

Structures of many-electron atoms

For systems with more than one electron, we cannot solve the Schrödinger equation for exact solutions. The reason will be discussed later. However, in this case we make the orbital approximation, by assigning each electron to occupy its own orbital, so that we can write the many-electron wavefunction as

$$\psi(r_1, r_2, \dots) = \psi_a(r_1) \psi_b(r_2) \dots$$

where the individual orbitals $\psi_a(r_i)$ specified by n, l , and m_l resemble to the hydrogenic orbitals but with an effective nuclear charge accounting for all the other electrons in the system.

The assignment of electrons to orbitals is called the electron configuration.

One important rule we need to keep in mind in assigning electrons to orbitals is the Pauli exclusion principle which states

No two electrons with the same quantum numbers, n, l, m_l , and s can occupy the same space.

Note: This is only true for half-integral spin particles known as fermions (electrons, for example) but not true for integral-spin particles, known as bosons.

Self-Consistent field theory (Hartree-Fock method)

For N -electron atom, the Hamiltonian is given by

$$\begin{aligned} \hat{H}_c &= -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \left(\frac{ze^2}{4\pi\epsilon_0} \right) \frac{1}{r_i} + \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r_{ij}} \\ &= \sum_{i=1}^N \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \left(\frac{ze^2}{4\pi\epsilon_0} \right) \frac{1}{r_i} + \sum_{j \neq i}^N \frac{1}{2} \left(\frac{e^2}{4\pi\epsilon_0} \right) \frac{1}{r_{ij}} \right\} \end{aligned}$$

kinetic energy
of the \bar{e}_i

electron-nucleus
attraction

electron-electron
repulsion term.

We hope to be able to separate the Hamiltonian into N independent terms then solve each term individually. However, due to the electron-electron repulsion term which indicates the energy of the i electron depend on the positions of all other electrons in the system. As a consequence, the Schrödinger equation

$$\hat{H}_c \Psi(r_1, r_2, \dots) = E \Psi(r_1, r_2, \dots)$$

is inseparable.

Well, when we cannot solve for exact solutions, we can start to make approximations to get the approximate solutions.

1) First, we approximate the electron-electron repulsion term, $\sum_{j \neq i} \frac{1}{r_{ij}}$, by an effective potential $V_{\text{eff}}(r_i)$ which depends only on the position of the electron i . This is known as the central-field approximation. \hat{H}_e is now separable.

$$V_{\text{eff}}(r_i) = \sum_{j \neq i} \int \frac{\rho_j^2}{r_{ij}} d^3r_j$$

2) Solve the Schrödinger equation for the electron i to obtain the orbital ψ_i and orbital energy E_i .

$$-\frac{\hbar^2}{2m} \nabla_i^2 \psi_i - \left(\frac{ze^2}{4\pi\epsilon_0} \right) \frac{1}{r_i} \psi_i + V_{\text{eff}}(r_i) \psi_i = E_i \psi_i$$

3) The orbital ψ_i is then used to calculate the average repulsion as in the step 1 but for another electron, say the j electron.

The whole procedure is repeated until the orbitals and orbital energies are converged, or are not too different from one cycle to the next. This is also known as the self-consistent procedure.

