B7.3 Further Quantum Theory Lecture 8

When combining angular momenta, we have two natural bases:

$|j_1, m_1; j_2, m_2\rangle$ diagonalize $(J^{(1)})^2$, $J_3^{(1)}$, $(J^{(2)})^2$, $J_3^{(2)}$

$|j_1, j_2; J, M\rangle$ diagonalize $(J^{(tot)})^2$, $J_3^{(tot)}$, $(J^{(1)})^2$, $(J^{(2)})^2$

In practice, it is useful to be able to move back and forth between these bases. Thus we need the expansion of a given basis vector of one type in terms of the other basis.

$$|j_1 j_2; J, M\rangle = \sum_{m_1, m_2} C_{j_1 j_2}(J, M; m_1, m_2)\, |j_1, m_1; j_2, m_2\rangle$$

The numbers $C_{j_1 j_2}(J, M; m_1, m_2) = \langle j_1, m_1; j_2, m_2 | j_1, j_2; J, M\rangle$ are known as "Clebsch-Gordan coefficients". By their definition, these coefficients satisfy a number of important properties:

▷ orthonormality: $\sum_{J,M} |C_{j_1 j_2}(J, M; m_1, m_2)|^2 = 1 = \sum_{m_1, m_2} |C_{j_1 j_2}(J, M; m_1, m_2)|^2$

▷ $\langle J, M | J', M'\rangle = \delta_{J,J'}\delta_{M,M'} = \sum_{m_2=-j_2}^{j_2} \sum_{m_1=-j_1}^{j_1} C^*_{j_1 j_2}(J, M; m_1, m_2)\, C_{j_1 j_2}(J', M'; m_1, m_2)$

▷ $\langle m_1, m_2 | m_1', m_2'\rangle = \delta_{m_1,m_1'}\delta_{m_2,m_2'} = \sum_{J,M} C_{j_1 j_2}(J, M; m_1, m_2) C_{j_1 j_2}(J, M; m_1', m_2')^*$

▷ selection rules: $C_{j_1 j_2}(J, M; m_1, m_2) = 0$ unless $M = m_1 + m_2$ & $|j_1 - j_2| \le J \le j_1 + j_2$.

How well-defined are these? Suppose the basis $|j_1, m_1; j_2, m_2\rangle$ is fixed. For each $J = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 - 1, j_1 + j_2$ we have a phase freedom in defining $|j_1, j_2; J, J\rangle$. But remaining states in irrep are fixed by $J_-^{(tot)}|J, M\rangle = \hbar\sqrt{J(J+1) - M(M-1)}\,|J, M-1\rangle$.

There are some standard conventions. First of all: $|J = j_1 + j_2, M = j_1 + j_2\rangle = |j_1, j_1; j_2, j_2\rangle$

Now acting w/ J_-: $|J, J-1\rangle = \sqrt{\frac{j_2}{j_1 + j_2}}\,|j_1, j_1; j_2, j_2 - 1\rangle + \sqrt{\frac{j_1}{j_1 + j_2}}\,|j_1, j_1 - 1; j_2, j_2\rangle$

Need to pick orthogonal state for $|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = \sqrt{\frac{j_1}{j_1 + j_2}}\,|j_1, j_1; j_2, j_2 - 1\rangle - \sqrt{\frac{j_2}{j_1 + j_2}}\,|j_1, j_1 - 1; j_2, j_2\rangle$

There is a generally agreed upon convention, sometimes called the "Condon-Shortley convention", to fix the signs of all the CG coefficients.

In general, $|j_1 j_2; J, J\rangle = c_1 |j_1, j_1; j_2, J-j_1\rangle + c_2 |j_1, j_1-1; j_2, J-j_1+1\rangle + \cdots + c_{j_1+j_2-J+1} |j_1, J-j_2; j_2, j_2\rangle$

↑ we demand this coefficient be positive (and in particular real).

With these conventions, all CG's are real, and there's an additional symmetry

$$C_{j_1 j_2}(J, M; m_1, m_2) = (-1)^{j_1+j_2-J} C_{j_2 j_1}(J, M; m_2, m_1)$$

Can compute by hand, but also easy to look up in tables (in Weinberg, for example).

