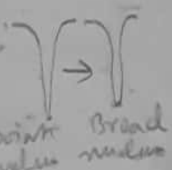
Hyperfine Structure

Hyperfine effect < hyperfine splitting (structure)
shifts (no splitting) isotope shifts

shifts:

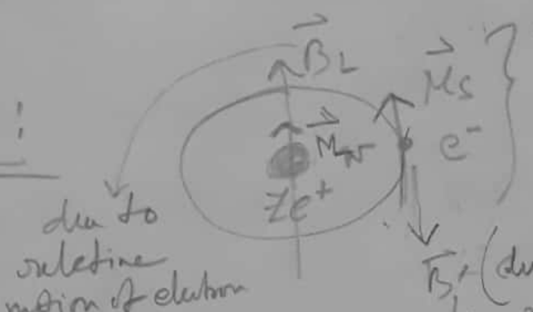
① KE Correction due to reduced mass (isotope shift) $\mu_e = \frac{m_e m_N}{m_e + m_N}$

② Volume effect: finite vol. of nucleus leads to modification near $r \to 0$:



Both the effects lead to lowering

Hyperfine str:



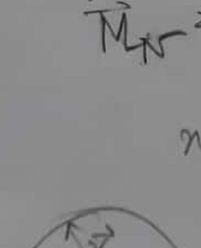
Interactions
$\vec{M}_N$ with $\vec{\mu}_s$
$\vec{M}_N$ with $\vec{B}_L$ ($\hat{I}$)

Interaction between $\vec{B}_L'$ and $\vec{\mu}_s$ has been already considered in $\hat{L}\cdot\hat{S}$ coupling.

- Total nuclear angular momentum operator $\hat{I}$
$\hat{I}$ is contributed by spins and orbital angular momentum of nucleons.
Associated nuclear magnetic moment $\vec{M}_N$:

$$\hat{M}_N = g_I \mu_N \frac{\hat{I}}{\hbar} \; ; \quad \mu_N = \frac{e\hbar}{2m_p} = \frac{\mu_B}{1836.15}$$

$g_I \to$ nuclear g factor



$$\vec{A}(\vec{r}) = -\frac{\mu_0}{4\pi}\left[\vec{M}_N \times \nabla\left(\frac{1}{r}\right)\right] = \frac{\mu_0}{4\pi}\left[\vec{M}_N \times \frac{\vec{r}}{r^3}\right]$$

$H' = H_1' + H_2'$; $H_1'\psi = -\frac{i\hbar e}{m}\vec{A}\cdot\nabla\psi$

$H_1' \to$ ($\vec{M}_N$ with $\hat{I}$), $H_2' \to$ (with $\hat{S}$)

$$= -\frac{i\hbar e}{m}\left(\frac{\mu_0}{4\pi}\right)\left[\vec{M}_N \times \nabla\left(\frac{1}{r}\right)\right]\cdot\nabla\psi$$

$$= \frac{\mu_0 e}{4\pi m r^3}\left[\vec{M}_N \times \vec{r}\right]\cdot\hat{p}\psi$$

$$H_1'\psi = \frac{\mu_0 e}{4\pi m r^3}\left[\hat{r}\times \hat{p}\psi\right]\cdot \vec{M}_N = \frac{\mu_0 e}{4\pi m}\hat{L}\psi\cdot\vec{M}_N$$

$$= \frac{\mu_0 e}{4\pi m r^3}\hat{L}\psi \cdot g_I \mu_N \frac{\vec{I}}{\hbar} = \frac{\mu_0}{4\pi} g_I \mu_N \mu_B \frac{2}{\hbar^2}\left(\frac{1}{r^3}\right)\hat{L}\cdot\hat{I}$$

→ coupling between $\vec{M}_N$ and an effective magnetic field $\left(\frac{\mu_0}{4\pi}\right)\frac{e\hat{L}\psi}{mr^2}$ created at the nucleus by the orbital motion of electron.

