

# Multi-Electron Atoms

## The Hamiltonian and the Central Field Approximation

Assuming we can make the same non-relativistic assumptions for multi-electron atoms as for two and one electron atoms, the Hamiltonian for these atoms is:

$$\hat{H} = \sum_j \frac{-\hbar^2}{2m} \nabla_j^2 + \sum_i \frac{-Ze^2}{4\pi\epsilon_0 |\mathbf{r}_i|} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

This is very hard to solve, even computationally. So we will make some simplifying assumptions. One assumption is that we can separate the electron-electron term into the central field potentials associated with each electron and a component which is the difference between the true situation and the approximate potential:

$$\hat{H} = \sum_j \left[ \frac{-\hbar^2}{2m} \nabla_j^2 + U(|\mathbf{r}_j|) \right] + \hat{H}_p \quad \text{where:}$$

$$\hat{H}_p = - \sum_j U(|\mathbf{r}_j|) + \left( \sum_i \frac{-Ze^2}{4\pi\epsilon_0 |\mathbf{r}_i|} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right)$$

We will treat the extra term  $\hat{H}_p$  as a perturbation.

If we know  $U(|\mathbf{r}|)$  this becomes much easier to solve, especially since the central field potentials are spherically symmetric so separation of variables is possible.

## Self-Consistent Atomic Orbital Calculations

So how do we work out  $\psi$ ? We use a technique in which we determine new "improved" potentials using the previous generation potential. This is a self-consistent solution and converges to the true solution.

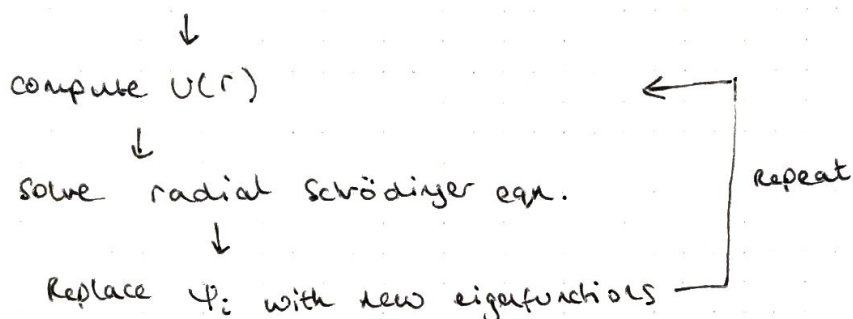
We determine  $U(\underline{r}_j)$  the spherical potential by effectively using a spherically averaged version of the classical e,e potential:

$$U(\underline{r}_j) = \frac{-Ze^2}{4\pi\epsilon_0|\underline{r}_j|} + \left\langle \sum_{i \neq j} \int \frac{e^2}{4\pi\epsilon_0|\underline{r}_j - \underline{r}_i|} |\Psi_i|^2 dV_i \right\rangle$$

- the triangle brackets indicate the average over angles  $\Theta, \varphi$

This method is called the Hartree method:

Initial guess for wavefunction  $\Psi_i(\underline{r})$



But the Hartree method does not take into account particle-exchange symmetry. With the Hartree-Fock method, we include the Pauli exclusion principle by building a wavefunction which is antisymmetric to particle exchange no matter which pair of electrons is exchanged. This is most easily done using the Slater determinant

$$\Psi(r_1, r_2, r_3, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Psi_1(r_1) & \Psi_1(r_2) & \dots & \Psi_1(r_N) \\ \Psi_2(r_1) & \Psi_2(r_2) & & \vdots \\ \vdots & & \ddots & \\ \Psi_N(r_1) & \dots & \dots & \Psi_N(r_N) \end{vmatrix}$$

Let's consider the case of the simplest set of multi-electron atoms, the alkali metal atoms.

## Aufbau Principle

The aufbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.

n \ l	0	1	2	3	4
1	1s				
2	2s	2p			
3	3s	3p	3d		
4	4s	4p	4d	4f	
5	5s	5p	5d	5f	5g

direction electrons fill up in

So this shows us that the order is

1s 2s 2p 3s 3p 4s 3d 4p

So 4s comes before 3d since it has lower energy.

