(4) Zeeman Effect in Hyperfine Structure.

If an atom has hyperfine structure, its energy levels will further split in the magnetic field. For simplicity, in our class we assume the magnetic field is not strong so that Zeeman splitting is much smaller than fine structure. In this case, the hyperfine interaction and the interaction with magnetic field can be regarded as the perturbation to fine structure. This perturbation Hamiltonian operator is

$$\Delta \hat{H} = \Delta \hat{H}_{hfs} + \Delta \hat{H}_{mag}.$$

where
$$\Delta \hat{H}_{hfs} = A\,(\hat{\vec{I}} \cdot \hat{\vec{J}}) + \frac{B}{I(2I-1)J(2J-1)} \times \left[3(\hat{\vec{I}}\cdot\hat{\vec{J}})^2 + \frac{3}{2}(\hat{\vec{I}}\cdot\hat{\vec{J}}) - \hat{\vec{I}}^2\,\hat{\vec{J}}^2\right]$$

$$\Delta \hat{H}_{mag} = -(\hat{\vec{\mu}}_J + \hat{\vec{\mu}}_I)\cdot\vec{B}$$
$$= +g_J m_J \mu_B B - g_I' m_I \mu_B B$$

Since $g_I' \ll g_J$, the 2nd term in $\Delta\hat{H}_{mag}$ is usually ignored. Using QM perturbation theory, the energy shift caused by the $\Delta\hat{H}_{hfs}$ and $\Delta\hat{H}_{mag}$ can be derived. The equation of it is called Breit-Rabi equation. Let us consider $J=1/2$ energy level (ground state of hydrogen and alkali atoms). Electric quadrupole $Q=0$. So we do not consider the electric quadrupole interaction.

$$\Delta\hat{H} = A\,(\hat{\vec{I}}\cdot\hat{\vec{J}}) + g_J m_J \mu_B B - g_I' m_I \mu_B B.$$

We introduce a parameter x to express the strength of the magnetic field:

$$\begin{cases} x = \dfrac{(g_J + g_I')\mu_B B}{A(I+1/2)} = \dfrac{(g_J + g_I')\mu_B B}{\delta E} \\ \delta E = A(I+1/2) \text{ — hyperfine splitting in zero } \vec{B}. \end{cases}$$

$$\therefore \Delta E = \langle \Delta\hat{H} \rangle$$

$$= -\frac{\delta E}{2(2I+1)} - m_F g_I' \mu_B B \pm \frac{\delta E}{2}\sqrt{1+\frac{4m_F}{2I+1}x+x^2},$$

— Breit–Rabi equation.

Where $m_F = \pm(I+1/2)$.

① when $B=0$, $\Delta E_{hfs} = \frac{I}{2I+1}\delta E$ (for $F=I+1/2$)

$\Delta E_{hfs} = -\frac{I+1}{2I+1}\delta E$ (for $F=I-1/2$)

$\Rightarrow \Delta E_{hfs}(F=I+1/2) - \Delta E_{hfs}(F=I-1/2) = \delta E.$

②. Under very weak magnetic field, F, m_F are good quantum numbers. $\sqrt{1+\frac{4m_F}{2I+1}x+x^2} \approx 1+\frac{2m_F}{2I+1}x.$

$(x \ll 1)$

Neglect the g_I' term, we have

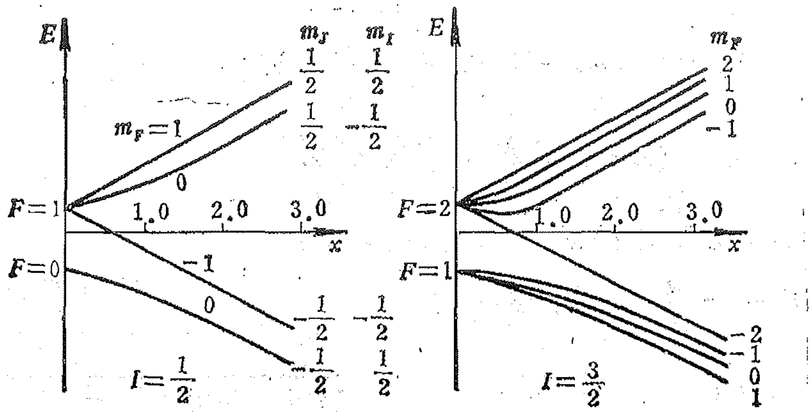
$$\Delta E = \Delta E_{hfs} \pm \frac{m_F}{2I+1}\delta E \cdot x. \quad \begin{cases} + \text{ for } F=I+1/2 \\ - \text{ for } F=I-1/2 \end{cases}$$

$$= \Delta E_{hfs} \pm \frac{1}{2I+1} g_J m_F \mu_B B$$

Each hyperfine energy level splits to sublevels with equal spacing.

