



UNIVERSITY OF  
CAMBRIDGE

NST Part II Physics  
Michaelmas Term 2022  
Dr Paula Alvarez Cartelle

# ADVANCED QUANTUM PHYSICS

## Handout 7

- 
- ▶ Multi-electron atoms
    - ▶ Periodic table
    - ▶ LS coupling (Hund's rules)
    - ▶ jj coupling

# Multi-electron Atoms

- The most important contributions to the Hamiltonian for an  $N$ -electron atom are :

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

$$\hat{H}_0 = \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right]$$

a sum of  $N$  independent hydrogen-like Hamiltonians

$$\hat{H}_1 = \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

electron-electron repulsion  
 $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$

$$\hat{H}_2 = \sum_{i=1}^N \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

spin-orbit interactions

- Relativistic corrections, hyperfine interactions etc. can be included as perturbations

## Multi-electron atoms (2)

- First, consider the dominant contribution,  $H_0$  :
  - The term  $H_0$  is the sum of  $N$  independent hydrogen-like Hamiltonians
  - It therefore possesses eigenstates which are products of  $N$  single-particle hydrogen-like states of the form  $|nlm_\ell\rangle|sm_s\rangle$
  - $(nl) = (1s), (2s), (2p), (3s), (3p), (3d), \dots$
- The energies and degeneracies of these single-particle states depend only on the principal quantum number  $n$  :
$$E_n = -\frac{Z^2}{n^2} R_\infty ; \quad g = \sum_{\ell=0}^{n-1} 2(2\ell + 1) = 2n^2$$
- The  $N$  electrons are identical particles; to take identical particle symmetry into account, we invoke the Pauli exclusion principle :
  - each electron must occupy a different single-particle state
  - we fill the available single-particle states one by one, starting with the lowest energy level :  $n = 1, 2, 3, \dots$

## Full (Closed) Shells

- Consider, for example, the (2p) subshell, with  $n = 2$  and  $\ell = 1$  :  
There are six available single-particle (2p) states, which can be written as
$$|m_\ell\rangle|m_s\rangle = |+1\rangle|\downarrow\rangle, \quad |+1\rangle|\uparrow\rangle, \quad |0\rangle|\downarrow\rangle, \quad |0\rangle|\uparrow\rangle, \quad |-1\rangle|\downarrow\rangle, \quad |-1\rangle|\uparrow\rangle$$
- If the (2p) subshell contains six electrons, only one overall state consistent with identical particle (fermion) exchange symmetry can be formed :

$$|\psi\rangle = \frac{1}{\sqrt{6!}} \begin{vmatrix} (1) & (2) & (3) & (4) & (5) & (6) \\ |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle \\ |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle \\ |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle \\ |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle \\ |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle \\ |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle \end{vmatrix}$$

- This produces a unique, *totally antisymmetric* overall wavefunction (antisymmetric under all possible interchanges  $1 \leftrightarrow 2, 1 \leftrightarrow 3, \dots, 2 \leftrightarrow 5, \dots, 5 \leftrightarrow 6$ , as required for identical fermions)

## Full (Closed) Shells (2)

- The Slater determinant expands out as a linear combination of  $6! = 720$  terms, such as

$$\frac{1}{\sqrt{6!}} \left( |+1\rangle|\downarrow\rangle \otimes |+1\rangle|\uparrow\rangle \otimes |0\rangle|\downarrow\rangle \otimes |0\rangle|\uparrow\rangle \otimes |-1\rangle|\downarrow\rangle \otimes |-1\rangle|\uparrow\rangle \right)$$

(1)              (2)              (3)              (4)              (5)              (6)

Each of the six electrons occupies a different (2p) state; all of the six available (2p) states are singly occupied

- Every one of the  $6!$  terms has

$$m_L = \sum_{i=1}^6 (m_\ell)_i = 0 ; \quad m_S = \sum_{i=1}^6 (m_s)_i = 0$$

and hence also

$$m_J = m_L + m_S = 0$$

The overall six-electron state therefore has zero total angular momentum :

$$J = L = S = 0$$

- For a (2p) subshell containing *less* than six electrons, multiple possible independent wavefunctions can be formed; this will be considered below

## Full (Closed) Shells (3)

- It is not possible to construct a totally antisymmetric wavefunction for a state containing *more* than six (2p) electrons
  - a (2p) subshell containing six electrons is full
- In general, a subshell ( $n\ell$ ) can accommodate at most  $2(2\ell + 1)$  electrons  
A full subshell ( $n\ell$ ) has all  $(2\ell + 1)$  values of  $m_\ell$  equally occupied
  - it has a charge distribution (probability density) with an angular component proportional to

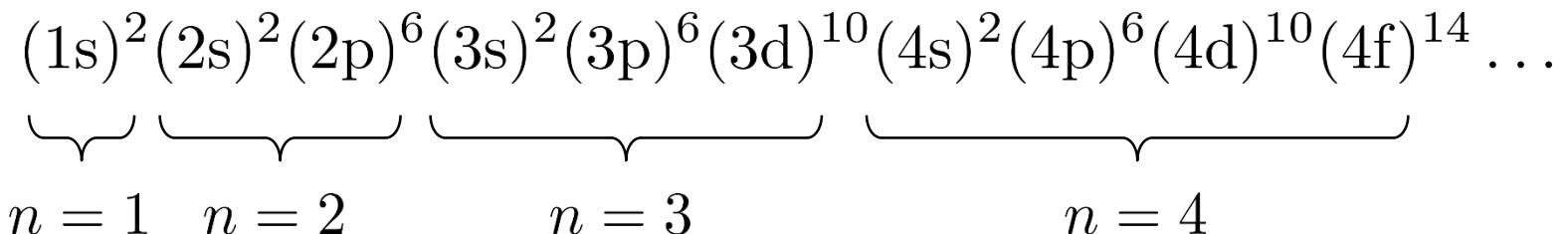
$$\sum_{m_\ell=-\ell}^{+\ell} |Y_{\ell m_\ell}(\theta, \phi)|^2 = \text{constant}$$

Hence the overall charge distribution is spherically symmetric (isotropic)

- In summary, a full subshell,  $(ns)^2$ ,  $(np)^6$ ,  $(nd)^{10}$ , ... has zero total angular momentum and an isotropic electronic charge distribution  
The total angular momentum quantum numbers of an atom are *effectively* determined by a small number of outer (valence) electrons

