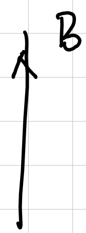
Zeeman splitting



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

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

Solution 1: $\omega = \omega_0$

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

$$\Rightarrow \quad \omega \simeq \omega_0 \pm \Omega_L \quad \text{since } \omega_0 \gg \Omega_L$$

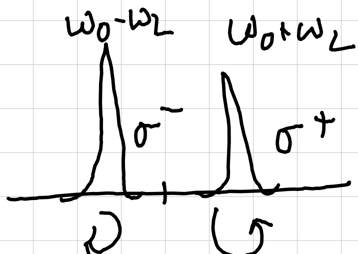
The corresponding eigenvectors are

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

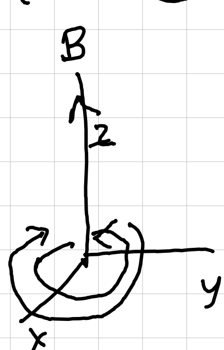
$$\vec{r} = \begin{pmatrix} \cos(\omega_0 + \Omega_L)t \\ \sin(\omega_0 + \Omega_L)t \\ 0 \end{pmatrix} \qquad \sigma_+$$

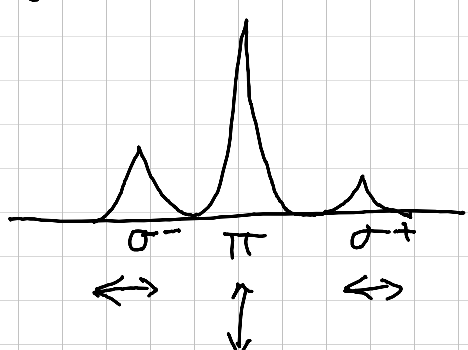
$$\vec{r} = \begin{pmatrix} 0 \\ 0 \\ \cos\omega_0 t \end{pmatrix} \qquad \pi$$

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



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





Magnetic field in atoms: (L-S coupling)

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

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

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

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

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

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

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

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 $f(\theta,\phi)$

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

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

Parity: (Mirror reflection)

Let $\hat{P}$ be the parity operater $\vec{r} \Rightarrow -\vec{r}$

$$\hat{P}\psi = \underbrace{P}_{\text{eigen value}}\psi$$

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

But $\lambda^2 = 1 \Rightarrow \lambda = +1$ (even) or $\lambda = -1$ (odd)

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.

Transitions

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

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

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

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

$$E = E\hat{e}$$

$$\text{Rate} \propto |eE|^2 \left| \int \Psi_2^* (\vec{r}.\hat{e}) \Psi_1 \, d^3r \right|^2$$

$$\downarrow$$

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

$$\langle 2|\vec{r}.\hat{e}|1\rangle = \underset{\text{radial}}{D_{12}} \; \underset{\text{angular}}{I_{ang}}$$

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

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

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

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

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

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

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

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

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

$$I^{\pi}_{ang} = A_\pi \int_0^{2\pi}\int_0^{\pi} Y^*_{\ell_2,m_2}(\theta,\phi)\cos\theta\, Y_{\ell_1,m_1}(\theta,\phi)\sin\theta d\phi$$

This integral has cylinderical symmetry about z-axis

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

Recall $Y \propto e^{im_\ell\phi}$

So $I^{\pi}_{ang}(\phi_0) = e^{i(m_{\ell_1}-m_{\ell_2})\phi_0} I^{\pi}_{ang}$

$m_{\ell_1}-m_{\ell_2}=0 \Rightarrow \boxed{\Delta m_\ell = 0}$

σ - transitions

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

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

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

$$I_{ang}^{\sigma^\pm} \propto \int_0^{2\pi}\int_0^{\pi} Y^*_{l_2,m_2} \sin\theta\, e^{\pm i\phi}\, Y_{l_1,m_1}\, d\Omega$$

Noting cylindrical 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 $\Delta m_l = 0, \pm 1$

We now look into the constraints from θ

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

where $m = 0, \pm 1$

we use Clebsch-Gordon coefficients

$$Y_{1,m} Y_{l_1,m_1} = A Y_{l_1+1, m_1+m} + B Y_{l_1-1, m_1+m}$$

and find

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

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

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

$$= (-1)^{l_1+l_2+1} \iint Y^*_{l_1,m_1}\, \vec{r}\, Y_{l_2,m_2}\, d\Omega$$

No change:

