F. Effects of Spin-Orbit Interaction in Atoms

Ignoring $\hat{H}'_{so}$:

$$\hat{H}_o \psi_{n\ell m_\ell \underset{\frac{1}{2}\text{ (always)}}{\underset{\parallel}{(s)}} m_s} = \underbrace{E_{n\ell}}_{\uparrow} \psi_{n\ell m_\ell (s) m_s} \qquad (17)$$

- for spherically symmetric $U(r)$
- for hydrogen, it is E_n

As discussed, can label these atomic states (each can hold an electron) by

$$(\ell, m_\ell, \underset{\frac{1}{2}\text{ always}}{\underset{\parallel}{s}}, m_s) \qquad \text{OR} \qquad (\ell, \underset{\frac{1}{2}\text{ always}}{\underset{\parallel}{s}}, j, m_j)$$

[there is an "n", understood]

Thus
$$\hat{H}_o \psi_{n\ell s j m_j} = E_{n\ell} \psi_{n\ell s j m_j} \qquad (18)$$
[same information]

$$\boxed{\text{What if } \hat{H}'_{so} \text{ is included, i.e. } \hat{H} = \hat{H}_o + \hat{H}'_{so} \text{ ?}}$$

Meaning:

- E_{21} for $2p$ states

$\hat{H}_0$ only

$$\left\{\begin{array}{lllll}
\psi_{211}(\vec{r})\,\alpha_z & \text{OR} & \psi_{211,+1/2} & \text{OR} & \psi_{211,\uparrow} \\
\psi_{211}(\vec{r})\,\beta_z & \text{OR} & \psi_{211,-1/2} & \text{OR} & \psi_{211,\downarrow} \\
\psi_{210}(\vec{r})\,\alpha_z & \text{OR} & \psi_{210,+1/2} & \text{OR} & \psi_{210,\uparrow} \\
\psi_{210}(\vec{r})\,\beta_z & \text{OR} & \psi_{210,-1/2} & \text{OR} & \psi_{210,\downarrow} \\
\psi_{21-1}(\vec{r})\,\alpha_z & \text{OR} & \psi_{21-1,1/2} & \text{OR} & \psi_{21-1,\downarrow} \\
\psi_{21-1}(\vec{r})\,\beta_z & \text{OR} & \psi_{21-1,-1/2} & \text{OR} & \psi_{21-1,\downarrow}
\end{array}\right.$$

are degenerate

6 $2p$ states with energy E_{21} OR E_{2p}

- For linear combinations: six in $\Rightarrow$ $\underbrace{\text{six out}}$

$\hat{H}_0$ only

$$j = \underset{l}{\underset{\uparrow}{1}} + \underset{s}{\underset{\uparrow}{1/2}} = 3/2 \Rightarrow m_j = 3/2,\ 1/2,\ -1/2,\ -3/2$$

$$j = 1 - 1/2 = 1/2 \Rightarrow m_j = 1/2,\ -1/2$$

$$(l,\ s,\ j,\ m_j)$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$

$$\underbrace{(1, 1/2, 3/2, 3/2),\ (1, 1/2, 3/2, 1/2),\ (1, 1/2, 3/2, -1/2),\ (1, 1/2, 3/2, -3/2);\ (1, 1/2, 1/2, 1/2),\ (1, 1/2, 1/2, -1/2)}_{\text{6 states also of energy } E_{21} \text{ considering } \hat{H}_0 \text{ only}}$$

Key Point $\hat{H} = \hat{H}_0 + \hat{H}'_{so}$

- $\hat{H}_0$ only $\begin{cases} (l, m_l, s, m_s) \\ (l, s, j, m_j) \end{cases}$ make no difference (one scheme is not better than the other)

- $\hat{H}_0 + \hat{H}'_{so}$ (l, s, j, m_j) scheme of labelling atomic states

  spin-orbit interaction

  makes 1st order perturbation theory easy to carry out

  (there is a difference)

Let's see...