penetration and shielding

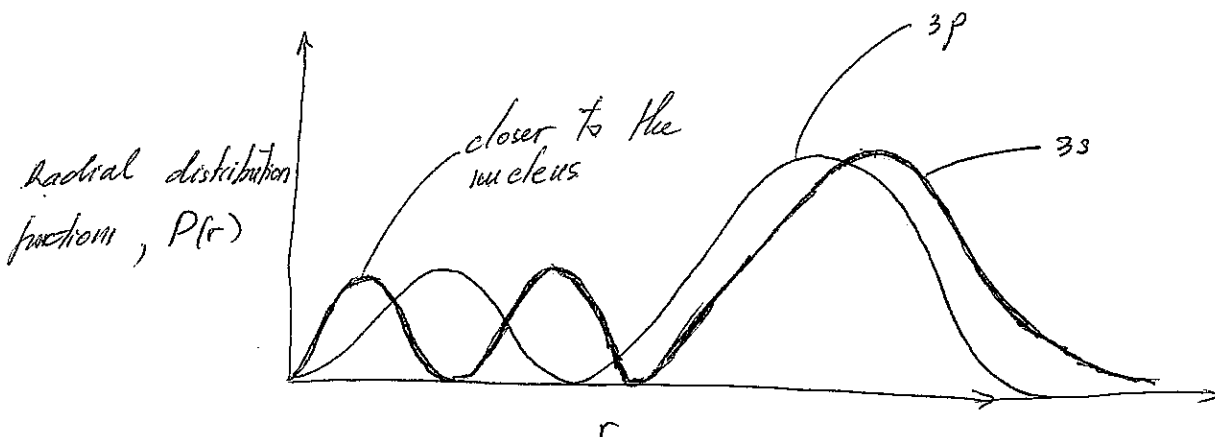
Recall that for the hydrogenic atoms, the energy levels depend only on n , thus orbitals with different angular quantum numbers l are degenerate, $E_{2s} = E_{2p}$, $E_{3s} = E_{3p} = E_{3d}$, etc. This is no longer true for many-electron atoms where s electrons generally lie lower in energy than p electrons, and p electrons lie lower in energy than d electrons for a given shell (n quantum number).

$$E_{2s} < E_{2p}$$

$$E_{3s} < E_{3p} < E_{3d}$$

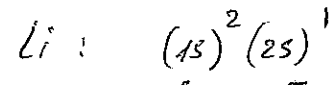
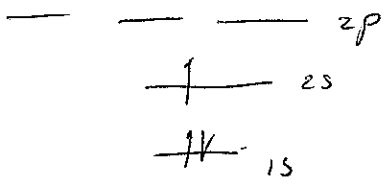
why?

An electron in a many-electron atom experiences an average repulsion from all other electrons in the system. We can also think of that as the other electrons shield the nuclear charge, thus the electron experiences an effective nuclear charge. So electrons which experience less shielding have larger Z_{eff} values, thus lower energies.



since 3s electron has greater penetration through the inner shell and gets closer to the nucleus than the 3p electron, thus it experiences less shielding, or has larger effective nuclear charge, and consequently, it has lower energy.