③. When $\vec{B}$ is strong, m_J, m_I are good quantum numbers, $J=\frac{1}{2}$ energy level split as $m_J = \pm 1/2$, then further split according to m_I values.

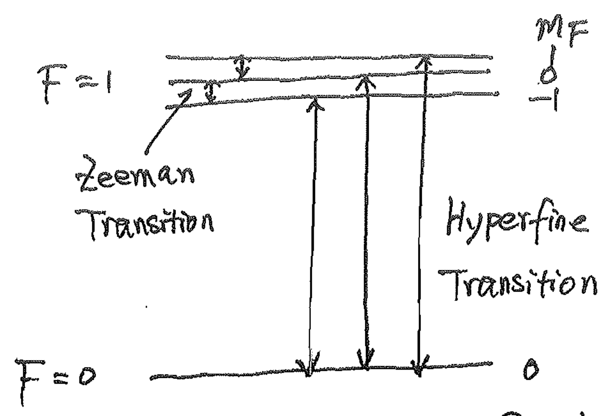
(4). If $\vec{B}$ is so large that magnetic interaction is larger or comparable to electron spin-orbit coupling, then we need to go back to consider fine structure with magnetic interaction and hyperfine interaction together.



For $J=1/2$, $I=1/2$ For $J=1/2$, $I=3/2$

Could you figure out why in the 2nd case ($J=1/2$, $I=3/2$), the energy levels for $F=1$, $m_F = -1, 0, 1$ is in opposite order than the $F=2$, $m_F=2,1,0,-1,-2$ levels?

(5) Magnetic Resonance:



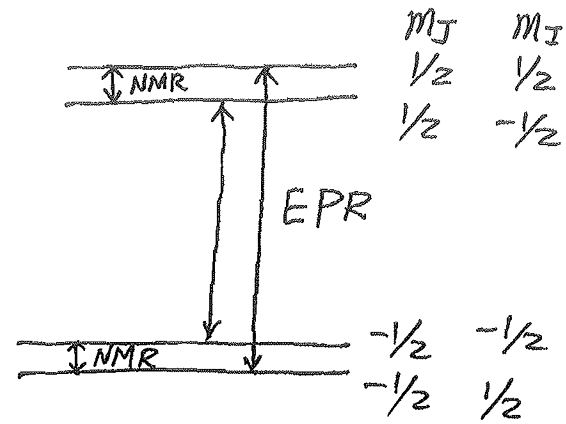
In weak magnetic field.

$\Delta F = \pm 1$, $\Delta m_F = 0, \pm 1$

(for hyperfine transition)

$\Delta F = 0$, $\Delta m_F = \pm 1$

(for Zeeman transition)



In strong magnetic field.

$\Delta m_J = \pm 1$, $\Delta m_I = 0$

(Electron Paramagnetic Resonance)

$\Delta m_J = 0$, $\Delta m_I = \pm 1$

(Nuclear Magnetic Resonance)

Magnetic Properties of matter:

① Diamagnetism ② Paramagnetism ③ Ferromagnetism

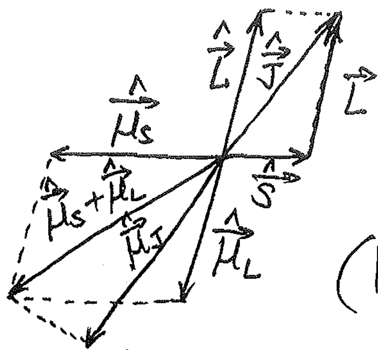
EPR and NMR and MRI:

These technologies have become very important approaches to study material structures, chemistry processes, medical diagnosis, etc.

You are encouraged to search on these topics and write a study report.

