Multi-Electron Atoms
The Vector Model of the Atom
(Note: Incomplete document)

Introduction

Direct solution of Schroedinger's Equation for an atom with two or more electrons is
impossible. Instead we have to resort to successively better and better approximations
(perturbation theory). The vector model is a semi classical representation of what the
increasingly sophisticated approximate solutions of Schroedinger's Equation are telling us.

In Schroedinger's Equation we need a representation of the potential energy of the electrons. At
a minimum the potential energy function should include all of the following:

- Central field potential energy, between the electrons and the nucleus
- Electrostatic electron-electron interactions
- Magnetic electron-electron interactions
- Interaction between the electrons and external fields
- Magnetic interactions between the electrons and the nucleus

We shall assume for the moment that the relative strengths of these interactions are in the order
given. This gives rise to the Russell Saunders, or LS coupling scheme. This will be the basis for
describing the energy levels of most of the atoms we shall be looking at. However, not all atoms
obey this hierarchy of interactions. For these atoms the relative ordering is different, and other
coupling schemes are possible. These will be briefly discussed at the end.

Central Field Approximation

The coarsest approximation for all atoms is the Central Field Approximation, in which the
potential energy function for the i\textsuperscript{th} electron is only dependent on the radial coordinate, and is
spherically symmetric

\[ U_i = U_i(r) \]

It is tempting to think of the Central Field Approximation to as representing the interaction
between the electron and the nucleus (with Z protons)

\[ U_i = U_i(r_i) = -\frac{Ze^2}{4\pi\varepsilon_o r_i} \]

However, if we restrict U\textsubscript{i} to this form, then the next term (the electron-electron interaction) will
not be a small approximation. We will therefore add to the electron-nucleus energy a term
which represents the interaction between the i\textsuperscript{th} electron and all the other electrons, but averaged

\[ U_i = U_i(r_i) = -\frac{Ze^2}{4\pi\varepsilon_o r_i} + \left[ \sum_{j\neq i} \frac{e^2}{4\pi\varepsilon_o r_{ij}} \right]_{av} \]

over all angles

For our purposes we will not worry about how this is done, on the result is important.

In this approximation, Schroedinger's equation can be separated into individual equations for
each of the electrons, with the equation for any one electron being the same as that for the
Hydrogen atom, except that the potential energy function is no longer strictly Coulombic because of the averaged electron-electron interaction. This leads to four key features of our description of the atom

1. The position part of any one electron's wave function can be split into radial and angular parts, as was the case with hydrogen.

\[ \psi_i(r_i, \theta_i, \phi_i) = R_i(r_i) Y_{l_i m_i}(\theta_i, \phi_i) \]

2. The angular part \( Y_{l_i m_i}(\theta_i, \phi_i) \) is exactly the same spherical harmonic that is calculated for the hydrogen atom, but the radial part is different.

3. The total wave function (including the spin part) is dependent on four quantum numbers; \( n_i, \ell_i, m_{\ell_i}, \) and \( m_s \). A fifth quantum number \( s_i \) is always equal to \( \frac{1}{2} \) and need not be specified.

4. The contribution to the energy by the \( i \)-th electron is only dependent on \( n_i \), as was the case with hydrogen.

In the Central Field Approximation any one electron is labeled by its value of \( n \) and \( \ell \), leaving \( m_{\ell} \) and \( m_s \) undefined. The value of \( \ell \) is always an integer, and is represented by a letter according to the table to the right. (Note: all letters are lower case.)

If all the electrons of the atom are labeled this way then the full label is known as a configuration. For example, the five electron atom beryllium might have the configuration \( 1s^22s^22p^2 \), showing that there are two 1s electrons, a single 2s electron, and two 2p electrons.

Pauli Exclusion Principle

The Pauli Exclusion Principle is most important in describing a multi electron atom. It states that now two electrons can have the same four quantum numbers \( n_i, \ell_i, m_{\ell_i}, \) and \( m_s \). This places quite a restriction on the possible configurations.

- For any given value of \( \ell \) there are \( 2\ell + 1 \) possible values of \( m_\ell \) with values \( -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \) and \( +\ell \). For each of these there are two possible values of \( m_s \), that is \(-\frac{1}{2}\) and \(+\frac{1}{2}\). That gives \( 2(2\ell+1) \) possible values of \( m_\ell \) and \( m_s \) for any given value of \( \ell \). These values are shown in the third column in the table above.

- For any value of \( n \) there are \( n \) possible values of \( \ell \), ranging from 0 to \( n-1 \). The total number of possible wave functions for any given value of \( n \) is therefore

\[ \sum_{0}^{n-1} 2(2\ell+1) = 2n^2 \]

For a two electron atom it is possible to have both electrons with quantum number \( n=1 \). However, with three electrons only two can have \( n=1 \), the third must have \( n=2 \) (or more). For lithium (\( Z=3 \)) the lowest energy configuration is therefore \( 1s^22s \). By the time we reach sodium in the periodic table (\( Z=11 \)), two of those electrons can have \( n=1 \), eight can have \( n=2 \), and the eleventh must have \( n=3 \) (or above). The lowest energy configuration of sodium is therefore \( 1s^22s^22p^63s \).
Before continuing it is worthwhile to have a semi-classical picture of the meaning of the quantum numbers \( \ell \) and \( s \). \( \ell \) is known as the orbital quantum number, and can be thought of as representing the angular momentum of the electron due to its orbit around the nucleus. This angular momentum is of course a vector, with a magnitude whose square is \( \ell(\ell+1)\hbar^2 \). The direction of the orbital angular momentum is constantly changing, such that its projection on the \( z \) axis is a constant, \( m_\ell \hbar \).

