

Two Electron Atoms/Ions

In this section we will shift focus from the single-electron atoms we have been studying and move onto two electron atoms. Helium is the atom with two electrons.

Two Electron Hamiltonian

The Schrödinger Hamiltonian for helium is given by:

this term
is the interaction
between
electrons

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}$$

where the subscripts on ∇ indicate the electron the derivatives are with respect to.

Note, just as with hydrogen, there will be a fine structure with all the corrections we described but they will be more complicated here.

The Wavefunction

First let's solve the problem neglecting the interaction between electrons. So:

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i} \right]$$

This is just the sum of 2 hamiltonians but with $2 \times$ the proton charge

To make this extend to other multi-electron systems, we will use Z for atomic number.

$$\hat{H}_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right]$$

for an ion (single electron):
$$\hat{H}_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Now we will scale using $r' = Zr$ so $r = \frac{r'}{Z}$ and $\nabla^2 = Z^2 \nabla'^2$

so
$$\hat{H}_0 = Z^2 \left[-\frac{\hbar^2}{2m} \nabla'^2 - \frac{e^2}{4\pi\epsilon_0 r'} \right]$$

This is just the hydrogen atom hamiltonian multiplied by Z^2 . So the new eigenfunctions will be scaled hydrogen eigenfunctions, using spatial coordinates $\underline{r}' = Z\underline{r}$

we will have to renormalise them by dividing by a divisor Z in each of the three dimensions. So our new eigenfunctions are:

$$\Psi_{n,l,m}(\underline{r}) = Z^{3/2} \Psi_{n,l,m}^H(\underline{r}')$$

Can we obtain the overall wavefunction of the atom from this? We saw in the Multiple Electron Systems chapter that we can use expansion theorem to write this as the sum of products of single-electron orbitals:

$$\Psi(\underline{r}_1, \underline{r}_2) = \sum_{(n_1, l_1, m_1)(n_2, l_2, m_2)} a_{n_1, l_1, m_1, n_2, l_2, m_2} \Psi_{n_1, l_1, m_1}(\underline{r}_1) \Psi_{n_2, l_2, m_2}(\underline{r}_2)$$

But electrons are indistinguishable and they are fermions.

If the particle exchange operator is used, the whole wavefunction including the spin part has to be antisymmetric.

This means the spatial part has to be symmetric or antisymmetric.

$$\text{so: } \Psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left(\Psi_{n_1, l_1, m_1}(\underline{r}_1) \Psi_{n_2, l_2, m_2}(\underline{r}_2) + \Psi_{n_2, l_2, m_2}(\underline{r}_1) \Psi_{n_1, l_1, m_1}(\underline{r}_2) \right)$$

$$\text{or } \Psi(\underline{r}_1, \underline{r}_2) = \frac{1}{\sqrt{2}} \left(\Psi_{n_1, l_1, m_1}(\underline{r}_1) \Psi_{n_2, l_2, m_2}(\underline{r}_2) - \Psi_{n_2, l_2, m_2}(\underline{r}_1) \Psi_{n_1, l_1, m_1}(\underline{r}_2) \right)$$

If we want both electrons to be in the same orbital, only the first is possible, since the second gives us 0 if $n_1, l_1, m_1 = n_2, l_2, m_2$

As the interaction term is symmetric under particle exchange, the wavefunctions above are the correct one for doing degenerate perturbation theory.

The first order perturbation to the energy is:

$$\Delta E^{(1)} = E_{\text{direct}} \pm E_{\text{exchange}} \quad (\pm \text{ depends on which of the two wavefunctions is used})$$

where

$$E_{\text{direct}} = \int \Psi_{n_1 l_1 m_1}^*(\mathbf{r}_1) \Psi_{n_2 l_2 m_2}^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \Psi_{n_1 l_1 m_1}(\mathbf{r}_1) \Psi_{n_2 l_2 m_2}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{\text{exchange}} = \int \Psi_{n_1 l_1 m_1}^*(\mathbf{r}_1) \Psi_{n_2 l_2 m_2}^*(\mathbf{r}_2) \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \Psi_{n_1 l_1 m_1}(\mathbf{r}_2) \Psi_{n_2 l_2 m_2}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

Notice in the E_{exchange} , \mathbf{r}_1 and \mathbf{r}_2 are swapped in the right hand product wavefunctions.

