The electron has a magnetic moment
\[ \mathbf{\mu} = -e \mathbf{s} / m \]
proportional to spin. However, electron moving around nucleus is a "current"
loop so entire atom has mag. moment \( \mathbf{\mu}_L \) prop to \( \mathbf{L} \) moment.

So we expect classically dipole -
dipole pot. eng.

\[ U \sim \mathbf{\mu} \cdot \mathbf{\mu}_L \sim \mathbf{L} \cdot \mathbf{L} \]

Simplest way to compute this is to compute \( \mathbf{B} \) field electron "feels" in
orbit - we change "reference frames" to
one where electron is at rest
and proton is orbiting.

Treat moving proton as current loop
that produces a mag. field \( \mathbf{B} \) at
center where electron is.
From Eq. 2102 we have

\[ B = \frac{\mu_0 I}{2r} \]

From circular loop, \( I = \frac{\text{Coulomb}}{\text{sec}} = \frac{e}{T} \)

Where \( T \) is orbital period. We connect to the momentum \( L \) via

\[ L = \left| I \times p \right| = rmv = r^2m \omega = \frac{2\pi r^2 m}{T} \]

\[ \omega = \frac{2\pi}{T} \]

\[ \Rightarrow T = \left[ \frac{L}{2\pi r^2 M} \right]^{-1} \]

\[ \Rightarrow I = \frac{e}{T} = \frac{eL}{2\pi r^2 M} \]

\[ \Rightarrow B = \frac{\mu_0 I}{2r} = \frac{\mu_0 eL}{4\pi^2 M r^3} \]

Maxwell's Eq \( \Rightarrow C = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \)

\[ \Rightarrow \mu_0 = \frac{1}{\varepsilon_0 C^2} \]

\[ B = \frac{1}{4\pi \varepsilon_0} \frac{1}{MC^2} \frac{e}{r^2} L \]

\[ \Rightarrow \frac{I}{L} = \frac{e}{1} \frac{1}{MC^2} \frac{e}{r^2} \frac{\varepsilon_0}{\frac{1}{2} L} \]

But "reference frame" trick requires a "force factor" since electron is accelerating, not inertial.
AGAIN PHYSICS GLUES POT. ERG.
OF DIPOLE \( \vec{M}_S \) IN MAG FLD
AS
\[ U = - \vec{M}_S \cdot \vec{B} \]
PUTTING HATSH ON GIVES
\[ \hat{H}' = - \vec{M}_S \cdot \left[ \frac{1}{2} k_0 \frac{1}{M^2 c^2} \frac{e}{r^3} \right] \]
\[ \hat{H}'_{so} = - \frac{k_0}{2} \frac{e^2}{M^2 c^2} \frac{1}{r^3} \vec{M}_S \cdot \vec{L} \]
\[ = + \frac{k_0}{2} \frac{e^2}{M^2 c^2} \frac{1}{r^3} \frac{e}{m} \vec{r} \cdot \vec{L} \]
\[ \hat{H}_{so} = \frac{1}{2} k_0 \frac{e^2}{M^2 c^2} \frac{1}{r^3} \vec{S} \cdot \vec{L} \]
SINCE \( \langle \vec{S} \rangle \sim \frac{1}{2} \frac{e}{m} \)
\( \langle \vec{L} \rangle \sim \frac{1}{r} \cdot \frac{e}{m} \)
\( \langle r^3 \rangle \sim a^3 \)
\[ E_{so} \sim \langle H_{so} \rangle \sim k_0 \frac{e^2}{M^2 c^2} \frac{1}{r^3} \frac{e}{m} \left( \frac{k_0 \frac{e}{m}}{k_0 \frac{e^2}{M^2 c^2} \frac{1}{r^3}} \right)^{-1} \sim \frac{k_0 e^2}{M^2 c^2} \frac{k_0 M^3 e^6}{k^6} \]
\[ \sim \frac{k_0 \frac{e^2}{M^2 c^2}}{k^4 c^4} \sim \frac{4 \mu_0}{k^4 c^4} \frac{M c^2}{k^4} \sim \frac{4}{k^4 M c^2} \]
As \( \mu \) PROVISED
\( \sim \propto M c^2 \)
\[
\hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(r)
\]

So now there is a problem

\[
\hat{H}_0 \neq \frac{\hbar^2}{2m} \nabla^2 + \hat{V}(r)
\]

Does not commute with \( \hat{S} \cdot \hat{L} \)

\[
[\hat{H}_0, \hat{S} \cdot \hat{L}] \neq 0
\]

So \( \hat{s} \) and \( \hat{l} \) are not "good" quantum numbers in this problem.