Similarly \( s \) is known as the spin\(^a\), with an angular momentum \( s \) with a magnitude whose square is \( s(s+1)\hbar \). Since \( s \) is always \( \frac{1}{2} \) the magnitude of \( s \) is always equal to \( \sqrt{\frac{1}{4}}\hbar \). The direction of the spin angular momentum is also constantly changing, such that its projection on the \( z \) axis is a constant, \( m_s \hbar \). This projection can only take on the values \( -\frac{1}{2}\hbar \) and \( +\frac{1}{2}\hbar \).

### Residual Electrostatic Interaction

The next approximation accounts for the electron-electron interaction more exactly. We have already partially accounted for the electron-electron interaction by adding in an angle-averaged energy. Now we must add as a perturbation term \( \Delta U \) which is the difference between the true interaction and the approximate angle-averaged energy

\[
\Delta U = \sum_{i \neq j} \frac{e^+}{\pi \epsilon_o r_{ij}} \left[ \sum_{i \neq j} \frac{e^+}{\pi \epsilon_o r_{ij}} \right]_{av}
\]

Calculations using \( \Delta U \) and perturbation theory are not trivial, and certainly beyond the scope of this class. You are referred to the reference books which are available in N136 for further information. We will instead discuss the results of the calculations using a semi classical model.

In a semi classical picture, the interaction between two electrons produces a torque on each electron, and that torque is responsible for changing the orbital angular momentum. In quantum mechanical terms the orbital quantum number \( \ell \) is no longer a constant, no longer a 'good' quantum number. However, if we take the two electrons together the torque on one is exactly equal to the torque on the other, but with opposite direction. Consequently the change in the orbital angular momentum of one electron is matched by an equal but opposite change in the orbital angular momentum of the other. Although neither angular momentum is constant, their sum is a constant. We will therefore switch from a description which relies on the individual orbital angular momenta of the electrons to one which relies on the total angular momentum

\[
\mathbf{L} = \sum_i \ell_i
\]

where the sum is over all the electrons of the atom. The result is a vector \( \mathbf{L} \) with a magnitude whose square is \( L(L+1)\hbar^2 \), with a direction which is constantly changing, and with a projection on the \( z \) axis which is a constant equal to \( m_L \hbar \).

Since the sum over the individual orbital angular momenta of the electrons is a vector sum more than one possible value of \( L \) is possible, depending on the relative orientations of the individual orbital angular momenta. The maximum possible value of \( L \) occurs when all the individual orbital angular momenta have the same direction. The minimum possible value occurs when the individual orbital angular momenta are oriented to make \( L \) the smallest possible positive integer (including 0). For the case of two electrons the result is

\(^{a}\) Although this has absolutely nothing to do with the electron spinning on its axis. Instead the spin is a measure of the magnetic properties of the electron, as will become evident when discussing spin-orbit coupling.
\[ |\ell_1 - \ell_2| \leq L \leq \ell_1 + \ell_2 \]

with \( L \) taking on all integer values between these limits. For example, for a d electron \((\ell_1 = 2)\) and an f electron \((\ell_2 = 3)\)

\[ 1 = |\ell_1 - \ell_2| \leq \ell_1 + \ell_2 = 5 \]

The possible values of \( L \) are therefore 1, 2, 3, 4, or 5. The results for various different combinations of \( \ell_1 \) and \( \ell_2 \) are tabulated to the right.

As with the individual electron orbital angular momenta the total orbital angular momenta is usually designated by a letter. The same letter scheme is used, except upper case letters are used.

**Pauli Exclusion Principle (again)**

The electrons which make up the atom are indistinguishable fermions. We can have no way of telling which electron is which. For example, suppose we have two electrons which we will arbitrarily label a and b, in the configuration 2s3p. If we write the spatial part of the wave function for these two electrons as

\[ \psi(2s3p) = \psi_a(2s) \psi_b(3p) \]

then we know for certain that electron a is the 2s electron and electron b is the 3p electron. This is not allowed. The correction is to write the spatial part of the wave function in a composite form

\[ \psi(2s3p) = \psi_a(2s) \psi_b(3p) + \psi_a(3p) \psi_b(2s) \]

such that if we now switch the labels a and b we end up with the same wave function we started with.

If we also include the spin part of the wave function then the Pauli Exclusion Principle demands that the total wave function for a fermion must be antisymmetric if the labels are reversed. This can be accomplished in one of two ways.

