HUND'S RULES

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.13.

We've seen how to find the possible ground states for some of the atoms at the start of the periodic table. However, each atom has only one ground state, so we need a way of finding it amongst all the possibilities.

We can eliminate some states immediately because they violate the Pauli exclusion principle. Look first at carbon, where we found 10 possible states. These states are formed by combining two electrons in the $2p$ shell, so we have two spins of 1/2 and two orbital angular momenta of 1 to combine. In order to form the ${}^1P_1$ state, we need total spin $S = 0$ and total orbital angular momentum $L = 1$. The $S = 0$ state is the singlet state, which is antisymmetric.

To get the $L = 1$ compound state from two $l = 1$ individual states, we can use the Clebsch-Gordan coefficients for combining spin. There are 3 states with $L = 1$ (with $M = -1, 0, 1$) and we can use the table of coefficients to construct them. As an example:

$$|10\rangle = \frac{1}{\sqrt{2}}\left(|1\ 1\rangle_1 |1\ -1\rangle_2 - |1\ -1\rangle_1 |1\ 1\rangle_2\right) \tag{1}$$

where the subscripts on the RHS indicate which electron the state describes. This function is antisymmetric (if we swap electrons 1 and 2, the function turns into its negative). The same is true for the states $|11\rangle$ and $|1-1\rangle$, so the $L = 1$ state is always antisymmetric. If we multiply two antisymmetric states, the result is a symmetric state, which is not allowed for fermions. Therefore, the ${}^1P_1$ state cannot occur in carbon.

By a similar process, we can eliminate ${}^3S_1$, since it is the product of the triplet spin state (symmetric) and the $|0\,0\rangle$ orbital state (also symmetric). We can also eliminate all three of the ${}^3D$ states, since they are products of the triplet spin and $L = 2$ states, which are all symmetric.

Thus for carbon, we are left with 5 candidates out of the original 10: ${}^1S_0$, ${}^1D_2$, ${}^3P_0$, ${}^3P_1$ and ${}^3P_2$. We can't use the exclusion principle any more since all of these states are anti-symmetric. At this point, we can resort to Hund's rules, which were worked out in 1927 by Friedrich Hund (a remarkable physicist if only because he lived to be 101). There are 3 rules, which

assume that we've already eliminated those states that violate the exclusion principle:

(1) Choose the states with highest spin S.
(2) Of those states, choose those with the highest orbital angular momentum L.
(3) If the subshell is no more than half full, choose $J = |L - S|$. Otherwise, choose $J = L + S$.

Applying the first rule to carbon selects the three states ${}^3P_0$, ${}^3P_1$ and ${}^3P_2$. The second rule doesn't get us any further, since all three states have the same $L = 1$. Since there are 2 electrons in a p shell (which can hold up to 6 electrons), the third rule tells us to choose $J = 1 - 1 = 0$ so the ground state of carbon is ${}^3P_0$.

A couple of other simple examples of Hund's rules:

In helium, the first rule says that an excited state (where one electron is in the ground state and the other is in an excited state) will have both spins parallel. Since the spin state is symmetric, this is orthohelium, so we'd expect orthohelium energies to be lower than the corresponding parahelium states, which is what is observed.

In boron, there are two possible states: ${}^2P_{1/2}$ and ${}^2P_{3/2}$. They both have the same values of S and L so we apply the third rule. As there is only one electron in the p shell, the preferred J is $J = |L - S| = \frac{1}{2}$ and the ground state is ${}^2P_{1/2}$.

The case of nitrogen is somewhat more complex since it involves three electrons, so we need a way of adding three angular momenta. We'll defer that to the next post.

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