Chapter 9: Multi-Electron Atoms – Ground States and X-ray Excitation

Up to now we have considered one-electron atoms. Almost all atoms are **multiple-electron atoms** and their description is more complicated due to the increase in the number of different interactions. Consider an atom with atomic number \( Z \). This atom will contain a nucleus with a charge \( Ze \) and \( Z \) electrons. To describe this system we need to consider the interactions between each electron and the nucleus and the interactions between the electrons. In order to describe such atoms, we will start with dealing with the strongest interactions first.

The description is complicated by the fact that the electrons are **identical particles**. In Classical Physics, identical particles can be distinguished on the basis of careful measurements. However, in Quantum Physics, electrons cannot be distinguished unless we disturb them.

First consider an atom with two electrons with no mutual interactions. The Schrödinger equation describing this system is

\[
-\frac{\hbar^2}{2m} \nabla_1^2 \psi_T \psi_T - \frac{\hbar^2}{2m} \nabla_2^2 \psi_T \psi_T + V_T \psi_T = E_T \psi_T
\]

The position of particle 1 is \((x_1, y_1, z_1)\); the position of particle 2 is \((x_2, y_2, z_2)\). If we assume there is no interaction between the electrons we can write the interaction potential as

\[
V_T(x_1, y_1, z_1, x_2, y_2, z_2) = V_1(x_1, y_1, z_1) + V_2(x_2, y_2, z_2)
\]

and the Schrödinger equation becomes

\[
-\frac{\hbar^2}{2m} \nabla_1^2 \psi_T - \frac{\hbar^2}{2m} \nabla_2^2 \psi_T + V_1 \psi_T + V_2 \psi_T = E_T \psi_T
\]

Consider the possibility that the wavefunction is the product of two wavefunctions: one associated with the particle 1 and one associated with particle 2:

\[
\psi_T(1,2) = \psi_\alpha(1) \psi_\beta(2)
\]

To determine if we can rewrite the wavefunction in this form, we need to substitute it in the Schrödinger equation:
\[
\left( -\frac{\hbar^2}{2m} \nabla_i^2 \psi_\alpha \right) \psi_\beta + \left( -\frac{\hbar^2}{2m} \nabla_2^2 \psi_\beta \right) \psi_\alpha + V_1 \psi_\alpha \psi_\beta + V_2 \psi_\alpha \psi_\beta = E_T \psi_\alpha \psi_\beta
\]

Dividing this equation by the wavefunction we obtain

\[
\left( -\frac{\hbar^2}{2m} \psi_\alpha + V_1 \right) / \psi_\alpha = E_1
\]

and

\[
\left( -\frac{\hbar^2}{2m} \psi_\beta + V_2 \right) / \psi_\beta = E_2
\]

In order for this equation to be satisfied for all positions of particles 1 and 2, the terms between the parentheses need to be constant. This requires that

\[
-\frac{\hbar^2}{2m} \psi_\alpha + V_1 \psi_\alpha = E_1 \psi_\alpha
\]

Since the \( V \) is the Coulomb potential, the wavefunctions \( \psi_\alpha \) and \( \psi_\beta \) are one-electron wavefunctions. The probability density distribution is

\[
\psi_T \psi_T^* = \left( \psi_\alpha (1) \psi_\beta (2) \right) \left( \psi_\alpha (1) \psi_\beta (2) \right) = \left( \psi_\alpha^*(1) \psi_\alpha (1) \right) \left( \psi_\beta^*(2) \psi_\beta (2) \right)
\]

In general, we cannot assume that the energies of the two states are the same, and the value of the wavefunction \( \psi_\alpha (1) \) will be different from the value of the wavefunction \( \psi_\beta (1) \). The probability density distribution will thus change when we exchange particles 1 and 2:

\[
\left( \psi_\alpha^*(1) \psi_\alpha (1) \right) \left( \psi_\beta^*(2) \psi_\beta (2) \right) \neq \left( \psi_\alpha^*(2) \psi_\alpha (2) \right) \left( \psi_\beta^*(1) \psi_\beta (1) \right)
\]

Since the probability density distribution changes when we exchange particles 1 and 2, we conclude that the particles are not indistinguishable. We thus conclude that the way we combined the two wavefunctions is not proper and the proposed total wavefunction is not a proper eigenfunction of the Schrödinger equation for a two-electron atom. There are however different ways of combining the two wavefunctions. For example, consider the following total wavefunctions:
\[ \psi_s(1, 2) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(1) \psi_\beta(2) + \psi_\beta(1) \psi_\alpha(2) \right\} \]

\[ \psi_A(1, 2) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(1) \psi_\beta(2) - \psi_\beta(1) \psi_\alpha(2) \right\} \]