- An antisymmetric spatial part and a symmetric spin part. For example, the composite spatial wave function above is symmetric, if we reverse a and b we get the same spatial wave function. The spin part of the wave function would therefore have to be antisymmetric, that is \( \sigma(b,a) = - \sigma(a,b) \).
- A symmetric spatial part and an antisymmetric spin part.

In the semi classical vector model the enforcement of the Pauli Exclusion Principle in conjunction with the Residual Electrostatic Interaction results in an addition of all the individual orbital angular momenta to produce the total angular momentum, as described above, and also the addition of the individual spin angular momenta to produce the total spin momentum of the atom

\[ S = \sum_i s_i \]
where the sum is again over all the electrons of the atom. The result is a vector \( \mathbf{S} \) with a magnitude whose square is \( S(S+1)\hbar^2 \), with a direction which is constantly changing, and with a projection on the z axis which is a constant equal to \( m_S \).

As we the case with the orbital angular momenta of the electrons, the vector sum of the individual spin angular momenta cannot produce more than one possible value of \( S \), depending on the relative orientations of the individual spin angular momenta. The maximum possible value of \( S \) occurs when all the individual spin angular momenta have the same direction. The minimum possible value occurs when the individual spin angular momenta are oriented to make \( S \) the smallest possible positive integer (including 0) or half-integer. For example, for four electrons the maximum possible value of \( S \) is 2 and the minimum is 0. With differences in the possible values of \( S \) having to be different by one, the only other value between these limits is 1. The possible values of \( S \) are therefore 0, 1, and 2. The results for some other number of electrons is shown to the right.

<table>
<thead>
<tr>
<th>#</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>2</td>
<td>0, 1</td>
</tr>
<tr>
<td>3</td>
<td>1/2, 3/2</td>
</tr>
<tr>
<td>4</td>
<td>0, 1, 2</td>
</tr>
<tr>
<td>5</td>
<td>1/2, 3/2, 5/2</td>
</tr>
<tr>
<td>6</td>
<td>0, 1, 2, 3</td>
</tr>
</tbody>
</table>

The values of \( L \) and \( S \) define a term in the energy diagram of the atom. Note that

- Any one configuration can produce multiple terms
  - For example a 2p2d configuration can produce terms with any combination of \( L = 1, 2, \) or 3, each with either \( S = 0 \) or 1
- Different configurations can produce terms with the same values of \( L \) and \( S \)
  - For example, a term with \( L = 1 \) and \( S = 0 \) can be produced from the configuration 1s2p, or the configuration 2s2p, or the configuration 2s3p, or the configuration 2p3d, or countless other configurations.

Terms are labeled by the configuration which produced it, and a designation \( ^{2S+1}L \) to denote the individual term. Remember \( L \) is designated by a letter, and the factor \( 2S+1 \), known as the multiplicity, is the number of possible values of \( m_S \) for a given value of \( S \). Some examples are

- Ground state of hydrogen 1s \( ^2S \) \( (L=0, S=\frac{1}{2}, \text{pronounced doublet } S) \)
- Ground state of helium 1s\(^2\) \( ^1S \) \( (L=0, S=1, \text{pronounced singlet } S) \)
- One of the excited states of helium 1s2p \( ^3P \) \( (L=1, S=1, \text{pronounced triplet } P) \)
- Ground state of sodium 1s\(^2\)2s\(^2\)2p\(^6\) \( ^2S \) \( (L=0, S=\frac{1}{2}, \text{pronounced doublet } S) \)
- First excited state of sodium 1s\(^2\)2s\(^2\)2p\(^6\)3p \( ^2P \) \( (L=0, S=\frac{1}{2}, \text{pronounced doublet } P) \)

### Spin Orbit Coupling

In the zeroth and first order approximations above we have dealt with the electrostatic properties of the electrons in the atom. Spin orbit coupling deals with the magnetic property of the atom, its intrinsic magnetic moment. This magnetic moment is usually expressed in terms of the spin

\[
\mu = g_s \mu_B S
\]

where \( \mu_B \) is known as the Bohr magneton (= \( e\hbar/2m \)) and \( g_s \) is the spin g factor which is very nearly equal to 2.\(^1\)

This magnetic moment can interact with any magnetic field. The case of an external field is

\(^1\) More exactly 2.0023193043622 ± 0.0000000000015, see http://physics.nist.gov/cgi-bin/cuu/Value?gem#mid
treated later (Zeeman effect). Internal fields can arise from three possible origins

1. *Spin-own orbit interaction.* As the electron moves in the electrostatic field of the nucleus, a relativistic transformation means that the electron partially perceives the electrostatic field as a magnetic field.

2. *Spin-other orbit interaction.* The orbit of any one electron around the nucleus can be though of (classically) as a small current. This circulating current gives rise to a magnetic field. For each electron there is then an interaction between its magnetic moment and the magnetic field produced all the other orbiting electrons.

3. *Spin-spin interaction.* Finally, since each electron is a small magnet, there is an interaction between the magnetic moment of any one electron and the magnetic moments of all the other electrons.

Zeeman Effect

Stark Effect

Hyperfine Structure

jj Coupling