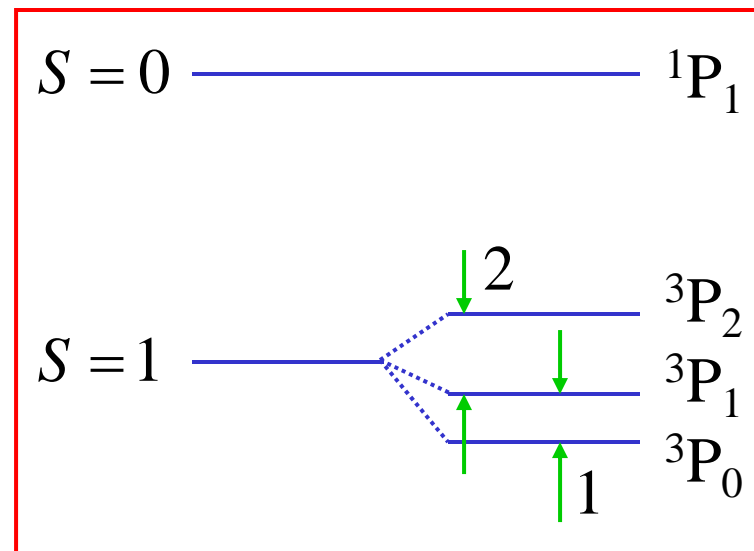


# Advanced Quantum Physics

## Lecture 20



David Ritchie

[www.sp.phy.cam.ac.uk/~dar11/pdf](http://www.sp.phy.cam.ac.uk/~dar11/pdf)

# Section 5: Atoms

5.1 The real hydrogen atom



5.2 Multielectron atoms

5.3 Coupling schemes

5.4 Atomic spectra

5.5 Atoms in a uniform magnetic field

## 5.2 (Continued) Central field approximation

- The Hamiltonian for a multielectron atom, neglecting spin and other relativistic effects is:

$$\hat{H} = \sum_i \left[ \underbrace{-\frac{\hbar^2}{2m_e} \nabla_i^2}_{\text{Kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r_i}}_{\text{Nuclear potential energy}} \right] + \sum_{i < j} \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\text{electron-electron repulsion}}$$

where  $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$  - the electron-electron repulsion term is complicated...

- The central field approximation assumes the e-e term contains a large spherically symmetric component. The following property of spherical harmonic functions,

$$\sum_{m=-\ell}^{\ell} |Y_{\ell m}|^2 = \text{constant (independent of } \theta, \phi)$$

shows that a closed shell with all values of  $m_\ell$  full will have a spherically symmetric charge distribution.

## Central field approximation (2)

- Given the spherically symmetric charge distribution for a closed shell, we can write  $\hat{H} = \hat{H}_0 + \hat{H}_1$  where:

$$\hat{H}_0 = \sum_i \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U(r_i) \right], \quad \hat{H}_1 = \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i U(r_i)$$

- $\hat{H}_0$  is a sum of terms for each electron so the wavefunction can be separated into product of wavefunctions for each electron.
- We solve Schrodinger's equation using  $\hat{H}_0$  and treat  $\hat{H}_1$  as a perturbation.
- The eigenfunctions of  $\hat{H}_0$  for each electron will be characterised by quantum numbers  $(n, l, m)$ .
- But  $\hat{H}_0$  no longer has a  $1/r$  variation.
- So the wavefunctions with different  $l$  for a given  $n$  will not be degenerate.
- The difficult part of the process is to estimate  $U(r)$  which depends on the wavefunction of all the electrons.
- This suggests an iterative approach.

## Central field approximation (3)

• An iterative method is provided by the *Self Consistent Field* approach:

(1) Guess  $U(r)$ , as  $r \rightarrow 0$  we expect  $U(r) \rightarrow 0$  corresponding to no screening.

• As  $r \rightarrow \infty$  we anticipate  $U(r) \rightarrow (Z-1)e^2 / 4\pi\epsilon_0 r$  which is perfect screening.

• We start with smooth behaviour for  $U(r)$  between these limits.

(2) Solve Schrodinger's equation numerically for energies and wavefunctions of single electron states:

$$\left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + U(r) \right) \psi_{nlm} = E_{nlm} \psi_{nlm}$$

(3) Estimate the ground state by filling levels, using the exclusion principle, until all the electrons are accounted for.

(4) Using wavefunctions improve  $U(r)$ . Charge density  $\rho(r) = e \sum |\psi_{nlm}|^2$  and Gauss' theorem will give the radial field, integration gives  $U(r)$ .

