## REAL ATOMS – the shell model

The Hamiltonian is

$$H = \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} \right) + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{e^2}{r_{ij}}.$$

$r_i$ is the distance between electron $i$ and the nucleus, and $r_{ij}$ is the distance between electrons $i$ and $j$. Note that each electron pair $ij$ appears exactly once.

The $N$-electron Schrödinger equation cannot be solved analytically for $N > 1$. One may start with an approximate Hamiltonian, written as a sum of one-electron terms,

$$H^{(0)} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m}\nabla_i^2 + V(\vec{r_i}) \right].$$

The equation is then separated into one-electron equations,

$$\left[ -\frac{\hbar^2}{2m}\nabla_i^2 + V(\vec{r_i}) \right] \psi_{\epsilon_i}(\vec{r_i}) = E_{n_i l_i} \psi_{\epsilon_i}.$$

$\epsilon_i$ collects the quantum numbers $n_i l_i m_i m_{si}$. The energy depends on $n$ and $l$ (it is $l$-independent only for an exactly Coulombic $V$). The determinant $\Psi = |\psi_{\epsilon_1}\psi_{\epsilon_2}\cdots\psi_{\epsilon_N}|$ will be an antisymmetrized eigenfunction of $H^{(0)}$.

Various choices may be used for $V$. The choice of the actual one-electron interaction $V = -\frac{Ze^2}{r_i}$ is not very good. A central potential is normally used, which depends on $r$ and not on $\vec{r}$. The general expression is $V(r_i) = -\frac{Ze^2}{r_i} + V^{\text{eff}}(r)$, where the second term approximates the effect of interaction with the other electrons. The orbitals may be written as a radial function multiplied by a spherical harmonic and a spin part,

$$\psi_{\epsilon_i} = R_{n_i l_i}(r_i) Y_{l_i m_i}(\theta_i, \varphi_i) \chi_{\frac{1}{2}, m_{si}},$$

and the radial equation is

$$\left\{\frac{1}{r_i^2}\frac{d}{dr_i}\left(r_i^2\frac{d}{dr_i}\right)-\frac{l(l+1)}{r_i^2}+\frac{2m}{\hbar^2}[E-V(r_i)]\right\}R_{n_il_i}(r_i)=0.$$

The orbitals in atoms are $1s, 2s, 2p, \cdots$. The energy depends on $n$ and $l$ (only on $n$ in 1-electron atoms). The orbitals may be ordered by energy, and the electrons put in the lowest orbitals. This is the aufbau principle. For a given $n$, the energy goes up with $l$. This happens because the radial equation includes the centrifugal potential $l(l+1)/r^2$, which keeps electrons in high-$l$ orbitals further away from the nucleus. The distribution of electrons in the orbitals is called electron configuration, e.g. $1s^22s^22p^2$ for C and $1s^22s^22p^5$ for F. The configuration is not sufficient to describe the atom. Thus, carbon atom has three low-energy atomic levels with the configuration $1s^22s^22p^2$. To understand atomic structure we need to look at the various angular momenta in the atom.

## Angular momenta in the atom

Electron $i$ has an orbital angular momentum $\vec{L}_i$ and a spin angular momentum $\vec{S}_i$. All these momenta are coupled. The individual $\vec{L}_i$ do not commute with $H$. The coupling scheme which works best in light atoms is the $LS$ coupling,

$$\vec{L}\equiv\sum_{i=1}^{N}\vec{L}_i \quad \vec{S}\equiv\sum_{i=1}^{N}\vec{S}_i \quad \vec{J}\equiv\vec{L}+\vec{S}.$$

The first two couplings (creating $\vec{L}, \vec{S}$) are the most important. They lead to splitting of level energies which do not depend only on the interactions between magnetic moments. This is similar to the singlet-triplet splitting in the 2-electron model, which does not come from magnetic interactions. The coupling between $\vec{L}$ and $\vec{S}$ to form $\vec{J}$ is magnetic in nature, like the spin-orbit coupling in 1-e atoms, and in light atoms involves small energies (fine structure).

If spin-orbit coupling is ignored, the determinants $\Psi$ constructed of $N$ orbitals may be characterized by the quantum numbers $nLSM_LM_S$ (the last four numbers correspond to the operators $L^2, S^2, L_z, S_z$, and $n$ differentiates between functions with the same angular momentum numbers), or $nLSJM_J$, belonging to the operators $L^2, S^2, J^2, J_z$. Only the second set remains valid when SO coupling is included.