So for Li atom (3 e⁻),



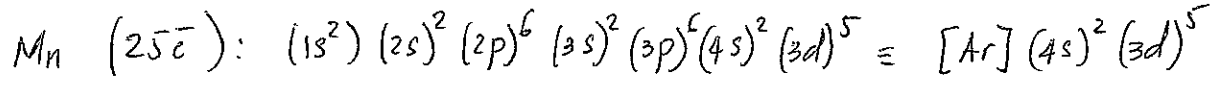
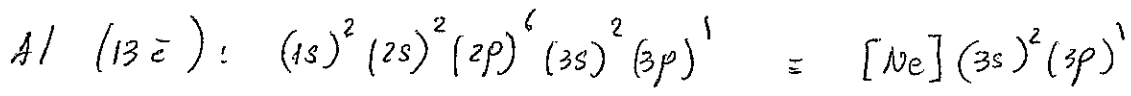
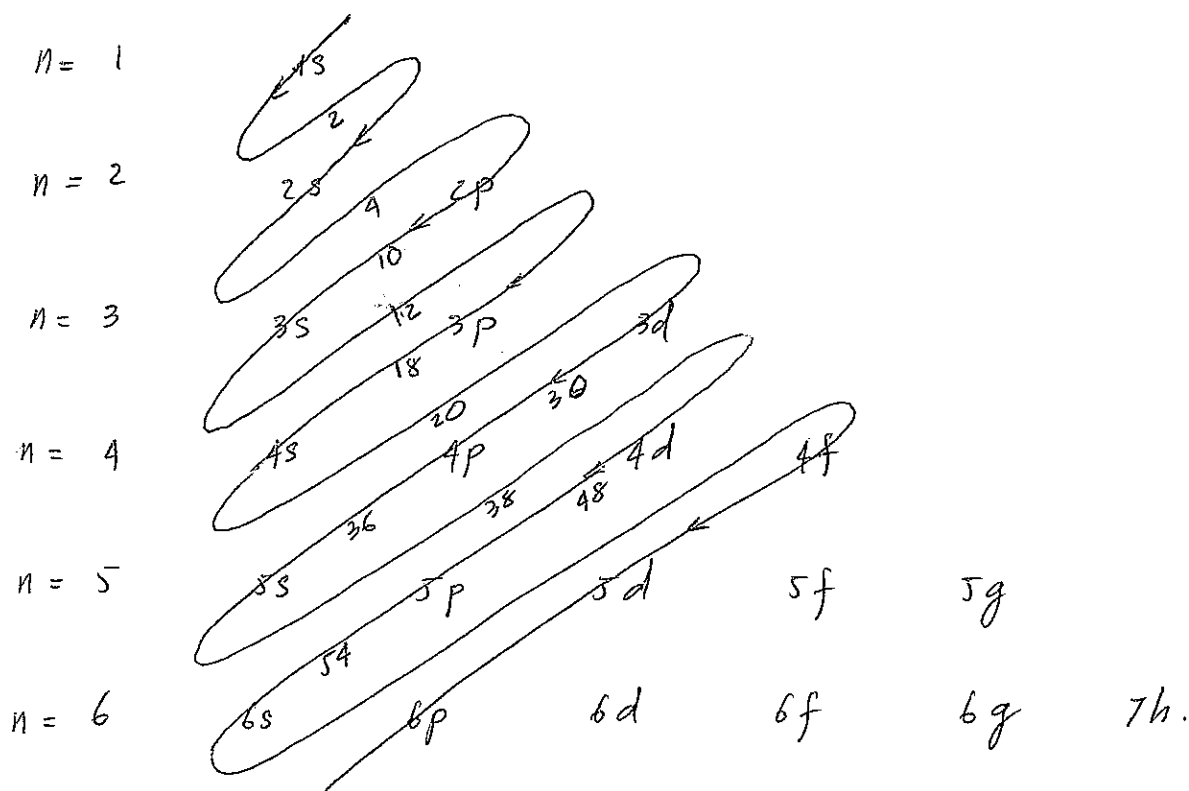
core electrons
(electrons in the inner shells)

valence electrons
(electrons in the outermost shell)

Remember: we can only put 2 e⁻ in each orbital due to the Pauli exclusion principle.

A general procedure for assigning electrons to orbitals is known as the Aufbau principle

$l =$	0	1	2	3	4	5
	s	p	d	f	g	h

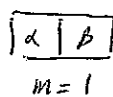
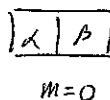
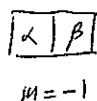


Note: The Aufbau principle gives only an approximate order of energies of the individual orbitals. To get more accurate answers we need to solve the many-electron Schrödinger equation.

Example 1: Consider a carbon atom with its electrons in the lowest-energy available orbitals to give the electron configuration $(1s)^2(2s)^2(2p)^2$.

We need to consider only the two $2p$ electrons.

Let first count how many different arrangements can the two $2p$ electrons have



6 slots for 2 identical \bar{e}

6 possibilities for the 1st \bar{e}
5 possibilities for the 2nd \bar{e} } $\Rightarrow 6 \times 5 = 30$ possibilities

but the 2 \bar{e} are identical, the ordering of \bar{e} makes no different $\Rightarrow \frac{1}{2}(30) = \boxed{15}$ possibilities

General: For n slots and m identical balls, there are

$$\frac{n!}{m!(n-m)!} \quad \text{possibilities for arranging}$$

m balls in n slots.