Key Ideas and Features: Qualitative Treatment

$$\hat{H} = \hat{H}_0 + \hat{H}'_{SO} = \hat{H}_0 + f(r)\,\hat{\vec{S}}\cdot\hat{\vec{L}} \qquad (19)$$

$H'_{SO} \to \hat{H}'_{SO}$
Go Quantum

Let's use our tools to handle $\hat{H}'_{SO}$ term!

- Recall: $\vec{J} = \vec{L} + \vec{S}$ (total AM)

[How to treat $\vec{S}\cdot\vec{L}$ term?]

[trick]

$$\vec{J}\cdot\vec{J} = J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S}$$

$$\Rightarrow \quad \vec{S}\cdot\vec{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right)$$

Go Quantum: $$\hat{\vec{S}}\cdot\hat{\vec{L}} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \qquad (20)$$

$$\therefore \quad \boxed{\hat{H} = \hat{H}_0 + \underbrace{\frac{f(r)}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)}_{\text{this is } \hat{H}'_{SO}\text{: handle it with } 1^{st} \text{ order perturbation theory}}} \qquad (21)$$

including spin-orbit interaction

Recall: $\hat{H} = \hat{H}_0 + \hat{H}'$

$$E_n \approx E_n^{(0)} + \underbrace{\langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}_{\text{1st order shift in energy}}$$

is the expectation value of $\hat{H}'$ with respect to the unexpected state $\psi_n^{(0)}$

In our context,

Unperturbed state is $\psi^{0}_{n l s j m_j}$, which has $\underbrace{E^{(0)}_{nl}}_{\substack{\text{0th order} \\ (\text{solutions to } \hat{H}_0)}}$

Recall: $\psi_{n l s j m_j}$

m_j goes into $\hat{J}_z$ eigenvalue

j goes into $\hat{J}^2$ eigenvalue

$$\hat{J}^2 \psi_{n l s j m_j} = j(j+1)\hbar^2 \psi_{n l s j m_j}$$

$$\hat{J}_z \psi_{n l s j m_j} = m_j \hbar \psi_{n l s j m_j}$$

$$\hat{L}^2 \psi_{n l s j m_j} = l(l+1)\hbar^2 \psi_{n l s j m_j}$$

$$\hat{S}^2 \psi_{n l s j m_j} = s(s+1)\hbar^2 \psi_{n l s j m_j} = \underset{\substack{\uparrow \\ s=\frac{1}{2}\ \text{(always for electron)}}}{\frac{3}{4}}\hbar^2 \psi_{n l s j m_j}$$

See General Angular momentum in Quantum Mechanics

- 1st order shift in energy due to $\hat{H}'_{so}$

$$\langle \psi_{nlsjm_j} | \hat{H}'_{so} | \psi_{nlsjm_j} \rangle = \langle \psi_{nlsjm_j} | \frac{f(r)}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) | \psi_{nlsjm_j} \rangle$$

$$= \left(j(j+1) - l(l+1) - \frac{3}{4} \right) \hbar^2 \left\langle \frac{f(r)}{2} \right\rangle \quad (22) \text{ Done!}$$

So what? p states ($l = 1$, $s = \frac{1}{2}$, thus $j = \frac{3}{2}$ and $\frac{1}{2}$)