## Multi-electron atoms (3)

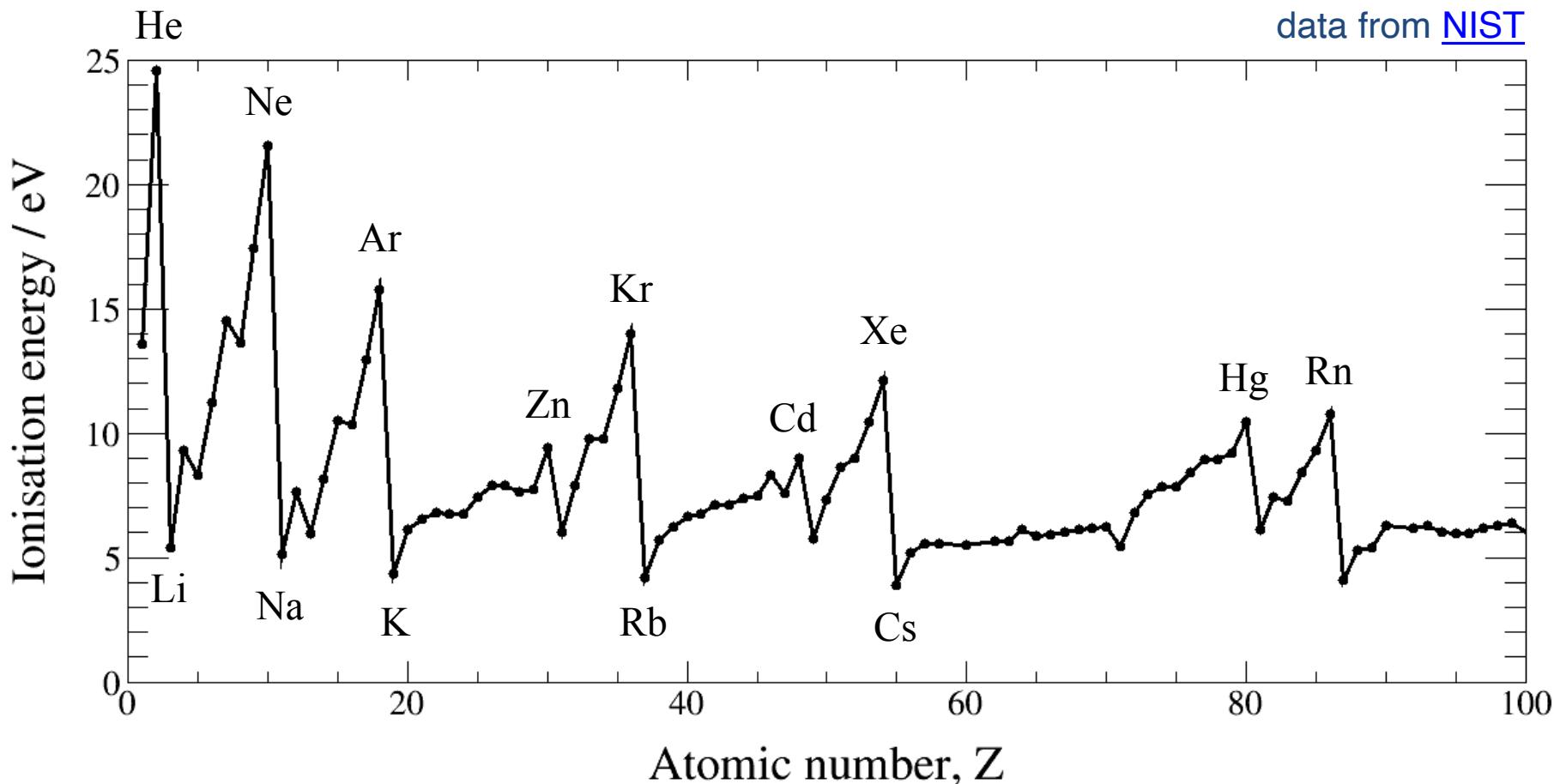
- Each energy level  $n$  can accommodate  $2n^2$  electrons, and on the basis of  $H_0$  alone, states would be filled in the order



- predict cumulative full shells at  $Z = 2, 10, 28, 60, 110, \dots$  which would be expected to be particularly stable
- But the *observed* stable configurations (the inert gases) are found at  $Z = 2, 10, 18, 36, 54, 86, \dots$ 
  - omission of the electron-electron interaction ( $H_1$ ) predicts the wrong stable configurations

Note also that  $Z = 30, 48, 80, \dots$  are relatively stable

## Ionisation energies



- The variation of ionisation energy with  $Z$  is generally smaller than expected  
For nuclear charge  $Ze$ , we might naïvely expect a dependence  $\sim Ze^2$ 
  - the outermost electrons are easier to remove than expected, so must be screened from the nucleus

# Central Field Approximation

- The Schrödinger equation for  $H_0 + H_1$  is difficult to solve because the electron-electron repulsion  $H_1$  is too large to be treated as a perturbation

Instead, resort to the ***central-field approximation*** (CFA) :

- assume that the electron-electron repulsion term contains a large spherically symmetric component arising from the “core” electrons
- In the CFA, radially symmetric “single-electron potentials”  $U_i(r_i)$  are introduced which accommodate the average effect of the other electrons

The Hamiltonian  $H_0 + H_1$  can then be repartitioned in a way which allows perturbation theory to be applied ...

The potentials  $U_i(r_i)$  are initially unknown; we will consider briefly below how they may be determined

## Central Field Approximation (2)

-- The Hamiltonian  $H$  is repartitioned as  $\hat{H} = \hat{H}'_0 + \hat{H}'_1$ , where

$$\hat{H}'_0 = \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U_i(r_i) \right]$$

$$\hat{H}'_1 = \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N U_i(r_i)$$

- $\hat{H}'_0$  contains most of the inter-electron repulsion
- $\hat{H}'_1$  is the residual Coulomb interaction, and is small enough to be treated as a perturbation

-- The Schrödinger equation for the unperturbed states,

$$\hat{H}'_0 \Phi = \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U_i(r_i) \right] \Phi = E \Phi$$

is separable into  $N$  single-particle equations of the form

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U_i(r_i) \right] \Phi_i = E_i \Phi_i$$

## Central Field Approximation (3)

- Each single-particle equation is in turn separable into a radial equation and spherical harmonic factors
  - ⇒ the eigenfunctions of  $H_0'$  for each electron will still be characterised by quantum numbers  $|nlm_\ell\rangle$  ( $\rightarrow$  we still have subshells s,p,d, ...)
- But:  $H_0'$  no longer contains a purely  $1/r$  potential term
  - for a given  $n$ , states with different  $\ell$  are no longer degenerate