Remember, each orbital can take 2 electrons

## Alkali Metals

The alkali metals are considered to be the simplest multi-electron atoms after helium because the highest energy electron is found in an orbital where it is most of the time the furthest electron from the nucleus. As we discussed with Helium, this electron experiences only a potential which is that of a nucleus with charge reduced by the number of electrons inside the outer electron. i.e., the other electrons have a "screening" effect. So the outer electron experiences a potential which is like that of a single positive charge at the nucleus, making it have Hydrogen-like states.

The energy levels of sodium are well approximated by the formula:

$$E_{n,l} = - \frac{R_y}{(n - \delta_l)^2}$$

where  $R_y$  is Rydberg energy  
and  $\delta_l$  is called quantum defect.

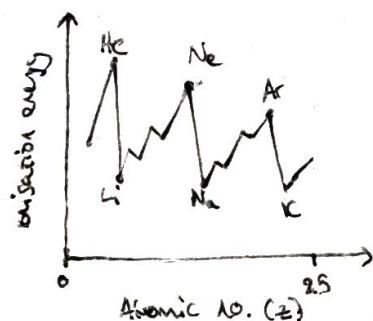
For sodium,  $\delta_l$  is: 1.35 for s states, 0.86 for p states, 0.01 for d states and effectively 0 for higher angular momenta.

The quantum defect term is due to taking into account the short amount of time an electron is close to the nucleus when orbiting. During this time, the electron encounters a much lower potential than if it was orbiting a hydrogen atom, due to all the other electrons outside it. This effect is captured using the quantum defect.

## Periodic Table

In the periodic table, elements are grouped by their electron configurations, the list of single electron orbitals which make it up. For example, the alkali metals are characterised by having a single outermost electron in a  $s$  orbital.

There are a number of trends in the periodic table, but perhaps the most important is ionisation energy. The <sup>first</sup> ionisation energy against atomic number plot is shown:



You will notice the noble gases (elements with filled  $p$  orbitals) are hardest to ionise and the alkali metals (elements with single  $s$  orbital) are easiest to ionise.



## Fine Structure of Multi-Electron Atoms

Now let's try and improve our model of multi-electron atoms by including the non-central component of the electron-electron interaction and a spin-orbit correction. The perturbation hamiltonians are:

$$\hat{H}_{\text{non-central}} = - \sum_j U(|\zeta_j|) + \left( \sum_i \frac{-Ze^2}{4\pi\epsilon_0 |\zeta_i|} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 |\zeta_i - \zeta_j|} \right)$$

$$\hat{H}_{\text{spin-orbit}} = \sum_j \xi_j(|\zeta_j|) \hat{L}_j \cdot \hat{S}_j$$

where the indices label the electrons.

The two perturbations above break the degeneracy of the modes in different ways, so the qualitative nature of the states obtained from perturbation theory is dependent on the relative strength of the two perturbations.

If one of the perturbations is dominant, then we solve by first treating the strong perturbation and determining new eigenstates and eigenenergies for the original hamiltonian plus the strong perturbation, and then treat the second perturbation as a perturbation of the new eigenstates and eigenenergies.

It turns out the non-central perturbation is more important in small  $Z$  atoms and the spin-orbit perturbation is more important in large  $Z$  atoms.

Interestingly, complete orbitals have 0 contribution to energies. In the spin-orbit case, this is because each spin up is cancelled out by a spin down. For non-central, it's because complete orbitals have a spherical charge distribution, so don't have a non-central potential.

## LS or Russell-Saunders Coupling

This is the case when the non-central perturbation is dominant. We need to work out which sets of degenerate eigenstates diagonalise the matrix representing the hamiltonian. We know that the eigenstates that do this will be eigenstates of an observable (and the perturbation hamiltonian) that commutes with the perturbation hamiltonian. We will use this fact to determine the correct basis set of wavefunctions. We know that if we rotate the whole atom with all its electrons, the problem is still symmetric. This symmetry means that the total orbital angular momentum squared is conserved as its  $z$  component, i.e.  $L$  and  $M_L$  are good quantum numbers. A similar argument is used to show the total spin quantum number  $S$  and the quantum number associated with the  $z$  component of spin are good quantum numbers.