The first term E_{direct} is simply what we would get if we worked out energy classically. The E_{exchange} term has no classical counterpart but is extremely important since it splits degeneracy between the symmetric and antisymmetric wave fns.

Exchange Term and Total Spin

The helium atom has two electrons with spin-half.

But we stated that we need particle exchange symmetry. So we can say the spins are not independent of each other and are instead given by the the antisymmetric $S=0$ state and the three symmetric $S=1$ states.

The $S=0$ state is always coupled to a particle exchange symmetric state and the $S=1$ state is always coupled to a antisymmetric spatial state.

Comparison with Experiments

In experiments we see that the energy levels for Helium are remarkably similar to Hydrogen, for all except the ground state of Helium. This is surprising since we worked out that if we ignore electron-electron interaction, the hamiltonian had a multiplication factor of Z^2 , so we expect the single particle energies of Helium to be 4x bigger than Hydrogen.

In fact, if we take the electron-electron interaction and the size of the orbitals into account, the experimental results make sense. Consider an electron in a highly excited large orbital. This electron will most of the time be found considerably further away than an electron in the 1s orbital.

If we use Gauss' law we can prove that the sum of the nuclear potential and the electron-electron potential for points further from the nucleus than the 1s orbital is the same as that for a point charge at the nucleus of a single proton atom. We say that the 1s electron "screens" one of the nuclear charges. Almost like the attractive force (from nucleus) and repulsive force (from 1s electron) cancel (although not exactly the same, just an easy way to think about it). So electrons in a high orbital have energies close to electrons in similar orbitals in Hydrogen.

Even in ground state of Helium, our no-electron interaction model predicts a much higher energy than if we include electron-electron interaction.

Optical Transitions

Let's try and understand the optical spectra of helium.

Let's first determine which transitions are optically allowed.

If we use the same dipole, long wavelength approximation as in previous chapters:

$$\hat{H}_p = \sum_{i=1,2} -e\mathbf{r}_i \cdot \mathbf{E}$$

where the sum is for each of the two electrons.

The matrix elements calculated with this operator involve terms of the form:

$$\int \Psi_{1212m1}^*(\mathbf{r}_1) \Psi_{1212m2}^*(\mathbf{r}_2) (-e\mathbf{r}_1) \Psi_{1313m3}(\mathbf{r}_1) \Psi_{1414m4}(\mathbf{r}_2) dV_1 dV_2$$

which we split into two integrals:

$$\underbrace{\int \Psi_{1212m1}^*(\mathbf{r}_1) (-e\mathbf{r}_1) \Psi_{1313m3}(\mathbf{r}_1) dV_1}_{\text{This will have the same selection rules as the hydrogen atom}} \underbrace{\int \Psi_{1212m2}^*(\mathbf{r}_2) \Psi_{1414m4}(\mathbf{r}_2) dV_2}_{\text{this is 0 unless the initial and final states are the same, i.e. } 1212m2 = 1414m4.}$$

This will have the same selection rules as the hydrogen atom

this is 0 unless the initial and final states are the same, i.e. $1212m2 = 1414m4$.
So only one electron can change at a time.

So we have the same selection rules as Hydrogen, and we require that only one electron can change at a time.

There is one more selection rule. Since the \hat{H}_p does not depend on spin, the spin states cannot change. So we cannot have $S=0$ and $S=1$ states linked by transitions.

This is why historically, we observe two types of helium series, one from $S=0$ and the other from $S=1$.