Lecture 19: Multi-electron atoms

Review: Basic Hydrogenic atom

Last semester we found the energy eigenstates and eigenvalues for hydrogenic atoms consisting of bound states between two oppositely charged point particles interacting through an attractive Coulomb potential. For the case of a charge +ze nucleus and one electron -e, relative motion Hamiltonian is (ignoring spin)

\[ \hat{H} = \frac{\hat{p}_r^2}{2m} - \frac{Ze^2}{r} = \frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 \hat{\alpha}^2}{2m r^2} - \frac{Ze^2}{r} \]

This is a central potential. We found the common eigenfunctions of \( \hat{H} \)

\[ |n, l, m_\ell\rangle \equiv R_{nl}(r) Y_{lm_\ell}^\ell(\Theta, \Phi) \]

with eigenvalues of \( \hat{H} \)

\[ E_n = -\frac{Z^2 \alpha^2}{n^2} \]

Recall: \( n = \) principal quantum number

Generally, for central potential, \( E \) depends on \( n_r \) (\# radial node) and \( l \).

For coulomb, \( n = n_r + l \) \Rightarrow Degeneracy \( n_r = 0, 1, \ldots n-1 \)

\[ \alpha = 0.5 \text{Å} = \text{Bohr radius} \]

\[ E = 13.6 \text{eV} \]

\[ R = \frac{e^2}{2\alpha} \]
Armed with the single electron orbitals and the Pauli exclusion principle, we can build up the periodic table. To build up the Pauli approximation, we neglect the interactions and treat each electron independently. We then fill in the orbitals one at a time:

**Multielectron atom: Shell Structure**

$$\ell = 0, \ldots, n-1$$

$$m_\ell = -\ell, -\ell+1, \ldots, 0, \ldots, \ell$$

$$m_s = \pm \frac{1}{2}$$

$$\ell = 0$$

1s

$$\ell = 1$$

2s, 2p

$$\ell = 2$$

3s, 3p, 3d

$$\ell = 3$$

4s, 3d, 4p, 4f

$$\ell = 4$$

5s, 4d, 5p, 4f, 5d, 5f

$$\ell = 5$$

6s, 5d, 6p, 5f, 6f, 6d, 6g

$$\ell = 6$$

7s, 6d, 7p, 6f, 7f, 6g, 7g, 7d

**Degeneracy:**

- Given \( \ell \)
- \( \ell = 0 \rightarrow m_\ell = 0 \)
- \( \ell = 1 \rightarrow m_\ell = -1, 0, 1 \)
- \( \ell = 2 \rightarrow m_\ell = -2, -1, 0, 1, 2 \)
- \( \ell = 3 \rightarrow m_\ell = -3, -2, -1, 0, 1, 2, 3 \)

**Total Quantum State:**

\( |n, \ell, m_\ell, m_s\rangle \)

**Electrons:**

A complete description of the state must include the spin of each electron. If we ignore the small magnetic effects, the energy spectrum is unchanged. The degeneracy of each state has now doubled.
Note: For multi-electron atoms, the different \( l \) states are no longer degenerate. This is because the total field seen by one electron is not purely \( \frac{1}{r} \), but a combination of \( \frac{1}{r} \) due to nucleus and the screening potential of other electrons.

Low angular momentum states \( \rightarrow \) small impact parameter with nucleus
\( \rightarrow \) stronger attraction
\( \rightarrow \) lower energy.

Thus, one should fill shells with lowest angular momentum first.
Example: Helium

The simplest multielectron atom is \( Z=2 \), Helium.

\[
\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \frac{(-e)(2e)}{r_1} + \frac{(-e)(2e)}{r_2} + \frac{(-e)(-e)}{1/r_2 - r_1}
\]

\[
= \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}
\]

\[
\hat{H}_i = \frac{\hat{p}_i^2}{2m} - \frac{2e^2}{r_i}
\]

Interaction of each electron with nucleus

Interaction of delta electrons with each other

If neglect \( \hat{H}_{12} \), the Hamiltonian is separable for one to electron. Each Hamiltonian \( \hat{H}_i \) is "hydrogenic" with orbitals \( |n, l, m_l, m_s \rangle \)

Neglecting \( \hat{H}_{12} \), the energy eigenvalues are the sum of two hydrogenic term with \( Z=2 \)

\[
E_{n_1, n_2}^{(0)} = -\frac{2^2 \beta R}{n_1^2} - \frac{2^2 \beta R}{n_2^2} = -4 \beta R (\frac{1}{n_1^2} + \frac{1}{n_2^2})
\]
In this crude approximation the ground state for "electron configuration" \((1s)^2\) \(n_1 = n_2 = 1\)

\[ E_{1,1}^{(0)} = -8 R = -108.8 \text{ eV} \]

This is about 30% larger in magnitude than measured ground state binding \(E_{\text{ground}} = -7.88 \text{ eV}\).

We have completely neglected the interaction of the electron with each other, this is a large effect!

