Zeeman splitting

classical view: lines are oscillators

$$m_e \frac{d\vec{v}}{dt} = -m_e \omega_0^2 \vec{r} - e\frac{v \times B}{c}$$

this is the principal line

$$\vec{B} = B\hat{z}$$

$$\ddot{r} + 2\Omega_L \dot{r} \times \hat{z} + \omega_0^2 \vec{r} = 0$$

$$\Omega_L = \text{Larmor frequency} \equiv \frac{eB}{2m_e c}$$

Since the incident field is oscillating $\propto e^{-i\omega t}$

assume

$$\vec{r} = \mathrm{Re}\left\{ \begin{pmatrix} x \\ y \\ z \end{pmatrix} e^{-i\omega t} \right\}$$

$$\Rightarrow \begin{pmatrix} \omega^2 & -2i\omega\Omega_L & 0 \\ 2i\omega\Omega_L & \omega_0^2 & 0 \\ 0 & 0 & \omega_0^2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \omega^2 \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The eigenvalues of ω^2 are given by

$$\begin{vmatrix} \omega_0^2-\omega^2 & -2i\omega\Omega_L & 0 \\ 2i\omega\Omega_L & \omega_0^2-\omega^2 & 0 \\ 0 & 0 & \omega_0^2-\omega^2 \end{vmatrix} = 0$$

detriment

$$\Rightarrow \left[\omega^4 - \left(2\omega_0^2 + 4\Omega_L^2\right)\omega^2 + \omega_0^4\right]\left[\omega^2-\omega_0^2\right] = 0$$

Solution 1: $\omega = \omega_0$

Solution 2, 3: $\omega^4 - \left(2\omega_0^2 + 4\Omega_L^2\right)\omega^2 + \omega_0^4 = 0$

$\Rightarrow$ $\omega \simeq \omega_0 \pm \Omega_L$ since $\omega_0 \gg \Omega_L$

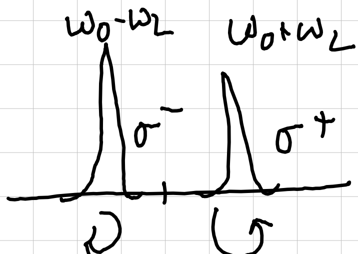
The corresponding eigenvectors are

$$\vec{r} = \begin{pmatrix} \cos(\omega_0 - \Omega_L)t \\ -\sin(\omega_0 - \Omega_L)t \\ 0 \end{pmatrix} \qquad \sigma_-$$

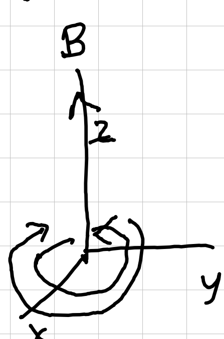
$$\vec{r} = \begin{pmatrix} \cos(\omega_0 + \Omega_L)t \\ \sin(\omega_0 + \Omega_L)t \\ 0 \end{pmatrix} \qquad \sigma_+$$

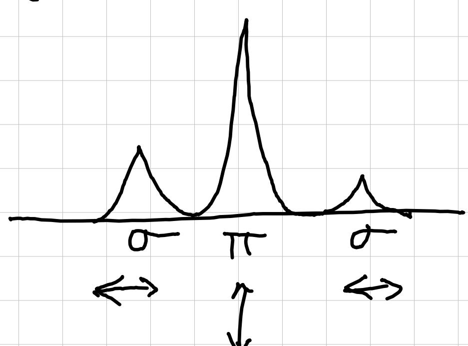
$$\vec{r} = \begin{pmatrix} 0 \\ 0 \\ \cos\omega_0 t \end{pmatrix} \qquad \pi$$

(as measured along $\hat{z}$)



(as measured $\perp$ to $\hat{z}$)





Magnetic field in atoms: (L-S coupling)

$$\mu = \mu_B \vec{L} + g_e \mu_B \vec{S}$$

$$H' = -\mu \cdot \vec{B} \quad \text{(external field)}$$

$$\mu_B = \frac{e\hbar}{2m_e c} \quad \text{Bohr magneton}$$

$$g_e = -2\left(1 + \frac{\alpha}{2\pi} + \cdots\right) \simeq -2$$

In L-S coupling. $\vec{J} = \vec{L} + \vec{S}$ is the basis.

