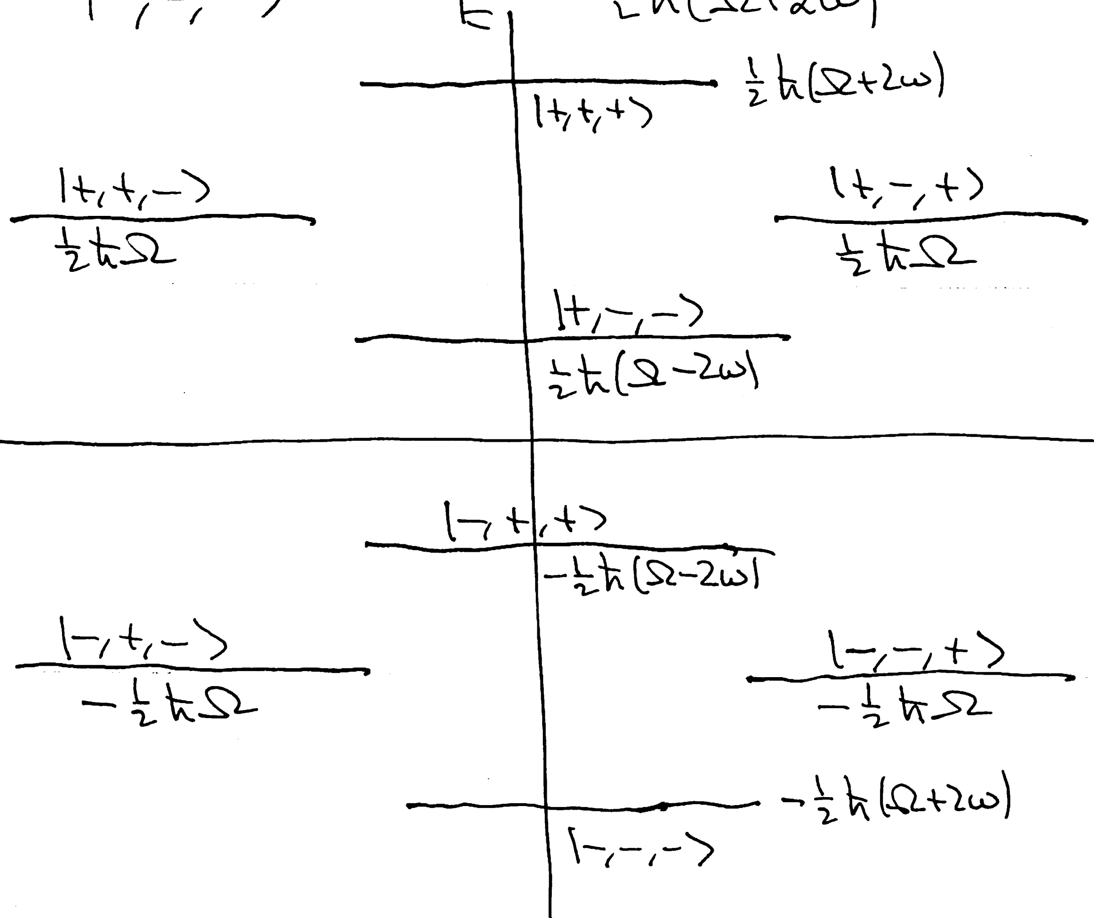
H_{XI} 6.) a) $H_0 = \Omega S_z + \omega I_{1z} + \omega I_{2z}$, $\Omega > 2\omega$

$$H_0 |\epsilon_s, \epsilon_1, \epsilon_2\rangle = \frac{\hbar}{2}\left[\Omega \epsilon_s + \omega(\epsilon_1 + \epsilon_2)\right] |\epsilon_s, \epsilon_1, \epsilon_2\rangle$$