Similarly as the $\vec{L}\cdot\vec{S}$ coupling term this term will also not have contribution from $l=0$

$$H_2' = -\vec{M}_S\cdot\vec{B} = -\left(g_s \mu_B \frac{\vec{S}}{\hbar}\cdot(\nabla\times A)\right) \quad ; \quad \bar{A} = -\frac{\mu_0}{4\pi}\left[\vec{M}_N\times\nabla\left(\frac{1}{r}\right)\right]$$

Recall

$$\nabla\times(A\times B) = A(\nabla\cdot B) - B(\nabla\cdot A) + (B\cdot\nabla)A - (A\cdot\nabla)B$$

$$\vec{\nabla}\times\bar{A} = -\nabla\times\left[\frac{\mu_0}{4\pi}\vec{M}_N\times\nabla\left(\frac{1}{r}\right)\right]$$

$$= -\frac{\mu_0}{4\pi}\left[\vec{M}_N\left(\nabla\cdot\nabla\left(\frac{1}{r}\right)\right) - \underbrace{(\vec{M}_N\cdot\vec{\nabla})\nabla\left(\frac{1}{r}\right)}_{\nabla(\vec{M}_N\cdot\nabla)\frac{1}{r}}\right]$$

$$H_2' = \frac{-\mu_0}{4\pi}\left[\vec{M}_S\cdot\vec{M}_N\,\nabla^2\left(\frac{1}{r}\right) - (\vec{M}_S\cdot\nabla)(\vec{M}_N\cdot\nabla)\frac{1}{r}\right]$$

$$= \frac{-\mu_0}{4\pi} g_s g_I \mu_B\mu_N \frac{1}{\hbar^2}\left[(-\hat{S})\cdot\hat{I}\,\underbrace{\nabla^2\left(\frac{1}{r}\right)}_{=-4\pi\delta r} - (-\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r}\right]$$

∴ let us see H_2' in two regimes: $r=0$ and $r\neq 0$.

<u>for $r\neq 0$</u> $\quad H_2' = \frac{\mu_0}{4\pi} g_s g_I \mu_B\mu_N \frac{1}{\hbar^2}(\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r}$

$$(\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r} = \sum_{ij} S_i I_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\left(\frac{1}{r}\right)$$

Now $\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\left(\frac{1}{r}\right) = \frac{3x_i x_j}{r^5}$ and $\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}\left(\frac{1}{r}\right) = \frac{3x_i^2}{r^5} - r^{-3}$

$$\therefore (S\cdot\nabla)(I\cdot\nabla)\frac{1}{r} = \sum_{ij} S_i I_j\left[\frac{\delta_{ij}}{r^3} - \frac{3x_i x_j}{r^5}\right]$$

$$= \sum_i \frac{S_i I_i}{r^3} - \frac{3}{r^5}\sum_i\sum_j S_i I_j x_i x_j$$

$$= \frac{\hat{S}\cdot\hat{I}}{r^3} - \frac{3}{r^5}\sum_i S_i x_i \sum_j I_j x_j$$

$$= \frac{S\cdot I}{r^3} - \frac{3}{r^5}(\hat{S}\cdot\vec{r})(\hat{I}\cdot\vec{r})$$

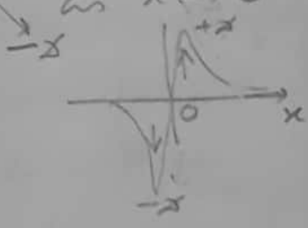
$$\therefore H'\Big|_{r\neq 0} = \frac{\mu_0}{4\pi} g_s g_I \mu_B \mu_N \frac{1}{\hbar^2}\frac{1}{r^3}\Big[\underbrace{3\frac{(\hat{S}\cdot\vec{r})(\hat{I}\cdot\vec{r})}{r^2} - \hat{S}\cdot\hat{I}}_{H_2'} + \underbrace{\hat{L}\cdot\hat{I}}_{\text{add } H_1' \text{ for } l\neq 0}\Big]$$

for $r=0$: valid for $l=0$ only

$$(\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r} = \sum_{ij} S_i I_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\left(\frac{1}{r}\right)$$