Appendix: Vector Model of Angular Momentum Coupling and Computation of g – Factor (Gyromagnetic Ratio)

(1) L – S Coupling of Electron:



(Figure 1)

As shown in Figure 1, the coupling of two angular momentum is given by

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

where $\hat{\vec{L}}$ is the orbital angular momentum,
$\hat{\vec{S}}$ is the electron spin angular momentum,
$\hat{\vec{J}}$ is the electron total angular momentum.

Corresponding magnetic moments are:

$$\begin{cases} \hat{\vec{\mu}}_L = -g_L \mu_B \hat{\vec{L}}, & g_L = 1 \quad \text{for single electron} \\ \hat{\vec{\mu}}_s = -g_S \mu_B \hat{\vec{S}}, & g_s = \tfrac{1}{2} \quad \text{for single electron} \\ \vec{\mu}_J = -g_J \mu_B \vec{J}. & \end{cases}$$

From the vector model, we want to derive g_J from known parameters like g_L, g_s, L, S, and J.

Notice that the sum $\hat{\vec{\mu}}_s + \hat{\vec{\mu}}_L$ is <u>NOT</u> equal to $\hat{\vec{\mu}}_J$, because $g_L \neq g_s$ and $\hat{\vec{\mu}}_s + \hat{\vec{\mu}}_L$ is <u>NOT</u> along the $\hat{\vec{J}}$ direction.

The projection of $\hat{\vec{\mu}}_s + \hat{\vec{\mu}}_L$ along $\hat{\vec{J}}$ direction is the $\hat{\vec{\mu}}_J$.

$$\therefore \quad \hat{\vec{\mu}}_J = \frac{(\hat{\vec{\mu}}_L + \hat{\vec{\mu}}_s)\cdot \hat{\vec{J}}}{\hat{\vec{J}}^2}\,\hat{\vec{J}} = \frac{\hat{\vec{\mu}}_L \cdot \hat{\vec{J}} + \hat{\vec{\mu}}_s \cdot \hat{\vec{J}}}{\hat{\vec{J}}^2}\,\hat{\vec{J}}$$

$$\therefore \hat{\vec{\mu}}_J = -\mu_B \frac{g_L \hat{\vec{L}}\cdot\hat{\vec{J}} + g_S \hat{\vec{S}}\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$

According to the definition of g_J: $\hat{\vec{\mu}}_J = -g_J \mu_B \vec{J}$,

We have $$g_J = \frac{g_L \hat{\vec{L}}\cdot\hat{\vec{J}} + g_S \hat{\vec{S}}\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}.$$

From the Law of Cosines, considering the vector model,

We have: $$\hat{\vec{L}}^2 = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2\hat{\vec{S}}\cdot\hat{\vec{J}} \Rightarrow \hat{\vec{S}}\cdot\hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2}{2}$$

$$\hat{\vec{S}}^2 = \hat{\vec{J}}^2 + \hat{\vec{L}}^2 - 2\hat{\vec{J}}\cdot\hat{\vec{L}} \Rightarrow \hat{\vec{L}}\cdot\hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{L}}^2 - \hat{\vec{S}}^2}{2}$$

Substitute $\hat{\vec{S}}\cdot\hat{\vec{J}}$ and $\hat{\vec{L}}\cdot\hat{\vec{J}}$ into g_J equation, we get

$$g_J = \frac{g_L(\hat{\vec{J}}^2 + \hat{\vec{L}}^2 - \hat{\vec{S}}^2) + g_S(\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2)}{2\hat{\vec{J}}^2}$$

The eigenvalues for $\hat{\vec{J}}^2$, $\hat{\vec{L}}^2$, $\hat{\vec{S}}^2$ are

$$\hat{\vec{J}}^2 \Rightarrow J(J+1),\quad \hat{\vec{L}}^2 \Rightarrow L(L+1),\quad \hat{\vec{S}}^2 \Rightarrow S(S+1)$$

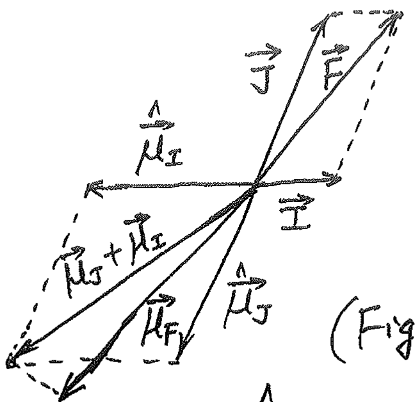
$$\therefore\quad g_J = \frac{\left\{ g_L[J(J+1)+L(L+1)-S(S+1)] + g_S[J(J+1)+S(S+1)-L(L+1)] \right\}}{2J(J+1)}$$