The numerical factor in these expressions ensures that the total wavefunctions are normalized:

\[ \langle \psi_s(1, 2) | \psi_s(1, 2) \rangle = \frac{1}{2} \langle \psi_\alpha(1) \psi_\beta(2) + \psi_\beta(1) \psi_\alpha(2) | \psi_\alpha(1) \psi_\beta(2) + \psi_\beta(1) \psi_\alpha(2) \rangle = \]

\[ = \frac{1}{2} \langle \psi_\alpha(1) \psi_\beta(2) | \psi_\alpha(1) \psi_\beta(2) \rangle + \frac{1}{2} \langle \psi_\beta(1) \psi_\alpha(2) | \psi_\beta(1) \psi_\alpha(2) \rangle + \]

\[ \frac{1}{2} \langle \psi_\beta(1) \psi_\alpha(2) | \psi_\alpha(1) \psi_\beta(2) \rangle + \frac{1}{2} \langle \psi_\alpha(1) \psi_\beta(2) | \psi_\beta(1) \psi_\alpha(2) \rangle = \]

\[ = \frac{1}{2} + \frac{1}{2} = 1 \]

These wavefunctions are symmetric and asymmetric under the exchange of particles 1 and 2:

\[ \psi_s(2, 1) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(2) \psi_\beta(1) + \psi_\beta(2) \psi_\alpha(1) \right\} = \psi_s(1, 2) \]

\[ \psi_A(2, 1) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(2) \psi_\beta(1) - \psi_\beta(2) \psi_\alpha(1) \right\} = -\psi_A(1, 2) \]

Their probability density distributions do not change under particle exchange:

\[ \psi_s^*(2, 1) \psi_s(2, 1) = \psi_s^*(1, 2) \psi_s(1, 2) \]

\[ \psi_A^*(2, 1) \psi_A(2, 1) = [-\psi_A(1, 2)] [-\psi_A(1, 2)] = \psi_A^*(1, 2) \psi_A(1, 2) \]

We note that the energy of both wave functions is the same:

\[ E_s = E_\alpha + E_\beta = E_A \]
and the symmetric and anti-symmetric states are thus degenerate states. The average distance between the two particles will be different for the two solutions.

Now consider what will happen when the two electrons have the same quantum numbers: \( \alpha = \beta \).

In this case, the wave functions will be equal to

\[
\psi_s(1,2) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(1) \psi_\alpha(2) + \psi_\alpha(1) \psi_\alpha(2) \right\} = \sqrt{2} \psi_\alpha(1) \psi_\alpha(2)
\]

\[
\psi_A(1,2) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(1) \psi_\alpha(2) - \psi_\alpha(1) \psi_\alpha(2) \right\} = 0
\]

We thus conclude that if the wavefunction describing the system is asymmetric, the particles cannot have the same quantum numbers. When the wavefunction describing the system is symmetric, the particles can have the same quantum numbers.

In 1925, Pauli concluded on the basis of his study of atomic structure that in multi-electron atoms no more than one electron can be in a given quantum state. This is called the Pauli exclusion principle. An alternative expression of the exclusion principle is the statement that the wavefunction describing a multiple-electron system must be asymmetric.

To construct asymmetric wavefunctions for multiple-electron atoms we can use the Slater Determinant:

\[
\psi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_\alpha(1) & \psi_\alpha(2) & \cdots \\
\psi_\beta(1) & \psi_\beta(2) & \\
\vdots & \vdots & \\
\end{vmatrix}
\]

Adding spin to the system increases the number of possible wavefunctions. To determine the number of possible ways of combining spin, let us start with a two-electron system:

- The spin of each electron is \( \frac{1}{2} \). Each electron can be in a state with \( m_s = +\frac{1}{2} \) and a state with \( m_s = -\frac{1}{2} \).

- The spin wavefunction can be represented by a symmetric and an asymmetric wavefunction:
\[ \psi_{A,\text{spin}} = \frac{1}{2} \sqrt{2} \{(+1/2, -1/2) - (-1/2, +1/2)\} \quad m_s = 0 \]

\[ \psi_{S,\text{spin}} = \begin{cases} 
(+1/2, +1/2) & m_s = 1 \\
\frac{1}{2} \sqrt{2} \{(+1/2, -1/2) + (-1/2, +1/2)\} & m_s = 0 \\
(-1/2, -1/2) & m_s = -1 
\end{cases} \]

