cdots + \cdots\right\}$$

$$\underset{(b)}{=} \left\{\left(\frac{1}{2}S_x^2 - \frac{1}{4}\mathbb{1}\right)\left(\frac{r^2-3x^2}{r^5}\right) + \cdots + \cdots - \frac{1}{2}(S_xS_y+S_yS_x)\frac{3xy}{r^5} + \cdots + \cdots\right\}$$

$$= \frac{1}{2}\left\{S_x^2\left(\frac{r^2-3x^2}{r^5}\right) + \cdots + \cdots - (S_xS_y+S_yS_x)\frac{3xy}{r^5} + \cdots + \cdots\right\}$$

$$H_{zfs} = \tilde{S} D S$$

$$\longrightarrow D_{xx} = \frac{1}{2}\frac{\mu_0}{4\pi} g^2 \beta_e^2 \left\langle \frac{r^2-3x^2}{r^5}\right\rangle \quad \text{etc.}$$

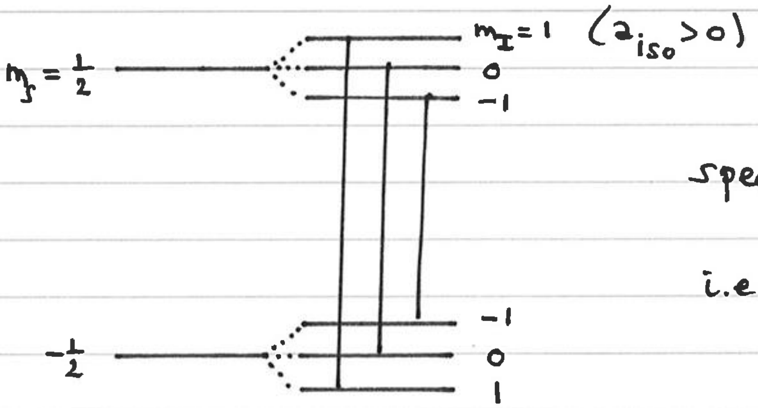
$\langle \cdots \rangle$ refers to the average over the spatial part of the electronic wave function.

$[\vec{r} = \vec{r}_1 - \vec{r}_2 \ ; \ x = x_1 - x_2]$

4 a. 9.5 GHz spectrum for solution at room temperature.
MTSL free tumbling : g and A anisotropy average out.

For $\vec{B} = (0, 0, B_0)$: $H = \beta_e g S_z B_0 + a_{iso} S_z I_z$

Hyperfine derives from ^{14}N: $I = 1 \rightarrow m_I = 1, 0, -1$



spectrum $\rightarrow a_{iso} \sim 1.6$ mT

i.e. $\frac{1}{3}(A_{xx} + A_{yy} + A_{zz}) = 1.6$ mT

275 GHz spectrum for frozen sample
spectrum shows g and A anisotropy : g_{xx} g_{yy} g_{zz} A_{zz}
(A_{xx} and A_{yy} not resolved)
the spectrum is dominated by the g anisotropy at this high magnetic field.

spectrum $\rightarrow A_{zz} \sim 3.6$ mT
$\rightarrow A_{xx} + A_{yy} \sim 1.2$ mT

b. 9.5 GHz spectrum : extra lines from hyperfine interaction with ^{13}C : $I = \frac{1}{2}$ (natural abundance 1.1 %)
275 GHz spectrum : extra lines from Mn^{2+} impurity $S = \frac{5}{2}$, $I = \frac{5}{2}$
$m_S = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition split into 6 lines of which 3 are visible.

c. guess spin Hamiltonian parameters and use garlic (9.5 GHz, isotropic) and pepper (275 GHz, rigid limit).

d. use chili for the slow-motion regime (note the difference at the two microwave frequencies.).

5 High spin Co(II) : $S = \frac{3}{2}$

Let us refer to the basis states as $|m_s\rangle$: $|\frac{3}{2}\rangle, |\frac{1}{2}\rangle, |-\frac{1}{2}\rangle, |-\frac{3}{2}\rangle$

$$H_{zfs} = \tilde{S} D S = D_x S_x^2 + D_y S_y^2 + D_z S_z^2$$ (x, y, z principal axes system of D tensor)

a. In order to determine the matrix representation of H_{zfs} in the basis $|m_s\rangle$, we have to calculate $S_j^2 |m_s\rangle$ for $j = x, y, z$ and $m_s = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