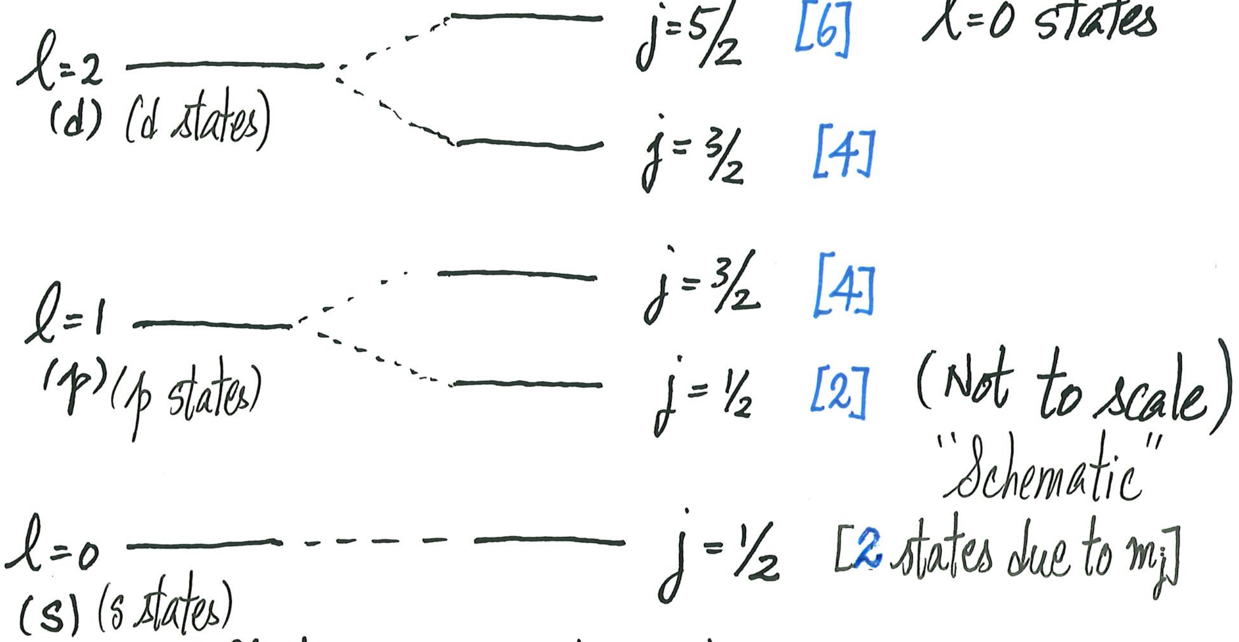
$j = \frac{3}{2}$ (4 states from m_j) : shift $= \left(\frac{3}{2} \cdot \frac{5}{2} - 2 - \frac{3}{4} \right) \hbar^2 \left\langle \frac{f(r)}{2} \right\rangle = \hbar^2 \left\langle \frac{f(r)}{2} \right\rangle$

$j = \frac{1}{2}$ (2 states from m_j) : shift $= \left(\frac{1}{2} \cdot \frac{3}{2} - 2 - \frac{3}{4} \right) \hbar^2 \left\langle \frac{f(r)}{2} \right\rangle = -2\hbar^2 \left\langle \frac{f(r)}{2} \right\rangle$

Key Idea: With spin-orbit interaction, $j = \frac{3}{2}$ states and $j = \frac{1}{2}$ states (different j's) have different energies. This is why we need to define $\vec{J}$.

$\ell = 0$ (s state) $\Rightarrow$ $j = 1/2$ only (also $s = 1/2$)

$$\therefore \left[\underbrace{j(j+1)}_{3/4} - \underbrace{\ell(\ell+1)}_{0} - 3/4 \right] \underbrace{= 0}_{\text{No effect on } \ell = 0 \text{ states}}$$



Effect of spin-orbit interaction on energy levels of a one-electron atom

[No External Applied Magnetic Field!]

Highly exaggerated!