- The symmetric and asymmetric wavefunctions corresponds to two values of the total spin of the two spin-½ particle system:

\[ S_{12} = 1: \quad \text{Triplet State, Symmetric, } \psi_{S,\text{spin}} \]

\[ S_{12} = 0: \quad \text{Singlet State, Asymmetric, } \psi_{A,\text{spin}} \]

Since the total wavefunction of the multi-electron atom must be asymmetric, the spin wavefunction will constrain the spatial wavefunction:

\[ \psi_{\text{multi-electron}} = \psi_{\text{spatial}} \psi_{\text{spin}} \]

Consider the following two possible configurations for a two-electron atom:

- **Singlet spin state.** When the system is in the singlet spin state, its spin wavefunction will be asymmetric. The spatial wavefunction must thus be symmetric:

\[ \psi_{\text{spatial}}(1, 2) = \frac{1}{2} \sqrt{2} \{\psi_\alpha(1)\psi_\beta(2) + \psi_\beta(1)\psi_\alpha(2)\} \]

When the two electrons are in the same spatial state, \( \alpha = \beta \), the probability density distribution will not be equal to zero even if the electrons are located at the same position \((1 = 2)\). For a system in the singlet spin state, we can find the two electrons close together.

- **Triplet spin state.** When the system is in the triplet spin state, its spin wavefunction is symmetric. The spatial wavefunction must thus be asymmetric:
If electrons 1 and 2 are located at the same position the spatial wavefunction is zero and the probability density distribution is thus also equal to 0. For a system in the triplet spin state, the two electrons cannot be located at the same position. In the triplet state it appears as if the electrons repel each other.

\[ \psi_{\text{spatial}}(1,2) = \frac{1}{2} \sqrt{2} \left\{ \psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2) \right\} \]

The preceding discussion shows that there is a coupling between the spin and the space variables. The electrons act as if a force is acting between them and the force depends on the relative orientation of their spin. This force is called the exchange force. The effect is shown schematically in the Figure on the right. The effect of the exchange force on the energy levels of Helium is shown in the Figure at the bottom of the page. The Figure shows the following features:

- The energy levels on the left are the energy levels that would be found if there is no Coulomb interaction between the electrons.
- The energy levels in the center are the energy levels that are found when the Coulomb interaction between the electrons is included. We see that the \( n = 1, n = 2 \) level is split. This is a result of the fact that the distance between the two electrons is somewhat larger.
when one electron is in the \((n = 1, \ell = 0)\) state and the other one is in the \((n = 2, \ell = 0)\) state compared to the situation in which one electron is in the \((n = 1, \ell = 0)\) state and the other one is in the \((n = 2, \ell = 1)\) state. The Coulomb repulsion between the two electrons will be less in former compared to the latter configuration. The level with \(\ell = 1\) is thus located at a slightly higher energy than the level with \(\ell = 0\).

- The levels on the right-hand side include the exchange force. Since the average distance between the electrons in the triplet state is larger than the average distance between the electrons in the singlet state, the energy of the triplet state will be less than the energy of the singlet state.

In order to describe multi-electron atoms we use the **Hartree theory**. This theory relies on multiple approximations and including gradually less important interactions. In order to describe a multi-electron atom we will start with considering the following forces:

- The attractive forces between the electrons and the nucleus. This force increases when \(r\) decreases.
- The repulsive forces between the electrons. This force decreases when \(r\) decreases. The reason that the force decreases is due to the fact that when the electron is located at small \(r\) the repulsive forces due to all other electrons add up to zero (see Figure below). When the electron is located near the edge of the atom, the repulsive forces do not cancel, but provide a net force point away from the center of the atom (see Figure below).

To describe the motion of the electrons we make the following assumptions:

- The atom has \(Z\) electrons and a nucleus with a positive charge \(Ze\).
- The electrons move independently.
- The effect of the presence of other electrons is included as a modification to the potential seen by the electron.
- Since the atom has spherical symmetry it is assumed that the potential also has spherical symmetry.
- When \(r\) approaches 0, it is assumed that the potential approaches

![Diagram showing electron orbital forces and potential regions](image.png)
\[ V \rightarrow \frac{1}{4\pi \varepsilon_0} \frac{Ze^2}{r} \]

The net charge seen by the electron is \( Ze \).

- When \( r \) approaches infinity, it is assumed that the potential approaches

\[ V \rightarrow \frac{1}{4\pi \varepsilon_0} \frac{e^2}{r} \]

The net charge seen by the electron is \( e \) which is the sum of the nuclear charge \( Ze \) and the charge due to \( Z-1 \) electrons.