The angular momentum $z$ components are added algebraically. This gives

$$M_L = \sum_{i=1}^{N} m_{li} \qquad M_S = \sum_{i=1}^{N} m_{si}.$$

The determinants satisfy

$$L_z\Psi = M_L\hbar\Psi, \qquad M_z\Psi = S_z\hbar\Psi.$$

For two non-equivalent electrons ($n_1l_1 \neq n_2l_2$), one may simply add the $l$'s and $s$'s vectorially, giving

$$L = |l_1 - l_2|, \cdots, l_1 + l_2 \text{ and } S = |s_1 - s_2|, \cdots, s_1 + s_2.$$

For example, if the open shells are one $2p$ and one $3p$ electrons, the allowed values are $L = |1-1|, \cdots, 1+1 = 0, 1, 2$ and $S = |\frac{1}{2} - \frac{1}{2}|, \cdots, \frac{1}{2} + \frac{1}{2} = 0, 1$. All possible combinations of $L$ and $S$ are allowed, and we get 6 energy levels (called terms). The terms are denoted by ${}^{2S+1}L$, where $L$ is the letter corresponding to the spd orbital notation but written as a capital letter, and $2S+1$ is a number. The 6 terms resulting from $2s3s$ are therefore

$$\begin{array}{llllll} L=0 & S=0 & {}^1\mathrm{S} & L=0 & S=1 & {}^3\mathrm{S} \\ L=1 & S=0 & {}^1\mathrm{P} & L=1 & S=1 & {}^3\mathrm{P} \\ L=2 & S=0 & {}^1\mathrm{D} & L=2 & S=1 & {}^3\mathrm{D} \end{array}$$

Closed shells always have $L=0, S=0$, so that only open shells need be taken into account when determining the atomic level structure. The $1s^2 2s^2 2p3p$ excited configuration of the carbon atom will therefore have the six energy levels listed above. Note that these levels indeed exist and have different energies, even though the electron configuration is identical. The orbital picture is not sufficient to fully describe the atomic structure, although it gives the major features.

Finding the terms resulting from equivalent electrons is more complicated, since Pauli's exclusion principle does not allow many of the possible combinations. It is easy to see that the $2p3p$ configuration has 36 determinants $(6\times 6)$. A $2p^2$ configuration will only have 15 allowed determinants: the first electron can go into any of the 6 spinorbitals of $2p$; the 2nd electron is allowed into one of the 5 remaining spinorbitals; and since electrons are indistinguishable, we must divide by 2. It is easy to find the $M_L$ and $M_S$ value of each determinant (the sums of $m_{li}$ and $m_{si}$, respectively); the $L$ and $S$ values, needed to define the terms, are more difficult. A straightforward way is to classify the determinants by the known $M_L$ and $M_S$ values and put them in a table:

| $M_S$ | $M_L = 2$ | 1 | 0 | $-1$ | $-2$ |
|---|---|---|---|---|---|
| 1 | | $p_1\alpha p_0\alpha$ | $p_1\alpha p_{-1}\alpha$ | $p_0\alpha p_{-1}\alpha$ | |
| 0 | $p_1\alpha p_1\beta$ | $p_1\alpha p_0\beta$<br>$p_0\alpha p_1\beta$ | $p_1\alpha p_{-1}\beta$<br>$p_0\alpha p_0\beta$<br>$p_{-1}\alpha p_1\beta$ | $p_0\alpha p_{-1}\beta$<br>$p_{-1}\alpha p_0\beta$ | $p_{-1}\alpha p_{-1}\beta$ |
| $-1$ | | $p_1\beta p_0\beta$ | $p_1\beta p_{-1}\beta$ | $p_0\beta p_{-1}\beta$ | |

To find the terms, we only need to know how many determinants appear in each box:

| $M_L =$ | 2 | 1 | 0 | $-1$ | $-2$ |
|---|---|---|---|---|---|
| $M_S = 1$ | | 1 | 1 | 1 | |
| 0 | 1 | 2 | 3 | 2 | 1 |
| $-1$ | | 1 | 1 | 1 | |