So  $L$  and  $S$  are good quantum numbers,  
hence the name LS coupling.

We expect states with the same electron configuration but different values of  $L$  and  $S$  to no longer be degenerate.

So what effect do  $L$  and  $S$  have on energy of the states?

Higher  $S$  means lower energy.  $\searrow$  the  $S$  is more important generally  
Lower  $S$  means lower energy

We can determine ground state of an atom within LS coupling using Hund's Rules.

# Hund's Rules

If we know the electron configuration and there is only one incomplete orbital, we can determine the ground state of an atom within LS. Hund's rules do not apply if there is more than one incomplete orbital (eg for Cr Chromium) and it cannot be used to determine the order of excited states of the atom. The rules are:

- 1) The state with maximum S lies lowest
- 2) For a given S, the state with maximum L lies lowest
- 3) For a given L and S,  $J = |L - S|$  for less than half filled orbitals and  $J = L + S$  for more than half filled orbitals.  
For exactly half-filled orbitals,  $L = 0$  and  $J = S$

Let's apply Hund's rules in a couple of examples.

Consider Carbon which has electron configuration  $(1s)^2(2s)^2(2p)^2$   
we fill this up as shown:

P

$m_l$	1	0	-1
$\uparrow$	X	X	
$\downarrow$			

d

	2	1	0	-1	-2
$\uparrow$	X	X	X	X	X
$\downarrow$	X				

f

	3	2	1	0	-1	-2	-3
$\uparrow$							
$\downarrow$							

Note, we started with the p orbital as it is the first unfilled orbital.

So now we can add up our values.

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

$$L = 1 + 0 = 1$$

The orbital is less than half filled

$$\text{so } J = |L - S| = 0$$

so in term notation:  $2S+1 L_J$  <sup>2 here is orbital</sup>

$$\Rightarrow 3P_0$$

Now let's consider iron:  $[Ar](4s)^2(3d)^6$

we will start in the d section.

$$\text{so } S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 2$$

$$L = 2 + 1 + 0 - 1 - 2 + 2 = 2$$

$$J = L + S = 4 \quad \therefore \Rightarrow 5D_4$$

In Hund's rules, start filling up the first incomplete table like a book (left  $\rightarrow$  right  $\rightarrow$  bottom left)



## Optical Selection Rules

We will treat optical transitions within the dipole approximation.  
The perturbation hamiltonian for light-atom interactions is:

$$\hat{H}_p = -e \sum_{i=1}^Z \mathbf{r}_i \cdot \underline{\mathbf{E}}$$

As with helium, this means only one electron can change its configuration at a time.

For the electron undergoing transition  $\Delta L = \pm 1$  and  $\Delta L = 0$  for all other transitions.

We also have for the total orbital angular momentum  $\Delta L = 0, \pm 1$

for spin we have  $\Delta S = 0$

Since  $J = L + S$ :  $\Delta S = 0, \pm 1$

We also therefore find  $\Delta M_J = 0, \pm 1$

## Zeeman Effect

The Zeeman effect is the effect of a magnetic field on atoms.

We will only consider cases of Zeeman effect where LS coupling is a good approximation.

We will also only work in one of two limits: The weak field limit where the energy associated with Zeeman effect is much smaller than the energy associated with spin-orbit coupling. And the strong field limit where the energy associated with Zeeman effect is much bigger than the energy associated with spin-orbit coupling. We will not work with the intermediate effect.

