Let's start with Helium. If we ignore the interaction term, the solution becomes separable:

$$\psi(r_1, r_2) = \psi_{nlm}(r_1)\psi_{n'l'm'}(r_2)$$

The functions $\psi_{nlm}(r_1)$ are the same as for the hydrogen atom, except that the nucleus has twice the charge and the states have four times the energy:

$$E = 4(E_n + E_{n'})$$

where $E_n = -13.6/n^2$ eV. This is off from the real energy by about 30%. The ground state is then

$$\psi_0(r_1, r_2) = \psi_{100}(r_1)\psi_{100}(r_2) = \frac{8}{\pi a^3}e^{-2(r_1 + r_2)/a}.$$

Note that the scale a (the Bohr radius) also changes accordingly. We can only construct a symmetric wavefunction:

$$\psi_0(r_1, r_2) = \frac{1}{\sqrt{2}}\left(\psi_0(r_1, r_2) + \psi_0(r_2, r_1)\right)$$

Because the wavefunction has to by anitsymmetric and the spacial part is symmetric, the spinor part has to be antisymmetric. Thus, the ground state has to be the singlet state.

$$\frac{1}{\sqrt{2}}(\downarrow\uparrow - \uparrow\downarrow) \qquad s = 0, m = 0$$

Let's look at the excited states. We keep one electron in the ground state.

$$\psi_{100}\psi_{nlm}$$

We can now construct symmetric and antisymmetric solutions.

The symmetric solutions have antisymmetric spinors (singlet) and are called parahelium. The antisymmetric ones have a symmetric spinor (triplet) and are called orthohelium.

The ground state has to be parahelium.

Symmetric spatial states bring the electrons closer together. Thus, they have a higher interaction energy. This is indeed what's observed. Parahelium has higher energies compared to orthohelium.

15 The Periodic Table

Let's piece together the groundstates of atoms using the wavefunctions ψ_{nlm}. This will of course be an approximation as we'll ignore the electron electron interaction. But let's see how far we get.

The periodic table is organized such that each row corresponds to a shell. When a shell is full, the next row starts. Because electrons have spin-$\frac{1}{2}$, we have two electrons in the $n = 0$ shell (hydrogen and helium). The next row has $l = 0, 1$ and $m = -1, 0, 1$ (four states). Thus, a total of 8 slots are available for electrons. If we continue like this, the periodic table's row should have the followung lengths

$$2, 8, 18, 32, 50, \ldots$$

However, in reality these are

$$2, 8, 8, 18, 18, \ldots$$

That's because we ignored electron-electron interactions.

Let's look at lithum ($Z = 3$). The $n = 1$ shell is filled and there is one electron in the $N = 2$ shell. We have $l = 0, 1$ orbitals available. Which one will it choose? Without electron-electron interactions, these orbitals would have the same energy. But that changes with electron-electron interactions.

For high l orbits, the electron will spend more time further away from the proton. Think of planets. Because it sees the other electrons from further away, the inner electrons are better at screening the nucleus, reducing the effective charge. Thus, the electron will prefer to be in a low l orbital as this state has a lower energy (more bound).

The screening effect can be so strong that an electon prefers the higher n value if it can have a lower l value. Potassium ($Z = 19$) is the first atom to make use of that. It chooses $n = 4, l = 0$ over $n = 3, l = 2$. The following illustration shows the different energy levels and let's you see which orbitals are filled.
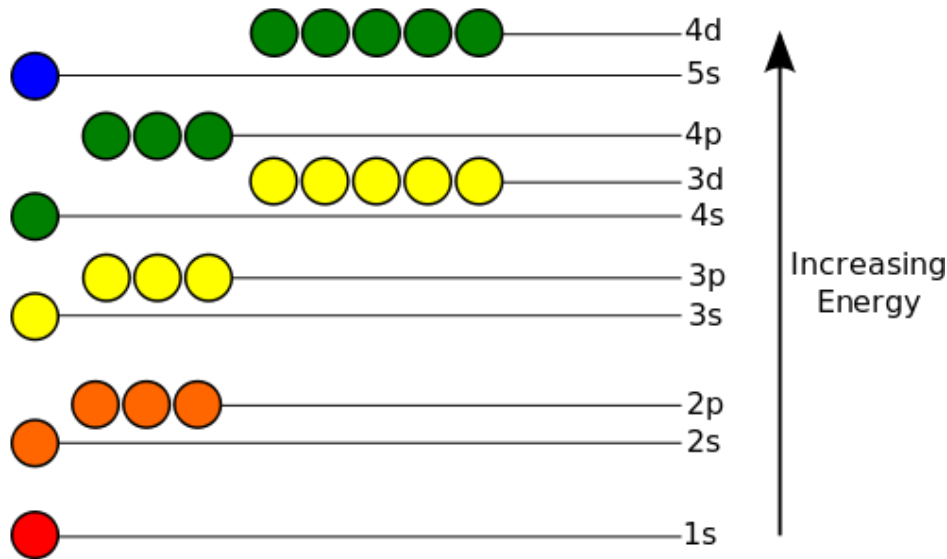
Let's look at carbon as an example. Carbon has two electrons locked into the first shell $(1s)^2$. It has another two locked up in the $(2s)^2$ orbital. The spins of those four electrons are locked so that they do not contribute to the total spin. Also, their orbital angular momentum is 0, so they will not contribute to the total angular momentum either.

The remaining two electrons are in the $l = 1$ orbital $(2p)^2$. Thus the total angular momentum L could be $0, 1$ or 2. The spins of the p-electrons could be in either the singlet or triplet configuration. Their spin could add up or not, thus giving a total spin of either 0 or 1.

The grand total (spin plus orbital angular momentum) could thus be $3, 2, 1$ or 0. It turns out there are rules to determine the right configuration, known at Hund's Rules. We will not discuss them any further but you should know how they are written:

$$^{2S+1}L_J$$

Hund's Rules

1. The state with the highest total spin S has the lowest energy.

2. For a given spin, the state with the highest total orbital angular momentum has the lowest energy.

3. If a subshell (n, l) is no more than half filled, then the lowest energy level has $J = |L - S|$. If it is more than half filled, then $J = L + S$ has the lowest energy.

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