We now take an extreme box, meaning that no functions appear above it or to its left. For example, $p_1\alpha p_0\alpha$ in the (1,1) box. It is easily seen that the function must belong to an $L = 1, S = 1$ term: obviously, it cannot have lower $L$ or $S$; if it had higher $L$, say $L = 2, S = 1$, there must have been a function with $M_L = 2, M_S = 1$. We therefore know that this function belongs to a $^3$S term, with $L = 1, S = 1$. This term has nine components, since $M_L = 1, 0, -1$ and $M_S = 1, 0, -1$, which sit in the appropriate boxes of the table. We do not know at this stage the form of all these functions, but we can drop one function from each of these boxes in the table, leaving

| $M_L =$ | 2 | 1 | 0 | $-1$ | $-2$ |
|---|---|---|---|---|---|
| $M_S = 1$ | | 0 | 0 | 0 | |
| 0 | 1 | 1 | 2 | 1 | 1 |
| $-1$ | | 0 | 0 | 0 | |

We repeat the procedure. The extreme function now sits in the (2,0) box, giving an $(L = 2, S = 0)$ or $^1$D term. Dropping the five functions belonging to this term, with $M_L = 2, 1, 0, -1, -2$ and $M_S = 0$, only one function is left, in the (0,0) box, which gives a $^1$S term. The $p^2$ configuration therefore gives rise to three terms, $^3$P, $^1$D, and $^1$S. This is indeed the situation in the spectrum of the carbon atom. The ground state is $^3$P, the next state is $^1$D 1.26 eV higher, and the third is $^1$S, 2.68 eV above the ground state. Note the large differences occurring between states which belong to the same $1s^2 2s^2 2p^2$ configuration. The fourth state of carbon belongs to the $1s^2 2s^1 2p^3$ configuration. It is a $^5$S state, 4.18 eV above the ground state.

The $LS$ terms may split (fine structure) because of the spin-orbit coupling. In contrast to the large differences between different terms of the same configuration, caused by different forms of the wavefunctions, the fine structure is caused by magnetic interactions, and is small for light elements. It is easy to understand the splitting by coupling $\vec{J} = \vec{L} + \vec{S}$. The $J$ values are given by vector addition of $L$ and $S$,

$$J = |L - S|, \cdots, L + S.$$

Thus the $^3$P term $(L = 1, S = 1)$ has $J = 0, 1, 2$, giving three sublevels denoted by $^3\mathrm{P}_0$, $^3\mathrm{P}_1$, $^3\mathrm{P}_2$, with energies 0, 0.0020 and 0.0054 eV, respectively. The other two states can have only one $J$ value, and are denoted by $^1\mathrm{D}_2$ and $^1\mathrm{S}_0$.

Hund's rules for level order:

1. The term with highest $S$ is lowest. We saw an example in the one-dimensional 2-fermion model.
2. Among terms with highest $S$, the term with highest $L$ is

lowest.

3. Within the same term, a sublevel with lower $J$ is lower if the open shell is less than half full, higher if the open shell is more than half full. About shells which are exactly half full (e.g. $p^3$), the lowest term always has $L = 0$ and maximum $S$, so there is no splitting; the higher terms have small splittings.

These rules work very well to determine the lowest level, less well for ordering the higher levels. In the carbon atom, we indeed get the order

$$ {}^3\mathrm{P}_0 < {}^3\mathrm{P}_1 < {}^3\mathrm{P}_2 < {}^1\mathrm{D}_2 < {}^1\mathrm{S}_0. $$

If the open shells involve some equivalent and some non-equivalent electrons (e.g. $2p^2 3s$), we use the procedure outlined above to find the terms for each group of equivalent orbitals, then combine the terms by vector addition. Combining the $^3$P of $p^2$ ($L = 1, S = 1$) with the $s$ electron ($l = 0, s = \frac{1}{2}$) gives $L = 1, S = \frac{3}{2}, \frac{1}{2}$ and the levels $^4$P and $^2$P. We also have to combine the $^1$D term with $s$, getting $^2$D, and the $^1$S with $s$, giving $^2$S. In all, the $2p^2 3s$ configuration will yield 4 terms: $^4$P, $^2$D, $^2$P and $^2$S.

## Functions

Above we found the terms resulting from arbitrary electron configurations. In order to determine energies and other properties, we need the wavefunctions (combinations of determinants) which belong to the various terms. It will normally suffice to know just one function of each term. Here we will see how this is done.