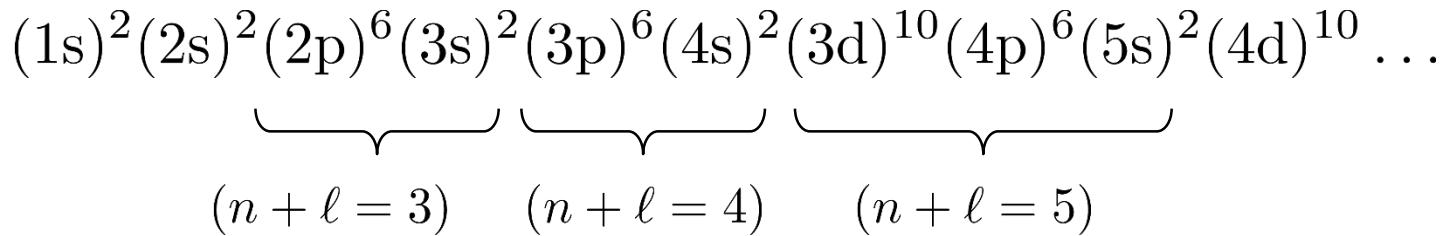
Larger  $\ell$  states are, on average, at larger radius

  - it needs less energy to remove the electron to infinity
  - larger  $\ell$  states have higher energy
- Thus, unlike zeroth-order hydrogen, where the energy depends only on  $n$ , for a more general potential  $U(r)$  the energy depends on both  $n$  and  $\ell$ 

The energies turn out to be ordered according to the value of  $n + \ell$ , with particularly large jumps in energy whenever a new value of  $n$  opens up

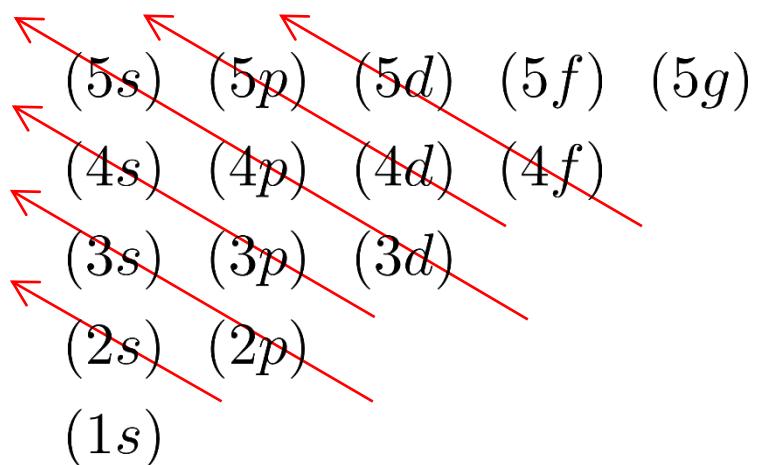
## Central Field Approximation (4)

- States are now filled in order of increasing  $n + \ell$  :



Known as the *aufbau principle*  
("build-up" principle)

The subshells are filled *diagonally*  
(not row by row)



- The values of  $Z$  for the inert gases,  $Z = 2, 10, 18, 36, 54, \dots$  now emerge naturally, whenever we first encounter a new value of  $n$

## Central Field Approximation (5)

- States corresponding to a given value of  $n$  form a *shell*  
States corresponding to given values of  $(n, \ell)$  form a *subshell*

Subshell	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	...
$n$	1	2	2	3	3	4	3	4	5	4	5	6	...
$\ell$	0	0	1	0	1	0	2	1	0	2	1	0	...
Degeneracy	2	2	6	2	6	2	10	6	2	10	6	2	...
Cumulative	<b>2</b>	4	<b>10</b>	12	<b>18</b>	20	30	<b>36</b>	38	48	<b>54</b>	56	...

- The sequence of occupied single-electron states predicts the *ground state configuration* of atoms
  - The outermost electrons are of the most interest – they govern chemical activity and optical spectra
- the inner closed shells can often be omitted - e.g. O is  $(2p)^4$

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

## Central Field Approximation (6)

- There are some exceptions to the expected aufbau filling order ; for example when the d and f subshells are being filled :
  - e.g. Cu ( $Z = 29$ ) is expected to have configuration  $(Ar)(4s)^2(3d)^9$  but actually has configuration  $(Ar)(4s)^1(3d)^{10}$
- The aufbau principle accounts for the structure of the Periodic Table
  - elements with similar configurations in their outermost shell have similar chemical properties

e.g. alkali metals :  
(Group I)

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

e.g. halogens :  
(Group VII)