(5) Return to step (2) and iterate until convergence

# Central field approximation – Hartree Fock

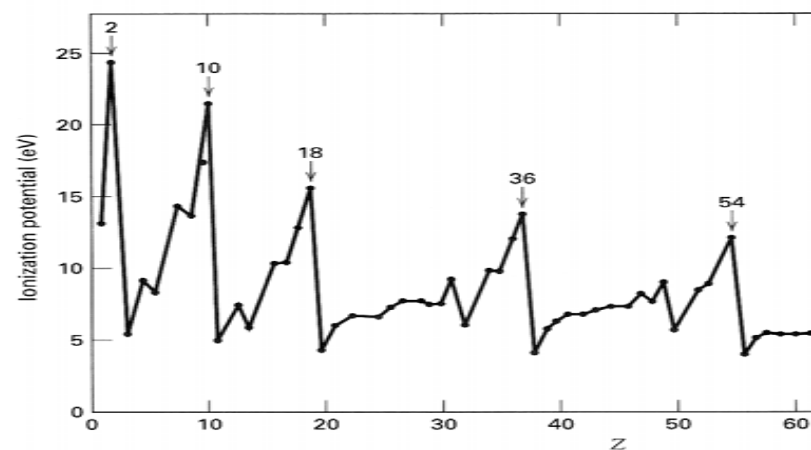
- This method takes account of exchange interactions.
- To do this we ensure the wavefunction including spin is antisymmetric under particle exchange.
- Use *Slater determinant*. For  $i^{th}$  electron where  $i = 1, 2, \dots, N$  wavefunction is  $\psi_k(\mathbf{r}_i)$ ,  $k$  is shorthand for set of quantum nos.  $(n, l, m_l, m_s)$
- Overall wavefunction:
 
$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \psi_1(\mathbf{r}_3) & \dots \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \psi_2(\mathbf{r}_3) & \dots \\ \psi_3(\mathbf{r}_1) & \psi_3(\mathbf{r}_2) & \psi_3(\mathbf{r}_3) & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}$$
- Each of  $N!$  terms in  $\Psi$  is a product of wavefunctions for each electron.
- $1/\sqrt{N!}$  factor normalizes
- Determinant changes sign if two columns exchanged – the same as  $\mathbf{r}_i \leftrightarrow \mathbf{r}_j$  this ensures wavefunction is antisymmetric under particle exchange.
- Determinant is zero for identical rows – so all wavefunctions must be different – satisfies Pauli exclusion principle.
- Note: If  $N = 2$  determinant reduces to:  $\frac{1}{\sqrt{2}} [\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)]$

## Central field approximation – Hartree Fock (2)

- Result of calculations: Eigenfunctions with quantum nos:  $n, l, m$ , and  $l < n$
- States with different  $l$  for given  $n$  are not degenerate.
- Smaller  $l$  lower energy – nucleus better screened for larger  $l$ .
- States with a particular value of  $n$  are a *shell*, pair of  $n, l$  values a *subshell*.

Subshell name	<i>1s</i>	<i>2s</i>	<i>2p</i>	<i>3s</i>	<i>3p</i>	<i>4s</i>	<i>3d</i>	<i>4p</i>	<i>5s</i>	<i>4d</i>	...
$n=$	<i>1</i>	<i>2</i>	<i>2</i>	<i>3</i>	<i>3</i>	<i>4</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>4</i>	...
$l=$	<i>0</i>	<i>0</i>	<i>1</i>	<i>0</i>	<i>1</i>	<i>0</i>	<i>2</i>	<i>1</i>	<i>0</i>	<i>2</i>	...
Degeneracy	<i>2</i>	<i>2</i>	<i>6</i>	<i>2</i>	<i>6</i>	<i>2</i>	<i>10</i>	<i>6</i>	<i>2</i>	<i>10</i>	...
Cumulative	<i>2</i>	<i>4</i>	<i>10</i>	<i>12</i>	<i>18</i>	<i>20</i>	<i>30</i>	<i>36</i>	<i>38</i>	<i>48</i>	...

- The values of  $Z$  for the inert gases: 2, 10, 18, 36 - which have a high ionization energy now emerge naturally corresponding to the no. of electrons just before a new shell (value of  $n$ ) is entered.



## Central field approximation – Hartree Fock (3)

- Use sequence of energy levels to predict ground state electronic configuration of atoms.