States	Energy	Degree of Degeneracy
$\|+,+,+\rangle$	$\frac{1}{2}\hbar(\Omega+2\omega)$	1
$\|+,+,-\rangle$	$\frac{1}{2}\hbar\Omega$	2
$\|+,-,+\rangle$	$\frac{1}{2}\hbar\Omega$	
$\|+,-,-\rangle$	$\frac{1}{2}\hbar(\Omega-2\omega)$	1
$\|-,+,+\rangle$	$-\frac{1}{2}\hbar(\Omega-2\omega)$	1
$\|-,+,-\rangle$	$-\frac{1}{2}\hbar\Omega$	2
$\|-,-,+\rangle$	$-\frac{1}{2}\hbar\Omega$	
$\|-,-,-\rangle$	$-\frac{1}{2}\hbar(\Omega+2\omega)$	1



II. 6.b) $W = a\vec{S}\cdot\vec{I}_1 + a\vec{S}\cdot\vec{I}_2$

$$\vec{S}\cdot\vec{I}_i = \tfrac{1}{2}\left[S_- I_{i+} + S_+ I_{i-}\right] + S_z I_{iz}$$

So

$$\vec{S}\cdot\vec{I}_1 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle = \tfrac{1}{4}\hbar^2 \epsilon_s \epsilon_1 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle$$
$$+ \tfrac{1}{2}\hbar^2\left[\tfrac{3}{4} - \epsilon_s(\epsilon_s - 1)\right]^{1/2}\left[\tfrac{3}{4} - \epsilon_1(\epsilon_1+1)\right]^{1/2} |\epsilon_s - 1, \epsilon_1 + 1, \epsilon_2\rangle$$
$$+ \tfrac{1}{2}\hbar^2\left[\tfrac{3}{4} - \epsilon_s(\epsilon_s + 1)\right]^{1/2}\left[\tfrac{3}{4} - \epsilon_1(\epsilon_1-1)\right]^{1/2} |\epsilon_s + 1, \epsilon_1 - 1, \epsilon_2\rangle$$

$$\boxed{\begin{aligned} &= \tfrac{1}{4}\hbar^2 \epsilon_s \epsilon_1 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle \\ &\quad + \tfrac{3}{8}\hbar^2 \,|\epsilon_s - 1, \epsilon_1 + 1, \epsilon_2\rangle + \tfrac{3}{8}\hbar^2 \,|\epsilon_s + 1, \epsilon_1 - 1, \epsilon_2\rangle \\ &= \vec{S}\cdot\vec{I}_1 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle \end{aligned}}$$

Likewise

$$\boxed{\begin{aligned} &\vec{S}\cdot\vec{I}_2 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle \\ &\quad = \tfrac{1}{4}\hbar^2 \epsilon_s \epsilon_2 \,|\epsilon_s, \epsilon_1, \epsilon_2\rangle \\ &\qquad + \tfrac{3}{8}\hbar^2 \,|\epsilon_s - 1, \epsilon_1, \epsilon_2 + 1\rangle + \tfrac{3}{8}\hbar^2 \,|\epsilon_s + 1, \epsilon_1, \epsilon_2 - 1\rangle \end{aligned}}$$

r.6.b.) Hence the matrix elements of $\vec{S}\cdot\vec{I}_i$ are

$$\langle \epsilon_s', \epsilon_1', \epsilon_2' \,|\, \vec{S}\cdot\vec{I}_1 \,|\, \epsilon_s, \epsilon_1, \epsilon_2 \rangle$$

=

	(+,+,+)	(+,+,−)	(+,−,+)	(+,−,−)	(−,+,+)	(−,+,−)	(−,−,+)	(−,−,−)
(+,+,+)	$\frac{1}{4}\hbar^2$	0	0	0	0	0	0	0
(+,+,−)	0	$\frac{1}{4}\hbar^2$	0	0	0	0	0	0
(+,−,+)	0	0	$-\frac{1}{4}\hbar^2$	0	$\frac{3}{8}\hbar^2$	0	0	0
(+,−,−)	0	0	0	$-\frac{1}{4}\hbar^2$	0	$\frac{3}{8}\hbar^2$	0	0
(−,+,+)	0	0	$\frac{3}{8}\hbar^2$	0	$-\frac{1}{4}\hbar^2$	0	0	0
(−,+,−)	0	0	0	$\frac{3}{8}\hbar^2$	0	$-\frac{1}{4}\hbar^2$	0	0
(−,−,+)	0	0	0	0	0	0	$\frac{1}{4}\hbar^2$	0
(−,−,−)	0	0	0	0	0	0	0	$\frac{1}{4}\hbar^2$