Note that the $i\neq j$ terms will be zero since:

$$\lim_{r\to 0}\frac{|\psi_{n00}|^2 x_i x_j}{r^5} \to 0$$ since it $\nearrow \infty$ as $x\to 0^+$ and $\searrow -\infty$ as $x\to 0^-$



$\therefore$ $i=j$ only survives.

$$(\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r} = \sum_i S_i I_i \frac{\partial^2}{\partial x_i^2}\left(\frac{1}{r}\right)$$

Due to sph sym of $|\psi_{n00}|^2$ the effect of $\frac{\partial^2}{\partial x^2}\left(\frac{1}{r}\right)$, $\frac{\partial^2}{\partial y^2}\left(\frac{1}{r}\right)$ and $\frac{\partial^2}{\partial z^2}\left(\frac{1}{r}\right)$ in $\langle n00|\frac{\partial^2}{\partial x_i^2}\left(\frac{1}{r}\right)|n00\rangle$ will be all same due to isotropy or sph sym. And we know $\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(r)$

$$\therefore \frac{\partial^2}{\partial x_i^2}\left(\frac{1}{r}\right) = \frac{1}{3}\nabla^2\left(\frac{1}{r}\right) = -\frac{4\pi}{3}\delta(r)$$ due to isotropy of sph. symm.

Recall,

$$\therefore H_2' = \frac{-\mu_0}{4\pi} g_s g_I \mu_B \mu_N\left[\hat{S}\cdot\hat{I}\,\nabla^2\left(\frac{1}{r}\right) - (\hat{S}\cdot\nabla)(\hat{I}\cdot\nabla)\frac{1}{r}\right]$$

$$= \frac{-\mu_0}{4\pi} g_s g_I \mu_B \mu_N\left[\hat{S}\cdot\hat{I}\right](-4\pi\delta(r))\left[1-\frac{1}{3}\right]$$

$l=0 \longrightarrow r=0$

$l\neq 0 \longrightarrow r\neq 0$

Energy shift for $l\neq 0$

Need to consider only $r\neq 0$

$$H' = \left(\frac{\mu_0}{4\pi} g_s g_I \mu_B \mu_N \frac{1}{\hbar^2}\right)\frac{1}{r^3}\left[\hat{\vec{L}}\cdot\hat{\vec{I}} - \hat{\vec{S}}\cdot\hat{\vec{I}} + 3\frac{(\hat{\vec{S}}\cdot\vec{r})(\hat{\vec{I}}\cdot\vec{r})}{r^2}\right]$$

$$= (\ )\frac{1}{r^3}\underbrace{\left[\hat{\vec{L}} - \hat{\vec{S}} + 3\frac{(\hat{\vec{S}}\cdot\vec{r})\vec{r}}{r^2}\right]}_{\vec{G}}\cdot\hat{\vec{I}} = (\ )\frac{1}{r^3}\hat{\vec{G}}\cdot\hat{\vec{I}}$$

Need to calculate $\langle\ |\frac{\hat{\vec{G}}\cdot\hat{\vec{I}}}{r^3}|\ \rangle$ where $|\ \rangle$ is a combination of electronic and nuclear wavefunction

To start with, $|\ \rangle \rightarrow |n l j m_j\rangle|I m_I\rangle \rightarrow |n l j m_j I m_I\rangle$

Since $\hat{\vec{I}}$ is a combination of $\vec{S}$ and $\vec{L}$ of nucleons much like $\hat{\vec{J}}$ of electrons. So one can think that the electronic wavefn will now also depend on nuclear coordinates and that part will be governed by I and m_I. We then need to check whether H' is diagonal in $|n l j m_j I m_I\rangle$ or not.

