Electronic and Fine Structure of multi-electron atoms

The LFS problem is pretty independent of the other atomic structure, but we must start at the beginning to understand the electronic energy levels and fine structure.

I. General principles:

For the present we will content ourselves with a qualitative treatment to obtain an overview of the energy spectrum. We will then be in a position to fill in some selected details. Much of what follows is based on the initial chapters of Södervall's text, "Atomic Spectra and Radiative Transitions."

A. Schrödinger Equation (S.E.)

Since this is strictly applicable only to single-particle systems, some approximations are clearly needed. The major ones are these:

1) Ignore relativistic and QED effects. They can be treated later as perturbations, and are always small, at least for low Z. In particular, we will later treat spin interactions by inserting the appropriate terms from the Pauli Hamiltonian into the S.E., generalizing somewhat for multiple electrons.

2) Make a central field approximation -- each electron moves in a spherically symmetric
potential $U(r)$ determined from the average motion of the other electrons and the nucleus. Deviations are usually treated as perturbations.

The approximate S.E. is then, for any electron,

$$\left(\frac{\hbar^2}{2m} \nabla^2 + U(r) + E\right) \psi_i = 0$$

Some central potential; dependent on which electron we are considering, etc.

The problem is separable just as in the example of the H atom, to give angular and radial parts:

$$\psi_i = R(r) Y_{lm} (\theta, \phi), \quad \text{with}$$

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \ell (\ell + 1) + U(r)\right) P(r) = E P(r)$$

and $P(r) \equiv r R(r)$.

So there is no m dependence of the energy, which makes sense, since an isolated atom shouldn't notice which way it is oriented.

Parity under inversion is same as for H atom:

Even $\ell \Rightarrow$ even parity.

Form of $U(r)$ is in general complicated, so solving for $P(r)$ is in general a numerical problem. We will assume that $U(r)$ behaves sensibly. In particular,

$$U(r) < 0 \quad \text{(attractive force)}$$

$$U(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

and $U(r) \rightarrow -\frac{Z e^2}{r}$ as $r \rightarrow 0$ (Coulomb attraction)

For a given $\ell$, electron $i$ will have some eigenvalue spectrum in this potential,
Label the eigenstates with the principal quantum number \( n = 1, 2, 3, \ldots \) in order of increasing energies. The energies will not necessarily obey the Rydberg formula.

The wave function of electron \( i \) can be written as

\[ \Psi_i = |n \ell m \rangle. \]

Adding in the spin of \( \frac{1}{2} \), we have more generally,

\[ \Psi_i = |n \ell \sigma \uparrow m, m \rangle. \] (4)

Parity is still just \((-1)^\ell\).

Next, consider total orbital angular momentum and total spin:

\[ \vec{L} = \sum_i \vec{l}_i \]
\[ \vec{S} = \sum_i \vec{s}_i. \] (5)

Convention: upper-case letters are used for properties of the complete \( n \)-electron wave function, lower case for the individual electrons.

Parity: determined by combining parities of the individual electrons. Taking a scalar (not vector) sum,
\[ \Sigma l_i = \text{even} \Rightarrow \text{even parity} \]
\[ \Sigma l_i = \text{odd} \Rightarrow \text{odd parity} \]

(These are quantum number, not momentum operators!)

B. Pauli exclusion principle: shells:

Since electrons are fermions, only one electron can occupy each quantum-mechanical state of the system. This is a special case of the more complete statement that the total wave function \( \Psi \) must be antisymmetric under the interchange of any two electrons. We can construct such a wave function from the \( \psi_i \)'s by setting up a Slater determinant:

\[
\Psi(\lambda_1, \lambda_2, \lambda_3, \ldots) = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc}
\psi_1(\lambda_1) & \psi_2(\lambda_1) & \cdots & \psi_N(\lambda_1) \\
\psi_1(\lambda_2) & \psi_2(\lambda_2) & \cdots & \psi_N(\lambda_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\lambda_N) & \psi_2(\lambda_N) & \cdots & \psi_N(\lambda_N)
\end{array} \right|
\]

(6)

\( \lambda_j \) = space & spin coordinates of j'th electron.
\( \psi_i \) = wave function for choice i of all quantum numbers, \( n, l, m, \) and \( m_s \).

