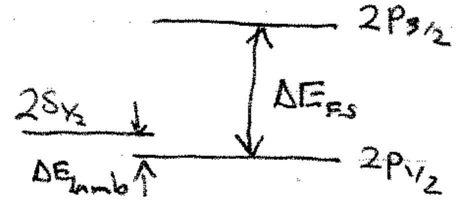
Problem Set #4 Solutions

Problem 1: Stark effect with Fine-structure

n=2 manifold of Hydrogen (including fine structure)



Stark effect perturbation: $\hat{H}_{int} = +e\hat{z}E_z$ (quantization axis along $\vec{E}$)

Recall spectroscopic notation: $nl_j \Rightarrow \underset{\overset{\uparrow}{n=2}}{2}\overset{\leftarrow l=0}{s}_{\frac{1}{2}\leftarrow j=1/2}$

For a given j, there are 2j+1 degenerate sublevels

$$\begin{cases} 2s_{1/2} \Rightarrow |2s_{1/2}, +1/2\rangle, \ |2s_{1/2}, -1/2\rangle \\ 2p_{1/2} \Rightarrow |2p_{1/2}, +1/2\rangle, \ |2p_{1/2}, -1/2\rangle \\ 2p_{3/2} \Rightarrow |2p_{3/2}, 3/2\rangle, \ |2p_{3/2}, 1/2\rangle, \ |2p_{3/2}, -1/2\rangle, \ |2p_{1/2}, -3/2\rangle \end{cases}$$

Since $\hat{H}_{int}$ acts only on the spatial degree of freedom, it will be useful to reëxpress the eigenstates above in terms of the "uncoupled" angular momentum basis. We did this in P.S.#8, problem 2 (521 Fall 2000). The results were

$$|2s_{1/2}, \pm 1/2\rangle = |2s, \overset{m_l}{\overset{\downarrow}{0}}\rangle \otimes |\overset{m_s}{\overset{\downarrow}{\pm\tfrac{1}{2}}}\rangle$$

$$|2p_{1/2}, \pm 1/2\rangle = \sqrt{\tfrac{1}{3}}\,|2p, 0\rangle \otimes |\pm 1/2\rangle - \sqrt{\tfrac{2}{3}}\,|2p, \pm 1\rangle \otimes |\mp \tfrac{1}{2}\rangle$$

$$|2p_{3/2}, \pm 1/2\rangle = \sqrt{\tfrac{2}{3}}\,|2p, 0\rangle \otimes |\pm 1/2\rangle + \sqrt{1/3}\,|2p, \pm 1\rangle \otimes |\mp \tfrac{1}{2}\rangle$$

$$|2p_{3/2}, \pm 3/2\rangle = |2p, \pm 1\rangle \otimes |\pm 1/2\rangle$$

(a) For weak fields $ea_0 E_z \gtrsim \Delta E_{Lamb}$, we can restrict our attention to the $(2s_{1/2}, 2p_{1/2})$ manifold

The matrix representation of $\hat{H}_{int}$ is block diagonal with no off-diagonal ~~elem~~ elements between different m_j as we will see below

Consider $m_j = 1/2$, 2 dim space

$$\hat{H}_0 + \hat{H}_{int} \doteq \begin{array}{cc} \begin{bmatrix} \Delta E_L & \epsilon \\ \epsilon^* & 0 \end{bmatrix} \\ |2s_{1/2}\rangle \quad |2p_{1/2}\rangle \end{array}$$

where ΔE_L = Lamb shift

$\epsilon = \langle 2p_{1/2}, \tfrac{1}{2} | \hat{H}_{int} | 2s_{1/2}, 1/2 \rangle$

To calculate ϵ, we use the uncoupled representation above:

$$\epsilon = \underset{-eE_z}{\wedge}\sqrt{\tfrac{1}{3}}\, \langle 2p,0|\hat{z}|2s,0\rangle \overset{1}{\cancel{\langle +\tfrac{1}{2}|+\tfrac{1}{2}\rangle}} - \sqrt{\tfrac{2}{3}}\, \langle 2p,1|\hat{z}|2s,0\rangle \underset{\text{orthogonal spin}}{\overset{0}{\cancel{\langle -\tfrac{1}{2}|+\tfrac{1}{2}\rangle}}}$$

From class $\langle 2p,0|\hat{z}|2s,0\rangle = -3a_0$

$$\Rightarrow \boxed{\epsilon = \mp\sqrt{3}\, e a_0 E_z} \quad \text{(real)}$$

Diagonalize $\hat{H} = \begin{bmatrix} \Delta E_L & 0 \\ 0 & 0 \end{bmatrix} + \epsilon \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

$$= \frac{\Delta E_L}{2}\hat{\mathbb{1}} + \frac{\Delta E_L}{2}\hat{\sigma}_z + \epsilon\, \hat{\sigma}_x$$

Eigenvalues $\boxed{E_{\pm} = \frac{\Delta E_L}{2} \pm \sqrt{\frac{(\Delta E_L)^2}{4} + \epsilon^2}}$

Eigenvectors: $|\pm\rangle = \cos\left(\frac{\Theta}{2}\right)|2p_{1/2}\rangle \pm \sin\left(\frac{\Theta}{2}\right)|2s_{1/2}\rangle$

where $\tan\Theta = \frac{2\epsilon}{\Delta E_L}$ ("mixing angle")

Note: ratio of coupling matrix element to energy separation

New splitting between perturbed $2s_{1/2}$ and $2p_{1/2}$

$$\Delta E_L' = E_+ - E_- = \sqrt{(\Delta E_L)^2 + 4\epsilon^2}$$

Find electric field such that $\Delta E_L' = 2\Delta E_L$

$$\Rightarrow \quad 4\epsilon^2 = 3(\Delta E_L)^2 \quad \Rightarrow \quad \epsilon = \frac{\sqrt{3}}{2}\Delta E_L$$

$$\Rightarrow \quad \sqrt{3}\, e\, a_0 E_z = \frac{\sqrt{3}}{2}\Delta E_L$$

$$\Rightarrow \quad \boxed{E_z = \frac{1}{2ea_0}\Delta E_L}$$

Now for the numbers. Remember, we are using c.g.s. units. The easiest thing to do is express ΔE_L in electron volts, so that $\frac{\Delta E_L}{e}$ is in volts.

Conversion: Planck's constant $h = 4.14 \times 10^{-15}$ eV · s

$$\Rightarrow \quad \Delta E_L = (10^9\ \text{Hz})(4.14 \times 10^{-15}\ \text{eV s}) = 4.14 \times 10^{-6}\ \text{eV}$$

$$a_0 = 0.5 \times 10^{-8}\ \text{cm} \quad 6.5\ \text{Å})$$

$$\boxed{E_z = \frac{4.14 \times 10^{-6}\ \text{V}}{10^{-8}\ \text{cm}} = 414\ \text{V/cm}}$$

What about the other m_j substates?