The following procedure is followed in order to determine the wavefunctions that describes the multi-electron atom:

1. Construct the potential \( V(r) \) using the procedure outlined above.
2. Solve the time-independent Schrödinger equation and determine the eigenfunctions.
3. Construct the ground state of the atom by filling the eigenfunctions obtained in step 2. If there are \( Z \) electrons in the atom, we will use the first \( Z \) eigenfunctions.
4. Calculate the spatial charge distribution by calculating the following charge density distribution for each electron: \(-e\langle \psi | \psi \rangle\).
5. Using the spatial charge distribution obtained in step 4, calculate a modified potential and go back to step 2.
6. Stop the cycle if the potential \( V \) converges. This also implies that \( \psi \) converges.

**Note:** the exclusion principle is used in step 3 but the asymmetric wavefunction requirement is not used.

When we follow these steps we can determine the wavefunction of the ground state of the multi-electron atom. Based on this wavefunction we can come to the following conclusions:

1. The wavefunction of the ground state can be written in the following way:

\[ \Psi_{n/m_s} = R_{n}^{m} (r) \Theta_{m_{l}} (\theta) \Phi_{m_{s}} (\varphi) \]

Same functions as we used for single-electron atoms Spin eigenfunction

2. The sum of the solutions for a given combination of \( n \) and \( \ell \) is spherically symmetric. For example, the probability density distribution for \( n = 2 \) and \( \ell = 1 \) is equal to
\[
\psi_{2,1} \ast \psi_{2,1} = \frac{1}{3} \left( \psi_{2,1,-1} \ast \psi_{2,1,-1} + \psi_{2,1,0} \ast \psi_{2,1,0} + \psi_{2,1,1} \ast \psi_{2,1,1} \right)
= \frac{1}{96\pi} \left( \frac{Z}{a_0} \right)^3 e^{-Zr/a_0} \left( \frac{Zr}{a_0} \right)^2
\]

The probability density distribution does not depend on the polar and azimuthal angle. It thus has spherical symmetry. The asymmetry of the charge distribution is due to the electrons in the highest energy state that is not fully occupied.

3. The \( r \) dependence of the wavefunction will be different for multi-electron atoms. For a given \( n \), electrons are found in a limited region of space (see Figure on the top of this page).

4. The spherical charge distributions imply that the modified potentials are also spherically symmetric:

\[
V_n(r) = -\frac{1}{4\pi\varepsilon_0} \frac{Z_n e^2}{r}
\]

In this equation, \( n \) is the principle quantum number and \( Z_n \) is the effective charge. It is found that \( Z_n \) has the following values:

- For the innermost shell (\( n = 1 \)): \( Z_n = Z - 2 \).
- For the next shell (\( n = 2 \)): \( Z_n = Z - 10 \). Note: 10 = 2 + 6 + 2.
- For the outermost shell: \( Z_n = n \).
5. The radius of the orbits of the \( n = 1 \) electrons decreases with increasing \( Z \):

\[
\bar{r} = \frac{a_0}{Z} \quad \Rightarrow \quad \bar{r}_1 = \frac{a_0}{Z} = \frac{a_0}{Z-2} = \bar{r}_{1,\mu}
\]

6. The energy of the innermost electrons becomes more negative with increasing \( Z \):

\[
E_1 = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2(2\hbar^2 n^2)} = Z^2 \left\{-\frac{\mu e^4}{(4\pi\varepsilon_0)^2(2\hbar^2)}\right\} = (Z-2)^2 E_{1,\mu}
\]

The binding energy of the innermost electron in the Hydrogen atom is \(-13.6 \text{ eV}\). If \( Z \) is large enough, the binding energy will exceed two times the rest mass of the electron. This happens when

\[
(Z - 2)^2 = \frac{E_1}{E_{1,\mu}} = \frac{2 \times 511,000}{13.6} = 75,147 \quad \Rightarrow \quad Z = 276
\]

7. The energy of the electrons in the outermost shell is equal to

\[
E_n = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2(2\hbar^2 n^2)} = -\frac{\mu n^2 e^4}{(4\pi\varepsilon_0)^2(2\hbar^2)} = -\frac{\mu e^4}{(4\pi\varepsilon_0)^2(2\hbar^2)} = E_{n,\mu}
\]

which is the energy of the ground state of the Hydrogen atom.

8. Electrons in the outermost shell move in an orbit with an average radius \( r \) equal to

\[
\bar{r} = \frac{n^2 a_0}{Z} = \frac{n^2 a_0}{n} = na_0
\]

Since \( n \) increases slowly when \( Z \) increases (for H \( n = 1 \), for Ne \( n = 2 \), etc.) the radius of the atom will only slowly increase with increasing \( Z \). For example, \( n \) doubles when \( Z \) increases by a factor of 10!