Back to spin-$\frac{1}{2}$:

$|1,1\rangle = |\tfrac{1}{2}, \tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle$ ——— $\longrightarrow C_{\frac{1}{2}\frac{1}{2}}(1,1; \tfrac{1}{2}, \tfrac{1}{2}) = 1$

$|1,0\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{1}{2}, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle + |\tfrac{1}{2}, -\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle\right) \longrightarrow C_{\frac{1}{2}\frac{1}{2}}(1,0; \pm\tfrac{1}{2}, \mp\tfrac{1}{2}) = \frac{1}{\sqrt{2}}$

$|1,-1\rangle = |\tfrac{1}{2}, -\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle$ ——— $\longrightarrow C_{\frac{1}{2}\frac{1}{2}}(1,-1; -\tfrac{1}{2}, -\tfrac{1}{2}) = 1$

$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|\tfrac{1}{2}, \tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle - |\tfrac{1}{2}, -\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle\right) \longrightarrow C_{\frac{1}{2}\frac{1}{2}}(0,0; \pm\tfrac{1}{2}, \mp\tfrac{1}{2}) = \pm\frac{1}{\sqrt{2}}$

Easy to check all the properties mentioned before.

Comment: from the CG's, one can form some very interesting objects called Wigner 3j-symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} C_{j_1 j_2}(j_3, -m_3; m_1, m_2) = C_{j_3 j_3}(0,0; m_3, -m_3) C_{j_1 j_2}(j_3, -m_3; m_1, m_2)$$

These describe how to combine three spins to get a spin-zero object. These objects have truly remarkable symmetries:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix}$$

$$= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_1 & \frac{1}{2}(j_2+j_3-m_1) & \frac{1}{2}(j_2+j_3+m_1) \\ j_2-j_3 & \frac{1}{2}(j_2-j_3-m_1)-m_3 & \frac{1}{2}(j_2-j_3+m_1)+m_2 \end{pmatrix}$$

$$= (-1)^{j_1+j_2+j_3} \begin{pmatrix} \frac{1}{2}(j_2+j_3+m_1) & \frac{1}{2}(j_1+j_3+m_2) & \frac{1}{2}(j_1+j_2+m_3) \\ j_1-\frac{1}{2}(j_2+j_3-m_1) & j_2-\frac{1}{2}(j_1+j_3-m_2) & j_3-\frac{1}{2}(j_1+j_2-m_3) \end{pmatrix}$$

Altogether, there are 72 symmetries of these symbols!

A standard implementation of these ideas is to the study of Hydrogen and similar atoms. Recall that for Hydrogen we have the Hamiltonian

$$H_{Hyd} = \frac{|\underline{p}|^2}{2m} - \frac{4\pi\epsilon_0 e^2}{|\underline{x}|}$$

acting on wave functions in $\mathbb{R}^3$. You studied the stationary states for this model in part A, where you found

$$\psi_{n,\ell}^{m'} = f_{n,\ell}(r) Y_\ell^{m'}(\phi,\theta) \qquad E_n = \frac{E_0}{n^2}, \; E_0 = \frac{-e^2}{8\pi\epsilon_0 a} \quad \left(a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}\right)$$

We won't revisit the derivation now (all the hard work is in finding the $f_{n,\ell}(r)$'s). Instead, let's look at the incorporation of the spin of the electron.

Electrons have spin-$\frac{1}{2}$, so the true Hilbert space here is $L^2(\mathbb{R}^3) \otimes \mathcal{H}_{spin-\frac{1}{2}} \cong L^2(\mathbb{R}^3) \oplus L^2(\mathbb{R}^3)$

$$|\psi\rangle \longleftrightarrow \begin{pmatrix} \psi_+(\underline{r}) \\ \psi_-(\underline{r}) \end{pmatrix} = |\psi_+ \otimes s=\tfrac{1}{2}\rangle + |\psi_- \otimes s=-\tfrac{1}{2}\rangle$$

Our Hamiltonian (for now) has no dependence on the spin of the electron, so we are just introducing a 2-fold degeneracy into the system, and we have a basis of stationary states

$$\psi_{n,\ell}^{m',m_s} = \psi_{n,\ell}^{m'}(r,\theta,\phi) \otimes |m_s\rangle$$

$n = 1, 2, \ldots$
$\ell = 0, \ldots, n-1$
$m' = -\ell, -\ell+1, \ldots, \ell-1, \ell$
$m_s = -1/2, 1/2$

However, the more natural basis will be the one where we add orbital and spin angular momentum, diagonalizing

$$\underline{J}^{(tot)} = \underline{L} + \underline{S} \qquad \text{(the square and the 3-component)}$$

