

## Spin representations and Pauli antisymmetry

Two electrons (for example, the outer two electrons in the carbon atom with configuration  $2p^2$ ) have well known symmetry properties that match well the antisymmetrization under exchange required by the Pauli principle. The vector model for adding  $s=1/2$  to  $s=1/2$  gives  $S=1$  or  $0$ , and the corresponding basis functions for these irreducible representations of the rotation group  $O(3)$  are

$$\begin{aligned} |11\rangle &= |\uparrow\uparrow\rangle \\ |10\rangle &= \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1-1\rangle &= |\downarrow\downarrow\rangle \end{aligned}$$

for the  $S=1$  spin triplet states, and

$$|00\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

for the  $S=0$  spin singlet. The triplet spin functions are eigenstates of particle exchange, with eigenvalue 1, whereas the spin singlet has eigenvalue -1. To make a total wave function which is antisymmetric under exchange (eigenvalue -1), the spatial part of the wave function  $\Psi(\vec{r}_1, \vec{r}_2)$  has to be antisymmetric under exchange for the triplet state, or symmetric under exchange for the singlet state. For example, suppose the electrons are placed in spatial orbitals  $|m\rangle$  and  $|m'\rangle$ . The triplet  $M_S=1$  state is

$$\frac{1}{\sqrt{2}} (\psi_m(\vec{r}_1)\psi_{m'}(\vec{r}_2) - \psi_{m'}(\vec{r}_1)\psi_m(\vec{r}_2)) |\uparrow\uparrow\rangle = A\{m \uparrow, m' \uparrow\},$$

that is, it is a single Slater determinant. However, the triplet and singlet  $M_S=0$  states are combinations of two Slater determinants,

$$[A\{m \uparrow, m' \downarrow\} \pm A\{m \downarrow, m' \uparrow\}] / \sqrt{2}.$$

Now consider three electrons, for example, in a free nitrogen atom, with  $2p^3$  configuration. The vector rule should be applied twice, first coupling two spins to give triplet  $S=1$  or singlet  $S=0$ , and then coupling a third  $s=1/2$ . This gives  $S=3/2$  and  $S=1/2$  from the triplet, and another  $S=1/2$  from the singlet. There are a total of  $2^3=8$  states. It is easy to find the quartet  $S=3/2$  states,

$$\begin{aligned} \left| \frac{3}{2}, \frac{3}{2} \right\rangle &= |\uparrow\uparrow\uparrow\rangle \\ \left| \frac{3}{2}, \frac{1}{2} \right\rangle &= [|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle] / \sqrt{3} \\ \left| \frac{3}{2}, -\frac{1}{2} \right\rangle &= [|\uparrow\downarrow\downarrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\downarrow\downarrow\uparrow\rangle] / \sqrt{3} \\ \left| \frac{3}{2}, -\frac{3}{2} \right\rangle &= |\downarrow\downarrow\downarrow\rangle \end{aligned}$$

which are symmetric under exchange. Therefore the  $^4S$  ground state of the N atom is thus

$$\Psi_{\frac{3}{2}, M_S} = \det \begin{pmatrix} \psi_1(\vec{r}_1) & \psi_0(\vec{r}_1) & \psi_{-1}(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_0(\vec{r}_2) & \psi_{-1}(\vec{r}_2) \\ \psi_1(\vec{r}_3) & \psi_0(\vec{r}_3) & \psi_{-1}(\vec{r}_3) \end{pmatrix} \left| \frac{3}{2}, M_S \right\rangle,$$

where the subscripts on the  $\psi$ 's are the  $m_l$  quantum numbers. The spatial part is antisymmetrized. The  $M_S = \pm 3/2$  partners are again single Slater determinants, whereas the  $M_S = \pm 1/2$  partners are sums of Slater determinants.

The spin basis functions for the two doublet  $S=1/2$  representations are built from states of the type  $|s_1, s_2, s_3\rangle$ , and are orthogonal to the four quartet functions shown above. They can be chosen to be, for  $M_S = +1/2$ ,

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle_A = [\omega^1 |\downarrow\uparrow\uparrow\rangle + \omega^2 |\uparrow\downarrow\uparrow\rangle + \omega^3 |\uparrow\uparrow\downarrow\rangle] / \sqrt{3}$$

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle_B = [\omega^{-1} |\downarrow\uparrow\uparrow\rangle + \omega^{-2} |\uparrow\downarrow\uparrow\rangle + \omega^{-3} |\uparrow\uparrow\downarrow\rangle] / \sqrt{3}$$

For  $M_S = -1/2$ , just reverse each spin. Here  $\omega = \exp(2\pi i/3)$  is a cube root of 1. Note that under interchange of electron number 1 with electron number 2, the states  $|1/2, 1/2\rangle_{A,B}$  transform into each other, since  $\omega^1 = \omega^{-2}$ , etc. Interchange of 2 and 3 takes  $|1/2, 1/2\rangle_A$  into  $\omega^2$  times  $|1/2, 1/2\rangle_B$ . Cyclic permutations take these states into powers of  $\omega$  times themselves. The net result is this. It is **not possible** to diagonalize the exchange operators using the basis functions of the irreducible spin representations  $S=1/2$ . The A and B type doublet spin basis functions are basis functions for a doubly degenerate  $E$  representation of the group  $P_3$  of permutations of three objects. Correct Pauli antisymmetrization of the complete wave function gets messy. Perhaps it is best not to ask for states which are products of pure spin representations times pure orbital representations.