Going back to the table of determinants, we can immediately find functions for two of the terms. For the $^3$P we may take $p_1\alpha p_0\alpha$, which sits alone in the (1,1) box; for the $^1$D term we have $p_1\alpha p_1\beta$ from the (2,0) box. More difficult is the $^1$S term, since the only box where it is represented is (0,0), which contains 3 determinants. We must find the combinations belonging to $^3$P and $^1$D in this box; the orthogonal combinations will be the $^1$S function.

For the $^3$P term, $^3\mathrm{P}(0,1) = p_1\alpha p_{-1}\alpha$. Applying $S^-$ (and ignoring $\hbar$, which cancels out on both sides)
$S^-\,{}^3\mathrm{P}(0,1) = \sqrt{2}\,{}^3\mathrm{P}(0,0)$,
$S^- p_1\alpha p_{-1}\alpha = (S_1^- + S_2^-)p_1\alpha p_{-1}\alpha = p_1\alpha p_{-1}\beta + p_1\beta p_{-1}\alpha$,
giving $^3\mathrm{P}(0,0) = \sqrt{\frac{1}{2}}(p_1\alpha p_{-1}\beta + p_1\beta p_{-1}\alpha)$.
The second determinant does not appear in the table; however, it is just the $p_{-1}\alpha p_1\beta$ determinant with a minus sign. We therefore write
$^3\mathrm{P}(0,0) = \sqrt{\frac{1}{2}}(p_1\alpha p_{-1}\beta - p_{-1}\alpha p_1\beta)$.
Note:

- When applying $S^-$ to $p_1\alpha p_{-1}\alpha$ we must use it as $S_1^- + S_2^-$.
- The normalization factor involved in applying $L^-$ is given by $\sqrt{(l+m)(l-m+1)}$, where $l, m$ correspond to the particular angular momentum used. Thus, application of $S^-$ to $^3\mathrm{P}(0,1)$ requires $l = S = 1$, $m = M_S = 0$, giving a factor of $\sqrt{2}$, and application of $S_1^-$ to $p_1\alpha$ means $l = s = \frac{1}{2}$, $m = m_s = \frac{1}{2}$, with the factor 1.
- Correct application results in a normalized function.

Looking now at the $^1$D term, we start from $^1\mathrm{D}(2{,}0)=p_1\alpha p_1\beta$

and apply $L^-$ twice to get to the (0,0) box.
$L^-$ $^1$D(2,0)=2 $^1$D(1,0)
$(L_1^- + L_2^-)p_1\alpha p_1\beta = \sqrt{2}(p_0\alpha p_1\beta + p_1\alpha p_0\beta)$
$^1$D(1,0)=$\sqrt{\frac{1}{2}}(p_0\alpha p_1\beta + p_1\alpha p_0\beta)$.
And again,
$L^-$ $^1$D(1,0)=$\sqrt{6}$ $^1$D(0,0)
$(L_1^- + L_2^-)\sqrt{\frac{1}{2}}(p_0\alpha p_1\beta + p_1\alpha p_0\beta) = (p_{-1}\alpha p_1\beta + p_0\alpha p_0\beta + p_0\alpha p_0\beta + p_1\alpha p_{-1}\beta)$
$^1$D(0,0)=$\sqrt{\frac{1}{6}}(p_{-1}\alpha p_1\beta + 2p_0\alpha p_0\beta + p_1\alpha p_{-1}\beta)$
We now need to find the combination of the three (0,0) determinants which is orthogonal to the two combinations we have. If we write this (unnormalized) combination as $p_{-1}\alpha p_1\beta + a \times p_0\alpha p_0\beta + b \times p_1\alpha p_{-1}\beta$, its overlap with the $^3$P(0,0) function is $1 - b$. The overlap with the $^1$D(0,0) function is $1 + 2a + b$. Both overlaps must vanish, giving $b = 1,\ a = -1$ so the desired function is (after normalization)
$^1$S(0,0)=$\sqrt{\frac{1}{3}}(p_{-1}\alpha p_1\beta - p_0\alpha p_0\beta + p_1\alpha p_{-1}\beta)$.

In this way we can find the atomic levels and corresponding functions. We can then proceed to calculate energies (including ionization potentials, excitation energies, electron affinities) and other properties (transition probabilities, spectrum, quadrupole moments etc.) These calculations are approximate, but can reach very high accuracy with sophisticated models and extensive computations.