For example :

$$\left.\begin{array}{l} S_+ |\tfrac{3}{2}\rangle = 0,\ S_- |\tfrac{3}{2}\rangle = \sqrt{3}\, |\tfrac{1}{2}\rangle \rightarrow S_x |\tfrac{3}{2}\rangle = \tfrac{1}{2}(S_+ + S_-)|\tfrac{3}{2}\rangle = \tfrac{1}{2}\sqrt{3}\, |\tfrac{1}{2}\rangle \\ S_+ |\tfrac{1}{2}\rangle = \sqrt{3}\, |\tfrac{3}{2}\rangle,\ S_- |\tfrac{1}{2}\rangle = 2\, |-\tfrac{1}{2}\rangle \rightarrow S_x |\tfrac{1}{2}\rangle = \tfrac{1}{2}\sqrt{3}\, |\tfrac{3}{2}\rangle + |-\tfrac{1}{2}\rangle \end{array}\right\}$$

$$\rightarrow S_x^2 |\tfrac{3}{2}\rangle = \tfrac{3}{4} |\tfrac{3}{2}\rangle + \tfrac{1}{2}\sqrt{3}\, |-\tfrac{1}{2}\rangle$$

etc. → matrix representation

$$\begin{array}{c|cccc} & |\frac{3}{2}\rangle & |-\frac{1}{2}\rangle & |\frac{1}{2}\rangle & |-\frac{3}{2}\rangle \\ \hline \langle\frac{3}{2}| & \frac{3}{4}D_x + \frac{3}{4}D_y + \frac{9}{4}D_z & \frac{1}{2}\sqrt{3}(D_x - D_y) & 0 & 0 \\ \langle-\frac{1}{2}| & \frac{1}{2}\sqrt{3}(D_x - D_y) & \frac{7}{4}D_x + \frac{7}{4}D_y + \frac{1}{4}D_z & 0 & 0 \\ \langle\frac{1}{2}| & 0 & 0 & \frac{7}{4}D_x + \frac{7}{4}D_y + \frac{1}{4}D_z & \frac{1}{2}\sqrt{3}(D_x - D_y) \\ \langle-\frac{3}{2}| & 0 & 0 & \frac{1}{2}\sqrt{3}(D_x - D_y) & \frac{3}{4}D_x + \frac{3}{4}D_y + \frac{9}{4}D_z \end{array}$$

Trace = $\frac{20}{4}(D_x + D_y + D_z)$

b To make the matrix traceless, subtract $(\frac{1}{4}\mathrm{Tr})\,1$

The two 2x2 matrices to be diagonalized become

$$\begin{pmatrix} -\frac{1}{2}D_x - \frac{1}{2}D_y + D_z & \frac{1}{2}\sqrt{3}(D_x - D_y) \\ \frac{1}{2}\sqrt{3}(D_x - D_y) & \frac{1}{2}D_x + \frac{1}{2}D_y - D_z \end{pmatrix}$$

$\frac{1}{2}(D_x - D_y) \equiv E$

$\mathrm{Tr}\, D = D_x + D_y + D_z = 0 \longrightarrow D_z - \frac{1}{2}(D_x + D_y) = \frac{3}{2} D_z \equiv D$

$$\begin{pmatrix} D & \sqrt{3}E \\ \sqrt{3}E & -D \end{pmatrix} \quad \text{diagonalization} \longrightarrow \ \mathcal{E} = \pm\sqrt{D^2 + 3E^2}$$

the same for the $|\frac{3}{2}\rangle / |-\frac{1}{2}\rangle$ and the $|\frac{1}{2}\rangle / |-\frac{3}{2}\rangle$ combinations.

Eigenstates:

e.g. $|\chi\rangle \equiv \cos\Theta\, |\frac{3}{2}\rangle + \sin\Theta\, |-\frac{1}{2}\rangle$

$(D - \mathcal{E})\cos\Theta + \sqrt{3}E\sin\Theta = 0$

$\mathrm{tg}\,\Theta = (\mathcal{E} - D)/\sqrt{3}E \longrightarrow \mathrm{tg}\, 2\Theta = \frac{\sqrt{3}E}{D}$

$\mathcal{E}_1 = \sqrt{D^2 + 3E^2}\ ; \quad |1\rangle = \cos\Theta\, |\frac{3}{2}\rangle + \sin\Theta\, |-\frac{1}{2}\rangle$

$\mathcal{E}_2 = -\sqrt{D^2 + 3E^2}\ ; \quad |2\rangle = \cos\Theta\, |-\frac{1}{2}\rangle - \sin\Theta\, |\frac{3}{2}\rangle$

$\mathcal{E}_3 = \sqrt{D^2 + 3E^2}\ ; \quad |3\rangle = \cos\Theta\, |-\frac{3}{2}\rangle + \sin\Theta\, |\frac{1}{2}\rangle$

$\mathcal{E}_4 = -\sqrt{D^2 + 3E^2}\ ; \quad |4\rangle = \cos\Theta\, |\frac{1}{2}\rangle - \sin\Theta\, |-\frac{3}{2}\rangle$

c For $D<0$ lower doublet $|1\rangle, |3\rangle$.