XI 6.b.) Likewise

$$\langle \epsilon_s', \epsilon_1', \epsilon_2' | \vec{S}\cdot\vec{I}_2 | \epsilon_s, \epsilon_1, \epsilon_2 \rangle$$

=

	(+,+,+)	(+,+,-)	(+,-,+)	(+,-,-)	(-,+,+)	(-,+,-)	(-,-,+)	(-,-,-)
(+,+,+)	$\frac{1}{4}\hbar^2$	0	0	0	0	0	0	0
(+,+,-)	0	$-\frac{1}{4}\hbar^2$	0	0	$\frac{3}{8}\hbar^2$	0	0	0
(+,-,+)	0	0	$\frac{1}{4}\hbar^2$	0	0	0	0	0
(+,-,-)	0	0	0	$-\frac{1}{4}\hbar^2$	0	0	$\frac{3}{8}\hbar^2$	0
(-,+,+)	0	$\frac{3}{8}\hbar^2$	0	0	$-\frac{1}{4}\hbar^2$	0	0	0
(-,+,-)	0	0	0	0	0	$\frac{1}{4}\hbar^2$	0	0
(-,-,+)	0	0	0	$\frac{3}{8}\hbar^2$	0	0	$-\frac{1}{4}\hbar^2$	0
(-,-,-)	0	0	0	0	0	0	0	$\frac{1}{4}\hbar^2$

c) So we need $\langle \epsilon_s', \epsilon_1', \epsilon_2' | W | \epsilon_s, \epsilon_1, \epsilon_2 \rangle$

XI 6.c) $\langle \epsilon_s', \epsilon_1', \epsilon_2' | W | \epsilon_s, \epsilon_1, \epsilon_2 \rangle$

$$= a\hbar^2 \times$$

$$\begin{array}{c|cccccccc}
 & (+,+,+) & (+,+,-) & (+,-,+) & (+,-,-) & (-,+,+) & (-,+,-) & (-,-,+) & (-,-,-) \\
\hline
(+,+,+) & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
(+,+,-) & 0 & 0 & 0 & 0 & \frac{3}{8} & 0 & 0 & 0 \\
(+,-,+) & 0 & 0 & 0 & 0 & \frac{3}{8} & 0 & 0 & 0 \\
(+,-,-) & 0 & 0 & 0 & -\frac{1}{2} & 0 & \frac{3}{8} & \frac{3}{8} & 0 \\
(-,+,+) & 0 & \frac{3}{8} & \frac{3}{8} & 0 & -\frac{1}{2} & 0 & 0 & 0 \\
(-,+,-) & 0 & 0 & 0 & \frac{3}{8} & 0 & 0 & 0 & 0 \\
(-,-,+) & 0 & 0 & 0 & \frac{3}{8} & 0 & 0 & 0 & 0 \\
(-,-,-) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2}
\end{array}$$

Recall first order (degenerate) RS perturbation theory

$$|\psi_n^{(0)}\rangle = \sum_{l=1}^{g_n} \psi_{nl} |\varphi_{n,l}\rangle$$

$$\sum_{k=1}^{g_n} \hat{H}'_{lk} \psi_{nk} = \epsilon_n^{(1)} \psi_{nl}$$

with

$$\langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle = \hat{H}'_{lk}$$

And non-degenerate case we have

$$\epsilon_n^{(1)} = \langle \varphi_n | \hat{H}' | \varphi_n \rangle$$

I. 6.c) So non-degenerate states have energy to first order

~~State~~

$$E_{(+,+,+)} = \tfrac{1}{2}\hbar(\Omega+2\omega) + \langle +,+,+|\overset{W}{\overset{\parallel}{H'}}|+,+,+\rangle$$

$$= \tfrac{1}{2}\hbar(\Omega+2\omega) + \tfrac{1}{2}a\hbar^2$$

$$E_{(-,-,-)} = -\tfrac{1}{2}\hbar(\Omega+2\omega) + \tfrac{1}{2}a\hbar^2$$

$$E_{(+,-,-)} = \tfrac{1}{2}\hbar(\Omega-2\omega) + \langle +,-,-|W|+,-,-\rangle$$

$$= \tfrac{1}{2}\hbar(\Omega-2\omega) - \tfrac{1}{2}a\hbar^2$$

$$E_{(-,+,+)} = -\tfrac{1}{2}\hbar(\Omega-2\omega) + \langle -,+,+|W|-,+,+\rangle$$

$$= -\tfrac{1}{2}\hbar(\Omega-2\omega) - \tfrac{1}{2}a\hbar^2$$

The degenerate states we need to consider the matrix els of W in their degenerate subspace (2×2) in each case.