Properties:

a) Any two identical wave functions \( \Rightarrow \) identical columns.
This gives \( \Psi = 0 \), recovering the conventional Pauli principle.

b) Any interchange of particles \( \Rightarrow \) interchange of rows
\( \Rightarrow \Psi \) changes sign (antisymmetric, as required).
Example -- The helium atom:

1) Ground state -- both electrons with \( n=1, l=0 \)
   (Notation -- \((1s)^2\))

   Writing the spin eigenstates as \( |\uparrow\rangle \) and \( |\downarrow\rangle \)
   
   \[ \Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{10} |\uparrow\rangle & \psi_{10} |\downarrow\rangle \\ \psi_{10} |\uparrow\rangle & \psi_{10} |\downarrow\rangle \end{vmatrix} \]

   \( \psi_{10} \) -- electron 1
   \( \psi_{10} \) -- electron 2

   \[ = |\psi_{10}\rangle |\psi_{10}\rangle \otimes \left( \frac{1}{\sqrt{2}} \left( |\uparrow\rangle - |\downarrow\rangle \right) \right) \]

   Thus the spins must be arranged antisymmetrically, with \( S=0 \) \( \Rightarrow \) singlet state. We could also have seen this by noting there cannot be two electrons with \( n=1, l=0 \), and the spins in the same direction.

   So the ground state is \( \frac{1}{\sqrt{2}} \), where the notation is always given by,

   \[ 2S+1 \]

   \( L \) -- eigenvalue of \( L^2 \)

   \((n\text{-electron operator})\)

2) First excited state -- 1s 2s configuration.

   Now there are 4 different ways to set up the 2-electron Slater determinant, since one electron is a 1s electron, the other is 2s, but also each spin can be + or -.

   \[ a) \quad \frac{1}{\sqrt{2}} \begin{vmatrix} 1s^+ > & 1s^- > \\ 1s^+ > & 1s^- > \end{vmatrix} \]

   \[ = \frac{1}{\sqrt{2}} (|1s\rangle|2s\rangle - |2s\rangle|1s\rangle) \otimes |++\rangle \]

   (symm. spins, antisymm. electrons)
b) \[ \begin{pmatrix} 1s \rightarrow 1s \rightarrow \\ 1s \rightarrow 1s \rightarrow \\ 1s \rightarrow 1s \rightarrow \end{pmatrix} = \frac{1}{\sqrt{2}} \left( |1s> |2s> - |2s> |1s> \right) \otimes \mid -- \rangle \] (same, with ++ \rightarrow --) 

\[ \text{(mixed)} \] 

\[(c) \frac{1}{\sqrt{2}} \begin{pmatrix} 1s + > 1s + > \\ 1s + > 1s + > \end{pmatrix} = \frac{1}{\sqrt{2}} \left( |1s> |1s> |+> - |2s> |1s> |+> \right) \] 

\[(d) \frac{1}{\sqrt{2}} \begin{pmatrix} 1s -> 1s + > \\ 1s -> 1s + > \end{pmatrix} = \frac{1}{\sqrt{2}} \left( |1s> |2s> |+> - |2s> |1s> |+> \right) \] 

In general, the exact eigenstates (so long as the 1s, 2s configuration is pure) will be some linear combination of these 4 Slater determinants.

For the particular case of the non-relativistic Hamiltonian, there are no terms in \( \vec{S} \), so it makes sense to write linear combinations of (c) and (d) where \( S^2 \) has well-defined eigenvalues, and the spin is separately either symmetric or anti-symmetric.

\[(c) + (d) \frac{1}{\sqrt{2}} \] gives \[ \frac{1}{\sqrt{2}} \left( |1s, 2s> - |2s, 1s> \right) \otimes \frac{1}{\sqrt{2}} \left( |++> + |-> \right) \] 

\[ (c) - (d) \frac{1}{\sqrt{2}} \] gives \[ \frac{1}{\sqrt{2}} \left( |1s, 2s> + |2s, 1s> \right) \otimes \frac{1}{\sqrt{2}} \left( |++> - |-> \right) \] 

Recalling \( \vec{S} = \vec{S}_1 + \vec{S}_2 \) and writing out \( S^2 \) explicitly, you can easily show, (or can show with 3-5 symbols) 

\[ |S=1, M_s = \pm 1 \rangle = |++> \] 

\[ |S=1, M_s = 0 \rangle = \frac{1}{\sqrt{2}} (|+-> + |->) \] 

\[ |S=0, M_s = 0 \rangle = \frac{1}{\sqrt{2}} (|+-> - |->) \]
Thus we have constructed the three triplet states,

\[ \frac{1}{\sqrt{2}} ( |1s \ 2s \rangle - |2s \ 1s \rangle ) \otimes \left| S = 1, M_S = 0, \pm \rightrangle \]  

(14)

and the singlet state (symm. electrons, antisymm. spins),

\[ \frac{1}{\sqrt{2}} ( |1s \ 2s \rangle + |2s \ 1s \rangle ) \otimes \left| S = 0, M_S = 0 \rightangle \]  

(15)

More systematically, we could have obtained wave functions of the form \((11) \rightarrow (13)\) using formal angular momentum theory. The Slater determinant (Eq. 6) gives a result in the uncoupled basis set with \(L_i, \ m_{i}; \) and \(M_{i};\) for each electron; we then need to convert to a coupled basis by taking appropriate linear combinations to form eigenstates of \(L^2, \ L_z, \ S^2\) and \(S_z\).