- No off-diagonal matrix elements between different m_j

Proof $\langle 2s_{1/2}\tfrac{1}{2}|\hat{H}_{int}|2p_{1/2},-\tfrac{1}{2}\rangle$

$$=+eE_z\Big[\left(\langle 2s,0|\langle\tfrac{1}{2}|\right)\hat{z}\left(|2p,0\rangle|-\tfrac{1}{2}\rangle\right)-\sqrt{\tfrac{2}{3}}\left(\langle 2s,0|\langle\tfrac{1}{2}|\right)\hat{z}\left(|2p,-1\rangle|\tfrac{1}{2}\rangle\right)$$

$$=+eE_z\left[\frac{1}{\sqrt{3}}\langle 2s,0|\hat{z}|2p,0\rangle\underbrace{\langle\tfrac{1}{2}|-\tfrac{1}{2}\rangle}_{0}-\sqrt{\frac{2}{3}}\underbrace{\langle 2s,0|\hat{z}|2p,-1\rangle}_{0}\langle\tfrac{1}{2}|\tfrac{1}{2}\rangle\right]$$

$=0$ ✓ and similary for $\langle 2s-\tfrac{1}{2}|\hat{H}_{int}|2p_{1/2},\tfrac{1}{2}\rangle$

- The 2×2 matrix representation for $m_j=-\tfrac{1}{2}$ is the <u>same</u> as for $m_j=\tfrac{1}{2}$ (try this yourself).

Thus in the 4-dim subspace of $(2s_{1/2},2p_{1/2})$ the representation of $\hat{H}$ is block-diagonal, with two degenerate sub-blocks

$$\hat{H}=\left[\begin{array}{cc|cc} E_L & \epsilon & & \\ \epsilon & 0 & \multicolumn{2}{c}{\smash{\raise.5ex\hbox{0}}} \\ \hline & & E_L & \epsilon \\ \multicolumn{2}{c|}{0} & \epsilon & 0 \end{array}\right]\begin{array}{l} m_j=\tfrac{1}{2} \\ \\ \\ m_j=-\tfrac{1}{2}\end{array}$$

Thus, the eigenvalue we found above are doublly degenerate

(b) Consider $ea_0 E_z \gtrsim \Delta E_{FS}$ ⇒ include all states in $n=2$

Again $\hat{H}$ is block diagonal, with no off-diagonal matrix element between different m_j. Those ~~case~~ block are also doubly degenerate for $\pm m_j$. As in class, there are no $p \to p$ matrix elements.

We must thus diagonalize the following 3x3 matrix

$$\hat{H} \doteq \begin{array}{c}\begin{bmatrix} \Delta E_L & \epsilon & \beta \\ \epsilon & 0 & 0 \\ \beta & 0 & \Delta E_{FS} \end{bmatrix} \\ \begin{array}{ccc} |2s_{1/2}\rangle & |2p_{1/2}\rangle & |2p_{3/2}\rangle \end{array}\end{array} \qquad m_j = \pm 1/2$$

note the $|2p_{3/2}, m_j = \pm 3/2\rangle$ is <u>unperturbed</u>

Here $\beta = \langle 2p_{3/2}, 1/2 | \hat{H}_{int} | 2s_{1/2}, 1/2\rangle$ (real)

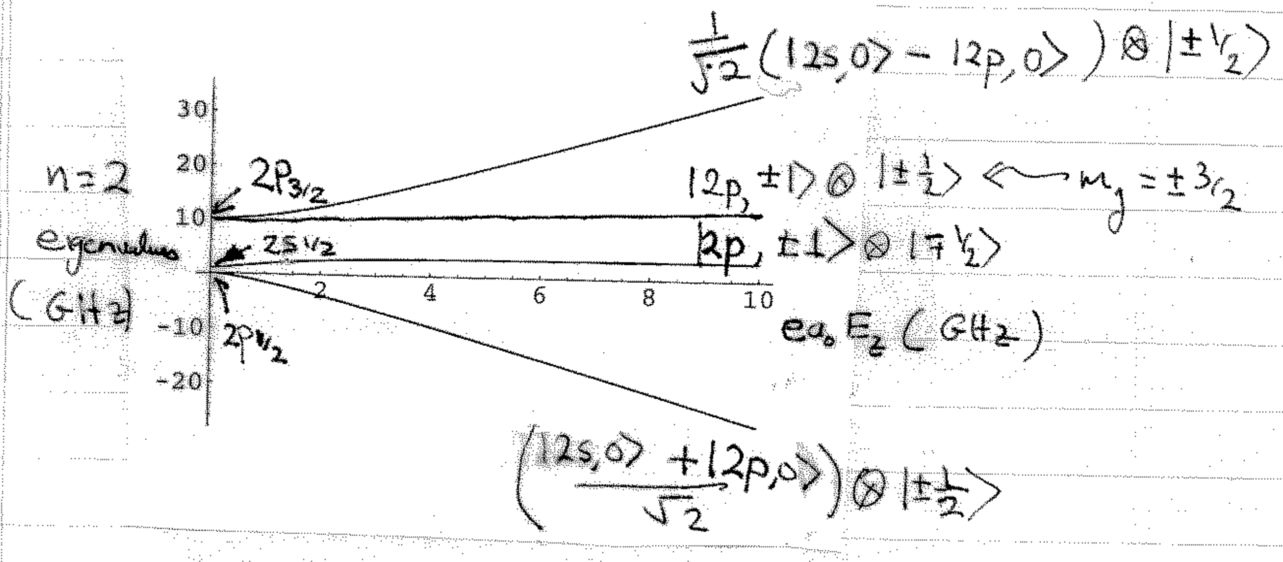
$$= -eE_z \left[\sqrt{\tfrac{2}{3}} \underbrace{\langle 2p, 0 | \hat{z} | 2s\, 0\rangle}_{-3a_0} \underbrace{\langle \tfrac{1}{2} | \tfrac{1}{2}\rangle}_{=1} + \sqrt{\tfrac{1}{3}} \langle 2p, 1 | \hat{z} | 2s, 0\rangle \overset{0}{\cancel{\langle -1/2 | 1/2\rangle}} \right.$$

$$\Rightarrow \boxed{\beta = \sqrt{6}\, e a_0 E_z}$$

$$\Rightarrow \quad \hat{H} \doteq \Delta E_L \begin{bmatrix} 1 & \sqrt{3}x & \sqrt{6}x \\ \sqrt{3}x & 0 & 0 \\ \sqrt{6}x & 0 & 10 \end{bmatrix} \qquad x \equiv \frac{e a_0 E_z}{\Delta E_L}$$

$\Delta E_L = 1\,\mathrm{GHz}$

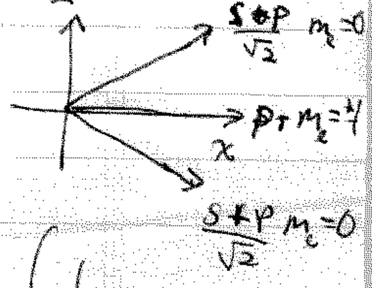
Solving for the eigenvalues numerically in the range $0 < x < 10$