$$\hat{H}' = \begin{array}{c} \\ (+,+,-) \\ (+,-,+) \end{array}\begin{array}{cc} (+,+,-) & (+,-,+) \\ \end{array}$$

$$\hat{H}' = \begin{array}{c|cc} & (+,+,-) & (+,-,+) \\ \hline (+,+,-) & 0 & 0 \\ (+,-,+) & 0 & 0 \end{array}$$

for $(+,+,-)$ & $(+,-,+)$ states

I.6.c.) Likewise

$$H' = \begin{array}{c|cc} & (-,+,-) & (-,-,+) \\ \hline (-,+,-) & 0 & 0 \\ (-,-,+) & 0 & 0 \end{array}$$ for the $(-,+,-)$ & $(-,-,+)$ states

$\boxed{\text{No first order energy shift for the degenerate states !!}}$

Energy ~~the~~ eigenstates: To find the energy eigenstates for the degenerate case in 0^{th} order we must use 2^{nd} order P.T.

Recall 2^{nd} order degenerate R-S P.T. from class notes:

$$\sum_{j=1}^{g_n} \left(\hat{H}'_{(2)}\right)_{kj} \mathcal{Y}_{nj} = \epsilon_n^{(2)} \mathcal{Y}_{nk}$$

$$\left(\hat{H}'_{(2)}\right)_{kj} = \sum_{m\neq n} \sum_{l=1}^{g_m} \frac{\langle \varphi_{n,k} | \hat{H}' | \varphi_{m,l}\rangle \langle \varphi_{m,l} | \hat{H}' | \varphi_{n,j}\rangle}{E_n^0 - E_m^0}$$

So we must find how the <u>other states</u> <u>mix</u> with the degenerate states in the H' matrix elements

6.c.) For the $(+,+,-)$ and $(+,-,+)$ states

$$H'_{(2)} = \frac{\begin{bmatrix} 0 & 0 & \frac{3}{8} & 0 & 0 & 0 \\ 0 & 0 & \frac{3}{8} & 0 & 0 & 0 \end{bmatrix} (a\hbar^2)^2 \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ \frac{3}{8} & \frac{3}{8} \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}}{\frac{1}{2}\hbar\Omega - \left[-\frac{1}{2}\hbar(\Omega - 2\omega)\right]}$$

$$\boxed{H'_{(2)} = \frac{\left(\frac{3}{8}a\hbar^2\right)^2}{\hbar(\Omega-\omega)} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}} = \epsilon \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$$

So eigenvalues are 0 and 2ϵ

eigenstates are $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$ for 0 and $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ for 2ϵ

So we have 2 energies (in 2nd order)

$$\boxed{\begin{aligned} E_{+1} &= 0 \quad \& \quad |E_{+1}\rangle = \frac{1}{\sqrt{2}}\left[|+,+,-\rangle - |+,-,+\rangle\right] \\ E_{+2} &= 2\epsilon \quad \& \quad |E_{+2}\rangle = \frac{1}{\sqrt{2}}\left[|+,+,-\rangle + |+,-,+\rangle\right] \end{aligned}}$$

I.6.a) Similarly for the $(-,+,-)$ & $(-,-,+)$ states

$$H'_{(2)} = \frac{\begin{bmatrix} 0 & 0 & 0 & \frac{3}{8} & 0 & 0 \\ 0 & 0 & 0 & \frac{3}{8} & 0 & 0 \end{bmatrix} (a\hbar^2)^2 \begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ \frac{3}{8} & \frac{3}{8} \\ 0 & 0 \\ 0 & 0 \end{bmatrix}}{-\frac{1}{2}\hbar\Omega - \left[\frac{1}{2}\hbar(\Omega - 2\omega)\right]}$$

$$\boxed{H'_{(2)} = \frac{-\left(\frac{3}{8}a\hbar^2\right)^2}{\hbar(\Omega-\omega)} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} = -\epsilon \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}}$$