However

\[
[\hat{H}_0, \hat{l}^2] = 0
\]

\[
[\hat{H}_0, \hat{s^2}] = 0
\]

\[
[\hat{H}_0, \hat{l} \pm \hat{s}] = 0
\]

So we define

\[
\hat{l} \equiv \hat{l} + \hat{s}
\]

The total angular momentum and its eigenvalues \( \hat{j} \equiv m_j \) are "good" new \( | j \ M_j \rangle \) basis states required.

Rules for \( j \) and \( m_j \)

\[
\hat{l^2} | j \ M_j \rangle = \hbar^2 j (j+1) | j \ M_j \rangle
\]

\[
\hat{s^2} | j \ M_j \rangle = \hbar^2 m_j | j \ M_j \rangle
\]

\[
l - s \leq j \leq l + s
\]

\[-j \leq m_j \leq +j\]
$|\psi_{100}\rangle$ is not good $|\psi_{nem}\rangle$

Using sum addition rules we need to find

$|\psi_{n,m_j}\rangle = |n, j, m_j\rangle$

$n = 0$

$s = \frac{1}{2}$

$| - s | \leq j \leq |s + 1 | \Rightarrow |\psi_{n,j}\rangle \in \frac{1}{2} \Rightarrow |j = \frac{1}{2}\rangle$

$\Rightarrow \frac{1}{2} \leq j \leq \frac{3}{2}$

$\Rightarrow -\frac{1}{2} \leq m_j \leq \frac{1}{2}$

$\Rightarrow m_j = \pm \frac{1}{2}$

$\Rightarrow |\psi_{100}\rangle \rightarrow \big\{ |\frac{1}{2}, \frac{1}{2}\rangle = \psi_{\frac{1}{2}, \frac{1}{2}}\rangle \big\}$

This explicitly includes spin $s = \frac{1}{2}$
Example 1st excited state

\[ \psi_{2\pi\sigma} = \psi_{\pi \sigma} \]

\[ l = 0 \quad j \in 10 - 1/2 \Rightarrow 10 + 1/2 \Rightarrow j = 1/2 \]

\[ m_j = \pm 1/2 \]

\[ \psi_{2\pi\sigma} \quad \psi_{1/2 \pm 1/2} \]

\[ \psi_{2\pi\pi} \quad l = 1 \]

\[ 11 - 1/2 \leq j \leq 11 + 1/2 \Rightarrow j = 1/2, 3/2 \]

\[ j = 1/2 \Rightarrow m_j = \pm 1/2 \]

\[ j = 3/2 \Rightarrow m_j = \begin{cases} 
3/2 \\
1/2 \\
-1/2 \\
-3/2 
\end{cases} \]

\[ \psi_{210} \]

\[ j = 1/2 \quad m_j = 1/2 \]

\[ m_j = -1/2 \]

Fig 6.9

Under 5.0 \( \text{H}^1 \) states of different \( j \) have degeneracy lifted, but states with same \( j \) but different \( m_j \) remain deg.
So goal is to take

\[ \hat{H}'_{so} = \frac{1}{2} \hbar \frac{e^2}{m^2 c^2} \frac{1}{r^3} \hat{\mathbf{s}} \cdot \mathbf{L} \]

and rewrite \( \hat{\mathbf{S}} \cdot \mathbf{L} \) in terms of \( \hat{\mathbf{S}}^2, \hat{\mathbf{L}}^2, \mathbf{S} \cdot \mathbf{L} \) (good) since

\[ [ \hat{H}_0, \hat{\mathbf{S}} \cdot \mathbf{L} ] \neq 0 \] \( \text{BAD} \)

\[ [ \hat{H}_0, \hat{\mathbf{S}}^2 ] = [ \hat{H}_0, \hat{\mathbf{L}}^2 ] = [ \hat{H}_0, \mathbf{S} \cdot \mathbf{L} ] \] \( \text{GOOD} \)

The crucial point is perturbation matrix

\[ W = \{ \langle \mathbf{n} \mathbf{m} | \hat{H}'_{so} | \mathbf{n} \mathbf{m} \rangle \} \]

is not diagonal in \( | \mathbf{n} \mathbf{m} \rangle \) basis

but is diagonal in

\[ W = \{ \langle \mathbf{n} \mathbf{m} | \mathbf{S} \cdot \mathbf{L} | \mathbf{n} \mathbf{m} \rangle \} \]

in \( | \mathbf{j} \mathbf{m}_j \rangle \) basis.

By switching \( | \mathbf{n} \mathbf{m} \rangle \to | \mathbf{j} \mathbf{m}_j \rangle \)

we can use non-degenerate perturbation theory!

