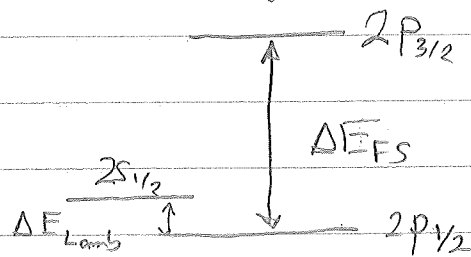


Physics 531: Atomic Physics

Problem Set #2 Solutions

Problem 1: Stark effect with Fine Structure

$n=2$ manifold of hydrogen (including fine structure)



Recall spectroscopic notation: $n l j$: e.g. $2s_{1/2}$ $\leftarrow \begin{matrix} n=2 \\ \downarrow \\ l=0 \\ \leftarrow \\ j=1/2 \end{matrix}$

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

sublevels specified by q -number m_j : $|n l j, m_j\rangle$

Stark effect perturbation: $\hat{H}_{int} = +e \hat{z} \mathcal{E}_z$ (\vec{E} along z -axis).

Since this interaction acts on the spatial (orbital) degree of freedom, it will be useful to re-express the eigenstates above in terms of the "uncoupled" angular momentum basis. We do this using the Clebsch-Gordan coefficients:

$$|n l j, m_j\rangle = \sum_{m_l, m_s} \langle j m_j | l m_l s m_s \rangle |l m_l\rangle |s m_s\rangle$$

$$\Rightarrow |2s_{1/2}, \pm \frac{1}{2}\rangle = |2s, 0\rangle \otimes |\pm \frac{1}{2}\rangle$$

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

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

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

- (a) For weak fields $ea_0 E_z \gtrsim \Delta E_{\text{Lamb}}$, 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 elements between different m_j as we will see below

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

$$\hat{H}_0 + \hat{H}_{\text{int}} = \begin{bmatrix} \Delta E_L & \epsilon \\ \epsilon^* & 0 \end{bmatrix} \quad \text{where } \Delta E_L = \text{Lamb shift}$$

$$\begin{matrix} |2S_{1/2}, 1/2\rangle & |2P_{1/2}, 1/2\rangle \end{matrix} \quad \epsilon = \langle 2P_{1/2}, 1/2 | \hat{H}_{\text{int}} | 2S_{1/2}, 1/2 \rangle$$

To calculate ϵ , we use the uncoupled representation above:

$$\epsilon = \underbrace{\frac{1}{\sqrt{3}} \langle 2p, 0 | \hat{z} | 2s, 0 \rangle}_{-eE_z} \underbrace{\langle \frac{1}{2}, \frac{1}{2} |}_{1} \hat{z} \underbrace{| \frac{1}{2}, \frac{1}{2} \rangle}_{0} - \frac{\sqrt{2}}{3} \langle 2p, 1 | \hat{z} | 2s, 0 \rangle \underbrace{\langle \frac{1}{2}, \frac{1}{2} |}_{\text{orthogonal spin}}$$

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

$$\Rightarrow \boxed{\epsilon = \frac{\sqrt{3}}{3} ea_0 E_z} \quad (\text{real})$$

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

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

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 $\Delta E'_L = 2\Delta E_L$

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

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

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

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 $h = 4.14 \times 10^{-15} \text{ eV} \cdot \text{s}$

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

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

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

(b) Consider $e a_0 E_z \vec{\sigma} \Delta E_{FS} \Rightarrow$ include all states in $n=2$

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

We must thus diagonalize the following 3×3 matrix

$$\hat{H} = \begin{bmatrix} \Delta E_L & \epsilon & \beta \\ \epsilon & 0 & 0 \\ \beta & 0 & \Delta E_{FS} \end{bmatrix} \quad m_j = \pm 1/2$$