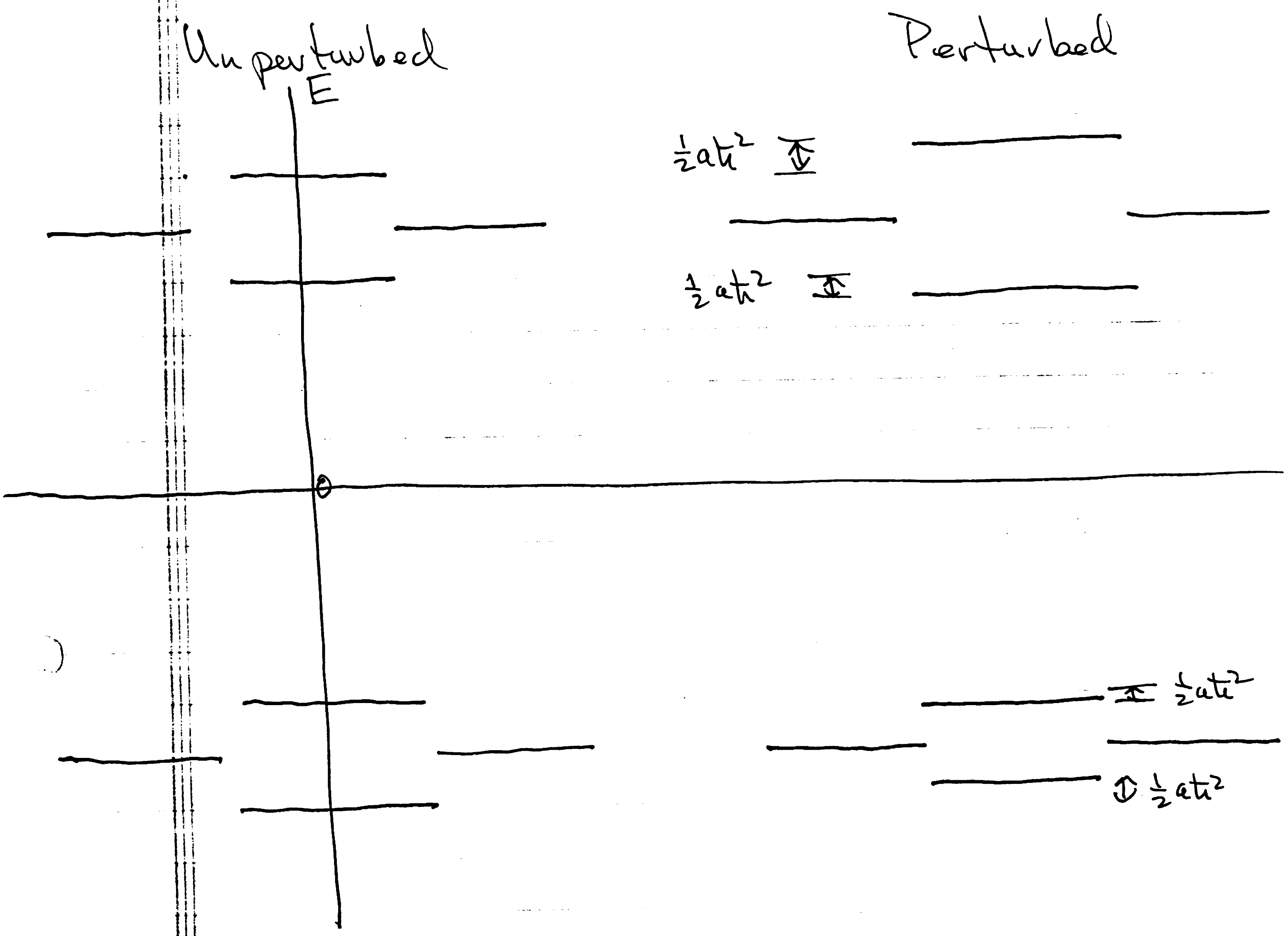
So eigenvalues are 0 and -2ϵ

with eigenstates $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$ for 0 & $\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ for -2ϵ