We take recourse to the result based on Wigner-Eckart theorem that we have used in weak field Zeeman effect.

Recall, $j(j+1)\hbar^2\langle l s j m_j|\hat{\vec{V}}|l s j m_j\rangle = \langle l s j m_j|(\hat{\vec{V}}\cdot\hat{\vec{J}})\hat{\vec{J}}|l s j m_j\rangle$

for $\vec{V} = V_x\hat{i} + V_y\hat{j} + V_z\hat{k}$ and $[J^2, J_z] = [J^2, J_y] = [J^2, J_x] = 0$

$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$

$\vec{J}$

$\Downarrow$

$$\Rightarrow j(j+1)\hbar^2\langle l s j m_j I m_I|(\hat{\vec{G}}\cdot\hat{\vec{I}})|l s j m_j I m_I\rangle$$

$$= \langle l s j m_j I m_I|\,(\underset{\vec{V}}{\hat{\vec{G}}}\cdot\hat{\vec{J}})\hat{\vec{J}}\cdot\hat{\vec{I}}\,|l s j m_j I m_I\rangle$$

Now, $\hat{\vec{G}} \cdot \hat{\vec{J}} = \left(\hat{\vec{L}} - \hat{\vec{S}} + 3 \frac{(\hat{\vec{S}} \cdot \vec{r})\vec{r}}{r^2} \right) \cdot (\hat{\vec{L}} + \hat{\vec{S}})$

$$= |\vec{L}|^2 - |\vec{S}|^2 + 3\frac{(\hat{\vec{S}} \cdot \vec{r})^2}{r^2} = |\vec{L}|^2 + 0 ; \because S^2 - \frac{3(\vec{S}\cdot\vec{r})^2}{r^2} = 0$$

Then the $\vec{G} \cdot \vec{J}$ part is diagonal in $|l s j m_j I m_I\rangle$

However $(\hat{\vec{I}} \cdot \hat{\vec{J}})$ is very similar to the $\hat{\vec{L}} \cdot \hat{\vec{S}}$ term. ($\vec{J} \equiv \vec{L}$, $\vec{I} \equiv \vec{S}$)

$\therefore$ like $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ let us define $\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}}$

Just as J^2, J_z, L^2, S^2 in this case F^2, F_z, I^2, J^2

$\therefore$ linear combination of $|n l s j m_j I m_I\rangle$ will give

$|n l s j m_j F m_F\rangle$ with $m_F = -F, -F+1, \dots 0 \dots F$

$$\hat{\vec{I}} \cdot \hat{\vec{J}} = \frac{1}{2}(F^2 - I^2 - J^2) \text{ diagonal in } |n l s j m_j F m_F\rangle$$

$$\therefore \Delta E = \left(\frac{\mu_0}{4\pi} g_s g_I \mu_B \mu_N \frac{1}{\hbar^2} \right) \left\langle n l s j m_j F m_F \middle| \frac{\hat{\vec{G}} \cdot \hat{\vec{I}}}{r^3} \middle| n l s j m_j F m_F \right\rangle$$

$$= (\ ) \left\{ \left\langle n l \middle| \frac{1}{r^3} \middle| n l \right\rangle \right\} \left\langle l s j m_j F m_F \middle| \frac{(\hat{\vec{G}} \cdot \hat{\vec{J}})(\hat{\vec{J}} \cdot \hat{\vec{I}})}{j(j+1)} \middle| \,''\, \right\rangle$$

$$= (\ ) \left\{ \frac{Z^3}{a_\mu^3 n^3 l(l+1)(l+\frac{1}{2})} \right\} \left\langle \middle| \frac{L^2 \frac{1}{2}(F^2 - I^2 - J^2)}{j(j+1)} \middle| \right\rangle ; \ a_\mu = a_0 \left(\frac{m}{\mu} \right)$$