$|2S_{1/2}\rangle$ $|2P_{1/2}\rangle$ $|2P_{3/2}\rangle$

note the $|2P_{3/2}, m_j = \pm 3/2\rangle$ is unperturbed

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

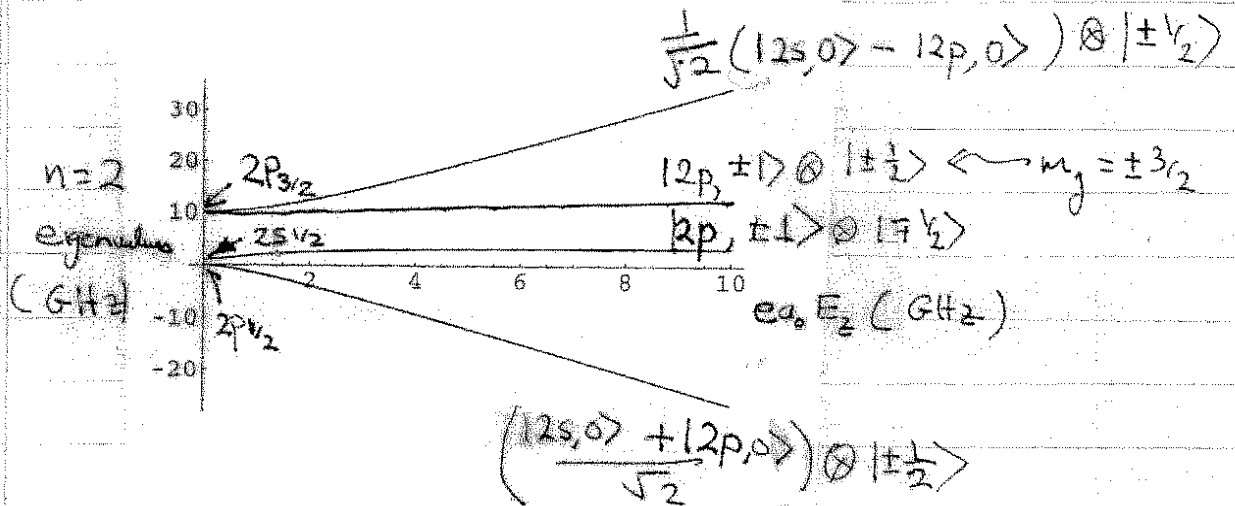
$$= -e E_z \left[\underbrace{\sqrt{\frac{2}{3}} \langle 2p, 0 | z | 2s, 0 \rangle}_{-3a_0} \underbrace{\langle \frac{1}{2}, \frac{1}{2} |}_{=1} + \sqrt{\frac{1}{3}} \langle 2p, 1 | z | 2s, 0 \rangle \right]$$

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

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

$\Delta E_L = 1 \text{ GHz}$

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

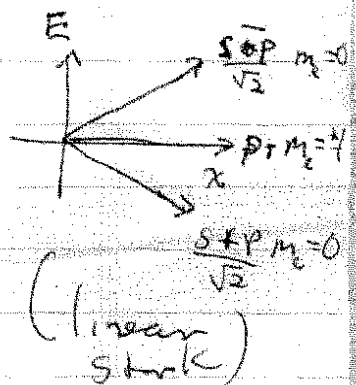


(c) Asymptotic behavior. Note for small x we recover the behavior of part (a) (the level $12P_{3/2}$ is too far away). For sufficiently large x the fine-structure is negligible and we recover the simple linear Stark shift discussed in class. That we cover the expected eigenvectors can be seen in the large x limit setting $\frac{\Delta E_{FS}}{x} = \frac{\Delta E_L}{x} = 0$

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

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

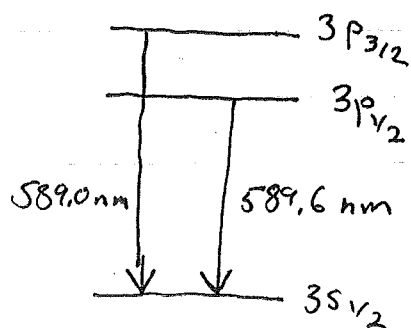
Eigenvectors
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Problem 2

Alkali atoms look a lot like Hydrogen with its one valence 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



These closely spaced spectral lines are known as D1 and D2.

Not to scale

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

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

C-G expansion

$$|nlj\rangle |FM_F\rangle = \sum_{m_j m_I} \langle FM_F | j m_j I m_I \rangle |j m_j\rangle \otimes |I m_I\rangle$$

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

radial wave function 3S understood

3S_{1/2} state F=2

$$|3S_{1/2}; F=2, M_F=2\rangle = \left| \frac{1}{2} \frac{1}{2} \right\rangle \otimes \left| \frac{3}{2} \frac{3}{2} \right\rangle \quad (\text{stretched state})$$

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

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

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

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

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

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

$$|3S_{1/2}; F=2, M_F=-2\rangle = \left| \frac{1}{2} -\frac{1}{2} \right\rangle \left| \frac{3}{2} -\frac{3}{2} \right\rangle$$

(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

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

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 radial wave funct.