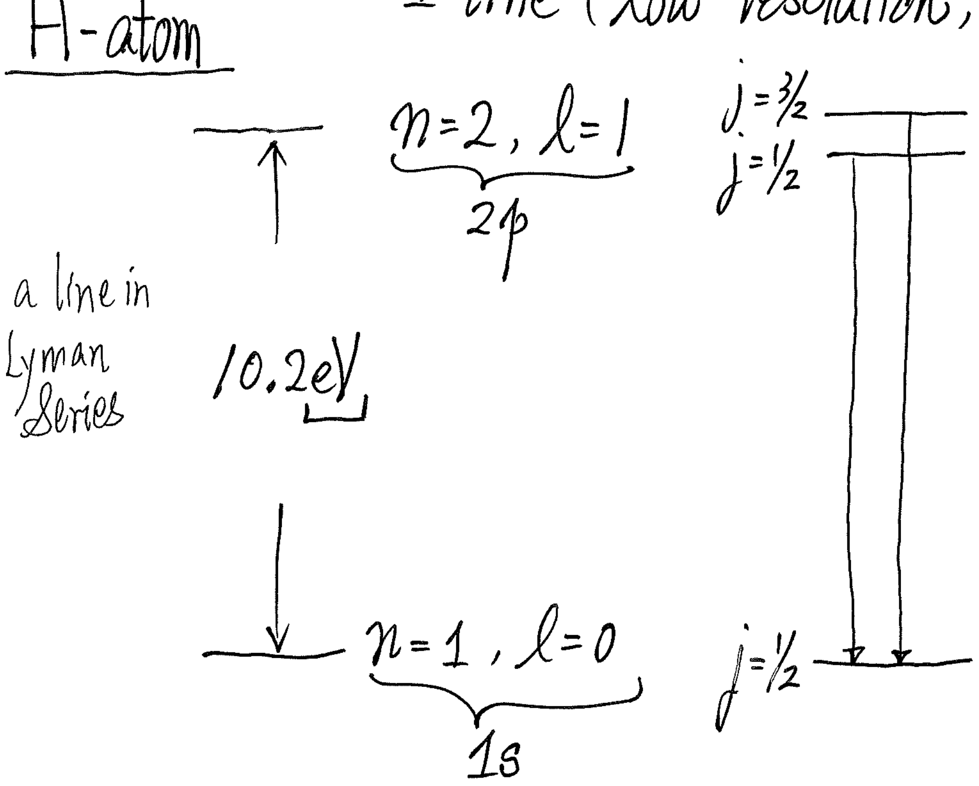
Recall: $|\vec{\mu}_s| \sim \mu_B$

$B_{int} \sim 0.7$ Tesla ~ 1 Tesla

$$\mu_s B_{int} \sim \underbrace{10^{-4}\ \text{eV}}_{\text{tiny compared to eV}}$$

- This <u>fine structure</u> has effect on spectral lines (no applied $\vec{B}$!)

$$\underbrace{2p \rightarrow 1s}_{\text{1 line (low resolution, }\overbrace{\text{ignoring}}^{\text{can't see}}\text{ spin-orbit interaction)}}$$



$\sim 2\mu_B B_{int} \sim 4.5\times\underbrace{10^{-4}\,eV}$ (not to scale)

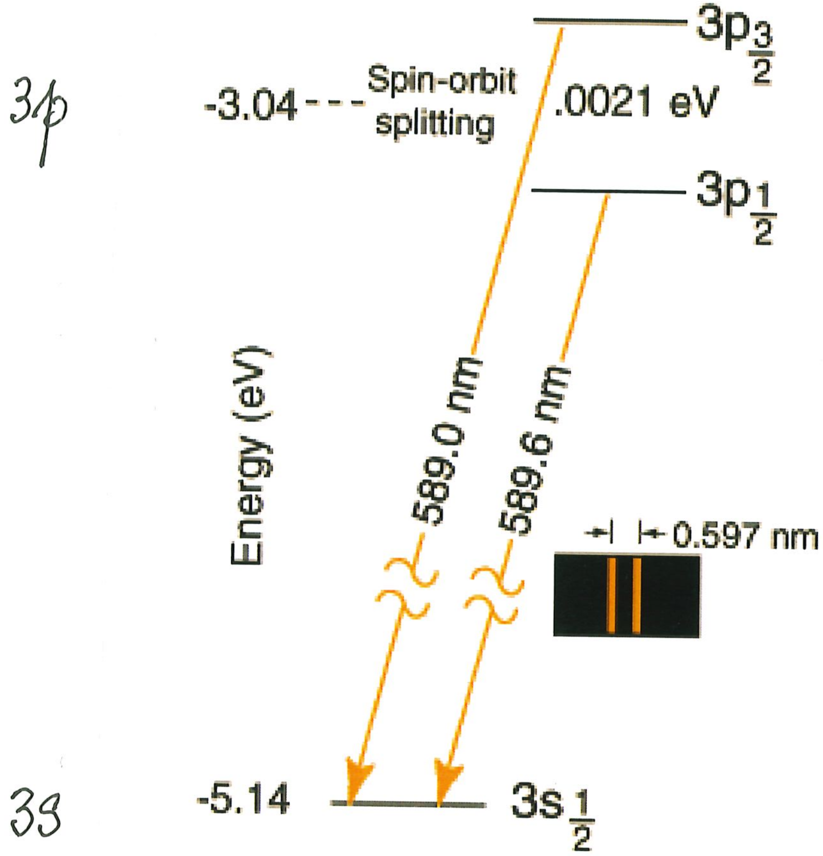
- $2p \rightarrow 1s$ transitions give a doubt of spectral lines separated by $\sim 5.4\times 10^{-4}$ nm in wavelength

