Combination of Spins

There is one more topic in the theory of angular momentum that we need to discuss. Now that we understand how one electron spin transforms under rotations, we can ask how a system of two or more electrons transforms.

A 2-electron system is described by two spinors

$$|\xi_1, \xi_2\rangle = \begin{pmatrix} \xi_1^1 \\ \xi_1^2 \end{pmatrix} \begin{pmatrix} \xi_2^1 \\ \xi_2^2 \end{pmatrix}$$

This representation is 4-dimensional. A basis is given by the 4 states

$$|\uparrow\uparrow\rangle \qquad |\uparrow\downarrow\rangle \qquad |\downarrow\uparrow\rangle \qquad |\downarrow\downarrow\rangle$$

The inner product in this 4-dimensional Hilbert space is

$$\langle \xi_1 \xi_2 | \eta_1 \eta_2 \rangle = \langle \xi_1 | \eta_1 \rangle \langle \xi_2 | \eta_2 \rangle = (\xi_1^{*a} \eta_1^a)(\xi_2^{*b} \eta_2^b)$$

We call this representation a *direct product* of two spin $\frac{1}{2}$ representations. The direct product of a spin j_1 and a spin j_2 representation has

$$(2j_1 + 1)(2j_2 + 1)$$

states.

The actions of a rotation on the 2-electron wavefunction is

$$\begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix}\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix} \rightarrow \mathcal{U}(\vec{\alpha})\begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix} \cdot \mathcal{U}(\vec{\alpha})\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix}$$

That is, we rotate each spin independently. Expanding this equation for small $\vec{\alpha}$ up to terms linear in $\vec{\alpha}$, we find

$$\begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix}\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix} \rightarrow \begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix}\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix} - i\vec{\alpha}\cdot\frac{\vec{\sigma}}{2}\begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix}\cdot\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix} - i\vec{\alpha}\cdot\begin{pmatrix}\xi_1^1\\ \xi_1^2\end{pmatrix}\cdot\frac{\vec{\sigma}}{2}\begin{pmatrix}\xi_2^1\\ \xi_2^2\end{pmatrix} + \cdots$$

Then the generator of angular momentum in this representation is

$$\vec{S} = \vec{S}_1 + \vec{S}_2$$

where $\vec{S}_1 = \hbar\vec{\sigma}/2$ acting on ξ_1 and $\vec{S}_2 = \hbar\vec{\sigma}/2$ acting on ξ_2.

I will now show that this product representation is not irreducible. Consider the state

$$|0\rangle = \frac{1}{\sqrt{2}}\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

The total S^z of this state is zero. Explicitly,

$$S^z|0\rangle = \frac{\hbar}{\sqrt{2}}\left[\frac{\sigma^z}{2}\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} + \begin{pmatrix}1\\0\end{pmatrix}\frac{\sigma^z}{2}\begin{pmatrix}0\\1\end{pmatrix} - \frac{\sigma^z}{2}\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix}\frac{\sigma^z}{2}\begin{pmatrix}1\\0\end{pmatrix}\right]$$

$$= \frac{\hbar}{\sqrt{2}}\left[+\tfrac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} + \left(-\tfrac{1}{2}\right)\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} - \left(-\tfrac{1}{2}\right)\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} - \left(+\tfrac{1}{2}\right)\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}\right]$$

$$= 0$$

It is less obvious how S^x and S^y act on this state. For S^x,

$$S^x |0\rangle = \frac{\hbar}{\sqrt{2}} \left[\frac{\sigma^x}{2} \begin{pmatrix}1\\0\end{pmatrix} \begin{pmatrix}0\\1\end{pmatrix} + \begin{pmatrix}1\\0\end{pmatrix} \frac{\sigma^x}{2} \begin{pmatrix}0\\1\end{pmatrix} - \frac{\sigma^x}{2} \begin{pmatrix}0\\1\end{pmatrix} \begin{pmatrix}1\\0\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix} \frac{\sigma^x}{2} \begin{pmatrix}1\\0\end{pmatrix} \right]$$

$$= \frac{\hbar}{2\sqrt{2}} \left[\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} + \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} - \begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} - \begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} \right] = 0$$

and similarly you can show that $S^y |0\rangle = 0$. The state $|0\rangle$ is thus a scalar, a spin 0 representation.