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

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

Stretched state $|3P_{3/2}; F=3 M_F=3\rangle = \left| \frac{3}{2} \frac{3}{2} \right\rangle \otimes \left| \frac{3}{2} \frac{3}{2} \right\rangle$

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$$|3P_{3/2}; F=3, M_F=2\rangle = \langle 32 | \frac{3}{2} \frac{3}{2} \frac{3}{2} \frac{1}{2} \rangle | \frac{3}{2} \frac{3}{2} \rangle \otimes | \frac{3}{2} \frac{1}{2} \rangle$$

$$+ \langle 32 | \frac{3}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \rangle | \frac{3}{2} \frac{1}{2} \rangle \otimes | \frac{3}{2} \frac{3}{2} \rangle$$

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

$$|3P_{3/2}; F=3, M_F=1\rangle = \langle 31 | \frac{3}{2} \frac{3}{2} \frac{3}{2} -\frac{1}{2} \rangle | \frac{3}{2} \frac{3}{2} \rangle | \frac{3}{2} -\frac{1}{2} \rangle$$

$$+ \langle 31 | \frac{3}{2} \frac{1}{2} \frac{3}{2} \frac{1}{2} \rangle | \frac{3}{2} \frac{1}{2} \rangle | \frac{3}{2} \frac{1}{2} \rangle$$

$$+ \langle 31 | \frac{3}{2} \frac{1}{2} \frac{3}{2} \frac{3}{2} \rangle | \frac{3}{2} -\frac{1}{2} \rangle | \frac{3}{2} \frac{3}{2} \rangle$$

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

$$|3P_{3/2}; F=3, M_F=0\rangle = \langle 30 | \frac{3}{2} \frac{3}{2} \frac{3}{2} -\frac{3}{2} \rangle | \frac{3}{2} \frac{3}{2} \rangle | \frac{3}{2} -\frac{3}{2} \rangle$$

$$+ \langle 30 | \frac{3}{2} \frac{1}{2} \frac{3}{2} -\frac{1}{2} \rangle | \frac{3}{2} \frac{1}{2} \rangle | \frac{3}{2} -\frac{1}{2} \rangle$$

$$+ \langle 30 | \frac{3}{2} -\frac{1}{2} \frac{3}{2} \frac{1}{2} \rangle | \frac{3}{2} -\frac{1}{2} \rangle | \frac{3}{2} \frac{1}{2} \rangle$$

$$+ \langle 30 | \frac{3}{2} -\frac{3}{2} \frac{3}{2} \frac{3}{2} \rangle | \frac{3}{2} -\frac{3}{2} \rangle | \frac{3}{2} \frac{3}{2} \rangle$$

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

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

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

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

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

$$|3P_{3/2}; F=3, M_F=-3\rangle = | \frac{3}{2} -\frac{3}{2} \rangle | \frac{3}{2} -\frac{3}{2} \rangle$$

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

$$\begin{aligned} |3p_{3/2} F=2, M_F=2\rangle &= \langle 2 | \begin{matrix} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \\ &= \frac{1}{\sqrt{2}} \left(| \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle - | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \right) \end{aligned}$$

$$\begin{aligned} |3p_{3/2} F=2, M_F=1\rangle &= \langle 2 | \begin{matrix} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & \frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & -\frac{1}{2} & \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \\ &= \frac{1}{\sqrt{2}} \left(| \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle - | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \right) \end{aligned}$$

$$\begin{aligned} |3p_{3/2} F=2, M_F=0\rangle &= \langle 2 | \begin{matrix} \frac{3}{2} & \frac{3}{2} & \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & \frac{1}{2} & \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & -\frac{1}{2} & \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle \\ &+ \langle 2 | \begin{matrix} \frac{3}{2} & -\frac{3}{2} & \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \\ &= \frac{1}{2} \left(| \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle + | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle - | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle \right. \\ &\quad \left. - | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{3}{2} \end{matrix} \rangle \right) \end{aligned}$$

Again

$$|3p_{3/2} F=2, M_F=-1\rangle = -\frac{1}{\sqrt{2}} \left(| \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle - | \begin{matrix} \frac{3}{2} & \frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle \right)$$

$$|3p_{3/2} F=2, M_F=-2\rangle = -\frac{1}{\sqrt{2}} \left(| \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle - | \begin{matrix} \frac{3}{2} & -\frac{1}{2} \end{matrix} \rangle | \begin{matrix} \frac{3}{2} & -\frac{3}{2} \end{matrix} \rangle \right)$$