$\mu \to$ reduced mass of electron

$$= (\ ) \{ \ \} \frac{l(l+1)\hbar^2}{j(j+1)} [F(F+1) - I(I+1) - j(j+1)]$$

$$F = \{ |I - j|, |I - j| + 1, \dots, I + j - 1, I + j \} \to \text{\# of values is smaller of } (2j+1) \text{ or } (2I+1)$$

$$= (\ ) \left\{ \frac{Z^3}{a_\mu^3 n^3} \right\} \frac{1}{j(j+1)(l+\frac{1}{2})} [F(F+1) - I(I+1) - j(j+1)]$$

for $l = 0$ (sph sym)

Recall $\Delta E = \left(\frac{\mu_0}{4\pi} g_s g_I \mu_B \mu_N\right) \frac{8\pi}{3} \langle \delta(r) \hat{S} \cdot \hat{I} \rangle$

$$\hat{F} = \hat{L} + \hat{S} + \hat{I}$$

$$|\hat{F}|^2 = |\hat{L}|^2 + |\hat{S}|^2 + |\hat{I}|^2 + 2 \hat{L} \cdot \hat{S} + 2 \hat{L} \cdot \hat{I} + 2 \hat{S} \cdot \hat{I}$$

$$\langle F^2 \rangle = \underbrace{\langle L^2 \rangle}_{=0 \text{ for } l=0} + \langle S^2 \rangle + \langle I^2 \rangle + 2 \langle \hat{L} \cdot \hat{S} \rangle + 2 \langle \hat{L} \cdot \hat{I} \rangle + 2 \langle \hat{S} \cdot \hat{I} \rangle$$

We already know from spin orbit coupling that $\langle \hat{L} \cdot \hat{S} \rangle$ is not contributed by $l=0$

Similarly $\langle \vec{L} \cdot \vec{I} \rangle$ will not be contributed by $l=0$

$$\therefore \langle F^2 \rangle = \langle S^2 \rangle + \langle I^2 \rangle + 2 \langle \hat{S} \cdot \hat{I} \rangle.$$

$$\langle \hat{S} \cdot \hat{I} \rangle = \frac{1}{2} \left[\langle F^2 \rangle - \langle S^2 \rangle - \langle I^2 \rangle \right]$$

$$\therefore \Delta E = (\quad) \frac{8\pi}{3} \langle nl | \delta(r) | nl \rangle \langle l s j m_j F m_F | \hat{S} \cdot \hat{I} | \rangle$$

$$= (\;) \left\{ |\psi_{n00}(0)|^2 \right\} \langle \, | \tfrac{1}{2} [F^2 - S^2 - I^2] | \, \rangle \frac{8\pi}{3}$$