$H_{eZ} = \beta_e \tilde{S} g B_0 = \beta_e |B_0| (S_x' g_x n_x + S_y' g_y n_y + S_z' g_z n_z)$

with $\vec{n} = (n_x, n_y, n_z)$ unit vector in the direction of $\vec{B_0}$.

matrix representation of H_{eZ} in the basis $|1\rangle, |3\rangle$:

$$\beta_e |B_0| \begin{pmatrix} n_z g_z \left(\frac{3}{2}\cos^2\Theta - \frac{1}{2}\sin^2\Theta\right) & \begin{matrix} n_x g_x (\sqrt{3}\cos\Theta\sin\Theta + \sin^2\Theta) \\ + i n_y g_y (-\sqrt{3}\cos\Theta\sin\Theta + \sin^2\Theta) \end{matrix} \\ \begin{matrix} n_x g_x (\sqrt{3}\cos\Theta\sin\Theta + \sin^2\Theta) \\ - i n_y g_y (-\sqrt{3}\cos\Theta\sin\Theta + \sin^2\Theta) \end{matrix} & -n_z g_z \left(\frac{3}{2}\cos^2\Theta - \frac{1}{2}\sin^2\Theta\right) \end{pmatrix}$$

Diagonalization

$$\longrightarrow \Delta\mathcal{E} = \pm\beta_e|B_0| \left\{ n_x^2 g_x^2 \left(\sqrt{3}\cos\theta\sin\theta + \sin^2\theta\right)^2 + n_y^2 g_y^2 \left(-\sqrt{3}\cos\theta\sin\theta + \sin^2\theta\right)^2 + n_z^2 g_z^2 \left(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\sin^2\theta\right)^2 \right\}^{1/2}$$

The upper doublet can be neglected as long as

$$\Delta\mathcal{E} \lll 2\sqrt{D^2+3E^2}$$

d. For $s=\frac{1}{2}$, $\Delta\mathcal{E} = \pm\frac{1}{2}\beta_e\left(n_x^2 g_x^2 + n_y^2 g_y^2 + n_z^2 g_z^2\right)$,

which is equivalent to the expression for the Kramers doublet above with effective g':

$$g_x' = g_x\left(2\sqrt{3}\cos\theta\sin\theta + 2\sin^2\theta\right)$$
$$g_y' = g_y\left(-2\sqrt{3}\cos\theta\sin\theta + 2\sin^2\theta\right)$$
$$g_z' = g_z\left(3\cos^2\theta - \sin^2\theta\right)$$

6 a $\rho_{11} = \langle 1|\chi\rangle\langle\chi|1\rangle = c_1 c_1^*$ etc.

$$\rightarrow \rho : \begin{pmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{pmatrix}$$

$$\langle S_x' \rangle = \mathrm{Tr}(\rho S_x') = \mathrm{Tr}\left[\begin{pmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{pmatrix} \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\right]$$

$$= \frac{1}{2}(c_1 c_2^* + c_2 c_1^*) = \mathrm{Re}\,\rho_{12}.$$

$$\langle S_y' \rangle = -\,\mathrm{Im}\,\rho_{12}.$$

$$\langle S_z \rangle = \frac{1}{2}(\rho_{11} - \rho_{22}).$$

b. $e^{i\theta}|\chi\rangle\langle\chi|e^{-i\theta} = |\chi\rangle\langle\chi|$

$$\langle A \rangle = \langle \chi|A|\chi\rangle = \mathrm{Tr}(\rho A)$$

c

$$\rho : \begin{pmatrix} p_1 & 0 \\ 0 & p_2 \end{pmatrix}$$

$$\frac{1}{2}\mathbb{1} + (p_1 - p_2) S_z' = \frac{1}{2}\begin{pmatrix} p_1 - p_2 + 1 & 0 \\ 0 & -p_1 + p_2 + 1 \end{pmatrix} \underbrace{=}_{[p_1 + p_2 = 1]} \begin{pmatrix} p_1 & 0 \\ 0 & p_2 \end{pmatrix}$$