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

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

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

$$|3p_{3/2}; F=1 M_F=-1\rangle = \sqrt{\frac{3}{10}} \left| \frac{3}{2} \frac{-3}{2} \right\rangle \left| \frac{3}{2} \frac{1}{2} \right\rangle - \sqrt{\frac{2}{5}} \left| \frac{3}{2} \frac{-1}{2} \right\rangle \left| \frac{3}{2} \frac{-1}{2} \right\rangle \\ + \sqrt{\frac{3}{10}} \left| \frac{3}{2} \frac{1}{2} \right\rangle \left| \frac{3}{2} \frac{-3}{2} \right\rangle$$

Finally!

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

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

$|00\rangle =$ equally weighted superposition of anticorrelated state $|j m\rangle |j -m\rangle$

The simplest example is the spin-singlet

$$|00\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

(b) Check using recursion relations

Start with stretched state

$$|F=3, M_F=3\rangle = \left| \frac{3}{2} \frac{3}{2} \right\rangle \otimes \left| \frac{3}{2} \frac{3}{2} \right\rangle$$

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

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

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

$$\hat{F}_- |F=3, M_F=2\rangle = \frac{1}{\sqrt{2}} \hat{J}_- \left| \frac{3}{2} \frac{1}{2} \right\rangle \otimes \left| \frac{3}{2} \frac{3}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{3}{2} \frac{1}{2} \right\rangle \otimes \hat{I}_- \left| \frac{3}{2} \frac{3}{2} \right\rangle + \frac{1}{\sqrt{2}} \hat{J}_- \left| \frac{3}{2} \frac{3}{2} \right\rangle \otimes \left| \frac{3}{2} \frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| \frac{3}{2} \frac{3}{2} \right\rangle \otimes \hat{I}_- \left| \frac{3}{2} \frac{1}{2} \right\rangle$$

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

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

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

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

(c) 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

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

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

$$M_F' = 1: \left(\frac{1}{2} \langle \frac{1}{2} \frac{1}{2} | \langle \frac{3}{2} \frac{1}{2} | - \frac{\sqrt{3}}{2} \langle \frac{1}{2} -\frac{1}{2} | \langle \frac{3}{2} \frac{3}{2} | \right) \hat{d}_z$$

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

$$= \frac{1}{2\sqrt{2}} \langle \frac{1}{2} \frac{1}{2} | \hat{d}_z | \frac{1}{2} -\frac{1}{2} \rangle \text{ using orthogonality}$$

$\uparrow \quad \uparrow$
 $j \quad m_j$ of $|L M_L\rangle$ states

$$= 0 \text{ from above}$$

$$M_F' = 0 \left(\frac{1}{\sqrt{2}} \langle \frac{1}{2} \frac{1}{2} | \langle \frac{3}{2} -\frac{1}{2} | - \frac{1}{\sqrt{2}} \langle \frac{1}{2} -\frac{1}{2} | \langle \frac{3}{2} \frac{1}{2} | \right) \hat{d}_z$$

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

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

$$M_F' = -1 \left(-\frac{1}{2} \langle \frac{1}{2} -\frac{1}{2} | \langle \frac{3}{2} -\frac{1}{2} | + \frac{\sqrt{3}}{2} \langle \frac{1}{2} \frac{1}{2} | \langle \frac{3}{2} -\frac{3}{2} | \right) \hat{d}_z$$

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

$$= -\frac{1}{2} \langle \frac{1}{2} -\frac{1}{2} | \hat{d}_z | \frac{1}{2} \frac{1}{2} \rangle = 0$$

(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 MUCH simpler and less tedious way of ~~instantly~~ determining this rule.