(c) Asymptotic behavior. Note for small x we recover the behavior of part (a) (the level $|2P_{3/2}\rangle$ is too far away). For sufficiently large x the fine-structure is negligible and we recover the simple linear stark shift discussed in class. That we cover the expected eigenvectors can be seen in the large x limit setting $\frac{\Delta E_{FS}}{x} = \frac{\Delta E_L}{x} = 0$

$$x \gg\!> 1 \Rightarrow \hat{H} \doteq -x \begin{bmatrix} 0 & \sqrt{3} & \sqrt{6} \\ \sqrt{6} & 0 & 0 \\ \sqrt{3} & 0 & 0 \end{bmatrix}$$

$\Rightarrow$ Eigenvalues $\{-3x, 0, 3x\}$



(linear Stark)

Eigenvectors (next page)

Eigenvectors:
(up to arbitrary overall phase)

$$\left(\begin{array}{ccc} |e_1\rangle & |e_2\rangle & |e_3\rangle \\ \begin{bmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} \end{bmatrix}, & \begin{bmatrix} 0 \\ -\sqrt{\frac{2}{3}} \\ \frac{1}{\sqrt{3}} \end{bmatrix}, & \begin{bmatrix} +\sqrt{\frac{1}{2}} \\ \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} \end{bmatrix} \end{array} \right)$$

in the ordered basis $(|2s_{1/2}\rangle, |2p_{1/2}\rangle, |2p_{3/2}\rangle)$ $m_j = \frac{1}{2}$

$$\Rightarrow |e_1\rangle = -\frac{1}{\sqrt{2}}|2s_{1/2}\rangle + \frac{1}{\sqrt{6}}|2p_{1/2}\rangle + \frac{1}{\sqrt{3}}|2p_{3/2}\rangle$$

$$= -\frac{1}{\sqrt{2}}|2s,0\rangle|\tfrac{1}{2}\rangle + \frac{1}{3\sqrt{2}}|2p,0\rangle|\tfrac{1}{2}\rangle - \cancel{\frac{1}{3}|2p,1\rangle|-\tfrac{1}{2}\rangle}$$
$$+ \frac{2}{3\sqrt{2}}|2p,0\rangle|\tfrac{1}{2}\rangle + \cancel{\frac{1}{3}|2p,1\rangle|-\tfrac{1}{2}\rangle}$$

$$\boxed{|e_1\rangle = -\frac{1}{\sqrt{2}}\left(|2s,0\rangle - |2p,0\rangle\right)\otimes|\tfrac{1}{2}\rangle} \checkmark$$

$$|e_2\rangle = -\sqrt{\frac{2}{3}}|2p_{1/2}\rangle + \frac{1}{\sqrt{3}}|2p_{3/2}\rangle = -\frac{\sqrt{2}}{3}|2p,0\rangle|\tfrac{1}{2}\rangle + \frac{2}{3}|2p,1\rangle|-\tfrac{1}{2}$$
$$+ \frac{\sqrt{2}}{3}|2p,0\rangle|\tfrac{1}{2}\rangle + \frac{1}{3}|2p,1\rangle|-\tfrac{1}{2}$$

$$\boxed{|e_2\rangle = |2p,1\rangle\otimes|-\tfrac{1}{2}\rangle} \checkmark$$

Same procedure $\Rightarrow$ $\boxed{|e_3\rangle = \frac{1}{\sqrt{2}}\left(|2s,0\rangle + |2p,0\rangle\right)\otimes|\tfrac{1}{2}\rangle}$ ✓

Note the $m_j = -1/2$ are the same asymptotes @ $m_s \rightarrow -m_j$

the $m_j = -3/2$ ~~asymptote~~ are flat throughout

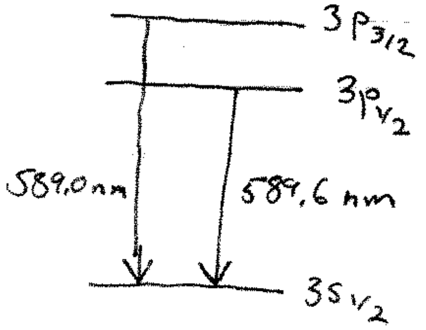
and yeild the remaining states $|2p,\pm1\rangle\otimes|\pm\tfrac{1}{2}\rangle$

Phys 522 P.S. #5 Solutions

Problem 1

Alkali atoms look a lot like Hydrogen with its one valance electron. The difference is that different l-values are nondegenerate due to the overlap of the valence wavefunction with the core.

Like Hydrogen spin-orbit coupling gives rise to fine structure



Not to scale

These closely spaced spectral lines are knows a D1 and D2.

The nuclear spin gives rise to hyperfine structure. For the common isotope with atomic mass 23 amu: ^{23}Na the nuclear spin is $I = 3/2$

(a) The total angular momentum $\vec{F} = \vec{I} + \vec{J}$ has possible values according to the triangle inequality

$$|I-J| \leq F \leq I+J$$

Ground state $3S_{1/2}$: $J = 1/2$ $I = 3/2$ $\Rightarrow F = 2$ or 1

Excited states: $3P_{1/2}$: $J = 1/2$ $I = 3/2$ $\Rightarrow F = 2$ or 1

$3P_{3/2}$: $J = 3/2$ $I = 3/2$ $\Rightarrow F = 3\ 2\ 1\ 0$

radial wave function 3S understoo

C-G expansion

$$|(nl_j)\ FM_F\rangle = \sum_{m_j\, m_I} \langle FM_F | j m_j\, I m_I\rangle\ |j m_j\rangle \otimes |I m_I\rangle$$

$$= \sum_{m_j} \langle FM_F | j m_j\, I\ m_F - m_j\rangle |j m_j\rangle \otimes |I\ M_F - m_j\rangle$$

3S$_{1/2}$ state F=2

$$\boxed{|3S_{1/2};\ F=2, M_F=2\rangle = |\tfrac{1}{2}\ \tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\ \tfrac{3}{2}\rangle}$$

(stretched state)

$$|3S_{1/2};\ F=2, M_F=1\rangle = \langle 21|\tfrac{1}{2}\tfrac{1}{2}\ \tfrac{3}{2}\tfrac{1}{2}\rangle\ |\tfrac{1}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle + \langle 21|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\ \tfrac{3}{2}\tfrac{3}{2}\rangle\ |\tfrac{1}{2}\ \text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle$$

$$\boxed{|3S_{1/2};\ F=2, M_F=1\rangle = \frac{\sqrt{3}}{2}|\tfrac{1}{2}\tfrac{1}{2}\rangle|\tfrac{3}{2}\tfrac{1}{2}\rangle + \frac{1}{2}|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle}$$

$$|3S_{1/2};\ F=2, M_F=0\rangle = \langle 20|\tfrac{1}{2}\tfrac{1}{2}\ \tfrac{3}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{1}{2}\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\text{-}\tfrac{1}{2}\rangle + \langle 20|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\ \tfrac{3}{2}\tfrac{1}{2}\rangle|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle$$

$$\boxed{|3S_{1/2};\ F=2, M_F=0\rangle = \frac{1}{\sqrt{2}}|\tfrac{1}{2}\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\text{-}\tfrac{1}{2}\rangle + \frac{1}{\sqrt{2}}|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle}$$