Since \( \hat{\mathbf{S}} \) and \( \hat{\mathbf{L}} \) act on spatial vs spin wave functions

\[ \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \chi = (\hat{\mathbf{L}} \cdot \chi) \cdot \hat{\mathbf{S}} \]

\[ = (\hat{\mathbf{S}} \cdot \chi) \cdot (\hat{\mathbf{L}} \cdot \chi) \]

\[ \Rightarrow [ \hat{\mathbf{S}}, \hat{\mathbf{L}} ] = 0 \] \( \text{commute} \)
\[ 
\hat{J}^2 = \frac{\hbar^2}{\mathbf{L}} \cdot \hat{J}^2 \\
= \left[ \hat{L}^2 + \frac{\hbar^2}{s} \right] \cdot \left[ \hat{L}^2 + \frac{\hbar^2}{s} \right] \\
= \hat{L}^2 \cdot \hat{L}^2 + \frac{\hbar^2}{s} \cdot \hat{L}^2 + \frac{\hbar^2}{s} \cdot \frac{\hbar^2}{s} \\
\Rightarrow \\
\frac{\hbar^2}{s} \cdot \hat{L}^2 = \hat{L}^2 + 2 \hat{L} \cdot \frac{\hbar^2}{s} + \frac{\hbar^2}{s} \\
\Rightarrow \\
\frac{\hbar^2}{s} \cdot \hat{L}^2 = \frac{1}{s} \left[ \hat{L}^2 - \frac{\hbar^2}{s} \hat{L}^2 \right] \\
\]

In the new basis |\( n_j m_j \rangle \)

This gives

\[ 
\hat{L} \cdot \frac{\hbar^2}{s} |n_j m_j \rangle = \frac{1}{s} \left[ \frac{\hbar^2}{s} |n_j m_j \rangle \\
- \hat{L}^2 |n_j m_j \rangle \\
- \frac{\hbar^2}{s} |n_j m_j \rangle \right] \\
\]

Since fixed \( j \) & \( s \) implies fixed \( L \)

We can show

\[ 
= \frac{1}{s} \left[ \frac{\hbar^2}{s} \hat{j} (j+1) |n_j m_j \rangle \\
- \frac{\hbar^2}{s} \hat{l}^2 (l+1) |n_j m_j \rangle \\
- \frac{\hbar^2}{s} \hat{s}^2 (s+1) |n_j m_j \rangle \right] \\
= \frac{1}{s} \left[ \frac{\hbar^2}{s} \hat{j} (j+1) - \frac{\hbar^2}{s} \hat{l}^2 (l+1) - \frac{\hbar^2}{s} \hat{s}^2 (s+1) \right] |n_j m_j \rangle \\
\]

\[ z = \sqrt{L} \]

\[ L = 0, 1, 2, \ldots \]

\[ |l-s| \leq j \leq |l+s| \]

\[ -j \leq m_j \leq +j \]
Hence using \( \frac{h}{2} \) - deg, perturbation theory.

\[
E_{so}^1 = \langle \hat{n}_{so} \rangle
\]

\[
= \langle n_j m_j \mid \frac{1}{2} k_0 \frac{e^2}{\hbar^2 c^2} \frac{\hbar^2}{2} \mid n_j m_j \rangle
\]

\[
= \langle n_j m_j \mid \frac{1}{2} k_0 \frac{e^2}{\hbar^2 c^2} \frac{\hbar^2}{2} \left[ j(j+1) - \ell(\ell+1) - \frac{3\hbar}{2} \right] \rangle \langle n_j m_j \mid \frac{1}{r^3} \rangle \langle n_j m_j \rangle
\]

\[
= \frac{1}{2} k_0 \frac{e^2}{\hbar^2 c^2} \frac{\hbar^2}{2} \left[ j(j+1) - \ell(\ell+1) - \frac{3\hbar}{2} \right] \langle n_j m_j \mid \frac{1}{r^3} \rangle \langle n_j m_j \rangle
\]

**BUT FINAL** \( \langle \frac{1}{r^3} \rangle \) **DOES NOT DEPEND ON SPIN ONLY SPATIAL \( \psi_{1e} \)**

\[
= \langle n_j m_j \mid \frac{1}{r^3} \mid n_j m_j \rangle = \langle n_{\ell m} \mid \frac{1}{r^3} \mid n_{\ell m} \rangle
\]

\[
= \frac{1}{2\pi} \int dV \psi_{n_{\ell m}}^* (\mathbf{r}) \frac{1}{r^3} \psi_{n_{\ell m}} (\mathbf{r})
\]