Problem 3: Zeeman effect in ground state of hydrogen

$$\hat{H} = \underbrace{A \hat{\mathbf{I}} \cdot \hat{\mathbf{S}}}_{\substack{\text{hyperfine} \\ \text{coupling}}} + \underbrace{g_e \mu_B \vec{B} \cdot \hat{\mathbf{S}} - g_p \mu_N \vec{B} \cdot \hat{\mathbf{I}}}_{\text{coupling to external } \vec{B}\text{-field}}$$

$$= \hat{H}_{\text{HF}} + \hat{H}_B$$

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

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

$\frac{\mu_B}{h} \approx 1.4 \text{ MHz/Gauss}$ (Bohr Magnetron)

\Rightarrow Weak $B \ll 1 \text{ kG}$ (1,000 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 coupled angular momentum:

$|F M_F, i, s\rangle$ (also principle quantum number n , and orbital l)

The shifts, to lowest nonvanish order are first order

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

(Next Page)

Now $\vec{I} \cdot \vec{S}$ is diagonal in this basis

$$\vec{I} \cdot \vec{S} = \frac{1}{2} (F(F+1) - \frac{3}{2})$$

But S_z is not. So, consider

$$\langle F' M_F' | \hat{S}_z | F M_F \rangle$$

Note $\hat{S}_z = \hat{S}_z \otimes \mathbb{1}_{\text{Nuc}}$ ← Identity on nucleus

Furthermore $[\hat{S}_z, \hat{F}_z] = 0 \Rightarrow$ No off-diagonal matrix elements between different M_F

Diagonal elements of \hat{S}_z

$$\begin{aligned} \langle F=0, M_F=0 | \hat{S}_z | F=0, M_F=0 \rangle &= \frac{1}{2} \left(\langle \uparrow_e | \hat{S}_z | \uparrow_e \rangle \langle \downarrow_p | \downarrow_p \rangle + \langle \downarrow_e | \hat{S}_z | \downarrow_e \rangle \langle \uparrow_p | \uparrow_p \rangle \right. \\ &\quad \left. - \langle \uparrow_e | \hat{S}_z | \downarrow_e \rangle \langle \downarrow_p | \uparrow_p \rangle - \langle \downarrow_e | \hat{S}_z | \uparrow_e \rangle \langle \uparrow_p | \downarrow_p \rangle \right) \\ &= \frac{1}{2} \left(\frac{1}{2} - \frac{1}{2} \right) = 0 \end{aligned}$$

orthogonal

$$\langle F=1, M_F=1 | \hat{S}_z | F=1, M_F=1 \rangle = \langle \uparrow_e | \hat{S}_z | \uparrow_e \rangle \langle \uparrow_p | \uparrow_p \rangle = +\frac{1}{2}$$

$$\langle F=1, M_F=-1 | \hat{S}_z | F=1, M_F=-1 \rangle = \langle \downarrow_e | \hat{S}_z | \downarrow_e \rangle \langle \downarrow_p | \downarrow_p \rangle = -\frac{1}{2}$$

$$\langle F=1, M_F=0 | \hat{S}_z | F=1, M_F=0 \rangle = 0 \text{ by same argument}$$

Off-diagonal elements of \hat{S}_z

$$\langle F=0, M_F=0 | \hat{S}_z | F=0, M_F=0 \rangle$$

$$= \frac{1}{2} (\langle \uparrow_e | \langle \downarrow_p | - \langle \downarrow_e | \langle \uparrow_p |) \hat{S}_z (| \uparrow_e \rangle | \downarrow_p \rangle + | \downarrow_e \rangle | \uparrow_p \rangle)$$

$$= \frac{1}{2} (\langle \uparrow_e | \langle \downarrow_p | - \langle \downarrow_e | \langle \uparrow_p |) (+\frac{1}{2} | \uparrow_e \rangle | \downarrow_p \rangle - \frac{1}{2} | \downarrow_e \rangle | \uparrow_p \rangle)$$

$$= \frac{1}{2}$$

Putting it all together,

$$A \vec{I} \cdot \vec{S} = A \begin{array}{c} \begin{array}{cccc} |F=0, M_F=0\rangle & |F=1, M_F=0\rangle & |F=1, M_F=1\rangle & |F=1, M_F=-1\rangle \\ \hline -\frac{3}{4} & & & \\ \hline \circ & -\frac{1}{4} & +\frac{1}{4} & \circ \\ \hline & & & \frac{1}{4} \end{array} \end{array}$$

$$2\mu_B B \hat{S}_z = 2\mu_B B \begin{array}{c} \begin{array}{ccc} \frac{1}{2} & & \\ \hline \frac{1}{2} & \circ & \\ \hline \circ & & \frac{1}{2} \\ \hline & & -\frac{1}{2} \end{array} \end{array}$$

Note: I have ordered the basis so that to $|F=0, M_F=0\rangle$ and $|F=1, M_F=0\rangle$ are next to each other