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

# The Periodic Table : by configuration

<b>H<sup>1</sup></b>														<b>He<sup>2</sup></b>			
1s														1s <sup>2</sup>			
<b>Li<sup>3</sup></b>	<b>Be<sup>4</sup></b>													<b>Ne<sup>10</sup></b>			
2s	2s <sup>2</sup>													2s <sup>2</sup> 2p <sup>6</sup>			
<b>Na<sup>11</sup></b>	<b>Mg<sup>12</sup></b>													<b>Ar<sup>18</sup></b>			
3s	3s <sup>2</sup>													3s <sup>2</sup> 3p <sup>6</sup>			
<b>K<sup>19</sup></b>	<b>Ca<sup>20</sup></b>	<b>Sc<sup>21</sup></b>	<b>Ti<sup>22</sup></b>	<b>V<sup>23</sup></b>	<b>Cr<sup>24</sup></b>	<b>Mn<sup>25</sup></b>	<b>Fe<sup>26</sup></b>	<b>Co<sup>27</sup></b>	<b>Ni<sup>28</sup></b>	<b>Cu<sup>29</sup></b>	<b>Zn<sup>30</sup></b>	<b>Ga<sup>31</sup></b>	<b>Ge<sup>32</sup></b>	<b>As<sup>33</sup></b>	<b>Se<sup>34</sup></b>	<b>Br<sup>35</sup></b>	<b>Kr<sup>36</sup></b>
4s	4s <sup>2</sup>	3d 4s <sup>2</sup>	3d <sup>2</sup> 4s <sup>2</sup>	3d <sup>3</sup> 4s	3d <sup>5</sup> 4s <sup>2</sup>	3d <sup>6</sup> 4s <sup>2</sup>	3d <sup>7</sup> 4s <sup>2</sup>	3d <sup>8</sup> 4s <sup>2</sup>	3d <sup>10</sup> 4s	3d <sup>10</sup> 4s <sup>2</sup>	4s <sup>2</sup> 4p	4s <sup>2</sup> 4p <sup>2</sup>	4s <sup>2</sup> 4p <sup>3</sup>	4s <sup>2</sup> 4p <sup>4</sup>	4s <sup>2</sup> 4p <sup>5</sup>	4s <sup>2</sup> 4p <sup>6</sup>	
<b>Rb<sup>37</sup></b>	<b>Sr<sup>38</sup></b>	<b>Y<sup>39</sup></b>	<b>Zr<sup>40</sup></b>	<b>Nb<sup>41</sup></b>	<b>Mo<sup>42</sup></b>	<b>Tc<sup>43</sup></b>	<b>Ru<sup>44</sup></b>	<b>Rh<sup>45</sup></b>	<b>Pd<sup>46</sup></b>	<b>Ag<sup>47</sup></b>	<b>Cd<sup>48</sup></b>	<b>In<sup>49</sup></b>	<b>Sn<sup>50</sup></b>	<b>Sb<sup>51</sup></b>	<b>Te<sup>52</sup></b>	<b>I<sup>53</sup></b>	<b>Xe<sup>54</sup></b>
5s	5s <sup>2</sup>	4d 5s <sup>2</sup>	4d <sup>2</sup> 5s <sup>2</sup>	4d <sup>4</sup> 5s	4d <sup>5</sup> 5s	4d <sup>6</sup> 5s	4d <sup>7</sup> 5s	4d <sup>8</sup> 5s	4d <sup>10</sup> -	4d <sup>10</sup> 5s	4d <sup>10</sup> 5s <sup>2</sup>	5s <sup>2</sup> 5p	5s <sup>2</sup> 5p <sup>2</sup>	5s <sup>2</sup> 5p <sup>3</sup>	5s <sup>2</sup> 5p <sup>4</sup>	5s <sup>2</sup> 5p <sup>5</sup>	5s <sup>2</sup> 5p <sup>6</sup>
<b>Cs<sup>55</sup></b>	<b>Ba<sup>56</sup></b>	<b>La<sup>57</sup></b>	<b>Hf<sup>72</sup></b> <i>4f<sup>14</sup></i>	<b>Ta<sup>73</sup></b>	<b>W<sup>74</sup></b>	<b>Re<sup>75</sup></b>	<b>Os<sup>76</sup></b>	<b>Ir<sup>77</sup></b>	<b>Pt<sup>78</sup></b>	<b>Au<sup>79</sup></b>	<b>Hg<sup>80</sup></b>	<b>Tl<sup>81</sup></b>	<b>Pb<sup>82</sup></b>	<b>Bi<sup>83</sup></b>	<b>Po<sup>84</sup></b>	<b>At<sup>85</sup></b>	<b>Rn<sup>86</sup></b>
6s	6s <sup>2</sup>	5d 6s <sup>2</sup>	5d <sup>2</sup> 6s <sup>2</sup>	5d <sup>3</sup> 6s <sup>2</sup>	5d <sup>4</sup> 6s <sup>2</sup>	5d <sup>5</sup> 6s <sup>2</sup>	5d <sup>6</sup> 6s <sup>2</sup>	5d <sup>9</sup> -	5d <sup>9</sup> 6s	5d <sup>10</sup> 6s	5d <sup>10</sup> 6s <sup>2</sup>	6s <sup>2</sup> 6p	6s <sup>2</sup> 6p <sup>2</sup>	6s <sup>2</sup> 6p <sup>3</sup>	6s <sup>2</sup> 6p <sup>4</sup>	6s <sup>2</sup> 6p <sup>5</sup>	6s <sup>2</sup> 6p <sup>6</sup>
<b>Fr<sup>87</sup></b>	<b>Ra<sup>88</sup></b>	<b>Ac<sup>89</sup></b>		<b>Ce<sup>58</sup></b> <i>4f<sup>2</sup></i>	<b>Pr<sup>59</sup></b> <i>4f<sup>3</sup></i>	<b>Nd<sup>60</sup></b> <i>4f<sup>4</sup></i>	<b>Pm<sup>61</sup></b> <i>4f<sup>5</sup></i>	<b>Sm<sup>62</sup></b> <i>4f<sup>6</sup></i>	<b>Eu<sup>63</sup></b> <i>4f<sup>7</sup></i>	<b>Gd<sup>64</sup></b> <i>4f<sup>7</sup></i>	<b>Tb<sup>65</sup></b> <i>5d</i>	<b>Dy<sup>66</sup></b> <i>4f<sup>8</sup></i>	<b>Ho<sup>67</sup></b> <i>4f<sup>10</sup></i>	<b>Er<sup>68</sup></b> <i>4f<sup>11</sup></i>	<b>Tm<sup>69</sup></b> <i>4f<sup>12</sup></i>	<b>Yb<sup>70</sup></b> <i>4f<sup>13</sup></i>	<b>Lu<sup>71</sup></b> <i>4f<sup>14</sup></i>
7s	7s <sup>2</sup>	6d 7s <sup>2</sup>		6s <sup>2</sup>	5d 6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>	6s <sup>2</sup>							
			<b>Th<sup>90</sup></b> -	<b>Pa<sup>91</sup></b> <i>5f<sup>2</sup></i>	<b>U<sup>92</sup></b> <i>5f<sup>3</sup></i>	<b>Np<sup>93</sup></b> <i>5f<sup>4</sup></i>	<b>Pu<sup>94</sup></b> <i>5f<sup>6</sup></i>	<b>Am<sup>95</sup></b> <i>5f<sup>7</sup></i>	<b>Cm<sup>96</sup></b> <i>5f<sup>7</sup></i>	<b>Bk<sup>97</sup></b> <i>6d</i>	<b>Cf<sup>98</sup></b> <i>7s<sup>2</sup></i>	<b>Es<sup>99</sup></b>	<b>Fm<sup>100</sup></b>	<b>Md<sup>101</sup></b>	<b>No<sup>102</sup></b>	<b>Lr<sup>103</sup></b>	

# PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

GROUP	RELATIVE ATOMIC MASS (1)																		18	
1	IA																		VIIA	
1	1 1.0079 H HYDROGEN	2 IIA																	2 4.0026 He HELIUM	
1	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM																		
2	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM																		
3	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	3 IIIIB	4 IVB	5 VB	6 VIB	7 VIIIB	8	9	10	11	IB	12	IIB	13	14	15	16	17	
4	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	Sc SCANDIUM	Ti TITANIUM	V VANADIUM	Cr CHROMIUM	Mn MANGANESE	Fe IRON	Co COBALT	Ni NICKEL	Cu COPPER	Zn ZINC	Al ALUMINIUM	Si SILICON	P PHOSPHORUS	S SULPHUR	Cl CHLORINE	Ar ARGON	VIIA	
5	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	Y YTTRIUM	Zr ZIRCONIUM	Nb NIOBUM	Mo MOLYBDENUM	Tc TECHNETIUM	Ru RUTHENIUM	Rh RHODIUM	Pd PALLADIUM	Ag SILVER	Cd CADMIUM	Ga GALLIUM	Ge GERMANIUM	As ARSENIC	Se SELENIUM	Br BROMINE	Kr KRYPTON		
6	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	Ta TANTALUM	W TUNGSTEN	Re RHENIUM	Os OSMIUM	Ir IRIDIUM	Pt PLATINUM	Au GOLD	Hg MERCURY	In INDIUM	Sn TIN	Sb ANTIMONY	Te TELLURIUM	I IODINE	Xe XENON				
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBINIUM	114 (289) Uuq UNUNQUADRIUM							

## LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM
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## ACTINIDE