Now use rule $\langle J\,{-M}|\, j_1\,{-m_1}\ j_2\,{-m_2}\rangle = (-1)^{j_1+j_2-j}\langle JM|\,j_1 m_1\, j_2 m_2\rangle$

$$\Rightarrow \boxed{|3S_{1/2};\ F=2;\ M_F=-1\rangle = \frac{\sqrt{3}}{2}|\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\text{-}\tfrac{1}{2}\rangle + \frac{1}{2}|\tfrac{1}{2}\,+\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\text{-}\tfrac{3}{2}\rangle}$$

$$\boxed{|3S_{1/2},\ F=2\ M_F=-2\rangle = |\tfrac{1}{2}\,\text{-}\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\text{-}\tfrac{3}{2}\rangle}$$

(stretched state)

The $3s_{1/2}$ state, $F=1$

We can determine these (up to an overall phase) just by orthogonality and selection rules. ~~Here~~ I will just use C-G coeffs

$$\boxed{\begin{aligned}
|3s_{1/2};\ F=1\ M_F=1\rangle &= \tfrac{1}{2}\,|\tfrac{1}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle - \tfrac{\sqrt{3}}{2}\,|\tfrac{1}{2}\,\tfrac{-1}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle \\
|3s_{1/2};\ F=1\ M_F=0\rangle &= \tfrac{1}{\sqrt{2}}\left(|\tfrac{1}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,{-1/2}\rangle - |\tfrac{1}{2}\,\tfrac{-1}{2}\rangle|\tfrac{3}{2}\,{+1/2}\rangle\right) \\
|3s_{1/2};\ F=1\ M_F=-1\rangle &= -\tfrac{1}{2}\,|\tfrac{1}{2}\,\tfrac{-1}{2}\rangle|\tfrac{3}{2}\,\tfrac{-1}{2}\rangle + \tfrac{\sqrt{3}}{2}\,|\tfrac{1}{2}\,{+1/2}\rangle|\tfrac{3}{2}\,\tfrac{-3}{2}\rangle
\end{aligned}}$$

We clearly see that $\langle F' M_F' | F M_F\rangle = \delta_{FF'}\,\delta_{M_F' M_F}$ for all states in this manifold

The $3p_{1/2}$ state $F=2$ or 1

These states have the same addition of $\vec{J}+\vec{I}$ as the $3s_{1/2}$ state and thus have the same decomposition in the uncoupled basis $|j M_j\rangle|I M_I\rangle$. These states differ from $3s_{1/2}$ in the <u>radial</u> wave funct.

$3p_{3/2}$ state $F=3$

Now $j=3/2$ $I=3/2$

Stretched state $\boxed{|3p_{3/2};\ F=3\ M_F=3\rangle = |\tfrac{3}{2}\,\tfrac{3}{2}\rangle \otimes |\tfrac{3}{2}\,\tfrac{3}{2}\rangle}$

(Next Page)

$$|3p_{3/2};\ F=3, M_F=2\rangle = \langle 3 2|\tfrac{3}{2}\tfrac{3}{2}\ \tfrac{3}{2}\tfrac{1}{2}\rangle\ |\tfrac{3}{2}\ \tfrac{3}{2}\rangle \otimes |\tfrac{3}{2}\ \tfrac{1}{2}\rangle$$

$$+ \langle 3 2|\tfrac{3}{2}\tfrac{1}{2}\ \tfrac{3}{2}\tfrac{3}{2}\rangle\ |\tfrac{3}{2}\ \tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\ \tfrac{3}{2}\rangle$$

$$\boxed{|F=3, M_F=2\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\ \tfrac{3}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle + |\tfrac{3}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle\right)}$$

$$|3p_{3/2};\ F=3, M_F=1\rangle = \langle 3 1|\tfrac{3}{2}\tfrac{3}{2}\ \tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle\ |\tfrac{3}{2}\ \tfrac{3}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle$$

$$+ \langle 3 1|\tfrac{3}{2}\tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\rangle\ |\tfrac{3}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle$$

$$+ \langle 3 1|\tfrac{3}{2}{-\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle\ |\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle$$

$$= \frac{1}{\sqrt{5}}|\tfrac{3}{2}\ \tfrac{3}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle + \sqrt{\frac{3}{5}}\ |\tfrac{3}{2}\tfrac{1}{2}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle + \frac{1}{\sqrt{5}}\ |\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}$$

$$|3p_{3/2};\ F=3, M_F=0\rangle = \langle 3 0|\tfrac{3}{2}\tfrac{3}{2}\ \tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle\ |\tfrac{3}{2}\ \tfrac{3}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle$$

$$+ \langle 3 0|\tfrac{3}{2}\tfrac{1}{2}\ \tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle\ |\tfrac{3}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle$$

$$+ \langle 3 0|\tfrac{3}{2}{-\tfrac{1}{2}}\ \tfrac{3}{2}\ \tfrac{1}{2}\rangle\ |\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle$$

$$+ \langle 3 0|\tfrac{3}{2}{-\tfrac{3}{2}}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle\ |\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle$$

$$= \frac{1}{2\sqrt{5}}\ |\tfrac{3}{2}\ \tfrac{3}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle + \frac{3}{2\sqrt{5}}|\tfrac{3}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle + \frac{3}{2\sqrt{5}}|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle$$

$$+ \frac{1}{2\sqrt{5}}|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle|\tfrac{3}{2}\ \tfrac{3}{2}\rangle$$

Again using the $M \to -M$ C-G rule

$$|3p_{3/2};\ F=3\ M_F=-1\rangle = \frac{1}{\sqrt{5}}|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle|\tfrac{3}{2}\ \tfrac{1}{2}\rangle + \sqrt{\frac{3}{5}}|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle + \frac{1}{\sqrt{5}}|\tfrac{3}{2}\ \tfrac{1}{2}\rangle|\tfrac{3}{2}\ {-\tfrac{3}{2}}$$

$$|3p_{3/2};\ F=3\ M_F=-2\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle|\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle + |\tfrac{3}{2}\ {-\tfrac{1}{2}}\rangle|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle\right)$$

$$|3p_{3/2};\ F=3\ M_F=-3\rangle = |\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle|\tfrac{3}{2}\ {-\tfrac{3}{2}}\rangle$$

Next Page

$3P_{3/2}$ F = 2 state

Again, up to a phase we can find these through selection rules and orthogonality to $3P_{1/2}$ F = 2 states. Here I will use C-G coefficients.