Substituting $g_L = 1$, $g_S = 2$ into the equation:

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$= \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

(2) Electron – Nucleus Coupling (I – J coupling)



(Figure 2)

Similar to L – S coupling, the I – J coupling is

$$\hat{\vec{F}} = \hat{\vec{J}} + \hat{\vec{I}}$$

where $\hat{\vec{J}}$ is the electron total angular momentum

$\hat{\vec{I}}$ is the nuclear spin angular momentum

$\vec{F}$ is the atomic total angular momentum

Corresponding magnetic moments are

$$\begin{cases} \hat{\vec{\mu}} = -g_J \mu_B \hat{\vec{J}} \\ \hat{\vec{\mu}}_I = g_I' \mu_N \hat{\vec{I}} = g_I \mu_B \hat{I}, \quad \left(\dfrac{g_I}{g_I'} = \dfrac{\mu_N}{\mu_B} = \dfrac{m_e}{M_P} \right) \\ \hat{\vec{\mu}}_F = -g_F \mu_B \hat{\vec{F}} \end{cases}$$

We want to derive g_F from g_J, g_I, J, I, F.

Again, $\hat{\vec{\mu}}_J + \hat{\vec{\mu}}_I$ is <u>NOT</u> equal to $\hat{\vec{\mu}}_F$. $\hat{\vec{\mu}}_F$ is the projection of $\hat{\vec{\mu}}_J + \hat{\vec{\mu}}_I$ along $\hat{\vec{F}}$ direction:

$$\hat{\vec{\mu}}_F = \frac{(\hat{\vec{\mu}}_J + \hat{\vec{\mu}}_I) \cdot \hat{\vec{F}}}{\hat{\vec{F}}^2} \hat{\vec{F}} = \frac{\hat{\vec{\mu}}_J \cdot \hat{\vec{F}} + \hat{\vec{\mu}}_I \cdot \hat{\vec{F}}}{\hat{\vec{F}}^2} \hat{\vec{F}}.$$

$$= -\mu_B \frac{g_J \hat{\vec{J}} \cdot \hat{\vec{F}} - g_I \hat{\vec{I}} \cdot \hat{\vec{F}}}{\hat{\vec{F}}^2} \hat{\vec{F}}$$

$$\therefore \quad g_F = \frac{g_J \hat{\vec{J}} \cdot \hat{\vec{F}} - g_I \hat{\vec{I}} \cdot \hat{\vec{F}}}{\hat{\vec{F}}^2} \hat{\vec{F}}.$$

From the law of cosines,

$$\hat{\vec{I}}^2 = \hat{\vec{F}}^2 + \hat{\vec{J}}^2 - 2\hat{\vec{F}}\cdot\hat{\vec{J}} \Rightarrow \hat{\vec{J}}\cdot\hat{\vec{F}} = \frac{\hat{\vec{F}}^2 + \hat{\vec{J}}^2 - \hat{\vec{I}}^2}{2}$$

$$\hat{\vec{J}}^2 = \hat{\vec{F}}^2 + \hat{\vec{I}}^2 - 2\hat{\vec{F}}\cdot\hat{\vec{I}} \Rightarrow \hat{\vec{I}}\cdot\hat{\vec{F}} = \frac{\hat{\vec{F}}^2 + \hat{\vec{I}}^2 - \hat{\vec{J}}^2}{2}$$

Also recall $\hat{\vec{J}}^2 = J(J+1)$, $\hat{\vec{I}}^2 = I(I+1)$, $\hat{\vec{F}}^2 = F(F+1)$.