- Fill up levels using exclusion principle:

- Outermost electrons of most interest – chemical activity or optical spectra

- Can often omit closed shells:– O is  $(2p)^4$

- Sometimes configuration is not correctly predicted in heavier atoms with close energy levels. Cu ( $Z=29$ ) would be expected to have  $(4s)^2(3d)^9$  but has  $(4s)^1(3d)^{10}$  - can happen when d and f subshells are being filled

- Basis of periodic table – expect elements with similar configurations in outermost shells to have similar chemical properties,

- e.g. alkali metals

Li	Na	K	Rb	Cs	Fr
$(2s)^1$	$(3s)^1$	$(4s)^1$	$(5s)^1$	$(6s)^1$	$(7s)^1$

- Halogens

F	Cl	Br	I	At
$(2p)^5$	$(3p)^5$	$(4p)^5$	$(5p)^5$	$(6p)^5$

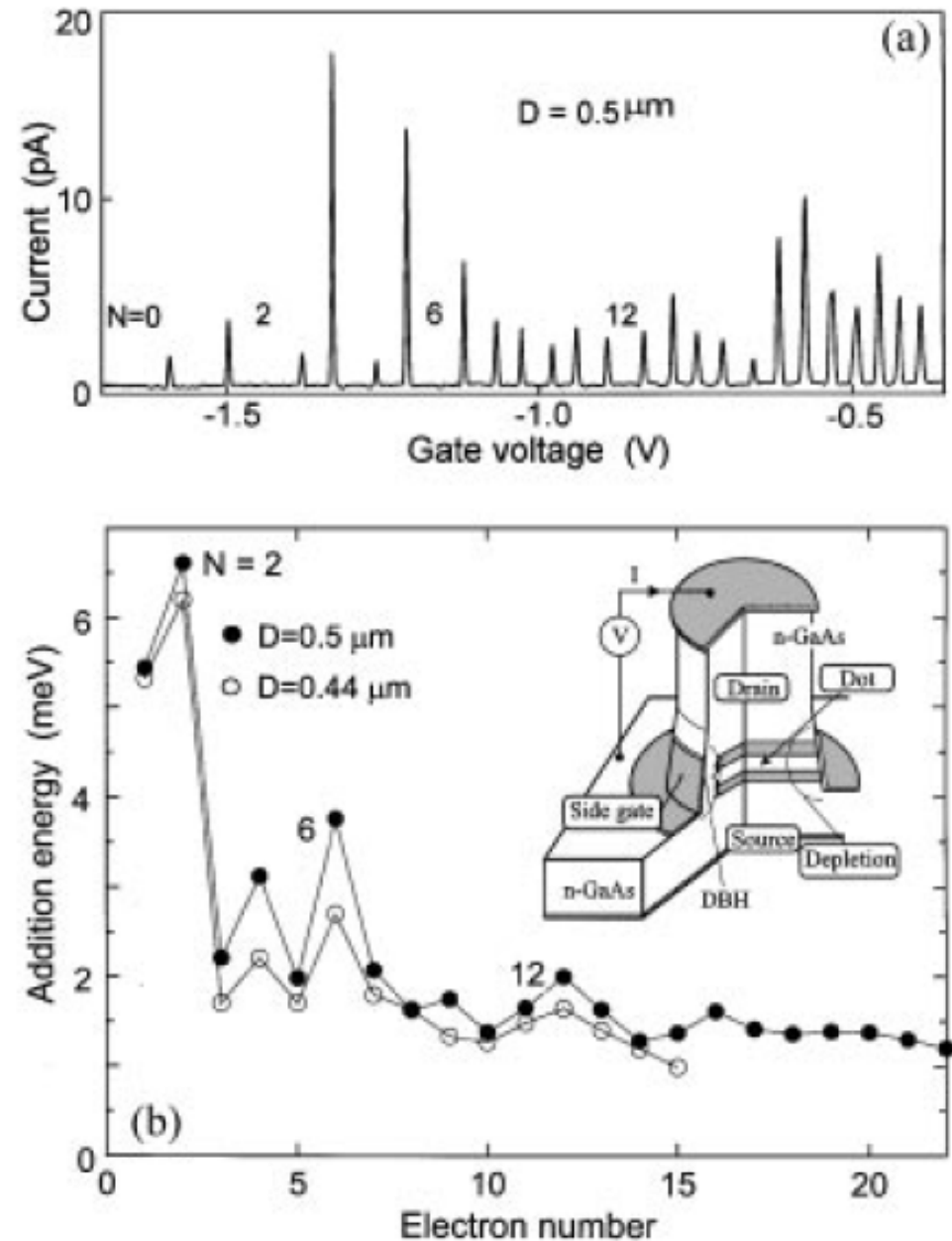
Element	Z	Configuration
H	1	$(1s)^1$
He	2	$(1s)^2$
Li	3	$(1s)^2(2s)^1$
O	8	$(1s)^2(2s)^2(2p)^4$