7 a. Liouville-von Neumann equation $i\hbar\dot{\rho} = [H,\rho]$

$$\rightarrow \rho(t) = \exp\left(\frac{-iHt}{\hbar}\right)\rho(0)\exp\left(\frac{iHt}{\hbar}\right)$$

$$H_1(t) = g\beta_e \tilde{S} B_1(t) = S'_x \hbar\omega_1 \quad \text{with } \omega_1 = \left(\frac{g\beta_e}{\hbar}\right)B_1$$

$$0 \rightarrow 0_+ : \rho(0_+) = \exp(-i\beta S_x)\,\rho(0)\,\exp(i\beta S_x)$$

b. $0_+ \rightarrow \tau_-$: $\rho(\tau_-) = \exp(-iH\tau)\,\rho(0_+)\,\exp(iH\tau)$

$\tau_- \rightarrow \tau_+$: $\rho(\tau_+) = \exp(-i\pi S'_x)\,\rho(\tau_-)\,\exp(i\pi S_x)$

$\tau_+ \rightarrow 2\tau$: $\rho(2\tau) = \exp(-iH\tau)\,\rho(\tau_+)\,\exp(iH\tau)$

$\rightarrow \rho(2\tau) =$ .... $\rho(0)$ ....

c

$$H: \begin{pmatrix} \varepsilon_1 & & & \\ & \varepsilon_2 & \phi & \\ \phi & & \varepsilon_3 & \\ & & & \varepsilon_4 \end{pmatrix} \qquad \exp(\pm iH\tau): \begin{pmatrix} e^{\pm i\varepsilon_1\tau} & & & \\ & e^{\pm i\varepsilon_2\tau} & & \phi \\ & \phi & e^{\pm i\varepsilon_3\tau} & \\ & & & e^{\pm i\varepsilon_4\tau} \end{pmatrix}$$

$$S'_x: \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} \qquad S'_y: \frac{i}{2}\begin{pmatrix} 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

$\exp(\pm i\beta S'_x)$:

$$\frac{1}{2}\begin{pmatrix} 1+\cos\beta & \pm i\sin\beta & \pm i\sin\beta & -1+\cos\beta \\ \pm i\sin\beta & 1+\cos\beta & -1+\cos\beta & \pm i\sin\beta \\ \pm i\sin\beta & -1+\cos\beta & 1+\cos\beta & \pm i\sin\beta \\ -1+\cos\beta & \pm i\sin\beta & \pm i\sin\beta & 1+\cos\beta \end{pmatrix}$$

d. $\langle S_x \rangle (2\tau) = \frac{1}{2}(p_1 - p_2 - p_3 + p_4) \sin 2\beta \sin (J + \omega_{dd})\tau$

$\langle S_y \rangle (2\tau) = (p_1 - p_4) \sin\beta \cos (J + \omega_{dd})\tau$

e. x-echo maximum for $\beta = \frac{\pi}{4}$ ($\frac{\pi}{4} - \pi$ sequence) and 0 for $\beta = \frac{\pi}{2}$

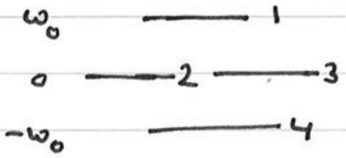
y-echo maximum for $\beta = \frac{\pi}{2}$ ($\frac{\pi}{2} - \pi$ sequence) and 0 for $\beta = \pi$

$\left.\begin{array}{l}\text{x-echo sin modulation}\\ \text{y-echo cos modulation}\end{array}\right\}$ 90° out-of-phase.

f. thermal equilibrium at $t=0$

take $\omega_A = \omega_B \equiv \omega_0$

weak coupling, level scheme for $J + \omega_{dd} = 0$



high-temperature approximation

$[p_1, p_2, p_3, p_4] = \frac{1}{4}[1-\delta, 1, 1, 1+\delta]$

with $\delta = \hbar\omega_0 / k_B T$

$$\left[\begin{array}{l} p_1 + p_2 + p_3 + p_4 = 1 \; ; \text{ suppose } p_2 = \frac{1}{4} \\ \qquad p_1 / p_2 = \exp\left(-\Delta E / k_B T\right) \approx 1 - \frac{\Delta E}{k_B T} \longrightarrow p_1 = p_2\left(1 - \frac{\hbar\omega_0}{k_B T}\right) \end{array}\right]$$

$\langle S_x \rangle (2\tau) = 0$

$\langle S_y \rangle (2\tau) = -\frac{1}{2}\delta \sin\beta \cos (J + \omega_{dd})\tau$

pure singlet at $t=0$: $|\chi\rangle = \frac{1}{\sqrt{2}}\left\{|\alpha_A \beta_B\rangle - |\beta_A \alpha_B\rangle\right\}$

$[p_1, p_2, p_3, p_4] = \frac{1}{2}[0, 1, 1, 0]$

$\langle S_x \rangle (2\tau) = -\frac{1}{2} \sin 2\beta \sin (J + \omega_{dd})\tau$

$\langle S_y \rangle (2\tau) = 0$