We get
$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_I \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} .$$

(3) In general, for any two angular momentum coupling:

$$\hat{\vec{J}} = \hat{\vec{j}}_1 + \hat{\vec{j}}_2 ,$$

$$\begin{cases} \hat{\vec{\mu}}_J = -g_J \mu_B \hat{\vec{J}} \\ \hat{\vec{\mu}}_{j_1} = -g_{j_1} \mu_B \hat{\vec{j}}_1 \\ \hat{\vec{\mu}}_{j_2} = -g_{j_2} \mu_B \hat{\vec{j}}_2 \end{cases}$$

We have
$$\hat{\vec{\mu}}_J = \frac{(\hat{\vec{\mu}}_{j_1} + \hat{\vec{\mu}}_{j_2})\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$
$$= -\mu_B \frac{g_{j_1}\hat{\vec{j}}_1\cdot\hat{\vec{J}} + g_{j_2}\hat{\vec{j}}_2\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$

$$\therefore g_J = g_{j_1}\frac{\hat{\vec{J}}_1\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2} + g_{j_2}\frac{\hat{\vec{j}}_2\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}$$

From the law of cosines, $\hat{\vec{j}}_1\cdot\hat{\vec{J}} = \dfrac{\hat{\vec{J}}^2 + \hat{\vec{j}}_1^2 - \hat{\vec{j}}_2^2}{2}$, $\hat{\vec{j}}_2\cdot\hat{\vec{J}} = \dfrac{\hat{\vec{J}}^2 + \hat{\vec{j}}_2^2 - \hat{\vec{j}}_1^2}{2}$

$$\therefore g_J = g_{j_1}\frac{J(J+1) + j_1(j_1+1) - j_2(j_2+1)}{2J(J+1)} - g_{j_2}\frac{J(J+1) + j_2(j_2+1) - j_1(j_1+1)}{2J(J+1)}$$

Another way to derive $\vec{I}\cdot\vec{F}$ and $\vec{J}\cdot\vec{F}$ is just to use the relationship $\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}}$

$$\Rightarrow \hat{\vec{J}} = \hat{\vec{F}} - \hat{\vec{I}}$$

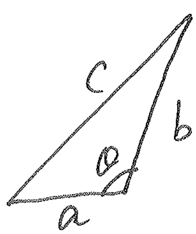
$$\therefore (\hat{\vec{J}})^2 = \hat{\vec{J}}\cdot\hat{\vec{J}} = (\hat{\vec{F}} - \hat{\vec{I}})\cdot(\hat{\vec{F}} - \hat{\vec{I}})$$

$$= (\hat{\vec{F}})^2 + (\hat{\vec{I}})^2 - 2\,\hat{\vec{I}}\cdot\hat{\vec{F}}$$

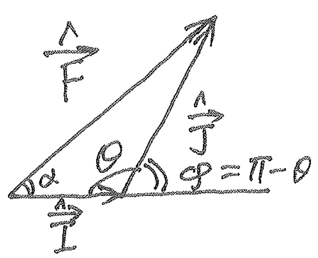
$$\Rightarrow \hat{\vec{I}}\cdot\hat{\vec{F}} = \frac{1}{2}(\hat{\vec{F}}^2 + \hat{\vec{I}}^2 - \hat{\vec{J}}^2)$$

Similarly, $\hat{\vec{J}}\cdot\hat{\vec{F}} = \frac{1}{2}(\hat{\vec{F}} + \hat{\vec{J}}^2 - \hat{\vec{I}}^2)$

<u>Note</u>: The law of cosines:



$$c^2 = a^2 + b^2 - 2ab\cos\theta \qquad \text{(in scalar)}$$



$$\hat{\vec{F}}^2 = \hat{\vec{I}}^2 + \hat{\vec{J}}^2 - 2IJ\cos\theta$$

$$\because \hat{\vec{I}}\cdot\hat{\vec{J}} = IJ\cos\varphi = IJ\cos(\pi-\theta)$$

$$= -IJ\cos\theta$$

$$\therefore \vec{F}^2 = \vec{I}^2 + \vec{J}^2 + 2\vec{I}\cdot\vec{J}$$

$$\vec{J}^2 = \vec{F}^2 + \vec{I}^2 - 2FI\cos\alpha$$

$$\because \vec{F}\cdot\vec{I} = FI\cos\alpha$$

$$\therefore \vec{J}^2 = \vec{F}^2 + \vec{I}^2 - 2\vec{F}\cdot\vec{I}$$

$$\Rightarrow \vec{F}\cdot\vec{I} = \frac{1}{2}(\vec{F}^2 + \vec{I}^2 - \vec{J}^2)$$