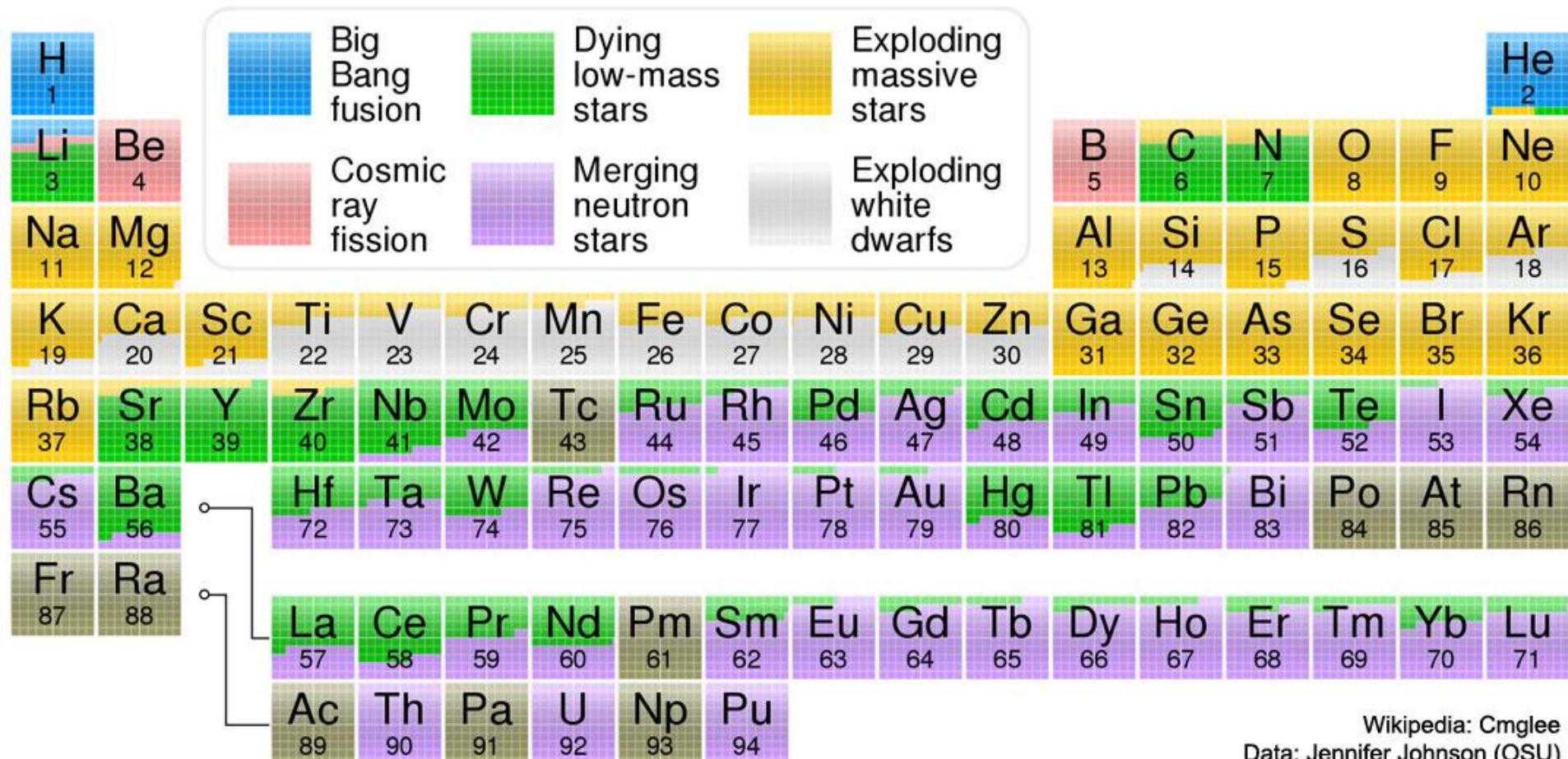
89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)  
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

# The Periodic Table : by origin



Wikipedia: Cmglee  
Data: Jennifer Johnson (OSU)

## The Self-Consistent Field Approach

- The difficult part is to estimate  $U(r)$ , which depends on the wavefunctions of *all* the electrons
  - use an iterative method known as the *Self-Consistent Field* approach :

- (1) Guess  $U(r)$ , taking a smooth function between the following limits :

$$U(r) \rightarrow 0 \quad (r \rightarrow 0) \quad (\text{no screening})$$

$$U(r) \sim \frac{(Z-1)e^2}{4\pi\epsilon_0 r} \quad (r \rightarrow \infty) \quad (\text{perfect screening})$$

Motivation :

$r \rightarrow 0$  : a given electron at the origin is surrounded by a cloud of  $(Z-1)$  other electrons which is isotropic on average  
→ expect  $U(r) \sim \text{constant}$ , independent of  $Z$

$r \rightarrow \infty$  : the  $(Z-1)$  other electrons are all effectively sitting at the origin

## The Self-Consistent Field Approach (2)

- (2) Solve Schrödinger's equation numerically to obtain the energies and wavefunctions of the single-electron states :

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + U(r) \right] \psi_{n\ell m_\ell}(\mathbf{r}) = E_{n\ell m_\ell} \psi_{n\ell m_\ell}(\mathbf{r})$$

- (3) Estimate the ground state by filling levels, using the exclusion principle, until all electrons are accounted for
- (4) Improve the estimate of  $U(r)$  using the wavefunctions obtained so far :
- the charge density is  $\rho(r) = e \sum |\psi_{n\ell m_\ell}|^2$
  - Gauss' theorem then gives the radial electric field
  - integration then gives an updated estimate of  $U(r)$
- (5) Return to step (2) and iterate until (hopefully) everything converges

# The Hartree-Fock Approximation

(Hartree Clerk-Maxwell prize)

- The *Hartree-Fock* approach takes account of exchange interactions by assuming initially that the solution has the form of a *single* Slater determinant :

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

where  $\psi_k(\mathbf{r}_i)$  is the wavefunction for the  $i$ 'th electron, and  $k$  is shorthand for the set of quantum numbers  $(n, \ell, m_\ell, m_s)$