# The periodic table of the elements

Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States																	
H <sup>1</sup> 1s															He <sup>2</sup> 1s <sup>2</sup>		
Li <sup>3</sup> 2s	Be <sup>4</sup> 2s <sup>2</sup>	The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters <i>s</i> , <i>p</i> , <i>d</i> , . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units $\hbar$ ; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.										B <sup>5</sup> 2s <sup>2</sup> 2p	C <sup>6</sup> 2s <sup>2</sup> 2p <sup>2</sup>	N <sup>7</sup> 2s <sup>2</sup> 2p <sup>3</sup>	O <sup>8</sup> 2s <sup>2</sup> 2p <sup>4</sup>	F <sup>9</sup> 2s <sup>2</sup> 2p <sup>5</sup>	Ne <sup>10</sup> 2s <sup>2</sup> 2p <sup>6</sup>
Na <sup>11</sup> 3s	Mg <sup>12</sup> 3s <sup>2</sup>											Al <sup>13</sup> 3s <sup>2</sup> 3p	Si <sup>14</sup> 3s <sup>2</sup> 3p <sup>2</sup>	P <sup>15</sup> 3s <sup>2</sup> 3p <sup>3</sup>	S <sup>16</sup> 3s <sup>2</sup> 3p <sup>4</sup>	Cl <sup>17</sup> 3s <sup>2</sup> 3p <sup>5</sup>	Ar <sup>18</sup> 3s <sup>2</sup> 3p <sup>6</sup>
K <sup>19</sup> 4s	Ca <sup>20</sup> 4s <sup>2</sup>	Sc <sup>21</sup> 3d 4s <sup>2</sup>	Ti <sup>22</sup> 3d <sup>2</sup> 4s <sup>2</sup>	V <sup>23</sup> 3d <sup>3</sup> 4s <sup>2</sup>	Cr <sup>24</sup> 3d <sup>5</sup> 4s	Mn <sup>25</sup> 3d <sup>5</sup> 4s <sup>2</sup>	Fe <sup>26</sup> 3d <sup>6</sup> 4s <sup>2</sup>	Co <sup>27</sup> 3d <sup>7</sup> 4s <sup>2</sup>	Ni <sup>28</sup> 3d <sup>8</sup> 4s <sup>2</sup>	Cu <sup>29</sup> 3d <sup>10</sup> 4s	Zn <sup>30</sup> 3d <sup>10</sup> 4s <sup>2</sup>	Ga <sup>31</sup> 4s <sup>2</sup> 4p	Ge <sup>32</sup> 4s <sup>2</sup> 4p <sup>2</sup>	As <sup>33</sup> 4s <sup>2</sup> 4p <sup>3</sup>	Se <sup>34</sup> 4s <sup>2</sup> 4p <sup>4</sup>	Br <sup>35</sup> 4s <sup>2</sup> 4p <sup>5</sup>	Kr <sup>36</sup> 4s <sup>2</sup> 4p <sup>6</sup>
Rb <sup>37</sup> 5s	Sr <sup>38</sup> 5s <sup>2</sup>	Y <sup>39</sup> 4d 5s <sup>2</sup>	Zr <sup>40</sup> 4d <sup>2</sup> 5s <sup>2</sup>	Nb <sup>41</sup> 4d <sup>4</sup> 5s	Mo <sup>42</sup> 4d <sup>5</sup> 5s	Tc <sup>43</sup> 4d <sup>6</sup> 5s	Ru <sup>44</sup> 4d <sup>7</sup> 5s	Rh <sup>45</sup> 4d <sup>8</sup> 5s	Pd <sup>46</sup> 4d <sup>10</sup> -	Ag <sup>47</sup> 4d <sup>10</sup> 5s	Cd <sup>48</sup> 4d <sup>10</sup> 5s <sup>2</sup>	In <sup>49</sup> 5s <sup>2</sup> 5p	Sn <sup>50</sup> 5s <sup>2</sup> 5p <sup>2</sup>	Sb <sup>51</sup> 5s <sup>2</sup> 5p <sup>3</sup>	Te <sup>52</sup> 5s <sup>2</sup> 5p <sup>4</sup>	I <sup>53</sup> 5s <sup>2</sup> 5p <sup>5</sup>	Xe <sup>54</sup> 5s <sup>2</sup> 5p <sup>6</sup>