For 2 $2p$ electrons,

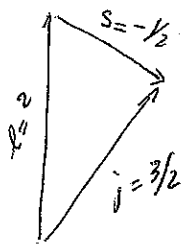
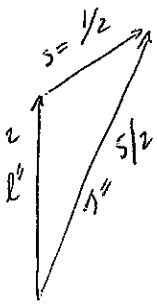
$$\frac{6!}{2!(6-2)!} = \frac{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot 6}{2 \times (1 \cdot 2 \cdot 3 \cdot 4)} = \frac{5 \times 6}{2} = \boxed{15}$$

For 2 electrons, there are two possibility for their spins,
(a) both parallel spins (b) opposite spins

Spectra of Complex atoms

Similar to the problem in solving the Schrödinger equation for many-electron atoms, the spectra of atoms become more complicated as the number of electron increases. As mentioned earlier, a moving charge will generate a magnetic field, thus the electron intrinsic spin motion generates a spin magnetic moment and its orbital motion around the nucleus generate a different magnetic moment called orbital magnetic moment. These two moments are coupled together. This coupling is known as the spin-orbit coupling. This can be represented by the vector representation of the total angular momentum of an electron, represented by the quantum number j and m_j .

Example an electron in $l=2$ state, what are the possible values of j .



Since an electron has two possible values of the spin, $s = \pm 1/2$.

\therefore Two possible values of j , $j = 5/2, 3/2$

Term symbols

The angular momentum of a many-electron atom is quantized, just as the angular momentum of the one-electron hydrogen atom. The angular momentum of a particular state of an atom is indicated by the term symbol for that state.

spin multiplicity $\rightarrow 2S+1$

J \rightarrow total orbital angular momentum

J \rightarrow total angular momentum
(spin and orbital).

Total orbital angular momentum: is the net orbital angular momentum from all electrons in the atom. It is quantized and is denoted by the L quantum number.

$$L = 0, 1, 2, 3, \dots$$

$$S, P, D, F, \dots$$

Note capital letters are for atoms, lower case letters, s, p, d, f, are for a single electron.

The total orbital angular momentum of two electrons with the individual orbital angular momentum quantum number l_1 and l_2 is

$$L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

For 2 p electrons, $l_1 = l_2 = 1$

$L = 2, 1, 0 \Rightarrow D, P, S$ terms.

Important note: A filled (closed) shell has zero total orbital angular momentum because the sum of all individual angular momentum in a shell is zero. Thus, we need to consider only the open shell when determining the term symbols. In other words, term symbols arise from different arrangements of electrons in the partially filled shell.

C: $(1s)^2(2s)^2(2p)^2 \rightarrow$ only 2 2p electrons contribute to the total angular momentum of the atom.

K: $(1s)^2(2s)^2(2p)^6 3s \rightarrow [Ne](3s)^1 \rightarrow$ only the 3s electron is needed in determining the term symbol.

Spin multiplicity: Similar to the total orbital angular momentum L , the total spin angular momentum, S , is given by

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

since $s_1 = s_2 = 1/2 \Rightarrow S = 0, 1$

If there is a third electron, the total spin angular momentum can be obtained by coupling the third electron spin to each of the s values for the first two spins.

$$S = \frac{3}{2}, \frac{1}{2} \quad \text{and} \quad S = \frac{1}{2}.$$

Spin multiplicity is the degeneracy level of the total spin S , and is given by $(2S+1)$.

$$\begin{array}{llll} S = 0 & \rightarrow & 2S+1 = 1 & \rightarrow \text{singlet state} \\ S = \frac{1}{2} & \rightarrow & 2S+1 = 2 & \rightarrow \text{doublet state} \\ S = 1 & \rightarrow & 2S+1 = 3 & \rightarrow \text{triplet state.} \end{array}$$

The total angular momentum:

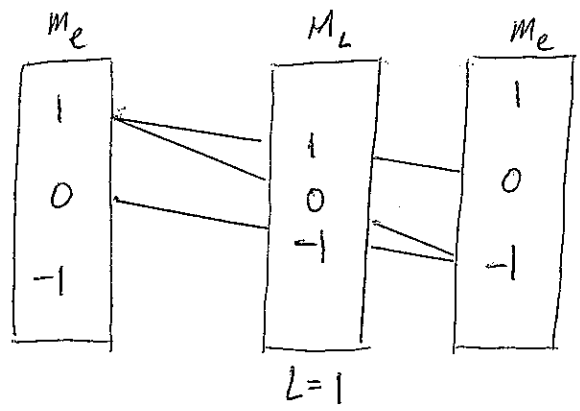
Similar to the spin-orbit coupling of a single electron which gives rise to the j quantum number, the spin-orbit coupling of all \bar{e} in an atom gives rise to the J quantum number. If such coupling is weak as in light atoms, the J values are integer or half-integer resulting from vector addition of L and S .

$$J = L+S, L+S-1, \dots, |L-S|$$

Let consider a couple of examples to show how one can obtain terms resulting from the contribution of two or more valence electron.

Case of two parallel spins

Electron #1	Atom	Electron #2
$n=2$		$n=2$
$l=1, s=1/2$		$l=1, s=1/2$



$S = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1$

$J = L + S, \dots, |L - S| = 2, 1, 0$

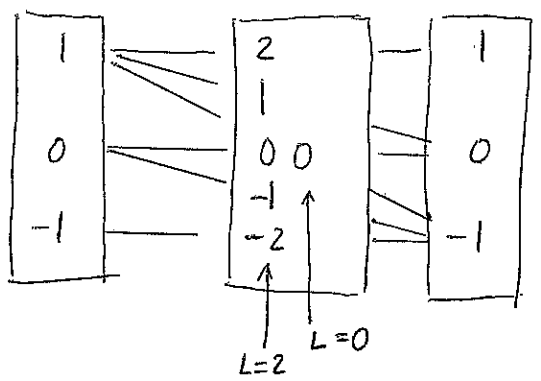
\therefore ${}^3P_2, {}^3P_1, {}^3P_0$ terms

Due to the Pauli exclusion principle, for electrons with the same $n, l,$ and s values, they cannot have the same m_l values.

Note: Electrons are indistinguishable thus different numbering of the electrons does not produce different states.

Case of two opposite spins

Electron #1	Atom	Electron #2
$n=2$		$n=2$
$l=1, s=1/2$		$l=1, s=-1/2$
m_l	M_L	m_l



$S = s_1 + s_2 = \frac{1}{2} - \frac{1}{2} = 0$

For $L=2, S=0$

$\Rightarrow J=2$

\therefore 1D_2

For $L=0, S=0 \Rightarrow J=0$

\therefore 1S_0

Note: A level with $L, S,$ and J specified has a degeneracy of $(2J+1)$.

The p^2 configuration gives

	3P_2	3P_1	3P_0	1D_2	1S_0	
*states.	5	3	1	5	1	\Rightarrow total of 15 states

✓ check.

Hund's rules

(a) For a given electron configuration, terms with the larger S has lower energy.