[This is how the name "<u>fine structure</u>" came from.]

- Don't confuse this with Zeeman effect. This is $\underbrace{\underline{\text{not}}\text{ Zeeman Effect.}}_{\underline{\text{No}}\text{ Applied }\vec{B}\text{-field.}}$
- To treat H-atom in full, we need relativistic QM.

Same physics works for the Sodium doublet

Sodium Atom



3s → 3p transition is split into $\underbrace{\text{a doublet}}_{\text{two spectral lines}}$

(D lines: D1 and D2)

Both lines are in visible range

Sodium: Bigger atom ⇒ stronger spin-orbit interaction
⇒ easier to see effect

subscript gives j (notation is called "Term Symbol")

Qualitative Ideas to take home:

- Orbital motion → $\vec{B}$ → acts on electron's own spin
- $$H'_{so} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L} \sim f(r)\vec{S}\cdot\vec{L}$$
- There is an internal $\vec{B}$-field (free-of-charge)
- States with same l but different j have different energies because
$$H'_{so} \sim \left\langle \frac{f(r)}{2} \right\rangle \left[j(j+1) - l(l+1) - s(s+1) \right] \hbar^2$$
- H'_{so} lifts degeneracy partially due to m_e according to values of j
- Spin-orbit interaction leads to splitting of one spectral line (low resolution) into closely spaced lines (high resolution) even in the absence of an external field ($\vec{B}_{ext} = 0$).

Quantitative Treatment : Hydrogen Atom

$$H'_{so} = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV(r)}{dr}\,\vec{S}\cdot\vec{L} \qquad (15)$$

H-atom: $V(r) = \dfrac{-e^2}{4\pi\varepsilon_0 r} \Rightarrow \dfrac{dV(r)}{dr} = \dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r^2}$

$$\boxed{H'_{so} = \frac{e^2}{8\pi\varepsilon_0}\,\frac{1}{m^2c^2}\,\frac{1}{r^3}\,\vec{S}\cdot\vec{L}} \qquad (23)$$

← for hydrogen atom [Griffiths' Eq. (6.60)]

$E^{(1)}_{so}$ = 1st order shift in energy due to H'_{so}

$$= \frac{e^2}{8\pi\varepsilon_0}\,\frac{1}{m^2c^2}\left\langle \psi_{nlsjm_j} \middle| \frac{1}{2r^3}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \middle| \psi_{nlsjm_j} \right\rangle$$

$$= \frac{e^2}{8\pi\varepsilon_0}\,\frac{1}{m^2c^2}\,\underbrace{\left\langle \frac{1}{r^3} \right\rangle}\,\frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - \frac{3}{4}\right)$$

$\left\langle \dfrac{1}{r^3} \right\rangle_{nl} = \displaystyle\int_0^\infty |R_{nl}(r)|^2\,\frac{1}{r^3}\cdot r^2\,dr$ = expectation value of $\frac{1}{r^3}$ w.r.t. state ψ_{nlsjm_j}

■ For hydrogen atomic states, $\left\langle \frac{1}{r^3} \right\rangle$ can be evaluated analytically[+].