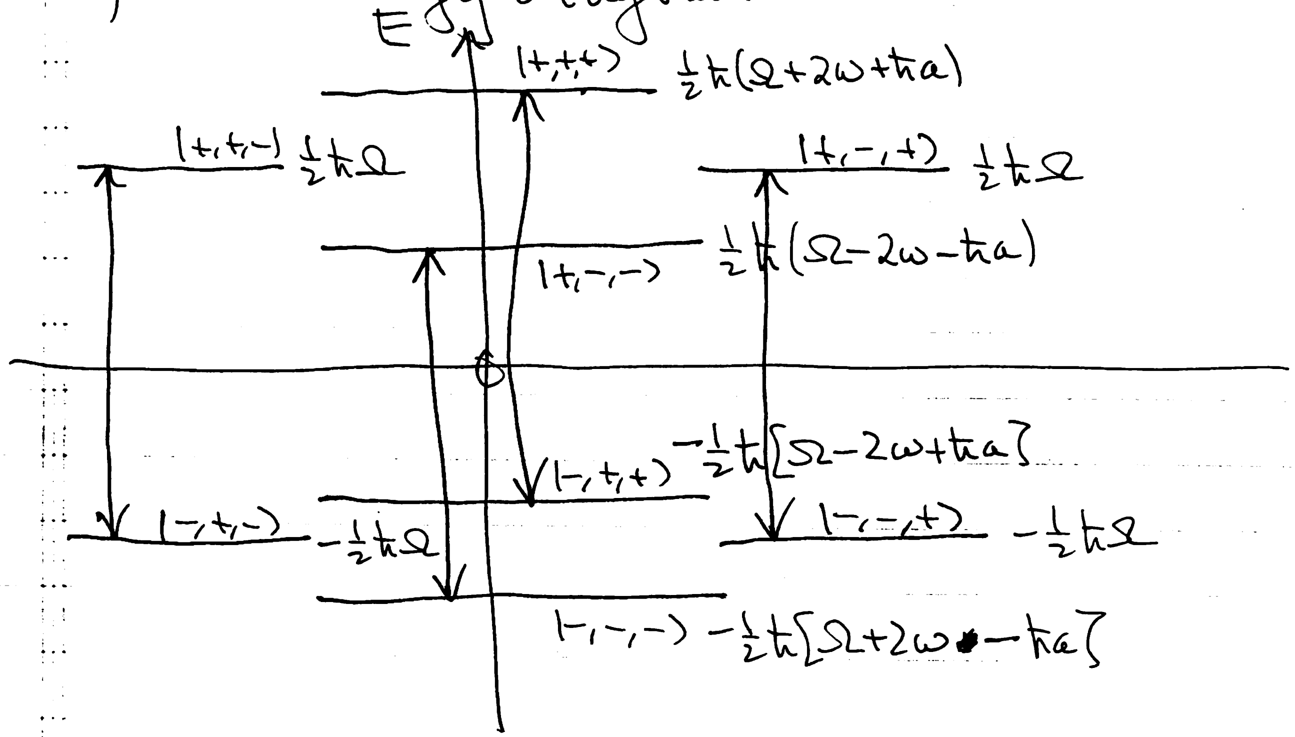
So we have 2 energies (in 2nd order)

$$\boxed{\begin{aligned} E_{-1} &= 0 \quad \& \quad |E_{-1}\rangle = \frac{1}{\sqrt{2}}\left[|-,+,-\rangle - |-,-,+\rangle\right] \\ E_{-2} &= -2\epsilon \quad \& \quad |E_{-2}\rangle = \frac{1}{\sqrt{2}}\left[|-,+,-\rangle + |-,-,+\rangle\right] \end{aligned}}$$

H XI. 6.(c) Energy Diagram (to first order in W only)