Cs <sup>55</sup> 6s	Ba <sup>56</sup> 6s <sup>2</sup>	La <sup>57</sup> 5d 6s <sup>2</sup>	Hf <sup>72</sup> 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	Ta <sup>73</sup> 5d <sup>3</sup> 6s <sup>2</sup>	W <sup>74</sup> 5d <sup>4</sup> 6s <sup>2</sup>	Re <sup>75</sup> 5d <sup>5</sup> 6s <sup>2</sup>	Os <sup>76</sup> 5d <sup>6</sup> 6s <sup>2</sup>	Ir <sup>77</sup> 5d <sup>9</sup> -	Pt <sup>78</sup> 5d <sup>9</sup> 6s	Au <sup>79</sup> 5d <sup>10</sup> 6s	Hg <sup>80</sup> 5d <sup>10</sup> 6s <sup>2</sup>	Tl <sup>81</sup> 6s <sup>2</sup> 6p	Pb <sup>82</sup> 6s <sup>2</sup> 6p <sup>2</sup>	Bi <sup>83</sup> 6s <sup>2</sup> 6p <sup>3</sup>	Po <sup>84</sup> 6s <sup>2</sup> 6p <sup>4</sup>	At <sup>85</sup> 6s <sup>2</sup> 6p <sup>5</sup>	Rn <sup>86</sup> 6s <sup>2</sup> 6p <sup>6</sup>
Fr <sup>87</sup> 7s	Ra <sup>88</sup> 7s <sup>2</sup>	Ac <sup>89</sup> 6d 7s <sup>2</sup>	Ce <sup>58</sup> 4f <sup>2</sup> 6s <sup>2</sup>	Pr <sup>59</sup> 4f <sup>3</sup> 6s <sup>2</sup>	Nd <sup>60</sup> 4f <sup>4</sup> 6s <sup>2</sup>	Pm <sup>61</sup> 4f <sup>5</sup> 6s <sup>2</sup>	Sm <sup>62</sup> 4f <sup>6</sup> 6s <sup>2</sup>	Eu <sup>63</sup> 4f <sup>7</sup> 6s <sup>2</sup>	Gd <sup>64</sup> 4f <sup>7</sup> 5d 6s <sup>2</sup>	Tb <sup>65</sup> 4f <sup>8</sup> 5d 6s <sup>2</sup>	Dy <sup>66</sup> 4f <sup>10</sup> 6s <sup>2</sup>	Ho <sup>67</sup> 4f <sup>11</sup> 6s <sup>2</sup>	Er <sup>68</sup> 4f <sup>12</sup> 6s <sup>2</sup>	Tm <sup>69</sup> 4f <sup>13</sup> 6s <sup>2</sup>	Yb <sup>70</sup> 4f <sup>14</sup> 6s <sup>2</sup>	Lu <sup>71</sup> 4f <sup>14</sup> 5d 6s <sup>2</sup>	
			Th <sup>90</sup> - 6d <sup>2</sup> 7s <sup>2</sup>	Pa <sup>91</sup> 5f <sup>2</sup> 6d 7s <sup>2</sup>	U <sup>92</sup> 5f <sup>3</sup> 6d 7s <sup>2</sup>	Np <sup>93</sup> 5f <sup>4</sup> 7s <sup>2</sup>	Pu <sup>94</sup> 5f <sup>6</sup> 7s <sup>2</sup>	Am <sup>95</sup> 5f <sup>7</sup> 7s <sup>2</sup>	Cm <sup>96</sup> 5f <sup>7</sup> 6d 7s <sup>2</sup>	Bk <sup>97</sup>	Cf <sup>98</sup>	Es <sup>99</sup>	Fm <sup>100</sup>	Md <sup>101</sup>	No <sup>102</sup>	Lr <sup>103</sup>	