$$H_{\text{Zeeman}} = -\frac{\langle \mu \cdot J \rangle \; \vec{J} \cdot \vec{B}}{J \cdot J}$$

$$= \frac{\langle L \cdot J \rangle + g_e \langle S \cdot J \rangle}{J(J+1)} \mu_B B J_z$$

Laplace Equation

$$\nabla^2 T = 0$$

Let: $T(r, \theta, \phi) = R(r)\, \Theta(\theta)\, \Phi(\phi)$

Solution: $$T = \begin{Bmatrix} r^{l} \\ r^{-l-1} \end{Bmatrix} P_l^m(\cos\theta) \begin{Bmatrix} e^{im\phi} \\ e^{-im\phi} \end{Bmatrix}$$

↑ Legendre polynomials

$l = 0, 1, 2, \ldots$
$m = -l, -l+1, \ldots, l-1, l$

Spherical harmonics:

$$Y_{l,m}(\theta, \phi) \equiv (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi (l+m)!}}\, P_l^m(\cos\theta)\, e^{im\phi}$$

Orthogonal: $\int Y_{l,m} Y^*_{l',m'}\, d\Omega = \delta_{ll'} \delta_{mm'}$

So you can expand any $f(\theta, \phi)$

$l=0 \quad Y_{1,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$

$$l=1 \begin{cases} Y_{1,\pm}(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi} \\ Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta \end{cases}$$

Parity: (Mirror reflection)

The mirror image of H atom has same engy level

$$\hat{P}(\psi(r)) = \lambda\psi(-\vec{r})$$

parity operator

$$\hat{P}(\hat{P}(\psi(r)) = \lambda^2\psi(\vec{r}) = \psi(\vec{r})$$

Thus $\lambda^2 = 1 \Rightarrow \lambda = \pm 1$

All EM wavefuctions should satisfy parity requirements

$$\hat{P}(Y_{l,m}) = (-1)^l Y_{l,m}$$

Thus, spherical harmonics enjoy both types of parity.

Clebsch-Gordon coefficients

Products of spherical harmonics can be rewritten as a sum over spherical harmonics.

e.x.

$$Y_{1,m}\, Y_{\ell_1, m_1} = A\, Y_{\ell_1+1, m_1+m} + B\, Y_{\ell_1-1, m_1+m}$$

Clebsch-Gordon coefficients

Transitions

The transition rate is computed using Fermi's golden rule.

The incident signal is $\vec{E}(t) = E_0 \, \mathrm{Re}(e^{i\omega t})\hat{e}$

① The wavelength is much larger than the size of the atom.

② Assume electric dipole, $H' = -e\vec{r}\cdot\vec{E}$

$$\text{Rate} \propto |eE_0|^2 \left| \int \psi_2^*(\vec{r}\cdot\hat{e})\psi_1 \, d^3r \right|^2$$

$$\downarrow$$

$$|\langle 2|\vec{r}\cdot\hat{e}|1\rangle|^2$$

$$\langle 2|\vec{r}\cdot\hat{e}|1\rangle = D_{12} \, I_{ang}$$

radial　　angular

$$D_{12} = \int_0^\infty R_{n_2,l_2}(r) \, r \, R_{n_1,l_1}(r) \, r^2 dr$$

$$I_{ang} = \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2,m_2}(\theta,\phi) \, \hat{r}\cdot\hat{e} \, Y_{l_1,m_1}(\theta,\phi) \, d\Omega$$

$\sin\theta \, d\theta \, d\phi$

$$\hat{r} = \frac{1}{r}\left(x\,\hat{x} + y\,\hat{y} + z\,\hat{z}\right)$$

$$= \sin\theta\cos\theta\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z}$$

$$\sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} - Y_{1,1}\right)$$

$$\sin\theta\sin\phi = i\sqrt{\frac{2\pi}{3}}\left(Y_{1,-1} + Y_{1,1}\right)$$

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\,Y_{1,0}$$

$$\hat{r} \propto Y_{1,-1}\,\frac{\hat{x}+i\hat{y}}{\sqrt{2}} + Y_{1,0}\,\hat{z} + Y_{1,1}\,\frac{-\hat{x}+i\hat{y}}{\sqrt{2}}$$