With classical approach we can show that an electron orbiting a nucleus with orbital ang. momentum  $\hat{\mathbf{L}}$  has magnetic moment  $\hat{\mathbf{\mu}}_L$ :

$$\hat{\mathbf{\mu}}_L = -\frac{e}{2m} \hat{\mathbf{L}}$$



$$\text{so } \hat{\underline{\mu}}_L = -\frac{e}{2m} \hat{L}$$

which we can use the Bohr magneton  $\hat{\mu}_B = -\frac{e\hbar}{2m}$  to rewrite as:

$$\hat{\underline{\mu}}_L = \frac{\mu_B}{\hbar} \hat{L}$$

We can show something similar for spin angular momentum  $\hat{S}$

$$\hat{\underline{\mu}}_S = g_s \frac{\mu_B}{\hbar} \hat{S} \quad \text{where } g_s \approx 2.00232$$

We can thus write the Perturbation Hamiltonian for the Zeeman effect as:

$$\begin{aligned} \hat{H}_{\text{Zeeman}} &= \frac{\mu_B}{\hbar} \sum_i (\hat{L}_i + g_s \hat{S}_i) \cdot \underline{B} \\ &= \frac{\mu_B}{\hbar} (\hat{L} + g_s \hat{S}) \cdot \underline{B} \end{aligned}$$

It should be clear that the eigenstates of  $\underline{J} = \underline{L} + \underline{S}$  are not eigenstates of the perturbation Hamiltonian. This is why we need the weak field and strong field limits. In the weak field limit the Zeeman effect only slightly shifts the energy of the total angular momentum operator, so we can apply the Zeeman perturbation last.

If we assume the magnetic field is along the z-axis:

$$\hat{H}_{\text{Zeeman}} = \frac{\mu_B}{\hbar} (\hat{L}_z + g_s \hat{S}_z) B$$

B is now a magnitude in z direction

We have already established that in the LS regime  $m_L$  and  $m_S$  are not good quantum numbers because of spin-orbit coupling.

we need to calculate the first order correction to the energies but in order to do this we will make use of a relationship which applies for both  $\hat{L}$  and  $\hat{S}$ :

$L_z$  and  $S_z$  can be replaced by their projection onto  $\underline{J}$ .

We won't prove this but it is true. what does this mean?

$$L_z \rightarrow (\hat{L} \cdot \hat{J}) \frac{\hat{J}_z}{J^2} = \frac{(\underline{L} \cdot \underline{J}) J_z}{J^2}$$

$$\text{so } S^2 = \underline{S} \cdot \underline{S} = (\underline{J} - \underline{L})(\underline{J} - \underline{L})$$

$$= J^2 + L^2 - 2\underline{J} \cdot \underline{L}$$

$$\Rightarrow \underline{J} \cdot \underline{L} = \frac{1}{2}(J^2 + L^2 - S^2)$$

we want to work out  $\langle L S J M_J | L_z | L S J M_J \rangle$

$$= \langle L S J M_J | \frac{J^2 + L^2 - S^2}{2J^2} | L S J M_J \rangle$$

$$= \frac{\hbar^2 J(J+1) + \hbar^2 L(L+1) - \hbar^2 S(S+1)}{2\hbar^2 J(J+1)} M_J$$

$$= \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} M_J$$

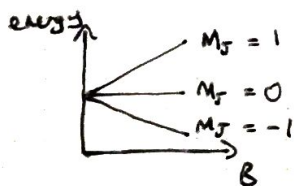
And we can do something similar for  $\langle L S J M_J | S_z | L S J M_J \rangle$

$$\text{This gives } \Delta E^{(1)} = \langle L S J M_J | \hat{H}_{Zeeman} | L S J M_J \rangle = \mu_B g_J M_J B$$

$$\text{where } g_J = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_s \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

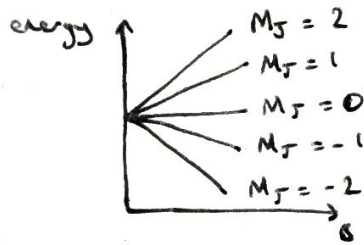
this is called the Landé factor.

so what does this tell us? well, if  $J=1$ , then  $M_J = -1, 0, 1$  so:



it tells us how the energy changes with the magnetic field.

If  $J=2$ , then  $M_J = -2, -1, 0, 1, 2$  and we would have:



At some field, the perturbation energy due to Zeeman effect will be greater than the level splitting caused by spin-orbit correction. In this limit we have to apply the Zeeman perturbation before the spin-orbit perturbation. This is the strong field limit and we find:

$$\Delta E^{(1)} = \mu_B (M_L + g_s M_S) B$$