## Artificial atoms

- Structures can be made from GaAs and AlGaAs which have properties similar to atoms.
- The GaAs quantum dot is filled with electrons which tunnel through AlGaAs barriers at certain 'gate' voltages with a peak in current measured for each electron added.
- Adding an electron to the dot requires a certain energy which is measured by the change in gate voltage between current peaks.
- The symmetry of the 2D harmonic oscillator potential for the electron confinement leads to complete filling of shells for 2, 6, 12... electrons – a sequence reflected in the electron addition energy data.



S Tarucha et al Phys Rev Lett **77**,3616 (1996)

## 5.3 Coupling Schemes

- In a partially filled subshell the angular momenta of electrons can couple in different ways giving different total angular momenta and energies.

- Consider the Hamiltonian:

- $\hat{H}_0$  includes K.E and central field

- $\hat{H}_1$  is the residual Coulomb energy

- $\hat{H}_2$  Spin orbit term

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

- Consider two scenarios:

- $\hat{H}_1 \gg \hat{H}_2$  - applies for light atoms, consider eigenstates of  $\hat{H}_0 + \hat{H}_1$  and treat  $\hat{H}_2$  as a perturbation – called **LS** or Russell-Saunders coupling

- $\hat{H}_1 \ll \hat{H}_2$  - applies in very heavy atoms or heavily ionised light atoms where electrons move faster and relativistic effects (such as spin-orbit interaction) more important. Scheme called **jj** coupling.

- Both schemes are approximations, real atoms cannot always be represented by either.

## LS coupling

$$\hat{H} \approx \hat{H}_0 + \underbrace{\sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{\hat{H}_1} + \underbrace{\sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i}_{\hat{H}_2}$$

• From the last slide:

• Consider the eigenstates of  $\hat{H}_0 + \hat{H}_1$  - the Hamiltonian must commute with  $\hat{\mathbf{J}}^2$  because of invariance under rotation, also commutes with total spin  $\hat{\mathbf{S}}^2$

• Since  $\hat{H}_1$  only involves internal interactions and is invariant under rotation of all electrons the Hamiltonian must commute with  $\hat{\mathbf{L}}^2$ .

• Energy levels characterised by angular momentum quantum nos.  $L, S, J$

• Ordering of energy levels given by *Hund's rules*:

(1) Combine the spins of the electrons to obtain possible values of total spin  $S$ . The largest permitted value of  $S$  lies lowest in energy.

(2) For each value of  $S$ , find the possible values of total orbital angular momentum  $L$ . The largest value of  $L$  lies lowest in energy.

(3) Couple the values of  $L$  and  $S$  to obtain the values of  $J$  (hence the name of the scheme). If the subshell is less than half full, the smallest value of  $J$  lies lowest; otherwise, the largest value of  $J$  lies lowest.

## LS coupling (2)

- In deciding on permitted values of  $L$  and  $S$ , by applying usual rules for adding angular momenta, ensure exclusion principle is respected.
- Hund's rules are empirical – there are exceptions.
- Try to understand physical origin:
  - (1) Maximising  $S$  makes the spin wave function as symmetric as possible. This tends to make the spatial wavefunction antisymmetric, and hence reduces the Coulomb repulsion.
  - (2) Maximising  $L$  also tends to keep the electrons apart. This is less obvious, though a simple classical picture of electrons rotating round the nucleus in the same or different senses makes it plausible.
  - (3) The separation of energies for states of different  $J$  arises from treating the spin-orbit term as a perturbation (fine structure). It can be shown (using the Wigner-Eckart theorem – beyond this course) that the energy separation is:

$$\langle JLS | \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | JLS \rangle \propto \langle JLS | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | JLS \rangle \propto \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)]$$

## LS coupling - Helium

- The ground state of He is  $(1s)^2$  and so  $L = S = J = 0$  - applies to any filled subshell.
- Consider an excited state  $(1s)^1(2p)^1$ , one electron excited to 2p level.
- We have  $S = 1$  or  $S = 0$ , with  $S = 1$  lying lowest (Hund 1).
- Combining orbital angular momenta:  $L = 1$
- So for  $S = 0$  we have  $J = 1$ , for  $S = 1$  we have  $J = 0, 1, 2$  with  $J = 0$  lying lowest in energy (Hund 3).
- Conventional to represent quantum nos. with 'Spectroscopic Term'  $^{2S+1}L_J$
- Superscript  $2S + 1$  gives no. of  $J$  values level is split into by spin-orbit term.
- $L$  value represented by a capital letter:
- $J$  represented by numerical value.

	S	P	D	F	G	H	...
$L=$	0	1	2	3	4	5	...

- So for the  $(1s)^1(2p)^1$  state of helium there are four possible states, with terms:  $^3P_0, ^3P_1, ^3P_2$  separated by the spin-orbit interaction and with  $^1P_1$  much higher in energy due to the Coulomb interaction.

## LS coupling – Helium (2)

• So for the  $(1s)^1(2p)^1$  state of helium there are four possible states, as shown.