$$|3P_{3/2}\ F=2,\ M_F=2\rangle = \langle 2\,2|\tfrac{3}{2}\,\tfrac{3}{2}\ \tfrac{3}{2}\,\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle$$
$$+ \langle 2\,2|\tfrac{3}{2}\,\tfrac{1}{2}\ \tfrac{3}{2}\,\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle$$
$$= \frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle\right)$$

$$|3P_{3/2}\ F=2\ \ M_F=1\rangle = \langle 2\,1|\tfrac{3}{2}\,\tfrac{3}{2}\ \tfrac{3}{2}\,-\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle$$
$$+ \langle 2\,1|\tfrac{3}{2}\,\tfrac{1}{2}\ \tfrac{3}{2}\,\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle$$
$$+ \langle 2\,1|\tfrac{3}{2}\,-\tfrac{1}{2}\ \tfrac{3}{2}\,\tfrac{3}{2}\rangle\,|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{3}{2}\rangle$$
$$= \frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle\right)$$

$$|3P_{3/2};\ F=2\ \ M_F=0\rangle = \langle 2\,0|\tfrac{3}{2}\,\tfrac{3}{2}\ \tfrac{3}{2}\,-\tfrac{3}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle$$
$$+ \langle 2\,0|\tfrac{3}{2}\,\tfrac{1}{2}\ \tfrac{3}{2}\,-\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle$$
$$+ \langle 2\,0|\tfrac{3}{2}\,-\tfrac{1}{2}\ \tfrac{3}{2}\,\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle$$
$$+ \langle 2\,0|\tfrac{3}{2}\,-\tfrac{3}{2}\ \tfrac{3}{2}\,\tfrac{3}{2}\rangle\,|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle\,|\tfrac{3}{2}\,\tfrac{3}{2}\rangle$$
$$= +\frac{1}{2}\left(|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle + |\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle\right.$$
$$\left. - |\tfrac{3}{2}\,-\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle\right)$$

Again

$3P_{3/2}$ $$|F=2\ M_F=-1\rangle = -\frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle\right)$$

$$|F=2\ M_F=-2\rangle = -\frac{1}{\sqrt{2}}\left(|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle\right)$$

$3p_{3/2}$ F=1 state

$$\boxed{|3p_{3/2};\ F=1\ M_F=1\rangle = \sqrt{\tfrac{3}{10}}\left(|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{-1}{2}\rangle\right) - \sqrt{\tfrac{2}{5}}\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle + \sqrt{\tfrac{3}{10}}\,|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle}$$

$$\boxed{|3p_{3/2};\ F=1\ M_F=0\rangle = \frac{1}{\sqrt{5}}\left(\tfrac{3}{2}|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle - \tfrac{1}{2}|\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle - \tfrac{1}{2}|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle + \tfrac{3}{2}|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle\right.}$$

$$\boxed{|3p_{3/2};\ F=1\ M_F=-1\rangle = \sqrt{\tfrac{3}{10}}\,|\tfrac{3}{2}\,\tfrac{-3}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{5}}\,|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle + \sqrt{\tfrac{3}{10}}\,|\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle}$$

Finally !

$$\boxed{|3p_{3/2};\ F=0\ M=0\rangle = \frac{1}{2}\left(|\tfrac{3}{2}\,\tfrac{3}{2}\rangle|\tfrac{3}{2}\,-\tfrac{3}{2}\rangle - |\tfrac{3}{2}\,\tfrac{1}{2}\rangle|\tfrac{3}{2}\,-\tfrac{1}{2}\rangle + |\tfrac{3}{2}\,-\tfrac{1}{2}\rangle|\tfrac{3}{2}\,\tfrac{1}{2}\rangle - |\tfrac{3}{2}\,-\tfrac{3}{2}\rangle|\tfrac{3}{2}\,\tfrac{3}{2}\rangle\right)}$$

This will always be an equally weighted ~~suppo~~ superposition, i.e. for $j + j \to J = 0$

$|0\ 0\rangle$ = equally weighted superposition of anti correllated state $|j\ m\rangle|j\ -m\rangle$

The simplest example is the spin-singlet

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

(b) Check using recursion relations

Start with streched state

$$|F=3 \;\; M_F=3\rangle = |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{3}{2}\rangle$$

$$\hat{F}_- = \hat{J}_- + \hat{I}_- \Rightarrow \hat{F}_- |F=3, M_F=3\rangle = \hat{J}_- |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \otimes \hat{I}_- |\tfrac{3}{2}\;\tfrac{3}{2}\rangle$$

$$\Rightarrow \sqrt{3(3+1) - 3(3-1)}\; |F=3, M_F=2\rangle = \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{3}{2}(\tfrac{3}{2}-1)} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)$$

$$\Rightarrow \boxed{|F=3, M_F=2\rangle = \frac{1}{\sqrt{2}} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)} \checkmark$$

$$\hat{F}_- |F=3, M_F=2\rangle = \frac{1}{\sqrt{2}} \hat{J}_- |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + \frac{1}{\sqrt{2}} |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \otimes I_- |\tfrac{3}{2}\;\tfrac{3}{2}\rangle$$

$$+ \frac{1}{\sqrt{2}} \hat{J}_- |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{1}{2}\rangle + \frac{1}{\sqrt{2}} |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \otimes I_- |\tfrac{3}{2}\;\tfrac{1}{2}\rangle$$

$$\sqrt{3(3+1) - 2(2-1)}\, |F=3, M_F=1\rangle = \frac{1}{\sqrt{2}} \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)} \left(|\tfrac{3}{2}\; -\tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2}\; -\tfrac{1}{2}\right.$$

$$+ \frac{2}{\sqrt{2}} \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{3}{2}(\tfrac{3}{2}-1)} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)$$

$$\Rightarrow \boxed{|F=3, M_F=1\rangle = \frac{1}{\sqrt{5}} \left(|\tfrac{3}{2}\; -\tfrac{1}{2}\rangle \otimes |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2}\; -\tfrac{1}{2}\rangle \right) + \sqrt{\frac{3}{5}} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)} \checkmark$$

$$\sqrt{3(3+1) - 0}\, |F=3, M_F=0\rangle = \frac{1}{\sqrt{5}} \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) + \tfrac{1}{2}(-\tfrac{1}{2}-1)} \left(|\tfrac{3}{2} -\tfrac{3}{2}\rangle |\tfrac{3}{2}\;\tfrac{3}{2}\rangle + |\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2} -\tfrac{3}{2}\rangle \right)$$

$$+ \frac{1}{\sqrt{5}} \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{3}{2}(\tfrac{3}{2}-1)} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle |\tfrac{3}{2} -\tfrac{1}{2}\rangle + |\tfrac{3}{2} -\tfrac{1}{2}\rangle |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)$$

$$+ \sqrt{\frac{3}{5}} \sqrt{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)} \left(|\tfrac{3}{2}\;\tfrac{1}{2}\rangle |\tfrac{3}{2} -\tfrac{1}{2}\rangle + |\tfrac{3}{2} -\tfrac{1}{2}\rangle |\tfrac{3}{2}\;\tfrac{1}{2}\rangle \right)$$

$$\checkmark \Rightarrow |F=3, M_F=0\rangle = \frac{1}{2\sqrt{5}} \left(|\tfrac{3}{2}\;\tfrac{3}{2}\rangle |\tfrac{3}{2} -\tfrac{3}{2}\rangle + |\tfrac{3}{2} -\tfrac{3}{2}\rangle |\tfrac{3}{2}\;\tfrac{3}{2}\rangle \right) + \frac{3}{2\sqrt{5}} \left(|\tfrac{3}{2}\tfrac{1}{2}\rangle |\tfrac{3}{2} -\tfrac{1}{2}\rangle + |\tfrac{3}{2} -\tfrac{1}{2}\rangle |\tfrac{3}{2}\tfrac{1}{2}\rangle \right)$$