For the electric field we will use the framework developed for Zeeman splitting

$$\hat{e} = A_{\sigma-}\left(\frac{\hat{x}-i\hat{y}}{\sqrt{2}}\right) + A_{\pi}\,\hat{z} + A_{\sigma+}\left(\frac{-\hat{x}+i\hat{y}}{\sqrt{2}}\right)$$

$$\hat{r}\cdot\hat{e} \propto A_{\sigma-}Y_{1,-1} + A_{\pi}Y_{1,0} + A_{\sigma+}Y_{1,+1}$$

π-transitions

Consider an oscillating electric field along $\hat{z}$

The $\hat{e}\cdot\hat{z} = A_\pi Y_{1,0} = A_\pi \cos\theta$

$$I^{\pi}_{ang} = A_\pi \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2,m_2}(\theta,\phi)\cos\theta\, Y_{l_1,m_1}(\theta,\phi)\sin\theta\, d\phi$$

This integral has cylinderical symmetry about z-axis

So I^{π}_{ang} should not change by rotation by ϕ_0

Recall $Y \propto e^{i m_l \phi}$

So $I^{\pi}_{ang}(\phi_0) = e^{i(m_{l_1}-m_{l_2})\phi_0}\, I^{\pi}_{ang}$

$m_{l_1} - m_{l_2} = 0 \quad \Rightarrow \quad \boxed{\Delta m_l = 0}$

σ - transitions

Consider (circular polarization) excitations in x-y plane (A_{σ^+}, A_{σ^-})

$$A_{\sigma^+} Y_{1,+1} \propto \sin\theta \, e^{i\phi}$$

$$A_{\sigma^-} Y_{1,1} \propto \sin\theta \, e^{-i\phi}$$

$$I_{ang}^{\sigma^+} \propto \int_0^{2\pi} \int_0^{\pi} Y^*_{\ell_2, m_2} \sin\theta \, Y_{\ell_1, m_1} \, d\Omega$$

Noting cylinderical symmetry

$$m_2 - m_1 + 1 = 0 \qquad m_2 - m_1 - 1 = 0$$

$$\therefore \quad \Delta m = \pm 1 \qquad (\text{RCP, LCP})$$

The σ and π transitions only take place for specific polarizations.

For unpolarized $\quad \Delta m_\ell = 0, \pm 1$

We now look into the constraints from θ

$$\cdot\ I_{avg} \propto \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2,m_2} Y_{1,m} Y_{l_1,m_1}\, d\Omega$$

we use Clebsch-Gordon coefficients

$$I_{avg} \propto A\,\delta_{l_2,l_1+1}\,\delta_{m_2,m_1+m} + B\,\delta_{l_2,l_1-1}\,\delta_{m_2,m_1+m}$$

So we find a new constraint

$$\boxed{\Delta l = \pm 1}$$

PARITY

It is a fact that parity operation should not change energy levels or transition rates

$$\hat{P}\left(\int_0^{\pi}\int_0^{\pi} Y^*_{l_1,m_1}\,\vec{r}\,Y_{l_2,m_2}\,d\Omega\right)$$

$$= (-1)^{l_1+l_2+1}\iint Y^*_{l_1m_1}\,\vec{r}\,Y_{l_2m_2}\,d\Omega$$

No change:

$$\Rightarrow \quad l_1+l_2+1 = \text{even}$$

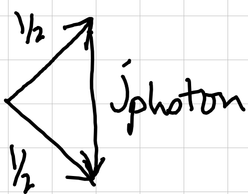
$$\Rightarrow \quad l_1+l_2 = \text{odd}.$$

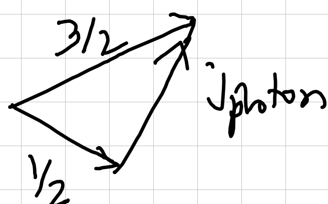
$$\Rightarrow \quad \Delta l = \pm 1$$

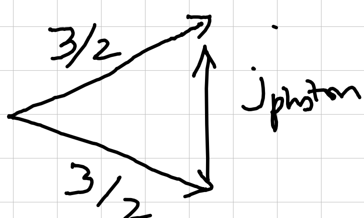
but $l=0 \nleftrightarrow l'=0$

ΔJ rule:

$\Delta j = 0, \pm 1$
(triangle rule)







Electric Dipole: selection rules
(in rough order of priority)

- $\Delta J = 0, \pm 1$ (but not $J=0$ to $J'=0$)

  Conservation of angular momentum

- Parity must change

  [For single electron Ψ_{nl}, $\Delta n = \text{any}$, $\Delta l = \pm 1$]

