Lecture 12 Highlights

One nice feature of $\vec{J}$ is the fact that it is a "constant of the motion" for the perturbed Hamiltonian $\mathrm{H}^0 + \mathrm{H}_{so}$. Hence although we loose m_ℓ and m_s as good quantum numbers, we gain j and m_j. This allows us to write the spin-orbit perturbation operator $\vec{S} \bullet \vec{L}$ in terms of "constants of the motion" as (using the definition of $\vec{J} = \vec{L} + \vec{S}$, squaring it, and solving for $\vec{S} \bullet \vec{L}$);

$$\vec{S} \bullet \vec{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right),$$

so the eigenvalues of $\vec{S} \bullet \vec{L}$ are $\frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)$, where $s = 1/2$ for the electron.

Finally we can calculate the first-order correction to the energy of the Hydrogen atom due to the spin-orbit perturbation. By the standard expression for first order energy correction:

$$E^1_{n,\ell,s,j} = \iiint \psi_n^{0*}\, \mathrm{H}_{so}\, \psi_n^0 \, d^3r$$

After substituting the appropriate Hydrogen atom wavefunctions (that we shall derive later) and spin-orbit Hamiltonian one arrives at;

$$E^1_{n,\ell,s,j} = \frac{\left|E_n^0\right|\alpha^2}{n} \frac{j(j+1) - \ell(\ell+1) - 3/4}{2\ell(\ell+\frac{1}{2})(\ell+1)}$$

(here we are using the fact that s=1/2 for the electron.) Note that this energy shift is on the order of the fine structure constant squared times the unperturbed eigenenergy, exactly the same form as the relativistic correction. When the two results are combined (Homework 4) the result is the fine structure formula:

$$\Delta E = E_n^{1\mathrm{Re}lativity} + E_n^{1SpinOrbit} = \frac{\left|E_n^0\right|\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n}{j+\frac{1}{2}}\right]$$

This correction is always negative and partially lifts the degeneracy of the unperturbed eigen-energies. See the schematic plot of the fine structure corrections to the energy levels of the Hydrogen atom elsewhere on the class web site.

What is the connection between the total angular momentum $\vec{J}$ and our old friends $\vec{L}, \vec{S}$?

If $\vec{J} = \vec{L} + \vec{S}$ and J^2 has eigenvalue $j(j+1)\hbar^2$, L^2 has eigenvalue $\ell(\ell+1)\hbar^2$, and S^2 has eigenvalue $s(s+1)\hbar^2$, then one might naively think that $j = \ell + s$. However this is not the whole story.

If we apply J_z to a souped-up Hydrogen atom product wave function which now includes spin, $\psi_{n,\ell,m_\ell,s,m_s}(r,\theta,\phi) \propto R_{n\ell}(r) Y_\ell^{m_\ell}(\theta,\phi)\left| s\ m_s \right\rangle$, where the spinor is denoted with the ket (s=1/2 for the electron), the result is:

$$J_z\psi_{n,\ell,m_\ell,s,m_s} = m_j\hbar\psi_{n,\ell,m_\ell,s,m_s}$$, and

$$J_z\psi_{n,\ell,m_\ell,s,m_s} = (L_z + S_z)\psi_{n,\ell,m_\ell,s,m_s}$$

The L_z operator sees only the spherical harmonic, while the S_z operator sees only the spinor ket. The result is:

$$J_z\psi_{n,\ell,m_\ell,s,m_s} = (m_\ell\hbar + m_s\hbar)\psi_{n,\ell,m_\ell,s,m_s}$$, leading to the conclusion that

$$m_j = m_\ell + m_s$$

However, if we operate with J^2 on this same Hydrogen atom wavefunction, the results are not so pretty. From the definition of $\vec{J} = \vec{L} + \vec{S}$, we know that $J^2 = L^2 + S^2 + 2\vec{L} \bullet \vec{S}$ (note that $\vec{L}$ and $\vec{S}$ commute with each other), and the $\vec{L} \bullet \vec{S}$ operator can be expressed as:

$$\begin{aligned} 2\vec{L} \bullet \vec{S} &= 2(L_xS_x + L_yS_y + L_zS_z) \\ &= 2L_zS_z + L_+S_- + L_-S_+ . \end{aligned}$$

using our old friends the raising and lowering operators. J^2 can now be written as:

$$J^2 = L^2 + S^2 + 2L_zS_z + L_+S_- + L_-S_+$$

Now consider applying this operator to a hydrogen atom product wavefunction of the form $\psi_{n,\ell,m_\ell,s,m_s}(r,\theta,\phi) = R_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)\left|\frac{1}{2}\ \frac{1}{2}\right\rangle$ for example (i.e. with a "spin up" electron):

$$J^2\psi_{n,\ell,m_\ell,1/2,1/2} = \left[\ell(\ell+1)\hbar^2 + \frac{3}{4}\hbar^2 + 2m_\ell\hbar\frac{\hbar}{2}\right]\psi_{n,\ell,m_\ell,1/2,1/2} + \hbar\hbar\sqrt{(\ell - m_\ell)(\ell + m_\ell + 1)}\psi_{n,\ell,m_\ell+1,1/2,-1/2}$$

where we have used results from Eq. [4.121] and page 174 of Griffiths. Note that this is no longer an eigen-equation because the raising and lowering operators have changed the m_ℓ and m_s values in the second term on the RHS. Apparently the eigenfunctions of J^2 are linear combinations of Hydrogen atom product wavefunctions $\psi_{n,\ell,m_\ell,s,m_s}(r,\theta,\phi)$ with different values of m_ℓ and m_s. This is consistent with the statement we made in the last lecture that the $\vec{L} \bullet \vec{S}$ operator mixes together different unperturbed Hydrogen atom states.

The eigenfunctions of J^2 can be expressed as linear combinations of states with different values of m_ℓ and m_s using the world-famous Clebsch-Gordan coefficients ($C^{\ell\ \ s\ \ j}_{m_\ell\ m_s\ m_j}$) as:

$$\left| j\ m_j \right\rangle = \sum_{m_\ell + m_s = m_j} C^{\ell\ \ s\ \ j}_{m_\ell\ m_s\ m_j} \left| \ell\ m_\ell \right\rangle \left| s\ m_s \right\rangle$$

Where the ket $\left|\ell\ m_\ell\right\rangle$ represents the spherical harmonics $Y_\ell^{m_\ell}$. The C-G coefficient values are given in Table 4.8 on page 188 of Griffiths. Remember that all of the coefficients should appear under a square root, with the minus sign (if any) out front.