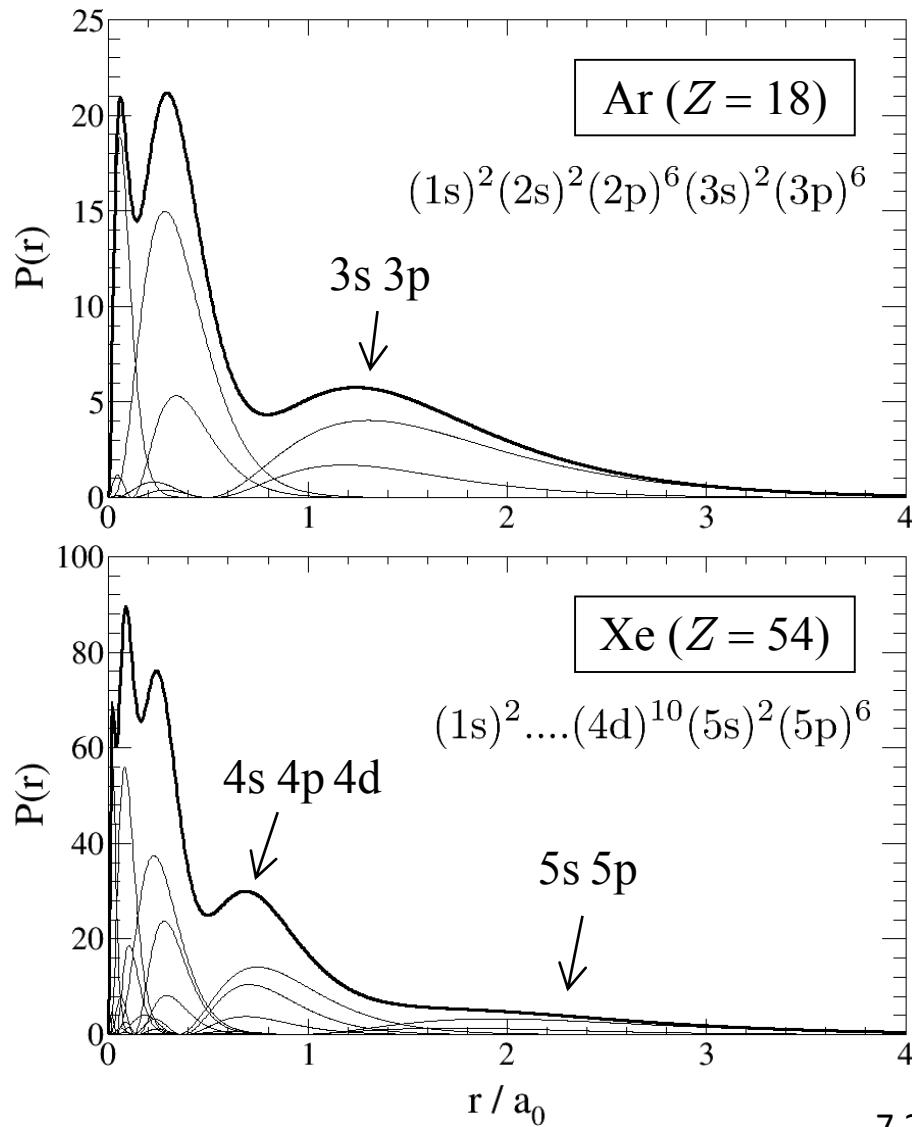
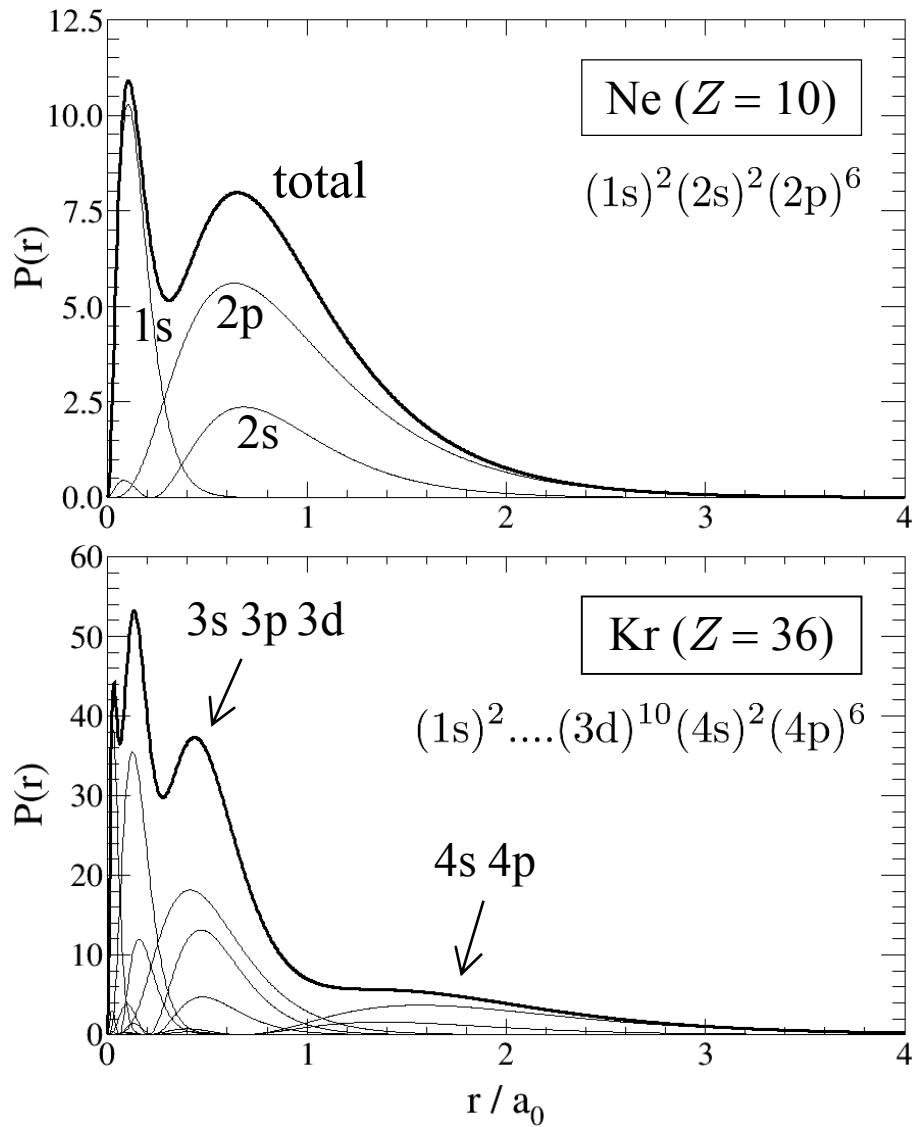
→ HF-CFA (Hartree-Fock Central Field Approximation)

- The results are available as tables of coefficients of parameterised functional orbitals [C.Bunge et al., At. Data & Nucl. Data Tables 53 \(1993\) 113](#)

The wavefunctions obtained can serve as inputs to more sophisticated calculations