So we define a new basis of spin/angular wave functions

$$\phi_{\ell,j}^{m} = \sum_{\substack{m',m_s \\ m'+m_s=m}} C_{\ell,\frac{1}{2}}(j,m_j m',m_s)\, Y_\ell^{m'}(\phi,\theta) \otimes |m_s\rangle$$

Here we have $j = \ell \pm \frac{1}{2}$ for $\ell \geq 1$ ($j = \frac{1}{2}$ for $\ell = 0$) by addition rules. Then the new basis of stationary states is given by

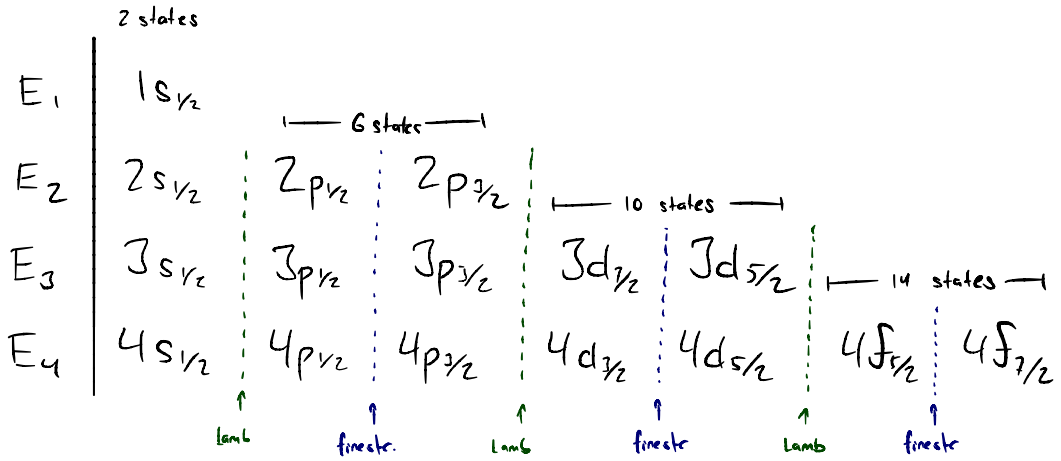
$$\psi_{n,\ell,j}^{m} = f_{n,\ell}(r)\, \phi_{\ell,j}^{m}$$

$(2j+1)$ states in orbital

For a given n, ℓ, j, this collection of states is known as the $n\ell_j$ orbital, with an alphabetical replacement for ℓ:

$\ell = 0 \longrightarrow$ s "sharp"
$\ell = 1 \longrightarrow$ p "principal"
$\ell = 2 \longrightarrow$ d "diffuse"
$\ell = 3 \longrightarrow$ f "fundamental"
$\vdots$ g $\vdots$

There is a lot of degeneracy amongst these states.



Two remarks:

- The Hydrogen Hamiltonian is an idealization; we expect real Hydrogen atoms to be more complicated. This leads to corrections to H that shift energy levels.
  - fine structure: j-dependant splitting
  - lamb shift: ℓ-dependant splitting
  - hyperfine structure: extra bifurcation due to nuclear degeneracy.
- Given the extra degeneracy, could there be a symmetry explanation? Yes! It turns out that for Hydrogen one can write $\underline{L} = \underline{A} + \underline{B}$ where $\underline{A}$ & $\underline{B}$ each obey A.M. commutation relations.

$$n=1: \quad \mathcal{H}_0^L \cong \mathcal{H}_0^A \otimes \mathcal{H}_0^B$$

$$n=2: \quad \mathcal{H}_0^L \oplus \mathcal{H}_1^L \cong \mathcal{H}_{\frac{1}{2}}^A \otimes \mathcal{H}_{\frac{1}{2}}^B$$

$$n=3: \quad \mathcal{H}_0^L \oplus \mathcal{H}_1^L \oplus \mathcal{H}_2^L \cong \mathcal{H}_{\frac{3}{2}}^A \otimes \mathcal{H}_{\frac{3}{2}}^A$$

etc.

Explains degeneracy amongst different ℓ-values! (This extra symmetry is, of course, broken by corrections.) This also leads to a completely algebraic derivation of the spectrum!

Keywords: (Laplace-)Runge-Lenz vector.

I've mentioned the idea of incorporating "small corrections" to the Hamiltonian. Our task next week will be to develop this notion in the form of "time-independant perturbation theory".