In this case \(L = 0\), so we need worry only about spins, where we have,

\[ |S, M \rangle = (-1)^{M - S} \sum_{m_1, m_2} \sqrt{2S + 1} (S_1 \ S_2 \ S \ S_1 \ S_2 \ S_1 \ S_2 \ S_1 \ S_2) |s_1, m_1, s_2, m_2 \rangle \]

For example, to get the state with \(S = 1, M = 0\),

\[ |1/2 \ 1/2 \ 1/2 \ 0 \rangle = (-1)^0 \sum_{m_1, m_2} \sqrt{3} \left( \begin{array}{c} 1/2 \ 1/2 \ 1 \\ m_1 \ m_2 \ 0 \end{array} \right) |1/2 \ m_1, 1/2 \ m_2 \rangle \]

\[ \Sigma m = 0 \Rightarrow \text{nonzero only for} \ 
\begin{array}{c} m_1 \ m_2 \\ 1/2 \ -1/2 \ \\
\end{array} \ (\text{and this (a)}) \]

\[ \begin{array}{c} 1/2 \ 1/2 \ 1/2 \ 0 \\ \end{array} \]

\[ \text{or in our earlier notation,} \]

\[ = \frac{1}{\sqrt{2}} \left( |1/2 + 1/2 \ 1/2 - 1/2 \rangle \right) + \left| 1/2 - 1/2 \ 1/2 + 1/2 \right\rangle \]

\[ = \frac{1}{\sqrt{2}} \left( |1 \rightarrow + \ 1 \rightarrow - \rangle \right), \text{same as Eq. (12)} \]

In general, \(L\) requires the same sort of treatment also.
Notes:

1. If we "turn on" the previously ignored two-electron Coulomb terms, going beyond the central field approximation,
\[ H' = \sum \frac{e^2}{r_{ij}} - \langle \sum \frac{e^2}{r_{ij}} \rangle \quad (\text{ph. avg}) \]

the singlet states will have a different energy than the triplet states, since the spatial part of the wave function differs. This separation of the spin multiplets from one another is a consequence of the Coulomb interaction alone, and arises because the Pauli principle prevents two electrons with the same spin from occupying the same spatial region.

\[ \Rightarrow \text{triplet wave function} \to 0 \text{ as } \frac{1}{r_i} \to \frac{1}{r'_i}. \]

2. Notation: \( \frac{1}{5} \) or \( {^3S} \). Further, since in small atoms usually only one electron is excited, we use the shorthand form, \( 2\frac{1}{5} \) and \( 2\frac{3}{5} \) for \((1s)(2s)\frac{1}{5}, \text{ etc.}\).\n
3. Degeneracy: In the central field approximation, all states with the same \( L \) have the same energy. This degeneracy is broken in the next order of approximation -- electrostatic interactions separate levels with different \( S \) as above. Further, relativistic terms like \( \vec{l_i} \cdot \vec{s_i} \) cause a fine structure, with up to \( 2S + 1 \) sublevels having different values of \( F \), where \( F = L + S \).


The most obvious consequence of the Pauli principle is that there is a limit to the number of electrons that can have a given value of \( n \).

For a given \( n \), and \( l \), \( 2(2l+1) \) values of \( m_l \) and \( m_s \) are possible. This restriction gives rise to the shell model for atomic structure.

For \( l=0 \), s shell: 2 electrons (maximum)
\[ l=1, \quad p \text{ shell: 6} \]
\[ l=2, \quad d \text{ shell: 10} \]
\[ l=3, \quad f \text{ shell: 14} \]

As one moves along the periodic table, these shells are filled more or less in order, with the principal quantum number increasing for each row.

Thus for H we have 1s
He \( 1s^2 \)
Li \( (1s^2) 2s \) (usually just written 2s)
\( \uparrow \)
Be \( (1s^2) 2s^2 2p^2 \) (usually written \( 2s^2 2p^2 \))
\( \uparrow \)
B \( (1s^2) (2s^2) (2p^6) 3s \) (usually written 3s)
\( \uparrow \)
and so on.

The nonreactive rare gases He, Ne, Ar, Kr, Xe, Rn correspond to completely filled shells, as is well known.

C. \( LS \) coupling; Terms

We have so far implicitly assumed that \( L \) and \( S \) are "good quantum numbers," that is, that the Hamiltonian commutes with \( L^2 \) and \( S^2 \).