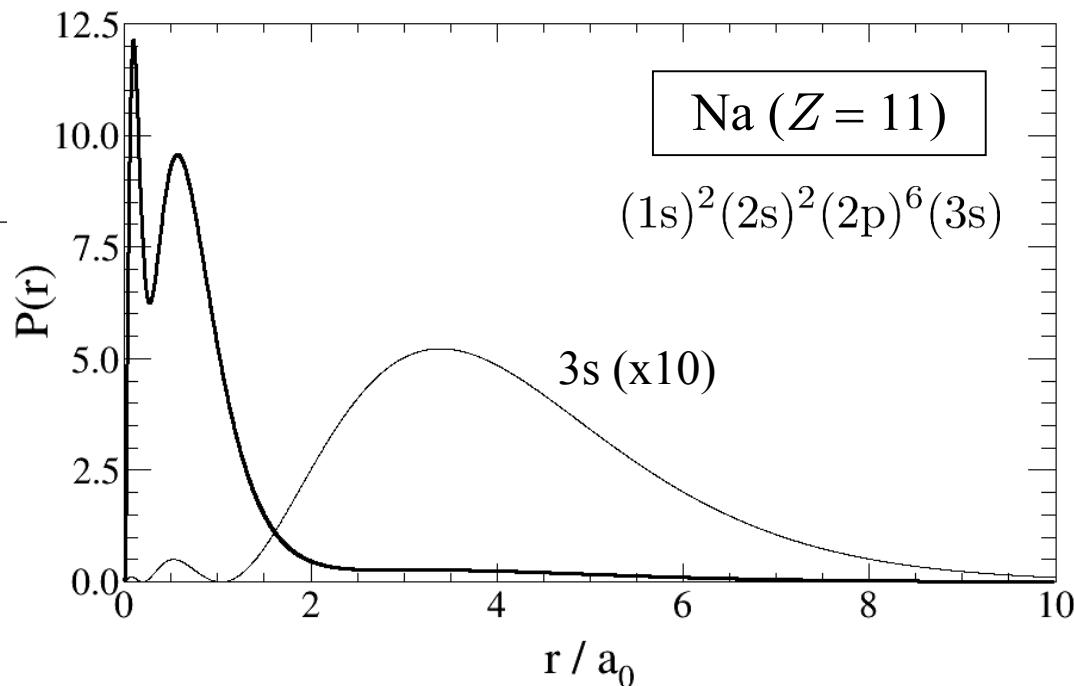
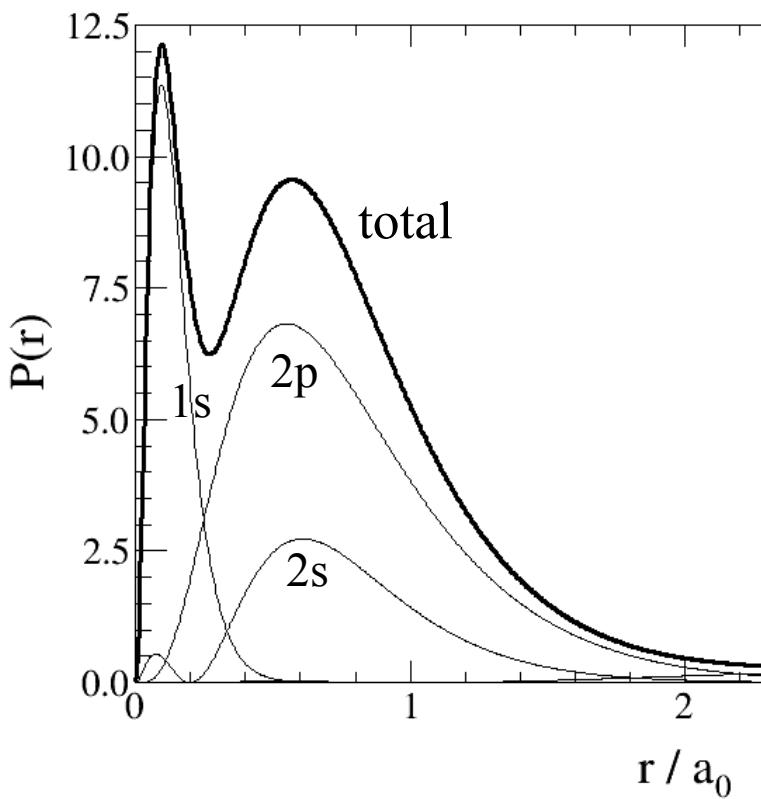
## Hartree-Fock wavefunctions : Radial densities

-- Electron radial probability densities for the inert gases :



## Hartree-Fock wavefunctions : Sodium

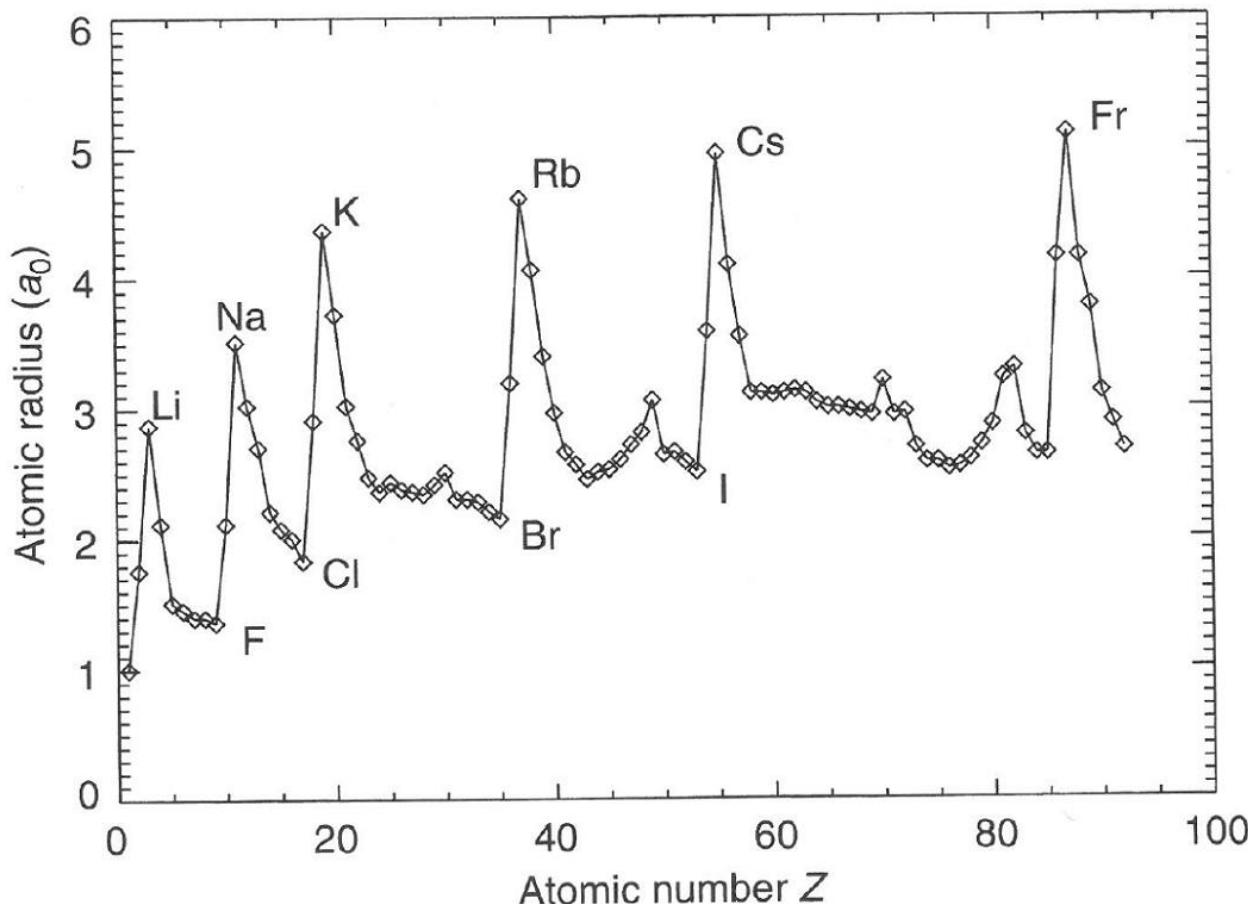
- Similarly for sodium :