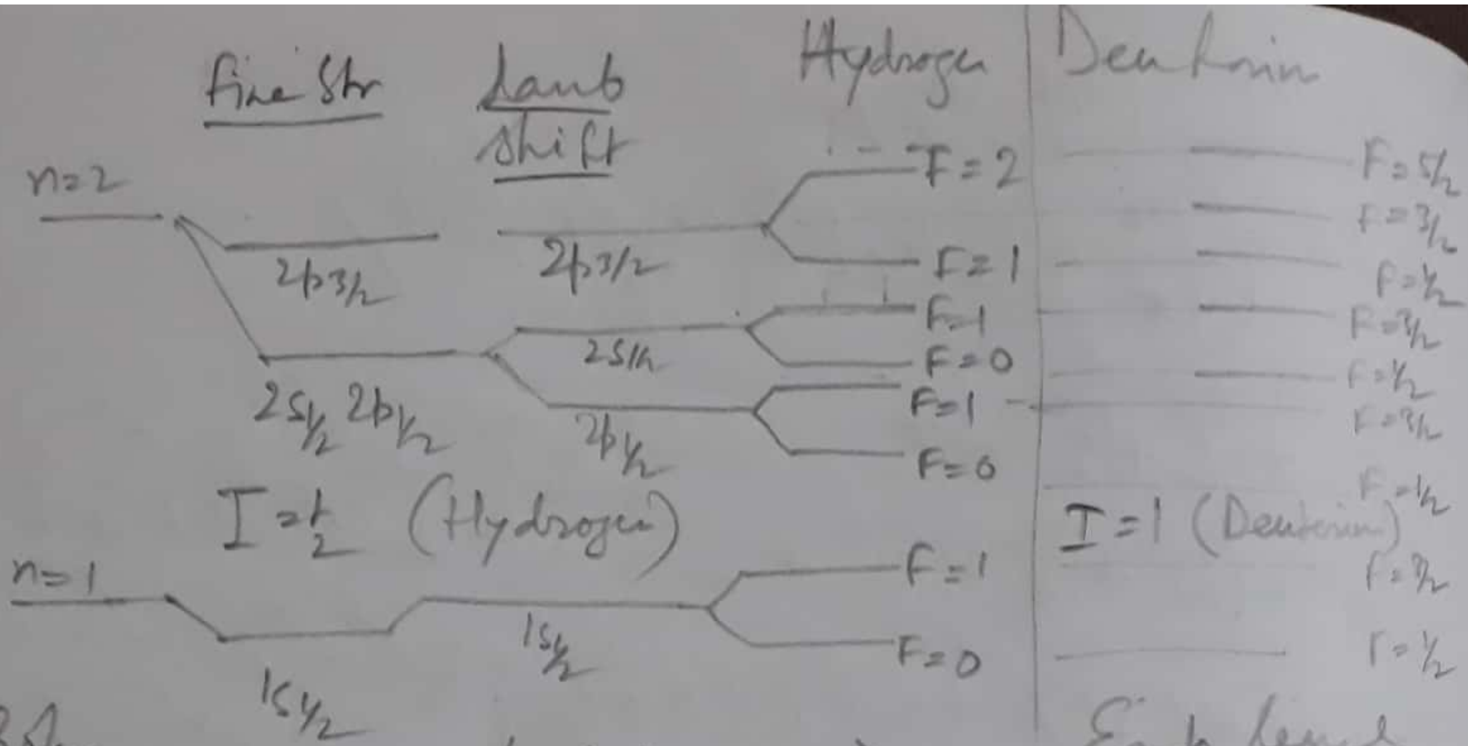
$$= (\;) \left\{ \frac{Z^3}{\pi a_\mu^3 n^3} \right\} \frac{1}{2} \left[F(F+1) - I(I+1) - s(s+1) \right] \frac{8\pi}{3}$$

$$= (\;) \left\{ \frac{Z^3}{a_\mu^3 n^3} \right\} \frac{4}{3} \left[F(F+1) - I(I+1) - s(s+1) \right]$$

Recall for $l \neq 0$ we had

$$\Delta E = (\,\text{''}\,) \left\{ \text{''} \right\} \frac{1}{j(j+1)(l+\frac{1}{2})} [\;\text{''}\;] = (\;) \{\;\} \frac{4}{3} [\;] \text{ for } j = \tfrac{1}{2}$$

$\therefore$ for any l : $\Delta E = \left(\frac{\mu_0}{4\pi} g_s g_I \mu_B \mu_N \right) \left\{ \frac{Z^3}{a_\mu^3 n^3} \right\} \frac{[F(F+1) - I(I+1) - j(j+1)]}{j(j+1)(l+\frac{1}{2})}$



Each level $(2F+1)$ degenerate

$|n\, l\, s\, j\, m_j\, F\, m_F\rangle$

Selection rule: $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$, $\Delta F = 0, \pm 1$

$\Delta s = 0$; $\Delta m_j = 0, \pm 1$, $\Delta m_F = 0, \pm 1$