Let us consider the expectation value of \(\hat{H}_{12}\) in the product state. First we must account for the fermion nature of the two electrons. Because the ground configuration has both electrons in the same \(1s\) spatial orbital, the spin state must be antisymmetric \(\Rightarrow \text{singlet}\)

\[ \left| \Phi_{\text{ground}} \right> = (1s \otimes 1s) \otimes |\chi_{\text{singlet}}\rangle \]

\[ = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \]  

\[ \langle \Phi_{\text{ground}} | \hat{H}_{12} | \Phi_{\text{ground}} \rangle = \]

\[ = \frac{e^2}{R_{12}} \left( \frac{R_{1s}^2 R_{2s}^2}{4\pi} \right)^2 \]

\[ \text{loss of algebra} = \frac{5}{2} R = 34 \text{ eV} \]
If we add this to the zeroth order contribution

\[ E_{1,1} = E_{1,1}^{(0)} + \langle 1s, 1s | H_{12} | 1s, 1s \rangle \]

\[ = -74.8 \text{ eV} \quad \text{not bad.} \]

We can in fact do better using more sophisticated approximation methods. An important one is the "variational approach" which we will not have time to cover in this course (see

What about excited states?

Consider the configuration \((1s)(nl)\) (one electron in ground orbital another in excited)

Two possibilities:

- Motional wave function even, spin odd (singlet)

\[ |\Phi_{\text{sing}}^{\text{sing}}\rangle = \left\{ \frac{1s\rangle 1n\rangle 2 + 1n\rangle 1s\rangle 2}{\sqrt{2}} \right\} |\chi_{\text{singlet}}\rangle \]

- Motional wave function odd, spin even (triplet)

\[ |\Phi_{\text{triplet}}\rangle = \left\{ \frac{1s\rangle 1n\rangle 2 - 1n\rangle 1s\rangle 2}{\sqrt{2}} \right\} |\chi_{\text{triplet}}\rangle \]
The interaction Hamiltonian has no explicit spin dependence. Nonetheless, the interaction strength depends on spin implicitly through the "exchange density" discussed in lecture 18.

If we consider the probability density for these two states

$$| \Phi_{\pm} (\vec{r}_1, \vec{r}_2) |^2 = \frac{1}{2} \left( | \phi_{15} (\vec{r}_1) |^2 | \phi_{ne} (\vec{r}_2) |^2 + | \phi_{ne} (\vec{r}_1) |^2 | \phi_{15} (\vec{r}_2) |^2 \right)$$

$$\pm \text{Re} \left\{ (\phi_{15} (\vec{r}_1) \phi_{ne}^* (\vec{r}_2)) \right\}$$

$$\pm \text{Re} \left\{ (\phi_{ne} (\vec{r}_1) \phi_{15}^* (\vec{r}_2)) \right\}$$

$$\text{positive } \#$$

$$\langle \frac{\hbar^2}{2m_e} \rangle_+ = \int d^3r_1 d^3r_2 \left| \Phi_{\pm} (\vec{r}_1, \vec{r}_2) \right|^2 \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$= \int d^3r_1 d^3r_2 \left| \phi_{15} (\vec{r}_1) \right|^2 \left| \phi_{ne} (\vec{r}_2) \right|^2 \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$\pm \int d^3r_1 d^3r_2 \pm \text{Re} \left\{ (\phi_{15} (\vec{r}_1) \phi_{ne}^* (\vec{r}_2)) \right\} \phi_{ne} (\vec{r}_1) \phi_{15}^* (\vec{r}_2) \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$= A \pm B$$

$$\text{direct term}$$

$$\text{exchange (quantum interference) term due to symmetrization}$$

Note: Both $A$ and $B$ are positive $\#$s with $A > B$. 
"Perturbed Spectrum" of He

\( 1^s \)

\( \downarrow A \)

\( \downarrow A + B \)

\( \downarrow A - B \)

Here we have introduced "term notation" for the energy levels of the multielectron state.

\[ \begin{align*}
\text{spin multiplicity} & \quad \Rightarrow 2s+1 \\
\text{total orbital angular momentum} & \quad \Rightarrow L
\end{align*} \]

\[ \text{Careful: "S" is used two different ways} \]

- Orbital state \( L=0 \) = "S-state"
- Spin quantum \# \( S = 0 \) = singlet
  \( \downarrow J \leq \text{triplet} \downarrow \)

More generally, we write term:

\[ 2s+1 \]

\[ L \quad J \leq \text{total spin + orbital ang. mom.} \]
L-S coupling.

At this point, we have represented the two electron state in terms of total orbital and total spin angular momentum, the common eigenstates of \( L^2, L_z, S^2, S_z \). Orbital and spin angular momentum are not coupled.

\[ |L, M_L \rangle \otimes |S, M_S \rangle \]

We can also consider the coupled representation of orbital and spin \( \ell, j, \ell_z, j_z, L^2, S^2, L_z, S_z \)

\[ |J \, M_J, L \, S \rangle = \sum_{M_L, M_S} C_{M_L, M_S} \, |L \, M_L \rangle \otimes |S \, M_S \rangle \]

For a given \( L \) and \( S \) the possible values of \( J \) must satisfy the "triangle inequality"

\[ |L - S| \leq J \leq L + S \]

Thus, for example, the 3P state of He has three possible "terms".

Here \( L = 1 \), \( S = 1 \) \( \Rightarrow \) \( J = 0, 1, 2 \)

\[ \Rightarrow \text{3P}_0, \text{3P}_1, \text{3P}_2 \]