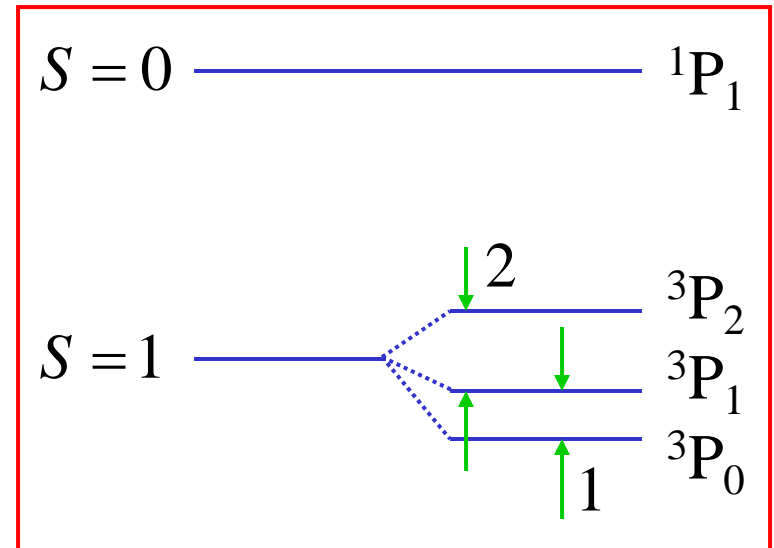
• From the equation for the energy separation due to the spin-orbit interaction (slide 13) the separation in energy between states  $J$  and  $J-1$  is:  $\propto J(J+1) - (J-1)J = 2J$

• This is an example of the Landé interval rule – the separation between a pair of adjacent levels in a fine structure multiplet is proportional to the larger  $J$  value involved

• Hence the fine structure splitting for  $^3P_2, ^3P_1$  compared to that for  $^3P_1, ^3P_0$  is in the ratio 2:1.

• In the case of He the situation is more complicated because the spin-orbit interaction between different electrons is not negligible and gives a contribution to the fine structure.

• Other excited states of He, of the form  $(1s)^1(nl)$  can be treated in the same way - again splitting into singlet and triplet states.



## LS coupling – Carbon

- Carbon – ground state configuration  $(2p)^2$ . There are two *equivalent* electrons in the unfilled subshell.
- The overall wavefunction must be anti-symmetric.
- If total spin  $S=0$  – anti-symmetric:  $\frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)$
- Total spin  $S=1$  - symmetric:  $\frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)$ ,  $\uparrow_1\uparrow_2$ ,  $\downarrow_1\downarrow_2$
- Choose values of  $L$  with correct symmetry for each value of  $S$ .

$m_l^1$	$m_l^2$	$M_L$
1	0	1
1	-1	0
0	-1	-1

• Anti-symmetric spatial state electrons have different  $m_l$

$\Rightarrow L = 1$

Hence  $S=1$

$m_l^1$	$m_l^2$	$M_L$
1	1	2
1	0	1
1	-1	0
0	0	0
0	-1	-1
-1	-1	-2

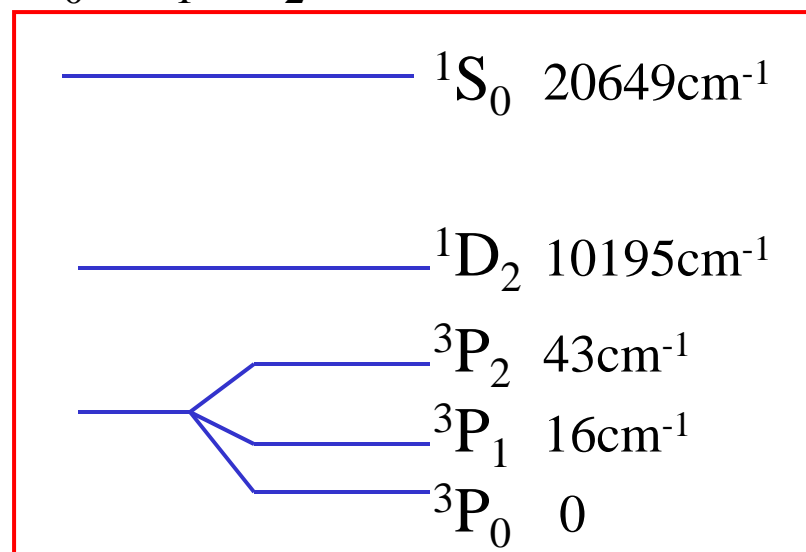
• Symmetric spatial state electrons have any  $m_l$