We must therefore diagonalize the 2x2 matrix

$$\hat{H}_{int} \equiv \begin{bmatrix} -\frac{3A}{4} & \mu_B B \\ \mu_B B & \frac{A}{4} \end{bmatrix} \begin{matrix} |F=0, M_F=0\rangle \\ |F=1, M_F=0\rangle \end{matrix}$$

$$= -\frac{A}{4} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \frac{A}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + \mu_B B \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

(Decomposed into Pauli matrices)

Solution:

Eigenvalues $E_{\pm} = -\frac{A}{4} \pm \sqrt{\frac{A^2}{4} + (\mu_B B)^2}$

Eigenvectors $|+\rangle = \cos \frac{\theta}{2} |F=0, M_F=0\rangle + \sin \frac{\theta}{2} |F=1, M_F=0\rangle$
 $|-\rangle = \sin \frac{\theta}{2} |F=0, M_F=0\rangle - \cos \frac{\theta}{2} |F=1, M_F=0\rangle$

where $\tan \theta = \frac{\mu_B B}{-A/2} \Rightarrow \theta = \pi - \tan^{-1}\left(\frac{2\mu_B B}{A}\right)$

Note limits $\bullet \mu_B B \ll \frac{A}{2} \Rightarrow \theta \rightarrow \pi$

$E_+ \rightarrow \frac{A}{4}$ $E_- \rightarrow -\frac{3A}{4}$

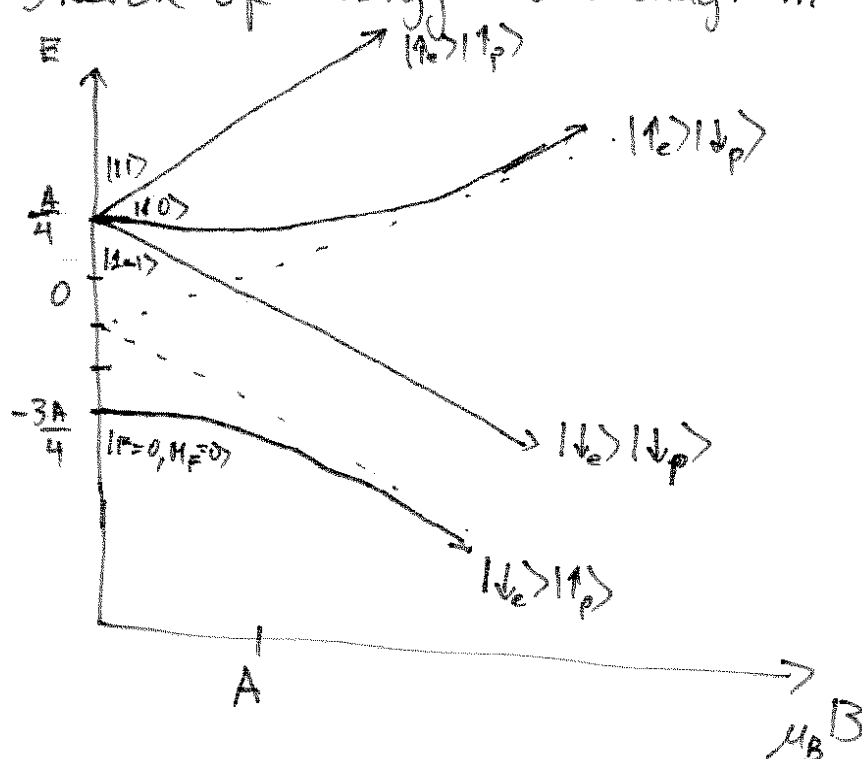
$|+\rangle \rightarrow |F=1, M_F=0\rangle$ $|-\rangle \rightarrow |F=0, M_F=0\rangle$

$\bullet \mu_B B \gg \frac{A}{2} \Rightarrow \theta \rightarrow \pi/2$ $E_{\pm} \rightarrow \pm \mu_B B$

$|+\rangle \Rightarrow |\uparrow_e\rangle |\downarrow_p\rangle$ $|-\rangle \Rightarrow |\downarrow_e\rangle |\uparrow_p\rangle$

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Sketch of energy level diagram



Key points:

- For small magnetic fields ($\mu_B B \ll \frac{A}{2}$) F, M_F are approximate "good quantum numbers". We then see a "linear Zeeman shifts" proportional to M_F .
- For large magnetic fields, the electron and proton spins decouple. Then $|SM_s\rangle|IM_p\rangle$ are approximate good quantum numbers. This is known as the "Paschen-Back" regime.