(6) Dipole matrix elements $\langle 3p_{1/2}\ F' M_F' |\ \hat{d}_z\ | 3s_{1/2}\ F\ M_F \rangle$

In problem set 1 we found

$\langle P_{1/2}\ m_j' |\ \hat{d}_z\ | S_{1/2}\ m_j \rangle$ <u>vanished</u> unless $m_j = m_j'$

Example: $\langle 3P_{1/2}\ F=1\ M_F' |\ \hat{d}_z\ | 3S_{1/2}\ F=1\ 0 \rangle$

$$M_F'=1: \left(\tfrac{1}{2} \langle \tfrac12\, \tfrac12 | \langle \tfrac32\, \tfrac12 | - \tfrac{\sqrt{3}}{2} \langle \tfrac12\, -\tfrac12 | \langle \tfrac32\, \tfrac32 | \right) \hat{d}_z \left(\tfrac{1}{\sqrt{2}} | \tfrac12\, \tfrac12 \rangle | \tfrac32\, -\tfrac12 \rangle - \tfrac{1}{\sqrt{2}} | \tfrac12\, -\tfrac12 \rangle | \tfrac32\, \tfrac12 \rangle \right)$$

$$= \frac{1}{2\sqrt{2}} \langle \underset{\overset{\uparrow}{j}}{\tfrac12}\, \underset{\overset{\uparrow}{m_j}}{\tfrac12} |\ \hat{d}_z\ | \tfrac12\, -\tfrac12 \rangle$$ using orthogonality of $|\cancel{I}\ m_I\rangle$ states

$= 0$ from above

$$M_F'=0 \left(\tfrac{1}{\sqrt{2}} \langle \tfrac12\, \tfrac12 | \langle \tfrac32\, -\tfrac12 | - \tfrac{1}{\sqrt{2}} \langle \tfrac12\, -\tfrac12 | \langle \tfrac32\, \tfrac12 | \right) \hat{d}_z \left(\tfrac{1}{\sqrt{2}} | \tfrac12\, \tfrac12 \rangle | \tfrac32\, -\tfrac12 \rangle - \tfrac{1}{\sqrt{2}} | \tfrac12\, -\tfrac12 \rangle | \tfrac32\, \tfrac12 \rangle \right)$$

$$= \tfrac{1}{2} \langle P_{1/2}\ \tfrac12 |\ \hat{d}_z\ | S_{1/2}\ \tfrac12 \rangle + \tfrac{1}{2} \langle P_{1/2}\ -\tfrac12 |\ \hat{d}_z\ | S_{1/2}\ -\tfrac12 \rangle$$

$$M_F'=-1 \left(-\tfrac{1}{2} \langle \tfrac12\, -\tfrac12 | \langle \tfrac32\, -\tfrac12 | + \tfrac{\sqrt{3}}{2} \langle \tfrac12\, \tfrac12 | \langle \tfrac32\, -\tfrac32 | \right) \hat{d}_z \left(\tfrac{1}{\sqrt{2}} | \tfrac12\, \tfrac12 \rangle | \tfrac32\, -\tfrac12 \rangle - \tfrac{1}{\sqrt{2}} | \tfrac12\, -\tfrac12 \rangle | \tfrac32\, \tfrac12 \rangle \right)$$

$$= -\tfrac{1}{2} \langle \tfrac12\, -\tfrac12 |\ \hat{d}_z\ | \tfrac12\, \tfrac12 \rangle = 0$$

(Next Page)

Thus we see the selection rule

$$\langle 3p_{1/2}\ F' M_F' \,|\, \hat{d}_z \,|\, 3s_{1/2}\ F M_F \rangle$$

vanishes unless $M_F = M_F'$

This is another example of the Wigner-Eckart theorem. We will find a <u>MUCH</u> simpler and less tedious way of instantly determining this rule

Problem 2: Zeeman effect in ground state of hydrogen

$$\hat{H} = \underbrace{A\,\hat{\vec{\imath}}\cdot\hat{\vec{s}}}_{\text{hyperfine coupling}} + \underbrace{g_e \mu_B \vec{B}\cdot\hat{\vec{s}} - g_p \mu_N \vec{B}\cdot\hat{\vec{\imath}}}_{\text{coupling to external } \vec{B}\text{-field}}$$

$$\equiv \hat{H}_{HF} + \hat{H}_B$$

(a) Weak field: $\mu_B B << A$.

$\frac{A}{h} \cong 1.42\,\text{GHz}$ for 1s of hydrogen

$\frac{\mu_B}{h} \cong 1.4\,\text{MHz/Gauss}$ (Bohr Magneton)

$$\Rightarrow \boxed{\text{Weak } B \underset{\sim}{<<} 1\,\text{kG} \quad (1,000 \text{ Gauss})}$$

In the weak-field limit $\hat{H}_B$ is a perturbation to $\hat{H}_{HF}$. The "good quantum numbers" are those that ~~eigen~~ define the eigenvector of $\hat{H}_{HF}$. These are the <u>coupled</u> angular momentum.

$$\boxed{|F M_F, i, s\rangle \quad \text{(also principle quantum number } n\text{, and orbital } l\text{)}}$$

The shifts, to lowest nonvanish order are first order

$$\delta E^{(1)}_{FM_F} = \langle F M_F, i, s|\, \hat{H}_B \,|F M_F, i s\rangle$$

(Next Page)

From Lecture, we have the eigenstates in coupled representation

$$F=1 \quad \begin{cases} |F=1,\ M_F=1\rangle = |++\rangle \\ |F=1,\ M_F=0\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle + |-+\rangle\right) \\ |F=1,\ M_F=-1\rangle = |--\rangle \end{cases}$$

$$F=0 \quad \left\{\ |F=0,\ M_F=0\rangle = \frac{1}{\sqrt{2}}\left(|+-\rangle - |-+\rangle\right)\right.$$