9. For small \( r \), the probability density distribution is proportional to \( r^{2\ell} \). The distribution in this region is not sensitive to the details of the potential. Since \( r < 1 \), the probability of finding a state with a high angular momentum at a given \( r \) is smaller than the probability of finding a state with a low angular momentum at that \( r \). Within a given \( n \) shell, the most negative state is the \( \ell = 0 \) state; the next state is the \( \ell = 1 \) state, etc.
The orbits of electrons in multi-electron atoms are specified by using the so-called spectroscopic notation \( n\ell \). The key ingredients of the spectroscopic notation are the principle quantum number \( n \) and angular momentum quantum number \( \ell \). States with different angular momentum quantum numbers are specified in the following way:

\[
\begin{array}{c|c}
\ell & \text{Spectroscopic Notation} \\
0 & s \\
1 & p \\
2 & d \\
3 & f \\
4 & g \\
5 & h \\
6 & i \\
\end{array}
\]

In terms of increasing energy, the sub-shells are arranged in the following way:

\[1s, 2s, 2p, 3s, 3p, 4s, 3d, \ldots\]

The rules for ordering the sub-shells are as follows:

- For a given outer sub-shell, lowest \( \ell \), lowest \( E \).
- For a given \( \ell \), the outer sub-shell with the lowest \( n \) has the lowest \( E \).

Note: the relative energies of sub-shells depend on the atomic number of the atom. For certain values of \( Z \) the ordering of the sub-shells will change (see Figure on the right).

Based on the energy of the levels shown in the Figure, additional rules for sub-shells are observed:

- Every \( p \) shell has a higher energy than the preceding \( s \) and \( d \) shells.
- Every \( s \) shell has a higher energy than the
preceding $p$ shell. Note: the energy difference is very large.

Based on our current understanding of the shell and sub-shell structure of multi-electron atoms we can

- Understand the properties of noble gasses. Noble gasses have filled outer $p$ shell. Because of the large gap between the $p$ shell and the next $s$ shell, the first excited state is far above the ground state and the atom is difficult to excite. The effect is a high ionization energy for noble gasses, as shown in the Figure on the top of this page.

As a result of the shell structure, the noble gas atoms are spherical. The charges of the noble atoms do not produce an electric field outside the atom, and noble gas atom do not interact chemically with other atoms.

- Understand the ionization energies, electron affinity, etc. These properties are related the properties of the last electron.

- A group of atoms, called the alkalis, have one loosely bound electron in the outer $s$ shell. This loosely-bound electron is easy to remove and as a result, these atoms have a low ionization energy.

- Another group of atoms, called the halogens, have one less electrons than is required to fill their outer $p$ shell. As a result, these atoms are very likely to pick up an electron to fill their outer $p$ shell. The halogens thus have a high electron affinity.

The chemical properties of atoms are primarily determined by the properties of the electrons in the outer shells. In order to determine the properties of electrons in the inner shells, X rays can be used. When energetic electrons interact with atoms, they can eject electrons from one of the inner shells and create a hole in this shell. This leaves the atom in a highly excited state. Consider the following scenario:

- An electron from the $1s$ shell is removed.
- The hole created in the $1s$ shell is filled with an electron from the $2p$ shell. When this happens, a photon is emitted with an energy equal to the energy difference of the $2p$ shell and the $1s$ shell.
- The hole in the $2p$ shell is filled with an electron from the $3d$ shell. When this happens, a photon is emitted with an energy equal to the energy difference of the $3d$ shell and the $2p$ shell.
- The hole continue to move up to higher-energy states.
The removal of an electron from an inner shell thus produces a cascade of low-energy photons, X-rays, which carry information about the energy structure of the inner shells of the atom. An example of an X-ray spectrum of Tungsten is shown in the Figure on the right.

When we look at the transitions in the atom, it appears as if the hole is jumping from low lying states to high lying states. The transitions made by the hole satisfy selection rules similar to those satisfied by electron transitions in the outer shells:

\[ \Delta \ell = \pm 1 \]

\[ \Delta j = 0, \pm 1 \]

The energies of the X-rays changes smoothly as function of \( Z \). For example the \( Ka \) lines have the following dependence on \( Z \):

\[ \frac{1}{\lambda} = C(Z - a)^2 \]

where \( a \) is a constant with a value between 1 and 2. A plot of the square-root of the inverse of the wavelength as function of \( Z \) should thus the a straight line. The slope of the line if the square-root of \( C \) and the line intercepts the horizontal axis at \( Z = a \). An example of this type of
data is shown in the Figure on the right.