$$\therefore \vec{B}' = -\frac{1}{c^2}\left(\frac{1}{r}\frac{dV(r)}{dr}\right)(\vec{r}\times\vec{v})$$

$$= -\frac{1}{mc^2 er}\left(\frac{dV(r)}{dr}\right)\underbrace{(\vec{r}\times m\vec{v})}_{\vec{L}}$$

$$= -\frac{1}{mc^2 er}\left(\frac{dV(r)}{dr}\right)\cdot\vec{L}$$

The quantum mechanical operator should arise as:

$$\hat{H}_{SO} = -\vec{\mu}_S \cdot \hat{\vec{B}}' = +\frac{1}{mc^2 er}\frac{dV(r)}{dr}\cdot\vec{L}\cdot\vec{\mu}_S$$ But $\vec{\mu}_S = \frac{e}{m}\vec{S}$

$$\therefore \hat{H}_{SO} = \frac{1}{m^2c^2 r}\frac{dV(r)}{dr}\hat{L}\cdot\hat{S}$$

From this we can expect:

$$\xi(r) = \frac{1}{m^2c^2r}\frac{dV(r)}{dr} = -\frac{e}{m^2c^2r}\frac{d\phi(r)}{dr}$$

This turns out to be off by a factor of 2 due to relativistic effects.

$$\xi(r) = \frac{1}{2m^2c^2r}\frac{dV(r)}{dr}$$

When $V(r) = -\frac{Ze^2}{4\pi\varepsilon_o r} \Rightarrow \frac{dV(r)}{dr} = +\frac{Ze^2}{4\pi\varepsilon_o r^2}$

then $$\xi(r) = \frac{Ze^2}{8\pi\varepsilon_o m^2c^2r^3}$$

6.2 Spin-orbit coupling to first order

Can set up the total Hamiltonian in the SO-coupled limit as:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}_{SO}$$

↓

Hamiltonian in the absence of SO coupling

Here $\hat{H}_{SO} = \xi(r)\hat{L}\cdot\hat{S}$

But $\hat{J}^2 = \left(\hat{L}+\hat{S}\right)^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\cdot\hat{S}$

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

$$\therefore \hat{H}_{SO} = \frac{1}{2}\xi(r)\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

Note: $\mathbf{H}_{SO}$ commute with each component, $\mathbf{J}^2$, $\mathbf{L}^2$, $\mathbf{S}^2$, and therefore all these operators have a common set of eigenfunctions when expressed in the coupled representation.

By perturbation theory can predict:

$$E_q^{(1)} = <\psi_q \,|\, \hat{H}^{(1)} \,|\, \psi_q>$$

where the Ψ_q's are wave functions in the coupled representation

Then: $$E_{n,\ell,s,j,m_j} = <n,\ell,s,j,m_j \,|\, \xi(r)\hat{L}\cdot\hat{S} \,|\, n,\ell,s,j,m_j>$$

$$= \frac{1}{2} <n,\ell,s,j,m_j \,|\, \xi(r)\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) |\, n,\ell,s,j,m_j>$$

Thus $$E_{SO}^{(1)} = \frac{1}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\hbar^2 <n,\ell,s,j,m_j \,|\, \xi(r) \,|\, n,\ell,s,j,m_j>$$

$$= \frac{1}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\hbar^2 <R_{n\ell} \,|\, \xi(r) \,|\, R_{n\ell}> \underbrace{<f(\theta,\phi,m_s) \,|\, f(\theta,\phi,m_s)>}_{=1}$$

$$= \frac{1}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\hbar^2 <\xi(r)>$$

Note that $$\xi(r) = \frac{Ze^2}{8\pi\varepsilon_o m^2 c^2} \cdot \frac{1}{r^3}$$

But $$\left\langle \frac{1}{r^3} \right\rangle = \int_0^\infty R_{n,\ell}^2(r) \frac{r^2}{r^3} dr = \frac{\left(\frac{Z}{a_o}\right)^3}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell + 1)}; \quad \ell > 0$$

$$\Rightarrow \hbar^2 < \xi(r) >= \frac{\hbar^2 Ze^2}{8\pi\varepsilon_o m^2 c^2} \cdot \frac{\left(\frac{Z}{a_o}\right)^3}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

But $$a_o = \frac{4\pi\varepsilon_o \hbar^2}{me^2}$$

$$\therefore \hbar^2 < \xi(r) >= \frac{Z^4 e^2 \hbar^2}{8\pi\varepsilon_o m^2 c^2 \left(\frac{4\pi\varepsilon_o \hbar^2}{me^2}\right)^3} \cdot \frac{1}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

$$= \frac{Z^4 e^8 m^3 \hbar^2}{8\pi\varepsilon_o m^2 c^2 (4\pi)^3 \varepsilon_o^3 \hbar^6} \cdot \frac{1}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

Fact: The Rydberg constant = R_H = ionization energy of the H-atom, is given by:

$$R_H = R_\infty = \frac{me^4}{8\varepsilon_o^2 h^3 c} = 109737.31\ cm^{-1}$$

This Rydberg constant assumes the nucleus has infinite weight relative to the electron which is an OK approximation even for hydrogen.

Finally, we can write: $$\hbar^2 < \xi(r) >= \frac{hc\alpha^2 R_\infty Z^4}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell + 1)}$$

where α is the dimensionless fine-structure constant = 7.29720×10^{-3}

$$\alpha = \frac{e^2}{\hbar c}$$

$$\therefore \hbar^2 < \xi(r) >= hc\xi_{n,\ell}$$

= spin-orbit coupling constant when $\xi_{n,l}$ is measured in cm^{-1}.

Note the Z^4 dependence. We can therefore expect SO interactions to become important for heavier elements.

Hence: $$E_{SO}^{(1)}(n,\ell,s,j) = \frac{1}{2}hc\xi_{n,\ell}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

and $$E(n,\ell,s,j) = E_n^{(0)} + E_{SO}^{(1)}(n,\ell,s,j)$$

$$= -\frac{Z^2e^2}{2n^2a_o(4\pi\varepsilon_o)} + \frac{1}{2}hc\,\xi_{n,\ell}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

Note: the energy does not depend on the quantum number m_j

Also **note:** the Z^2 dependence for H-like (1 electron) atoms: He^+, Li^{2+}, etc.