Where $|\pm, \pm\rangle$

electron spin up/down

proton spin up/down

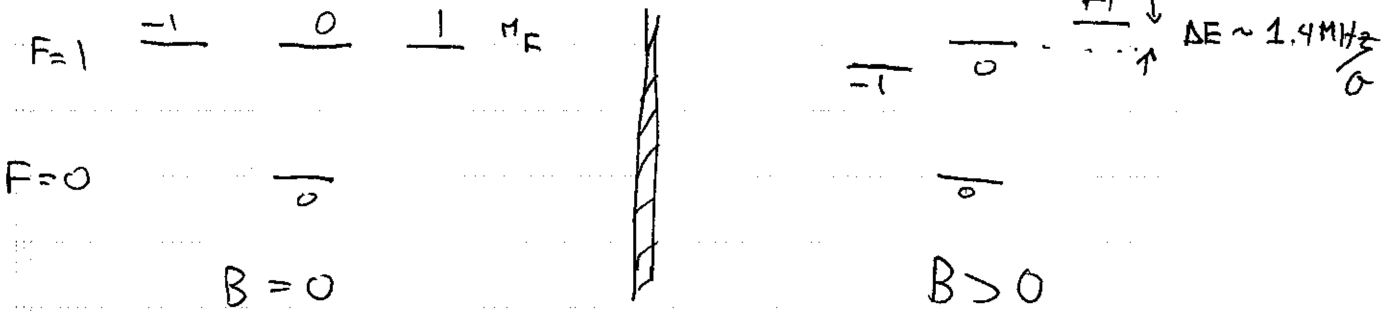
Aside: In the uncoupled basis

$$\langle m_s', m_i' | \hat{H}_B | m_s, m_i\rangle = g_e \mu_B B\, m_s\, \delta_{m_s m_s'} - \cancelto{\text{neglect}}{g_p \mu_N B\, m_i\, \delta_{m_i m_i'}}$$

In the weak field regime $\mu_N B$ is negligible

$$\Rightarrow \boxed{\begin{aligned} \delta E^{(1)}_{F=1, M_F=1} &= g_e \frac{\mu_B B}{2} \cong \left(1.4\ \text{MHz}/\text{Gauss}\right) B \\ \delta E^{(1)}_{F=1, M_F=0} &= 0 \\ \delta E^{(1)}_{F=1, M_F=-1} &= -g_e \frac{\mu_B B}{2} \cong \left(-1.4\ \text{MHz}/\text{Gauss}\right) B \\ \delta E^{(1)}_{F=0, M_F=0} &= 0 \end{aligned}}$$

Zeeman Shifts in Weak-field limit



Zeeman shift linear w/ B

(b) In the very strong field limit (Pashen-Back regime) $\hat{H}_B$ is dominant; $\hat{H}_{HF}$ is a perturbation

$\hat{H}_B$ commutes with $\hat{S}_z$ and $\hat{i}_z$ (taking $\vec{B}$ in the z-direction) ⟹ Good quantum numbers are the "uncoupled representation"

$$|s\, m_s\rangle |i\, m_i\rangle$$

- To zeroth order, the energy levels are the eigenstates of $\hat{H}_B$

$$\boxed{E^{(0)}_{m_s,m_i} = g_e \mu_B B m_s - \cancel{g_p \mu_N B m_i}} \quad \text{Typically negligible}$$

Again linear in B, but near degenerate in m_i

- The first-order correction (due to hyperfine coupling)

$$\delta E^{(1)}_{m_s m_i} = \langle m_s m_i | A \hat{\vec{I}} \cdot \hat{\vec{S}} | m_s m_i \rangle = A \langle m_s m_i | \left(\frac{\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+}{2} + \hat{I}_z \hat{S}_z \right| m_s m_i \rangle$$

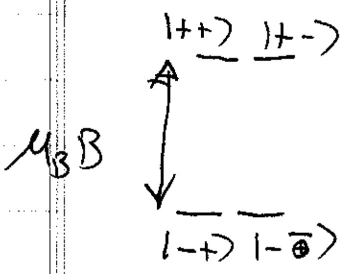
$$\Rightarrow \boxed{\delta E^{(1)}_{m_s m_i} = A m_s m_i}$$

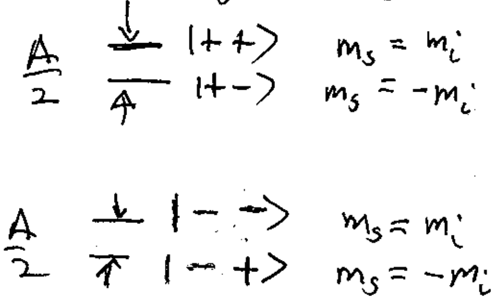
(b) Continued

$$\Rightarrow \quad \delta E^{(1)}_{m_s m_i} = \frac{A}{4} \qquad m_s = m_i = \pm\frac{1}{2}$$

$$\delta E^{(1)}_{m_s m_i} = -\frac{A}{4} \qquad -m_s = m_i = \pm\frac{1}{2}$$

Zeeman shift in Pashen-Back regime





No Hyperfine
(neglecting nuclear)

Note: For very very large fields such that $\mu_N B >> A$ the nuclear spin cannot be neglected and nuclear spin-up is shifted down in energy relative to nuclear spin-down.

(Next Page)

(c) Exact diagonalization in 1s subspace

$$\hat{H} = \underbrace{A\hat{\vec{I}}\cdot\hat{\vec{S}}}_{\hat{H}_{HF}} + \underbrace{g_e\mu_B B\hat{S}_z - g_p\mu_N B\hat{I}_z}_{\hat{H}_B}$$

Consider: $\hat{F}_z = \hat{S}_z + \hat{I}_z$

Since $[\hat{S}_z, \hat{F}_z] = 0$ and $[\hat{I}_z, \hat{F}_z] = 0$

$$\Rightarrow [\hat{H}_B, \hat{F}_z] = 0$$

Also, since $\vec{I}\cdot\vec{S} = \frac{F^2 - I^2 - S^2}{2}$

and $[\hat{F}^2, \hat{F}_z] = 0$, $[\hat{I}^2, \hat{F}_z] = 0$, $[\hat{S}^2, \hat{F}_z] = 0$

$$\Rightarrow [\hat{H}_{HF}, \hat{F}_z] = 0$$

$$\Rightarrow \boxed{[\hat{H}, \hat{F}_z] = 0}$$

$\Rightarrow$ $\hat{H}$ is block-diagonal in subspaces with a given value of $\hat{F}_z$

(Next Page)

We will write a matrix representation of $\hat{H}$ is the coupled basis. The three possible values of M_F determine three subspaces

$\underline{M_F = 1}$: Only one state: $|F=1, M_F=1\rangle$

$\underline{M_F = -1}$: Only one state: $|F=1, M_F-1\rangle$

$\underline{M_F = 0}$: 2D subspace $\underbrace{|F=0, M_F=0\rangle \text{ and } |F=1, M_F=0\rangle}$

$\hat{H}_{HF}$ is diagonal in this basis. $\hat{H}_B$ has off-diagonal elements in the $M_F = 0$ subspace.