$$({}^3P_2, {}^3P_1, {}^3P_0) < ({}^1D_2, {}^1S_0).$$

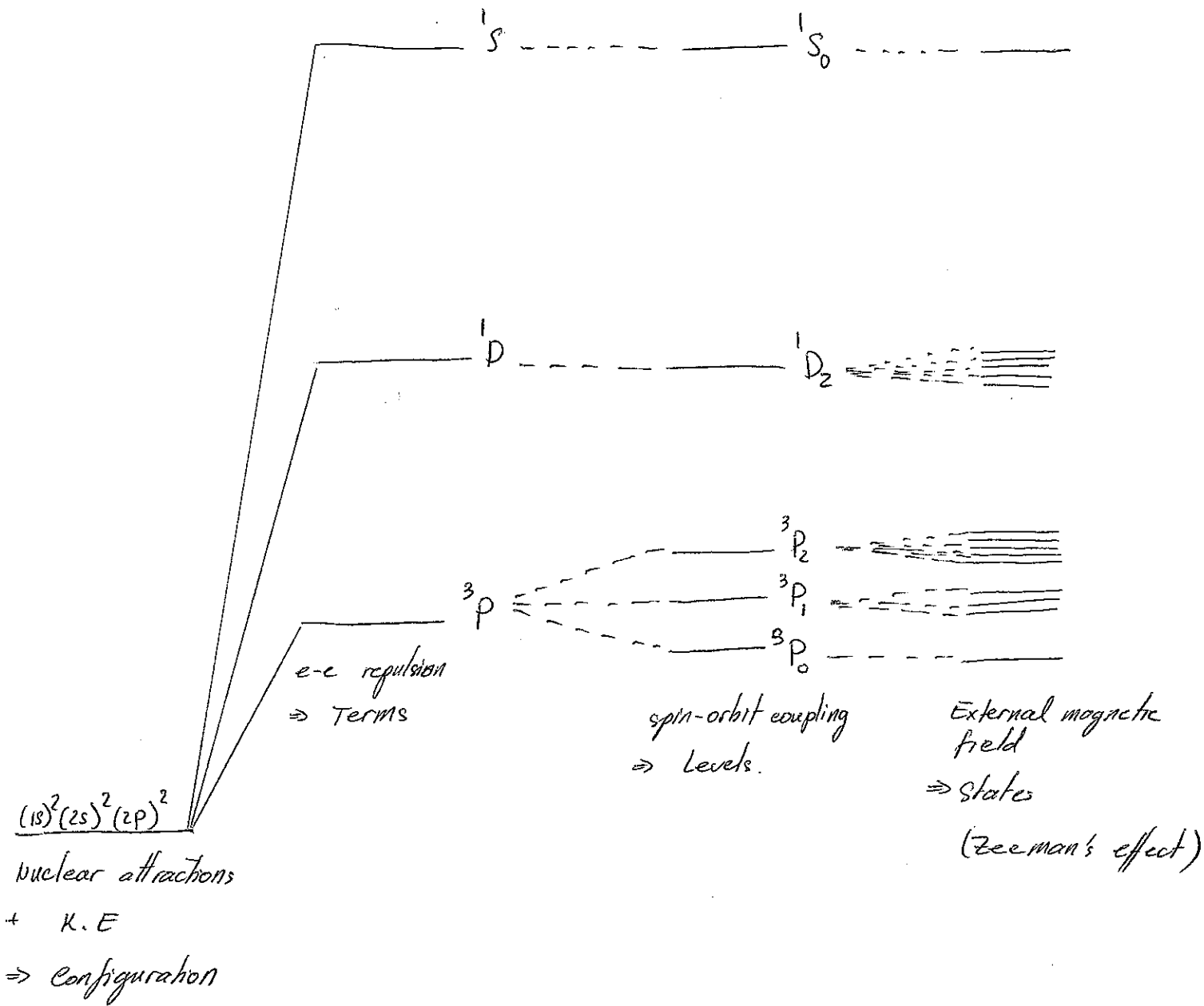
(b) subsequently, for a given S , term with the larger L has lower energy

$$({}^3P_2, {}^3P_1, {}^3P_0) < {}^1D_2 < {}^1S_0$$

(c) For a given L, S arising from electrons in a single subshell (i.e. same n and l), the smaller J lies lower in energy if the sub-shell is less than half-filled; the larger J lies lower in energy if the sub-shell is more than half-filled.

$${}^3P_0 < {}^3P_1 < {}^3P_2 < {}^1D_2 < {}^1S_0$$

Summary for the carbon ground state given by the $(1s)^2(2s)^2(2p)^2$ electron configuration.