- $\Delta L = 0, \pm 1$ ($L=0 \nLeftrightarrow L'=0$)

- $\Delta S = 0$ electric dipole does not interact with spin wave-functions

Electric Dipole

$\Delta J = 0, \pm 1 \; (J=0 \not\to J'=0)$

Parity change

$\Delta n \geq 1, \Delta l = \pm 1$

$\Delta L = 0, \pm 1$

$\Delta S = 0$

Magnetic Dipole

"

No parity change

$\left.\begin{array}{l}\Delta l = 0 \\ \Delta n = 0\end{array}\right\}$ no jump

$\Delta L = 0$

$\Delta S = 0$

Semi-forbidden, Intercombination, Inter-system

$\Delta S \neq 0$

N II] 2143 $^3P_2 - {}^5S_2$

Forbidden: magnetic (see above)

electric dipole

[N II] 5756 $^1D_2 - {}^1S_0$

Hyperfine lines:

Spin-orbit coupling was the interaction between the orbit of proton and spin of electron.

$\Rightarrow$ fine-structure lines

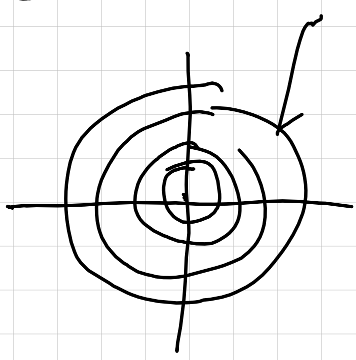
Hyperfine structure: interaction of both spin and orbit of electron with magnetic moment of nucleus.

- This will be $\left(\frac{m_e}{M_p}\right)$ smaller than fine structure
- It will depend on the magnetic moment of the nucleus.

Consider Hydrogen 1s'

$$\psi_{1s}(r) = \frac{1}{\sqrt{4\pi}}\left(\frac{1}{a_0}\right)^{3/2} 2e^{-\rho}$$

$$\rho = r/a_0$$



Magnetic moment:

$$M(r)\,d^3r = -g_e \mu_B \vec{S} |\psi_{1s}(r)|^2 d^3r$$

at $r=0$ $\quad |\psi_{1s}(0)|^2$ is finite

$$B_e(0) = \frac{2}{3} M(0) \qquad \text{(classical resut)}$$

$$H' = -\vec{\mu_I}\cdot\vec{B_e}$$

$$H' = g_I \mu_N I \; \frac{2}{3} g_e \mu_B |\psi_{1s}(0)|^2$$

$$= A\, \vec{I}\cdot\vec{S}$$

where I is the nuclear spin

$$\vec{F} = \vec{I} + \vec{J} \qquad \text{total angular momentu}$$

$$E_{HFS} = A\langle I.J\rangle$$

$$= \frac{A}{2}\left\{F(F+1) - I(I+1) - J(J+1)\right\}$$

ex. H' $\;{}^1S_{1/2}$ $\quad J = 1/2,\; I = 1/2$

$$A = \frac{2}{3} g_e \mu_B g_I \mu_N \frac{Z^3}{\pi a_0^3 n^3}$$

For nucleus:

$$\mu = g \frac{e}{2m_p c} I$$ ← spin angular momentum

μ_N = nuclear magneton $= \frac{e\hbar}{2m_p c}$

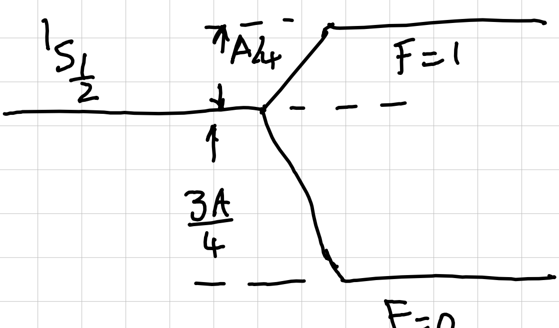
$g_p = +5.585\ldots$ D $0.857\ldots$

$g_n = -3.826\ldots$ T $2.978\ldots$

21-cm hyperfine line of HI

Substituting physical values

$$\frac{\Delta E_{HFS}}{h} = 1.42 \text{ GHz}$$



$g_2 = 3$ $E_2 = 5.87\,\mu eV$

$A_{21} = 2.88 \times 10^{-15}\,s^{-1}$

$g_1 = 1$ $E_1 = 0$