Ordering the basis $\{ |\underset{F}{1}, \underset{M_F}{1}\rangle, |1 -1\rangle, |1 0\rangle, |0,0\rangle \}$

$$\hat{H} = \underbrace{\begin{bmatrix} \frac{A}{4} & 0 & 0 & 0 \\ 0 & \frac{A}{4} & 0 & 0 \\ 0 & 0 & \frac{A}{4} & 0 \\ 0 & 0 & 0 & -3\frac{A}{4} \end{bmatrix}}_{\hat{H}_{HF}} + \underbrace{\begin{bmatrix} (g_e \mu_B - g_p \mu_N)\frac{B}{2} & 0 & 0 & 0 \\ 0 & -(g_e \mu_B - g_p \mu_N) B & 0 & 0 \\ 0 & 0 & 0 & \langle 10|\hat{H}_B|00\rangle \\ 0 & 0 & \langle 00|\hat{H}_B|10\rangle & 0 \end{bmatrix}}_{\hat{H}_B}$$

Aside: $$\langle 10|\hat{H}_B|00\rangle = \left(\frac{\langle +-| + \langle -+|}{\sqrt{2}}\right)\left(g_e \mu_B B \hat{S}_z - g_p \mu_N \hat{I}_z\right)\left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}}\right)$$

$$= \frac{g_e \mu_B B}{2} + \frac{g_p \mu_N B}{2}$$

In the $M_F = \pm 1$ subspaces $|1,1\rangle$ and $|1,-1\rangle$ are eigenvectors of the total Hamiltonian, with eigenvalue

$$\boxed{E(M_F=\pm 1) = \frac{A}{4} \pm (g_e\mu_B - g_p\mu_N)\frac{B}{2}}$$

In the $M_F=0$ subspace, we must diagonalize the 2X2 block

$$\hat{H}_{M_F=0} = \begin{bmatrix} \frac{A}{4} & (g_e\mu_B + g_p\mu_N)\frac{B}{2} \\ (g_e\mu_B+g_p\mu_N)\frac{B}{2} & -\frac{3A}{4} \end{bmatrix}$$

$$= A\begin{bmatrix} \frac{1}{4} & \frac{x}{2} \\ \frac{x}{2} & -\frac{3}{4} \end{bmatrix}$$

where $\boxed{x \equiv (g_e\mu_B+g_p\mu_N)\frac{B}{A}}$

Eigenvalues: $A\left(-\frac{1}{4} \pm \frac{1}{2}\sqrt{1+x^2}\right)$

$$\Rightarrow \boxed{E_\pm(M_F=0) = -\frac{A}{4} \pm \frac{A}{2}\sqrt{1+x^2}}$$

Check w/ Breit-Rabi formula

$$E_\pm(M_F) = -g_p\mu_N B m_F - \frac{A}{4} \pm \frac{A}{2}\sqrt{1+2m_F x + x^2}$$

$M_F = \pm 1$ $\quad E_\pm(\pm 1) = \mp g_p\mu_N B - \frac{A}{4} \pm \frac{A}{2}(x \pm 1)$

Here 1D, so only one root (+ ~~root~~ for $M_F=+1$
− root for $M_F=-1$)

$$\Rightarrow E(M_F=\pm 1) = \frac{A}{4} \pm \frac{A}{2}x \mp g_p \mu_N B$$

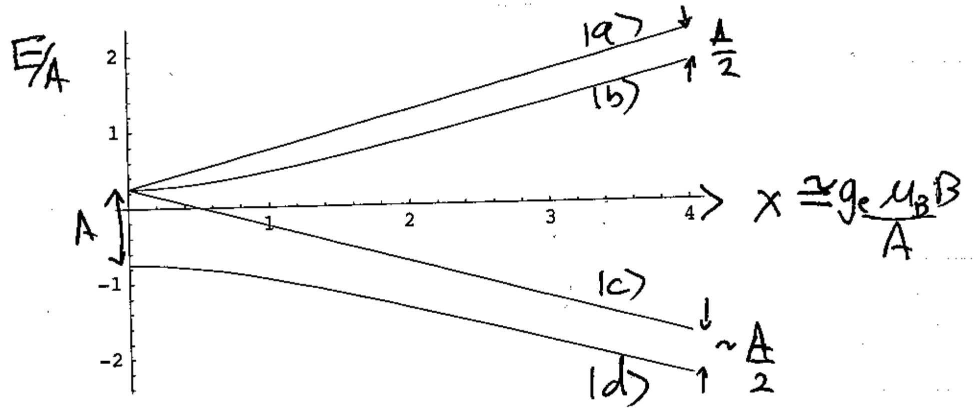
$$= \frac{A}{4} \pm (g_e \mu_B + g_p \mu_N)\frac{B}{2} \mp g_p \mu_N B$$

$$\Rightarrow \boxed{E(M_F \pm 1) = \frac{A}{4} \pm (g_e \mu_B - g_p \mu_N)\frac{B}{2}}$$ ✓

For $M_F = 0$, we have two roots

$$\boxed{E(M_F=0) = -\frac{A}{4} \pm \frac{A}{2}\sqrt{1+x^2}}$$ ✓

(d)



Breit - Rabi diagram (neglecting nuclear magneton)

- For $x \ll 1$ (weak field) we see shifts within the hyperfine manifold $|F M_F\rangle$
- For $x \gg 1$ (strong field) the spins decouple and separately shift.

$|a\rangle = |F=1, M_F=1\rangle = |++\rangle$

$|c\rangle = |F=1, M_F - 1\rangle = |--\rangle$

$|b\rangle \longrightarrow |F=1, M_F=0\rangle$ (weak) $\quad |+-\rangle$ (strong)

$|d\rangle \rightarrow |F=0, M=0\rangle$ (weak) $\quad |-+\rangle$ (strong)

(e) Asymptotic expansions

- For $M_F = \pm 1$, the eigenvalue has the same form, independent of B (stretched state)

$$E(M_F = \pm 1) = \frac{A}{4} \pm g_e \mu_B B \quad (\text{neglecting } \mu_N)$$

- For $M_F = 0$ we must expand $-\frac{A}{4} \pm \frac{A}{2}\sqrt{1+x^2}$

Weak Field $\quad x = \frac{\mu_B B}{A} \ll 1$

$$\delta E^{(1)}(M_F = \pm 1) = \pm g_e \mu_B B$$

$$\delta E^{(1)}(M_F = 0) = 0 \quad (\text{no shift in first order})$$

Strong Field $\quad x \gg 1$

$$\delta E^{(1)}(M_F = \pm 1) = \frac{A}{4} = (\pm\tfrac{1}{2})(\pm\tfrac{1}{2})A \quad ✓$$

$$\delta E^{(1)}(M_F = 0) = -\frac{A}{4} = (\pm\tfrac{1}{2})(\mp\tfrac{1}{2})A \quad ✓$$

These agree with perturbation theory