**Can be integrated directly or by trick**

**Prob 6.35**

\[
\langle \frac{1}{r^3} \rangle = \frac{1}{\ell (\ell + \frac{1}{2})(\ell + 1) \hbar^3 a^3}
\]

\[
E_{so}^1 = \frac{1}{2} k_0 \frac{e^2}{\hbar^2 c^2} \frac{\hbar^2}{2} \left[ j(j+1) - \ell(\ell+1) - \frac{3\hbar}{2} \right] \frac{\ell (\ell + \frac{1}{2})(\ell + 1) \hbar^3 a^3}{\ell (\ell + 1)} \Rightarrow \text{Eq 6.64}
\]

\[
\psi_{1e} = \frac{\hbar^2}{k_0 M c^2} \left( \frac{k_0 e^2}{\hbar c} \right)^4 \Rightarrow \gamma_4 M c^2
\]

\[
k_0 = \frac{1}{\sqrt{\pi} \epsilon_0 c} \Rightarrow a = \frac{\hbar^2}{k_0 M e^2} \Rightarrow \alpha = \frac{k_0 e^2}{\hbar c}
\]

\[
\Rightarrow \frac{k_0 \frac{e^2}{\hbar^2 c^2} \frac{\hbar^2}{a^2}}{M e^2} \Rightarrow \frac{k_0 M^3 e^6}{\hbar^6 c^2} = \frac{k_0 y M e^8}{\hbar^4 c^2}
\]
\[ E_{20}^{(0)} = \left( \frac{\hbar}{2} \right)^4 M c^2 \left[ \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{\hbar^3} \right] n < \frac{4}{3} \]

Using Prob 6.11
\[ E_{nm}^{(0)} = E_{nm}^{(0)} = -\frac{\alpha^2 M c^2}{2 n^2} \]

Bohr energy

\[ \frac{\hbar^4 M c^2}{h^3} \]

\[ \frac{n^4}{2M c^2} \]

\[ \frac{\hbar^4 M c^2}{2 n^4} = \frac{n}{M c^2} \left[ \frac{E_{nm}^{(0)}}{E_{nm}^{(0)}} \right]^2 \]

\[ E_{20}^{(1)} = \frac{\left( E_{nm}^{(0)} \right)^2}{M c^2} \left\{ \frac{\hbar^4 M c^2}{2 n^4} \right\} = \frac{1}{2} \left[ \frac{4n}{n} - \frac{3}{4} \right] \]

\[ \text{Eq. 6.65} \]

Since \[ E_{20}^{(1)} \] and \[ E_{20}^{(1)} \] both \( n < \frac{4}{3} \)

We combine them to get " Fine Structure"

Correctly

\[ E_{FS}^{(1)} = E_{20}^{(1)} + E_{20}^{(1)} \]

\[ = \left[ \frac{\left( E_{nm}^{(0)} \right)^2}{M c^2} \right] \left\{ \frac{n}{2} \left[ \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{\ell(\ell+\frac{1}{2})(\ell+1)} \right] - \frac{1}{2} \left[ \frac{4n}{n} - \frac{3}{4} \right] \right\} \]

\[ = \frac{\left( E_{nm}^{(0)} \right)^2}{M c^2} \left\{ \text{see Prob 6.17 using} \quad j = \ell + \frac{1}{2} \right\} \]

This simplifies to...

\[ E_{FS}^{(1)} = \frac{\left( E_{nm}^{(0)} \right)^2}{2 M c^2} \left( 3 - \frac{4n}{j+\frac{1}{2}} \right) \]

\[ \text{Eq 6.66} \]
Derivation of Eq. 6.66

Problem 6.17

With the plus sign, \( j = l + 1/2 \ (l = j - 1/2) \) : \hspace{1em} \text{Eq. 6.57} \Rightarrow \ E_{r}^{1} = -\frac{(E_n)^2}{2mc^2} \left( \frac{4n}{j} - 3 \right)

Equation 6.65 \Rightarrow \ E_{so}^{1} = \frac{(E_n)^2}{mc^2} \left( j(j+1) - \frac{(j - \frac{1}{2})(j + \frac{1}{2}) - \frac{3}{4}}{j} \right)

\[ = \frac{(E_n)^2}{mc^2} \frac{n(j^2 + j - j^2 - \frac{3}{4} - \frac{3}{4})}{j(j + \frac{1}{2})j(j + \frac{3}{2})} = \frac{(E_n)^2}{mc^2} \frac{n}{j(j + \frac{1}{2})}. \]

\[ E_{ls} = E_{r}^{1} + E_{so}^{1} = \frac{(E_n)^2}{2mc^2} \left( -\frac{4n}{j} + 3 + \frac{2n}{j(j + \frac{1}{2})} \right) \]

\[ = \frac{(E_n)^2}{2mc^2} \left( 3 + \frac{2n}{j(j + \frac{1}{2})} \left( 1 - 2 \left( j + \frac{1}{2} \right) \right) \right) = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right). \]

With the minus sign, \( j = l - 1/2 \ (l = j + 1/2) \) : \hspace{1em} \text{Eq. 6.57} \Rightarrow \ E_{r}^{1} = -\frac{(E_n)^2}{2mc^2} \left( \frac{4n}{j + 1} - 3 \right).