XI.6.d.) From energy diagram

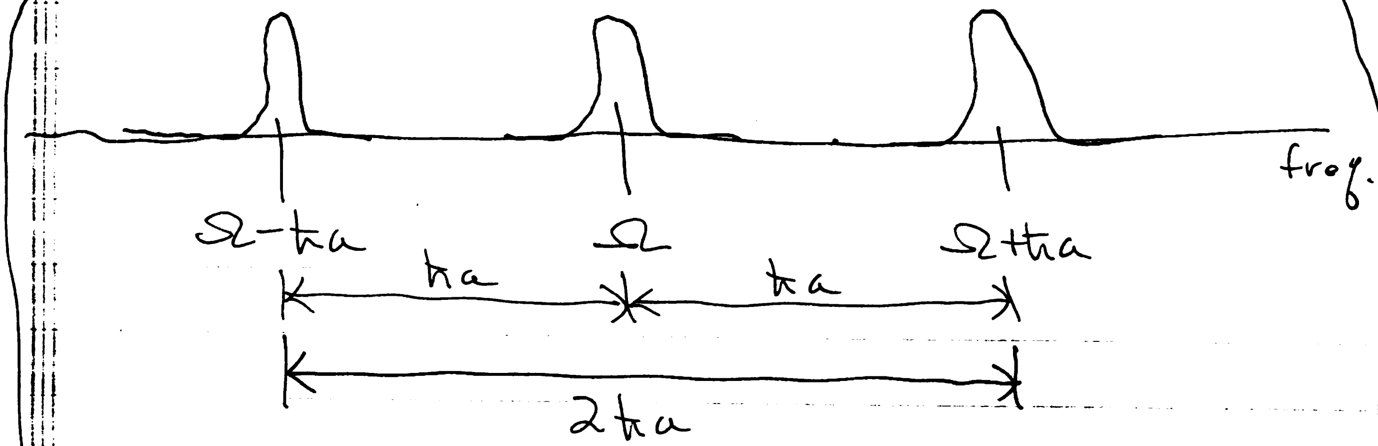


Recall $S_x = \frac{1}{2}[S_+ + S_-]$. So we can only connect states that flip the S_z spin for $\langle S_x \rangle$

Bohr frequencies are these energy differences$/\hbar$

$$\boxed{\begin{gathered}\text{2 cases of frequency } \Omega \\ \tfrac{1}{2}[\Omega+2\omega+\hbar a]+\tfrac{1}{2}[\Omega-2\omega+\hbar a] = \Omega+\hbar a \\ \tfrac{1}{2}[\Omega-2\omega-\hbar a]+\tfrac{1}{2}[\Omega+2\omega-\hbar a] = \Omega-\hbar a\end{gathered}}$$

I.6.d.) EPR spectrum:



Measure frequency between resonance lines to determine a.

e.) $\Omega = \omega = 0$ $\boxed{H = W = a\vec{S}\cdot\vec{I}}$

α.) where $\vec{I} = \vec{I}_1 + \vec{I}_2$

$\boxed{\vec{I}^2 \text{ has e.v. } \hbar^2 i(i+1) \quad i = 0, 1}$

Consider $\{S_z, \vec{I}^2, I_z\}$ eigenstates

$$\boxed{\begin{gathered} |\epsilon_s, 0, 0\rangle = \frac{1}{\sqrt{2}}\left[|\epsilon_s, +, -\rangle - |\epsilon_s, -, +\rangle\right] \\ \text{2-states with } i = 0 \end{gathered}}$$

1 at. 6. e.)

α.)

$$\boxed{\begin{aligned} &|e_s, 1, 1\rangle = |\epsilon_s, +, +\rangle \\ &|e_s, 1, 0\rangle = \tfrac{1}{\sqrt{2}}\left[|\epsilon_s, +, -\rangle + |\epsilon_s, -, +\rangle\right] \\ &|e_s, 1, -1\rangle = |e_s, -, -\rangle \\ &\text{6 states with } i = 1 \end{aligned}}$$

Note $[\vec{I}^2, \vec{S}] = 0 = [\vec{I}^2, \vec{I}]$

$$\Rightarrow [\vec{I}^2, \vec{S}\cdot\vec{I}] = 0$$

$$\Rightarrow \langle \epsilon_s, 0, 0 | [\vec{I}^2, \vec{S}\cdot\vec{I}] | \epsilon_s', 1, I_z\rangle = 0$$

$$\|$$

$$0 = -\hbar^2 1(1+1)\langle \epsilon_s, 0, 0 | \vec{S}\cdot\vec{I} | \epsilon_s', 1, I_z\rangle$$

$$\Rightarrow \boxed{\langle \epsilon_s, 0, 0 | \vec{S}\cdot\vec{I} | \epsilon_s', 1, I_z\rangle = 0}$$

