3.27 The helium atom with ground and first excited states with Pauli exclusion

In section 3.21, we found the ground state energy of the helium atom, treating the mutual electron repulsion in first order perturbation theory. However, we did not take into consideration the effects of the electron spin and the Pauli exclusion principle. All we did was to mention that the two electrons had opposite spin projections and could be labeled accordingly.

Taking the spin of the electrons into consideration explicitly and observing the Pauli exclusion principle, including the proper anti-symmetry of the wave function for identical fermions, gives for the ground state

\[ \Phi_{nn', (\vec{r}_1, \vec{r}_2)} = \Phi_{11, (\vec{r}_1, \vec{r}_2)} = \phi_{10}(\vec{r}_1) \phi_{10}(\vec{r}_2) X_{\text{singlet}} \]

where

\[ X_{\text{singlet}} = \frac{1}{\sqrt{2}} (\chi^+_1 \chi^-_2 - \chi^-_1 \chi^+_2) \]

and (recall from our discussion of addition of two \( \frac{1}{2} \) angular momenta)

\[ \chi_+ = (0^1) , \chi_- = (0^1). \]

The spatial wave functions here are the single particle (one electron) ground state wave functions obtained for the hydrogen atom and the product of the two is, of course, symmetric under the exchange of the (1) and (2) particle labels (since they are identical). It is for this reason that we must use the anti-symmetric total spin 0 (singlet) spin state, so that the whole wave function is anti-symmetric, as required by the Pauli principle.

The first excited state of the helium atom corresponds to one of the electron sitting in the next higher energy eigenstate with \( n = 2 \). In that case, the two single electron spatial wave functions no longer have the same form and switching the labels would change the combined wave function if it were a simple product of the two single electron functions.
We therefore have two possible combinations for the spatial wave function:

\[ \Phi_{12}^t (\vec{n}_1, \vec{n}_2) = \frac{1}{\sqrt{2}} \left( \Phi_{100}(\vec{n}_1) \Phi_{2lm}(\vec{n}_2) + \Phi_{2lm}(\vec{n}_1) \Phi_{100}(\vec{n}_2) \right) \chi_{\text{Sing}}. \]

or,

\[ \Phi_{12}^{(u)} (\vec{n}_1, \vec{n}_2) = \frac{1}{\sqrt{2}} \left( \Phi_{100}(\vec{n}_1) \Phi_{2lm}(\vec{n}_2) - \Phi_{2lm}(\vec{n}_1) \Phi_{100}(\vec{n}_2) \right) \chi_{\text{trip}}. \]

where

\[ \chi_{\text{trip}} = \begin{cases} 
\chi_+^{(1)} \chi_+^{(2)} \\
\frac{1}{\sqrt{2}} \left( \chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)} \right) \\
\chi_-^{(1)} \chi_-^{(2)}
\end{cases} \]

which is orthogonal to the spin singlet.
The first excited state of helium with the exclusion principle and electron repulsion

We now briefly consider the first excited state of the helium atom together with mutual electron repulsion. We only need to do this for $m = 0$, since the perturbation $V$ commutes with $J_z$ and therefore the corresponding shift in energy must be independent of the projection.

The interaction term (the perturbation) is given by

$$
\Delta E = \langle \Phi_i | H' | \Phi_i \rangle \\
= \frac{1}{2} \alpha_{t1} c \int d^3r_1 \int d^3r_2 \left[ \phi_{100}^*(\vec{r}_1) \phi_{2lm}^*(\vec{r}_2) \pm \phi_{2lm}^*(\vec{r}_1) \phi_{100}^*(\vec{r}_2) \right] \\
\times \frac{1}{|\vec{r}_1 - \vec{r}_2|} \left( \phi_{100}^*(\vec{r}_1) \phi_{2lm}(\vec{r}_2) \pm \phi_{2lm}^*(\vec{r}_1) \phi_{100}(\vec{r}_2) \right) \\
= \frac{1}{2} \alpha_{t1} c \int d^3r_1 \int d^3r_2 \left[ \phi_{100}^*(\vec{r}_1) \phi_{2lm}^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{100}(\vec{r}_1) \phi_{2lm}(\vec{r}_2) \\
\pm \phi_{100}^*(\vec{r}_1) \phi_{2lm}^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{2lm}(\vec{r}_1) \phi_{100}^*(\vec{r}_2) \\
\pm \phi_{2lm}^*(\vec{r}_1) \phi_{100}^*(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{100}(\vec{r}_1) \phi_{2lm}(\vec{r}_2) \\
\pm \phi_{2lm}(\vec{r}_1) \phi_{100}(\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{2lm}^*(\vec{r}_1) \phi_{100}^*(\vec{r}_2) \right]
$$