Equation 6.65 \Rightarrow \ E_{so}^{1} = \frac{(E_n)^2}{mc^2} \left( j(j+1) - \frac{(j + \frac{1}{2})(j + \frac{3}{2}) - \frac{3}{4}}{j + \frac{1}{2}} \right)

\[ = \frac{(E_n)^2}{mc^2} \frac{n(j^2 + j - j^2 - 2j - \frac{3}{4} - \frac{3}{4})}{(j + \frac{1}{2})(j + 1)(j + \frac{3}{2})} = \frac{(E_n)^2}{mc^2} \frac{-n}{(j + 1)(j + \frac{1}{2})}. \]

\[ E_{ls} = \frac{(E_n)^2}{2mc^2} \left[ -\frac{4n}{j + 1} + 3 + \frac{2n}{(j + 1)(j + \frac{1}{2})} \right] = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{2n}{(j + 1)(j + \frac{1}{2})} \left[ 1 + 2 \left( j + \frac{1}{2} \right) \right] \right) \]

\[ = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right). \] For both signs, then, \( E_{ls} = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j + \frac{1}{2}} \right). \) QED
we have \( E_{\text{rem}}^{\text{tot}} = E_{nj}^{\text{tot}} \approx E_{n}^{(0)} + E_{n}^{(i)} \)

\[ = E_{\text{rem}}^{(0)} + \left( \frac{E_{\text{rem}}^{(0)}}{2MC^2} \right)^2 \left( 3 - \frac{4\pi}{j+1/2} \right) \]

using \( E_{\text{rem}}^{(0)} = -\frac{k^2MC^2}{2n^2} = -13.6\text{ eV} \)

\[ E_{nj}^{\text{tot}} = -\frac{k^2MC^2}{2n^2} + \left[ \frac{k^2MC^2}{2n^2} \right]^2 \frac{1}{2MC^2} \left( 3 - \frac{4\pi}{j+1/2} \right) \]

\[ = -\frac{k^2MC^2}{2n^2} \left\{ 1 - \frac{k^2MC^2}{2n^2} \frac{1}{2MC^2} \left( 3 - \frac{4\pi}{j+1/2} \right) \right\} \]

\[ = -\frac{k^2MC^2}{2n^2} \left\{ 1 + \frac{k^2}{4n^2} \left[ \frac{\frac{n}{j+1/2} - \frac{3}{4}}{n} \right] \right\} \]

\[ E_{nj} = -\frac{13.6\text{ eV}}{n^2} \left\{ 1 + \frac{k^2}{n^2} \left[ \frac{n}{j+1/2} - \frac{3}{4} \right] \right\} \]

since smallest \( \frac{n}{j+1/2} \) can be is \( \frac{1}{\sqrt{2}} = 2 \)

the shift is always negative does not depend on \( mj \) but only \( j \) in so states with same \( j \) but different \( mj \) deg.
\[ \psi_{n\ell m} \]

\[ n = 1 \quad \ell = 0 \quad m = 0 \]

\[ E_{1/2}^{(1)} = E_{FS}^{(1)} \]

\[ |n j m_j\rangle \]

\[ n = 2 \quad \ell = 0 \quad m = 0 \]

\[ E_{3/2}^{(1)} = E_{FS}^{(1)} \]

\[ |n j m_j\rangle \]

\[ n = 2 \quad \ell = 1 \quad m = 0 \]

\[ |2 \frac{3}{2} m_j\rangle \text{ is quadrupole deg.} \]

\[ m_j = \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{3}{2} \]

\[ |2 \frac{1}{2} m_j\rangle \text{ is double deg.} \]

\[ m_j = \pm \frac{1}{2} \]

Sodium is hydrogen-like. The famous sodium doublet is the state

\[ |2 \frac{1}{2} m_j\rangle \text{ vs. } |2 \frac{3}{2} m_j\rangle \]

\[ \delta = 589.0 \text{ nm} \]

\[ \Delta \ell = 589.0 \text{ nm} \]

\[ |1 \frac{1}{2} \pm \frac{1}{2}\rangle \]