The remaining three states orthogonal to $|0\rangle$,

$$|11\rangle = |\uparrow\uparrow\rangle \qquad |10\rangle = \frac{1}{\sqrt{2}} \left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right] \qquad |1\,{-1}\rangle = |\downarrow\downarrow\rangle$$

are eigenvectors of S^z with, respectively, $S^z = +\hbar, 0, -\hbar$. They form a spin 1 representation of angular momentum. Those of you who followed the lecture on the general theory of angular momentum can verify this in complete detail by showing explicitly that

$$S^- |11\rangle = \sqrt{2}\, |10\rangle \qquad S^- |10\rangle = \sqrt{2}\, |1\,{-1}\rangle$$

as predicted by our general theory.

Notice that $|0\rangle$ is *antisymmetric* with respect to interchange of the two spins, while the states $|1m\rangle$ are symmetric with respect to interchange of the spins. This is not an accident. It can be shown that the states in the product representation that are antisymmetric under interchange transform only among themselves under rotations, and that this is also true for the states that are symmetric under interchange.

All in all, we have shown that the product of two spin $\frac{1}{2}$ representations can be decomposed into the sum of a spin 0 representation and a spin 1 representation,

$$\frac{1}{2} \otimes \frac{1}{2} = 0 \oplus 1$$

With this understanding, we can make sense of some of the unclear statements that I made in my discussion of the energy levels of real atoms. Let's return, for example, to the discussion of the ground states of the C atom. These states have 2 electrons in the 2P levels. By the Pauli exclusion principle, the total electron wavefunction must be antisymmetric. Each electron can be in one of $2 \times 3 = 6$ possible states. The number of totally antisymmetric states of 2 electrons is then

$$\frac{6 \cdot 5}{2!} = 15 \quad \text{states}$$

These states can have one of two forms, first, symmetric in the orbital state and antisymmetric in spin,

$$\frac{3 \cdot 4}{2!} \times 1 = 6 \text{ states}$$

second, antisymmetric in the orbital state and symmetric in spin,

$$\frac{3 \cdot 2}{2!} \times 3 = 9 \text{ states}$$

The number of states in the two classes adds correctly to 15.

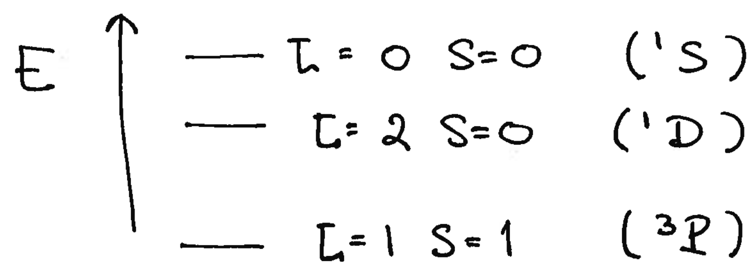
The total spin angular momentum in the two cases is 0 and 1, respectively. To work out the total orbital angular momentum of these states, we need to decompose the product of two $\ell = 1$ representations into representations of definite total $\vec{L} = \vec{L}_1 + \vec{L}_2$. It can be shown that

$$1 \otimes 1 = 0 \oplus 1 \oplus 2$$

The spin 1 is the antisymmetric part (3 states); the spin 0 and spin 2 terms form the symmetric part (6 states).

It turns out that the states that are antisymmetric in their orbital configuration have lower energy. In these states, the electrons are, on the average, further apart, so they experience less Coulomb repulsion. Between the spin 0 and spin 2 states, the spin 2 states have lower energy.

The energy spectrum of the 15 ground states of C is then



This is exactly the structure of the energy spectrum shown for C in the lecture on real atoms.

To work with quantum mechanics in a serious way, it is essential to be able to decompose products of spin representations into irreducible parts. I have discussed some methods for solving this problem in the lecture on the general theory of angular momentum. You will learn more about this in Physics 131.