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

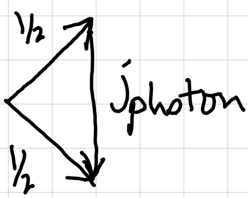
$\Rightarrow \quad l_1+l_2 = \text{odd}.$

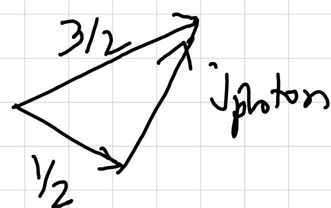
$\Rightarrow \quad \Delta l = \pm 1$

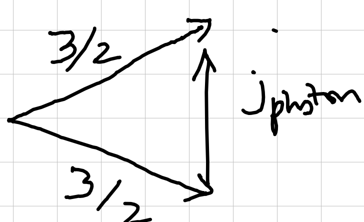
but $l=0 \not\leftrightarrow l'=0$

The triangle rule: must be able to construct triangle

$$\boxed{J=0 \not\leftrightarrow J'=0}$$







$J=0$ to $J'=0$ is completely forbidden

VIA SINGLE PHOTON DECAY

Electric Dipole: selection rules (E1)

(in rough order of priority)

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

  Conservation of angular momentum of photon

- Parity must change

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

- $\Delta L = 0, \pm 1$ ($L=0 \not\leftrightarrow L'=0$)

- $\Delta S = 0$ electric dipole does not interact with spin wave-functions
  so, spin wavefunctions should be in the same spin family

NOTATION:

Semi-forbidden, Intercombination, Inter-system

$\Delta S \neq 0$

N II] 2143 $^3P_{\frac{1}{2}} - {}^5S_{\frac{?}{2}}$

Notice "]"

Forbidden lines:

magnetic dipole (M1)
electric quadrupole (E2)
magnetic quadrupole (M2)

ex. [N II] 5756 $^1D_2 - {}^1S_0$ ← (E2)

Notice "[ ]"

COMPARISON: E1 vs M1

Electric Dipole (E1)	Magnetic Dipole (M1)
$\Delta J = 0, \pm 1$ $(J=0 \not\to J=0)$	"
Parity change	No parity change
$\Delta n \geq 1$, $\Delta l = \pm 1$	$\left.\begin{array}{l}\Delta l = 0 \\ \Delta n = 0\end{array}\right\}$ no jump
$\Delta L = 0, \pm 1$	$\Delta L = 0$
$\Delta S = 0$	$\Delta S = 0$

Electric Quadrupole (E2)

For single electron species

$$\Delta l = 0, \pm 2$$

$$\Delta m_l = 0, \pm 1, \pm 2$$

$$\Delta m_s = 0$$

Generally

$$\Delta j = 0, \pm 1, \pm 2$$

$$\Delta m_j = 0, \pm 1, \pm 2$$

(but $j=0 \not\Leftrightarrow j=0$, $j=\frac{1}{2} \not\Leftrightarrow j=\frac{1}{2}$, $j=0 \Leftrightarrow j=1$)

Lyα λ1216 Å — A-coefficient

$1s\ {}^1S_{\frac{1}{2}} \rightarrow 2p\ {}^1P_{3/2}$ — $6.2\times10^8\ s^{-1}$ (electric dipole)

$2p\ {}^1P_{1/2}$ — $6.2\times10^8\ s^{-1}$

CIII] λ1908.7 — $1.14\times10^2\ s^{-1}$

$(1s^2)2s^2\ {}^1S_0 \rightarrow (1s^2)2s2p\ {}^3P_1^0$

[CIII] λ1906.7

$(1s^2)2s^2\ {}^1S_0 \rightarrow (1s^2)2s2p\ {}^3P_2^0$ (M2!)

(Magnetic Quadrupole

$[\mathrm{O\,III}]$ λ 4958.6 (vacuum)

$(1s^2)2s^2 2p^2\ ^3P_1 \rightarrow (1s^2)2s^2 2p^2\ ^1D \cdots 6.2\times10^{-3}\,s^{-1}$ (magnetic)

$4.6\times10^{-6}\,s^{-1}$ (E-quad

$[\mathrm{C\,II}]$ 157.6 μm

$(1s^2)2s^2 2p\ ^2P^0_{1/2} \rightarrow (1s^2)2s^2 2p\ ^2P^0_{3/2}$ $2.3\times10^{-6}\,s^{-1}$ (magnetic)