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)\, n^3 a_0^3}$$

for given n, ℓ $\quad$ a_0 = Bohr radius $= \frac{4\pi\varepsilon_0 \hbar^2}{m e^2}$

$$E_{SO}^{(1)} = \frac{e^2}{8\pi\varepsilon_0} \frac{1}{m^2c^2} \frac{\hbar^2}{2} \frac{\left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right]}{\ell(\ell+\frac{1}{2})(\ell+1)\, n^3 a_0^3}$$

$$= \underset{\substack{\nearrow \\ \frac{-13.6}{n^2}\,\text{eV} \rightarrow \text{unperturbed energy}}}{E_n^{(0)}} \cdot \underbrace{\left(\frac{E_n^{(0)}}{mc^2} \right)}_{\boxed{\text{Important factor}}} \underbrace{\left[\frac{n\left[j(j+1) - \ell(\ell+1) - \frac{3}{4} \right]}{\ell(\ell+\frac{1}{2})(\ell+1)} \right]}_{\text{"order 1"}} \qquad (24)$$

$$\approx \frac{\text{eV}}{0.511\,\text{MeV}} \approx 10^{-5}$$

$$E_n^{(0)} = \frac{-e^2}{8\pi\varepsilon_0 n^2 a_0} = \frac{-13.6}{n^2}\,\text{eV}$$

$$mc^2 = 0.511\,\overbrace{\text{MeV}}^{\text{scale}}$$

= rest energy of electron

$$\Rightarrow E_{SO}^{(1)} = E_n^{(0)} \cdot \left(\text{a factor} \sim 10^{-5} \right)$$

[shift is tiny compared with $E_n^{(0)}$] (make sense)

[+] Students are not expected to know to evaluate it. Calculation is similar to evaluating $\left\langle \frac{1}{r} \right\rangle$ and $\left\langle \frac{1}{r^2} \right\rangle$.

The Fine Structure Constant : $\alpha \approx 1/137$

The ratio
$$\frac{|E_n^{(0)}|}{mc^2} = \frac{1}{mc^2}\cdot\frac{e^2}{8\pi\varepsilon_0 n^2 a_0} = \frac{e^2}{mc^2}\cdot\frac{1}{8\pi\varepsilon_0 n^2}\cdot\frac{me^2}{4\pi\varepsilon_0\hbar^2}$$

$$= \underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2}\cdot\frac{1}{2n^2}$$

"order α^2" $\rightarrow$
$$\equiv \alpha^2\cdot\frac{1}{2n^2} \qquad \text{where } \alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}$$

all fundamental constants

= <u>fine structure constant</u>

$$= \underbrace{\left(\frac{1}{137}\right)^2}_{\sim 10^{-5}}\cdot\frac{1}{2n^2} \qquad (25)$$

Why is α important?

- $\alpha^2 \sim \frac{|E_1^{(0)}|}{mc^2} \sim \frac{\text{GS energy}}{\text{electron rest energy}}$, $\quad \alpha = \frac{v_1}{c} = \frac{\text{speed in "}n=1\text{" Bohr orbit}}{\text{speed of light}}$

  $\therefore$ α characterizes how important relativistic effects are
- $\alpha \sim \frac{1}{137}$ provides a small parameter for accuracy of QED [perturbation works]

Treating $\hat{H}'_{SO}$ in Hydrogen Atom

Nice stuff -

- Can do integrals in 1st order perturbation exactly
- See tininess of effect and α^2 order clearly

Bad stuff -

- Lightest atom
  ⇒ $\underbrace{\text{tininess of effect}}$

Another effect (relativistic correction) happens to be roughly as "big"

Bigger atoms have stronger spin-orbit interaction
⇒ Don't need to worry about another effect

Another $\alpha^2 E_n^{(0)}$ shift: Relativistic correction to kinetic energy term[†]

