Lecture 19 Highlights

Now, back to the He atom. The ground state of He must put both of the electrons in to the lowest energy single-particle state ψ_{100} (promoting one of the two electrons to the next available state is too energetically costly). This will put the two electrons into a symmetric space wavefunction. To make the overall wavefunction anti-symmetric under exchange of all the coordinates of the two identical fermions, we must have an anti-symmetric spin wavefunction. The spin singlet wavefunction will do the trick;

$$\Psi_{He}^{GS}(1,2) = \psi_{100}(1)\psi_{100}(2)\left|0\ 0\right\rangle$$

The unperturbed eigenstate has a ground state energy of $E_T = -108.8\,\text{eV}$.

Now if we include the Coulomb repulsion perturbing Hamiltonian, the first-order correction to the energy is given by;

$$E_{GS}^{1} = \left\langle \Psi_{He}^{GS}\middle|\text{H}'\middle|\Psi_{He}^{GS}\right\rangle$$

$$= \iiint d^3x_1 \iiint d^3x_2 \psi_{100}^{*}(1)\psi_{100}^{*}(2)\left\langle 0\ 0\right| \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1 - \vec{r}_2\right|}\psi_{100}(1)\psi_{100}(2)\left|0\ 0\right\rangle$$

This integral can be done analytically (see Griffiths, page 300), and yields $E_{GS}^{1} = +34\,\text{eV}$. The first-order corrected ground state energy of He is predicted to be $E_{GS} = E_T + E_{GS}^{1} = -74.8\,\text{eV}$. The measured ground state energy of He is 78.98 eV, within 5% of our estimate.

What is the first excited state of He? Clearly one of the electrons must be promoted from the n=1 state to the n=2 state. But now there are two choices, $\ell = 0$ (code-letter s) or $\ell = 1$(code-letter p). The short-hand for these two states is 1s2s and 1s2p. The 1s2s configuration has a lower energy than the 1s2p for the following reason. The first electron (1s) resides in a Hydrogenic state with strong binding energy and small average radius. The second electron goes into an n=2 state with less binding energy and a larger average radius. The n=2 electron will experience a partially screened nucleus, since the 1s electron "wraps around" the nucleus and reduces its effective charge from +2e to something closer to +e. This weakens the attraction that the n=2 electron experiences with the nucleus, and is called 'screening'. Now the orbital angular momentum comes in to play. An electron in an $\ell = 0$ state will spend more time traveling through the nucleus and penetrating the inner 1s screening cloud (at least classically), compared to a 2p electron that will be in more of a traditional high angular momentum classical "orbit" about the nucleus. This allows the 1s electron to enjoy a stronger attraction to the nucleus, without paying too high a price in terms of Coulomb repulsion from the 1s electron. This same general idea explains many un-expected features of the periodic table.

There are now many ways to write down the excited state wavefunctions (super-scripts "A" and "S" stand for Antisymmetric and Symmetric, respectively):

$$\Psi_{1s2s}^{SA}(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)\right\}\left|0\ 0\right\rangle$$

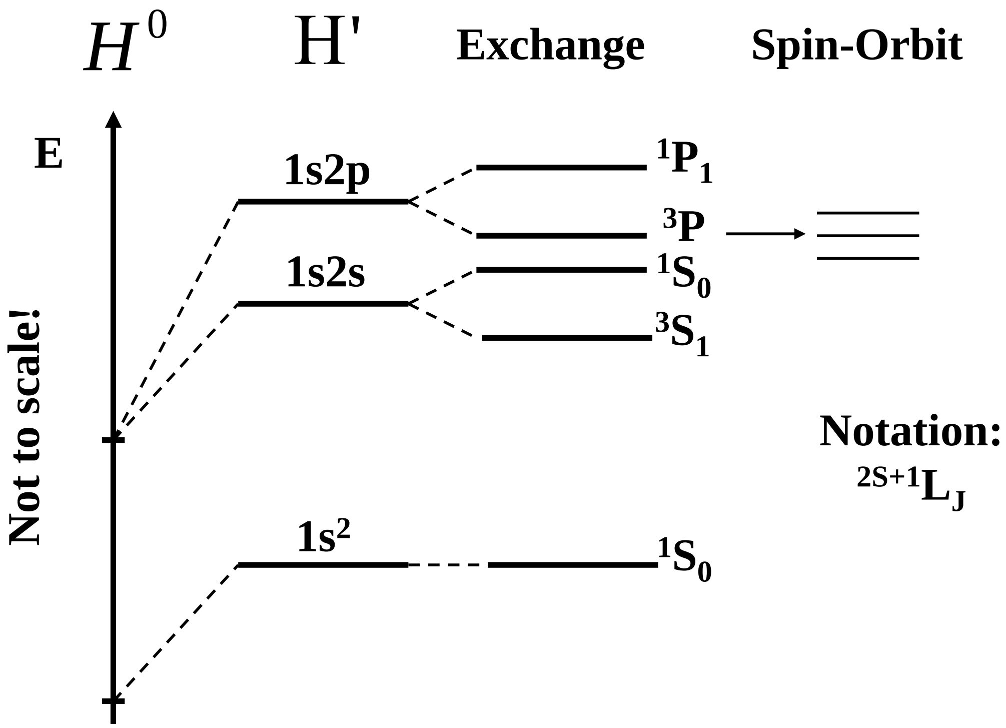
or $$\Psi_{1s2s}^{AS}(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)\right\}\left|1\ m\right\rangle$$, with $m = +1, \quad 0, \quad -1$

and $$\Psi^{SA}_{1s2p}(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_{1s}(1)\psi_{2p}(2) + \psi_{1s}(2)\psi_{2p}(1)\right\}\left|0\;0\right\rangle$$

or $$\Psi^{AS}_{1s2p}(1,2) = \frac{1}{\sqrt{2}}\left\{\psi_{1s}(1)\psi_{2p}(2) - \psi_{1s}(2)\psi_{2p}(1)\right\}\left|1\;m\right\rangle, \text{ with } m = +1, \quad 0, \quad -1$$

The anti-symmetric space wavefunctions will have lower energy than their symmetric counterparts because of the “exchange splitting” discussed in the last lecture.

He Atom Low-Lying States



These energy level orderings agree with the experimental data on He, as posted on the NIST Atomic Spectra Database web site.