β.) $\vec{J} = \vec{S} + \vec{I}$ $\quad$ $\vec{J}^2$ has e.v. $\hbar^2 j(j+1)$

with $j = 1+\tfrac{1}{2}, 1-\tfrac{1}{2}, 0+\tfrac{1}{2}$

$$\boxed{j = \tfrac{3}{2}, \tfrac{1}{2}, \tfrac{1}{2}}$$

II.6.e.3.) Consider the $\{\vec{J}^2, J_z, \vec{I}^2\}$ eigenstates

4 states with $j=\frac{1}{2}$

$$\left|\tfrac{1}{2}, M=\pm, 0\right\rangle = \frac{1}{\sqrt{2}}\left[\left|\overset{S_z}{\underset{\epsilon_s}{\pm}}, \overset{I_{1z}}{\underset{\epsilon_1}{+}}, \overset{I_{2z}}{\underset{\epsilon_2}{-}}\right\rangle - |\pm,-,+\rangle\right]$$

$$\left|\tfrac{1}{2}, M=+, 1\right\rangle = \sqrt{\tfrac{2}{3}}\,\left|\overset{S_z}{\epsilon_s}=-, \overset{\vec{I}^2}{i}=1, \overset{I_z}{I_z}=1\right\rangle - \frac{1}{\sqrt{3}}|+,1,0\rangle$$

$$\left|\tfrac{1}{2}, M=-, 1\right\rangle = \frac{1}{\sqrt{3}}|-,1,0\rangle - \sqrt{\tfrac{2}{3}}\,|+,1,-1\rangle$$

---

4 states with $j=3/2$

$$\left|\tfrac{3}{2}, M=\tfrac{3}{2}, 1\right\rangle = |\epsilon_s=+, i=1, I_z=1\rangle = |+,+,+\rangle$$

$$\left|\tfrac{3}{2}, M=\tfrac{1}{2}, 1\right\rangle = \sqrt{\tfrac{2}{3}}\,|\epsilon_s=+, i=1, I_z=0\rangle + \sqrt{\tfrac{1}{3}}\,|\epsilon_s=-, i=1, I_z=1\rangle$$

$$\left|\tfrac{3}{2}, M=-\tfrac{1}{2}, 1\right\rangle = \frac{1}{\sqrt{3}}|\epsilon_s=+, i=1, I_z=-1\rangle + \sqrt{\tfrac{2}{3}}\,|\epsilon_s=-, i=1, I_z=0\rangle$$

$$\left|\tfrac{3}{2}, M=-\tfrac{3}{2}, 1\right\rangle = |\epsilon_s=-, i=1, I_z=-1\rangle$$

$$\left(2\otimes 3 = 4 \oplus 2 \oplus 2\right)$$

VI 6. e. 3) Now $\vec{J}^2 = \vec{S}^2 + \vec{I}^2 + 2\vec{S}\cdot\vec{I}$

So $W = \frac{a}{2}\left[\vec{J}^2 - \vec{S}^2 - \vec{I}^2\right]$

$$\boxed{E_{j,s,i} = \frac{\hbar^2 a}{2}\left[j(j+1) - \tfrac{3}{4} - i(i+1)\right]}$$

So

$E_{\frac{1}{2},\frac{1}{2},0} = 0$ degeneracy $= 2$

$E_{\frac{1}{2},\frac{1}{2},1} = -\hbar^2 a$ degeneracy $= 2$

$E_{\frac{3}{2},\frac{1}{2},1} = \frac{1}{2}\hbar^2 a$ degeneracy $= 4$

$\{\vec{J}^2, J_z\}$ is not CSCO, $|\tfrac{1}{2}, \kappa (= \pm)\rangle$ is doubly degenerate

$\{\vec{I}^2, \vec{J}^2, J_z\}$ is a CSCO, all 8 states have unique labels.