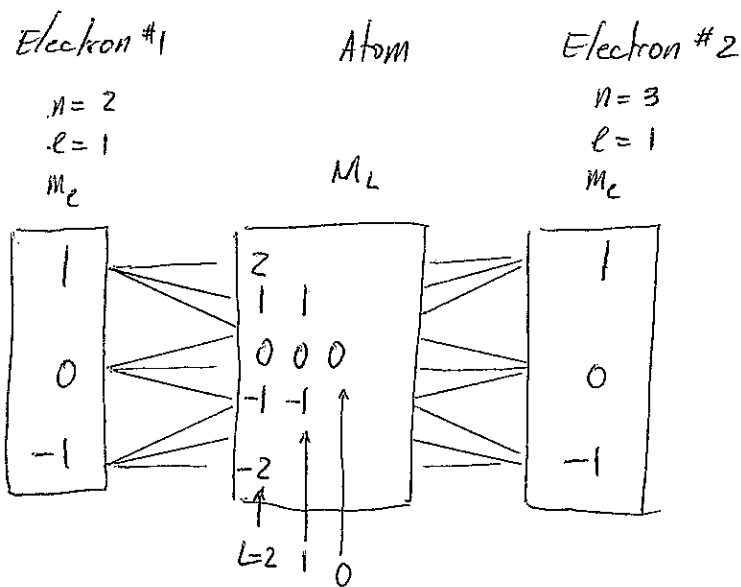
Example 2: Now let consider the excited state of the carbon atom with its electron configuration given by $(1s)^2 (2s)^2 (2p)^1 (3p)^1$.

Again we need to consider only the $(2p)(3p)$ valence electrons. Since the two e^- have different principal quantum number n , they can have all possible values of m_l and s .

$n=3$, $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m_l = -1$ $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m = 0$ $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m = 1$ 6 slots, one $e^- \Rightarrow$ 6 possibilities.

$n=2$ $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m = -1$ $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m = 0$ $\begin{array}{|c|c|} \hline & \\ \hline \end{array}$ $m = 1$ 6 slots, one $e^- \Rightarrow$ 6 possibilities.

\Rightarrow total of $6 \times 6 = 36$ possibilities



$s = 0, 1$ (9 possibilities for 2 e^-).

3D 1D 3P 1P 3S 1S

* states: $3 \times 5 + 1 \times 5 + 3 \times 3 + 1 \times 3 + 3 \times 1 + 1 \times 1 = 36$ states
 ✓ check.

From Hund's rules: ${}^3D < {}^3P < {}^3S < {}^1D < {}^1P < {}^1S$

note the third Hund's rule is not applicable since $n_1 \neq n_2$.

3D has $L=2, S=1 \Rightarrow {}^3D_3, {}^3D_2, {}^3D_1$

3P has $L=1, S=1 \Rightarrow {}^3P_2, {}^3P_1, {}^3P_0$

3S has $L=0, S=1 \Rightarrow {}^3S_1$

1D has $L=2, S=0 \Rightarrow {}^1D_2$

1P has $L=1, S=0 \Rightarrow {}^1P_1$

1S has $L=0, S=0 \Rightarrow {}^1S_0$

short cut:

For electrons with different n quantum numbers, or l quantum numbers, all possible terms can arise.

For example: $(2p)(3p)$.

$l_1 = 1, l_2 = 1 \Rightarrow L = 2, 1, 0 \Rightarrow D, P, S$ terms.
 $S = 1, 0$ for spin.

$\Rightarrow \therefore {}^3D, {}^1D, {}^3P, {}^1P, {}^3S, {}^1S$ terms.

Selection rules:

As mentioned earlier, the selection rule arises from the conservation of the total angular momentum during a transition, and from the fact that photon has an intrinsic spin of 1.

The same rule is applied for atoms, however it is simpler to express it in terms of the term symbols.

$$\Delta S = 0 \quad \rightarrow \text{since photon does not affect the spin.}$$

$$\Delta L = 0, \pm 1 \quad \rightarrow \text{results from } \Delta l = \pm 1$$

$$\Delta J = 0, \pm 1 \quad \rightarrow \text{but } J_1 = 0 \text{ cannot go to } J_2 = 0$$

Example.

$${}^2P_{3/2} \rightarrow {}^2S_{1/2} \quad \Delta L = -1, \Delta J = -1 \quad (\text{allowed}).$$

$${}^1D_2 \not\rightarrow {}^3P_1 \quad \Delta S = 2 \quad (\text{forbidden}).$$