$\Rightarrow L = 0, 2$

Hence  $S=0$

## LS coupling – Carbon (2)

- From the previous slide we have  $S=0, L=0$  &  $2$  and  $S=1, L=1$ .
- This gives the terms;  $^1S_0, ^1D_2$  and  $^3P_0, ^3P_1, ^3P_2$ .
- The largest value of  $S$  lies lowest in energy (Hund 1). So the  $^3P_0, ^3P_1, ^3P_2$  states lie below the  $^1S_0, ^1D_2$  states.
- The largest value of  $L$  lies lowest in energy so the  $^1D_2$  state is lower than the  $^1S_0$  state (Hund 2).
- The subshell is less than half full (2 electrons in 2p) so the smallest value of  $J$  lies lowest i.e increasing energy  $^3P_0, ^3P_1, ^3P_2$  (Hund 3).
- Note that the Landé interval rule is approximately obeyed.



Not to scale!

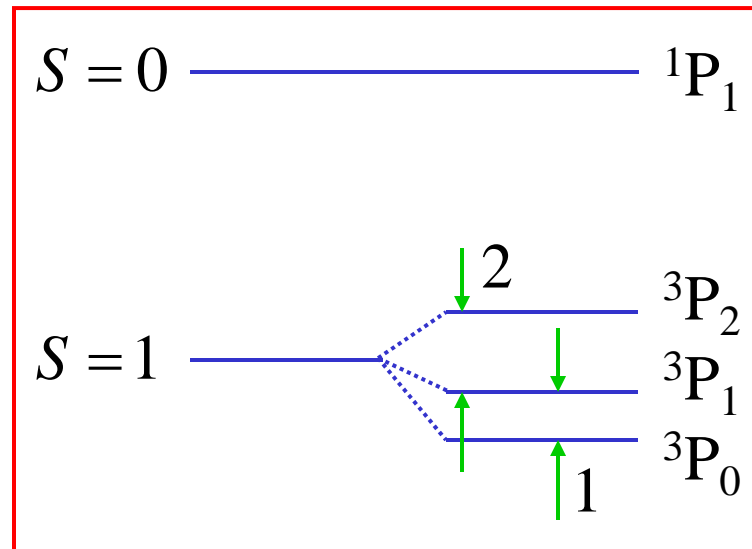
## Coupling Schemes: LS coupling

- But for excited state of carbon e.g.  $(2p)^1(3p)^1$  electrons no longer equivalent - they have different radial wavefunctions.
- So combine any of  $S=0,1$  with  $L=0,1,2$  to give (in order of increasing energy):  ${}^3D_{1,2,3}$   ${}^3P_{0,1,2}$   ${}^3S_1$   ${}^1D_2$   ${}^1P_1$   ${}^1S_0$
- *Final example* – ground state of Oxygen  $(2p)^4$
- Although there are 4 electrons in  $(2p)$  subshell the maximum value of  $S$  is  $S=1$  – this is because there are only three values of  $m_l=0,1,-1$  and one of these must contain two electrons with opposite spin. So the maximum value of  $M_l$  is  $+1$  – achieved by having electrons with  $m_s=+1/2$  in the other  $m_l$  states.
- Hence the allowed quantum nos.  $L, S, J$  are the same as for Carbon  $(2p)^2$ .
- This is a general result – the allowed quantum numbers for a subshell with  $n$  electrons are the same as for a subshell with  $n$  holes.
- Hence the energy levels for the  $O$  ground state configuration are the same as for  $C$  except that the fine structure is inverted.

## Lecture 20 - Summary

- Multielectron atoms (continued).
- Hamiltonian for a multielectron atom.
- The central field approximation and the self consistent field approach.
- The effect of exchange interactions (Hartree-Fock) – explanation of ionization energies of the elements and the periodic table.
- Coupling schemes – consider Coulomb and spin-orbit terms in Hamiltonian.
- If Coulomb  $\gg$  spin-orbit use LS or Russell-Saunders coupling.
- If Coulomb  $\ll$  spin-orbit use jj coupling.
- Hund's rules - used to determine the ground state in LS coupling regime.
- Examples - LS coupling applied to helium, carbon and oxygen.

# Lecture 20



**The End!!**

([www.sp.phy.cam.ac.uk/~dar11/pdf](http://www.sp.phy.cam.ac.uk/~dar11/pdf))