Helium:

$1s^2\ ^1S_0 \longrightarrow 1s2s\ ^1S_0$ $J=0$ to $J=0$

Absolutely forbidden via single photon

$\Rightarrow$ decay via two photon

$1s^2\ ^1S_0 \longrightarrow 1s2s\ ^3S_1$

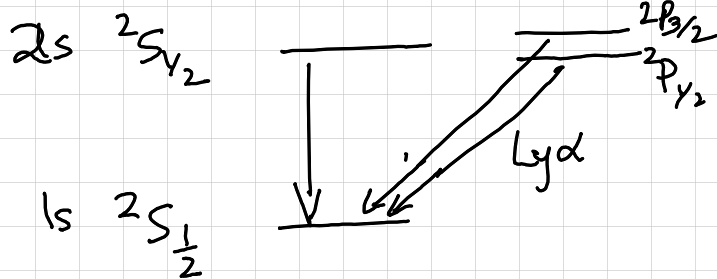
this is semi-forbidden, $\Delta S \neq 0$.

$A^{-1} \simeq 2.3$ hours

Hydrogen $1s\ ^2S_{1/2} \leftrightarrow 2s\ ^2S_{1/2}$

This is a very special forbidden transition

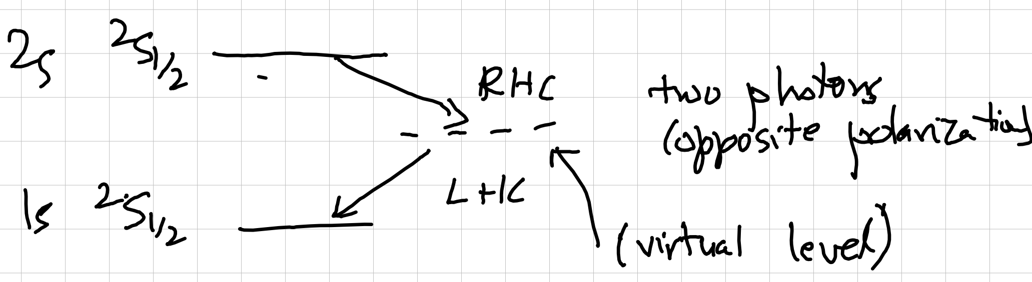
Hydrogen:



Magnetic Dipole (M1)

$1s\ ^2S_{1/2} \rightarrow 2s\ ^2S_{1/2} \quad A = 2.5 \times 10^{-6}\ s^{-1}$

However two-photon decay is faster



$A \simeq 10\ s^{-1}$

Hyperfine lines:

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

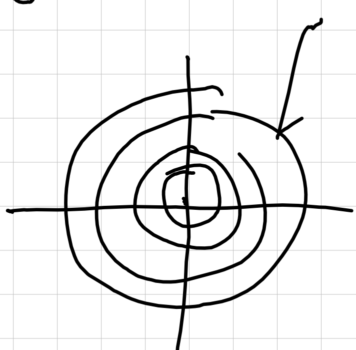
$\Rightarrow$ fine-structure lines

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

$\rho = r/a_0$



Magnetic moment:

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

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

$$B_e(0) = \frac{2cM(0)}{3} \qquad \text{(classical result)}$$

$$H' = -\vec{\mu}_I \cdot \vec{B}_e$$

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

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

where I is the nuclear spin

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

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

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

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

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

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 $0.857\ldots$

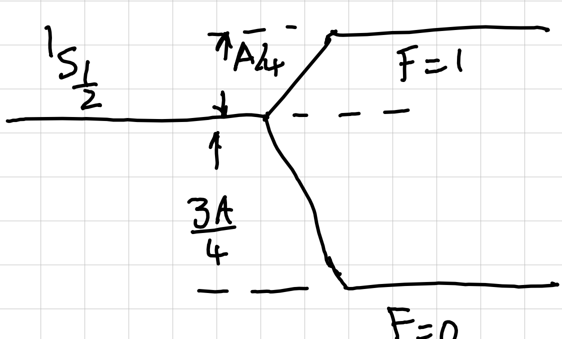
$g_n = -3.826\ldots$ T $2.978\ldots$

21-cm hyperfine line of HI

Substituting physical values

$$\frac{\Delta E_{HFS}}{h} = 1,420,405,751.768 \text{ Hz}$$

(maser)



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

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

$g_1 = 1$ $E_1 = 0$