- H'_{so} leads to shift of order $\alpha^2 E_n^{(0)}$
- To be fair, should also consider relativistic correction in $\hat{T}$
- In $\hat{H}_0$, $\hat{T} = \frac{\hat{p}^2}{2m}$ but $\frac{p^2}{2m}$ is Newtonian (non-relativistic)

$$\text{k.e.} = \sqrt{c^2p^2 + m^2c^4} - mc^2 \approx \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{H'_{rel}}$$

Important for H-atom (special case)

H'_{rel} = perturbation term due to relativistic correction

$$E^{(1)}_{rel} = \text{shift (1st order) due to } H'_{rel}$$

$$= \langle \psi_{nlm_l} | H'_{rel} | \psi_{nlm_l} \rangle$$

$$= -E_n^{(0)} \underbrace{\underbrace{\left(\frac{E_n^{(0)}}{mc^2}\right)}_{\alpha^2 \cdot \frac{1}{2n^2}} \cdot \left[\frac{2n}{l+\frac{1}{2}} - \frac{3}{2}\right]}_{\sim 10^{-5}}$$

(Same order of magnitude as H'_{so} for H-atom)

[†] See Sample Question 14

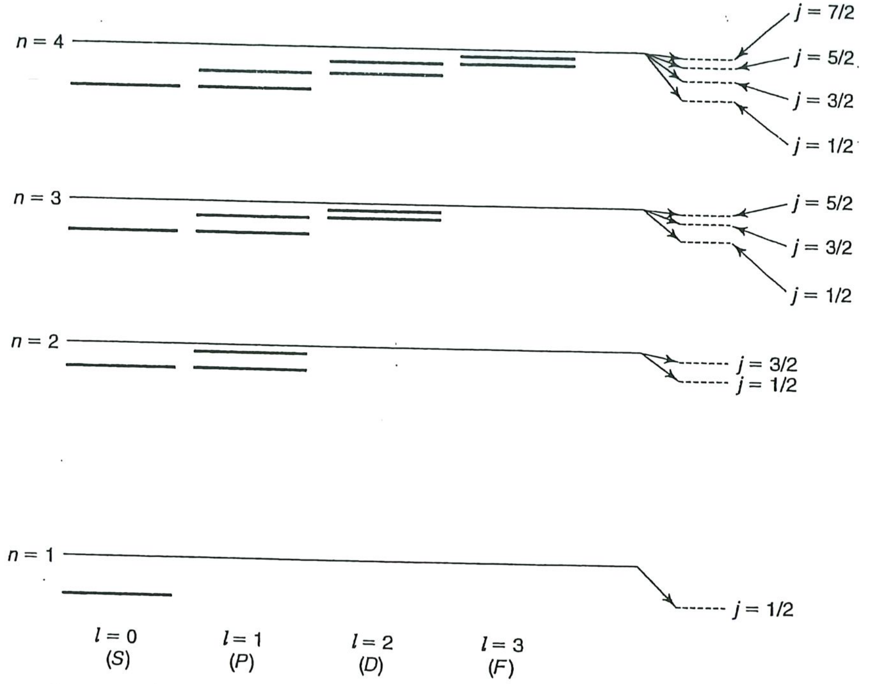
- $E_{SO}^{(1)}$ and $E_{rel}^{(1)}$ are both of the same order "$\alpha^2 E_n^{(0)}$" for hydrogen
- Complete discussion on fine structure in hydrogen atom requires the combined effect of Spin-orbit interaction AND relativistic correction
- Put 1st order results together

$$E_{nj} = \frac{-13.6\,(\text{eV})}{n^2}\left[1+\frac{\alpha^2}{n}\underbrace{\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)}_{\substack{\bullet\ \text{due to } H'_{so} \text{ and } H'_{rel} \\ \bullet\ \text{order } \alpha^2 \\ \boxed{\bullet\ \text{depends on } n \text{ and } j}}}\right] \qquad (26)$$

$E_n^{(0)}$ ↗

↗ 0th order Schrödinger Eq. with $\frac{-e^2}{4\pi\varepsilon_0 r}$ only ($\hat{H}_0$ only)

Hydrogen atom's fine structure (Eq. (26))



Energy levels of hydrogen, including fine structure (not to scale).