Now, switch (1) ↔ (2) in the last two terms, which we can do, due to the symmetry of $V(\varphi)$.
The second term in the integral is called the exchange term and comes from the Pauli principle for fermions. It's sign is positive for total spin 0 (the singlet state) and negative for total spin 1 (the triplet state). This changes the energy shift and the singlet and triplet states are no longer degenerate. We won't evaluate the integrals here. They can be done analytically, in a way similar to what we did for the ground state energy of the helium atom earlier, but the math associated with it provides no further insight at this point. So, let's rewrite this result as

$$\Delta E = \alpha \hbar c \int d^3 r_1 \int d^3 r_2 \left[ \phi^*_{100} (\vec{r}_1) \phi^*_{2l_m} (\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{100} (\vec{r}_1) \phi_{2l_m} (\vec{r}_2) \right]$$

$$\quad + \phi^*_{100} (\vec{r}_1) \phi^*_{2l_m} (\vec{r}_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{2l_m} (\vec{r}_1) \phi_{100} (\vec{r}_2)$$

To find out which energy is lower/higher (singlet or triplet), we can use the operator corresponding to the inner product between the electron spin operators to rewrite the energy shift, as follows

$$\Delta E_{2e}^{(s)} = \alpha \hbar c \left( I_{2e} + K_{2e} \right)$$

or

$$\Delta E_{2e}^{(t)} = \alpha \hbar c \left( I_{2e} - K_{2e} \right)$$

To find out which energy is lower/higher (singlet or triplet), we can use the operator corresponding to the inner product between the electron spin operators to rewrite the energy shift, as follows

Total spin $$\hat{S} = \hat{S}_1 + \hat{S}_2$$

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2 \hat{S}_1 \cdot \hat{S}_2$$
So,
\[ 2 \hat{S}_1 \cdot \hat{S}_2 = \hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2 \]

Using the singlet or triplet states \( m_s = 0 \), we get
\[ 2 \hat{S}_1 \cdot \hat{S}_2 \times \hat{s}_f = (\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \frac{1}{\sqrt{2}} (x^a x^{a_2} + x^b x^{b_2}) \]
\[ = (\hat{t}^a s(s+1) - \frac{3}{4} t_a^2 - \frac{3}{4} t_a^2) \times \hat{s}_f \]

So,
\[ \frac{2}{\hbar^2} \hat{S}_1 \cdot \hat{S}_2 = S(s+1) - \frac{3}{2} = \begin{cases} \frac{1}{2} & S=1 \text{ triplet} \\ -\frac{3}{2} & S=0 \text{ singlet} \end{cases} \]

Or, using \( \hat{S} = \frac{\hbar}{2} \hat{s} \), we have that
\[ -\frac{1}{2} (1 + \hat{S}_1 \cdot \hat{S}_2) = \begin{cases} -1 & S=1 \text{ triplet} \\ +1 & S=0 \text{ singlet} \end{cases} \]

So we can write the energy shift as
\[ \Delta E_{2e} = I_{2e} - \frac{1}{2} (1 + \hat{S}_1 \cdot \hat{S}_2) \kappa_{2e} \]

Both integrals turn out to be positive and we therefore have
\[ I_{ne} - \kappa_{ne} < I_{ne} + \kappa_{ne} \]
The corresponding spectrum for helium therefore looks like:

\[ (1s^2) \quad (1s)(2s) \quad (1s)(2p) \]

\[ \begin{array}{c}
1s \quad \text{singlet} \\
1s, 3p, 3s \quad \text{triplet} \\
3p_{1,3,5} \quad \text{triplet} \\
1s_0 \quad \text{singlet}
\end{array} \]

If you recall our discussion of the nuclear potential between the neutron and the proton, when we did addition of angular momentum, you can see that that potential

\[ V = V_0(r) + \vec{\sigma}_1 \cdot \vec{\sigma}_2 V_1(r) \]

has this exchange term as well, which is also a result of the Pauli principle for the two fermions involved \((n, p)\).

The consequences of the Pauli principle are far reaching and extend into almost every subarea of physics.