- A single 3s valence electron lies largely outside a neon-like core

## Hartree-Fock wavefunctions : Atomic radii

- Atomic radii grow only slowly overall with  $Z$ , with larger “spikes” in radius at the positions of the alkali metals :

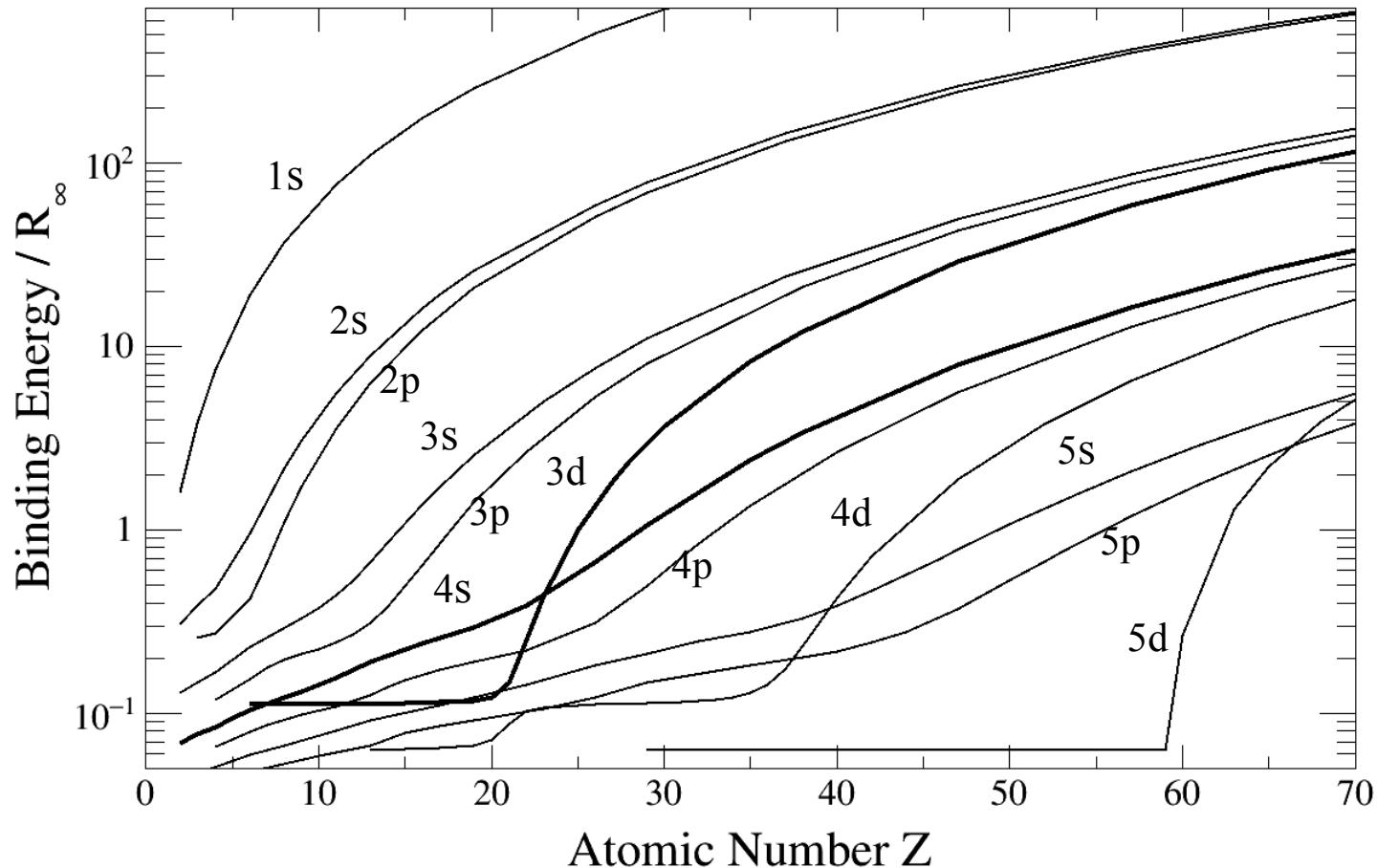


## Hartree-Fock : subshell energies

- Approximate values of subshell binding energies can be obtained by solving Schrödinger's equation for a central potential of the form

$$V(r) = (Ze/r) \phi(r/\mu); \quad \mu = 0.8853 a_0 / Z^{1/3}$$

[R. Latter, Phys. Rev. 99 \(1955\) 510](#)



# Configuration Quantum Numbers

- So far, we have only considered the *ground state* atomic configurations for each element

e.g.  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^1$  for potassium ( $Z = 19$ )

Now consider also atomic *excited states*, and the overall quantum numbers  $J, L, S, \dots$  of ground and excited states

- For example, carbon has a ground state configuration  $(2p)^2$  ;  
It also has a variety of excited states where one of the valence electrons is promoted to a higher energy subshell :

$(2p)(3s), (2p)(4s), \dots (2p)(3p), (2p)(4p), \dots (2p)(3d), (2p)(4d), \dots$

- For the ground state,  $(2p)(2p)$ , the two electrons can occupy the same spatial state, in which case they cannot occupy the same spin state

For excited states however, the two electrons always occupy *different* spatial states, and there are no such restrictions

## Configuration Quantum Numbers (2)

- For the configuration (2p)(3s), for example, the quantum numbers are

$$\ell_1 = 1, \ell_2 = 0 \Rightarrow L = \ell_1 \otimes \ell_2 = 1$$

$$s_1 = 1/2, s_2 = 1/2 \Rightarrow S = s_1 \otimes s_2 = 1, 0$$
$$\Rightarrow J = L \otimes S = 2, 1, 0$$

Hence the configuration (2p)(3s) gives the possible terms

$$(2S+1)L_J = \boxed{^1P_1, ^3P_{2,1,0}}$$

- Similarly, for (2p)(3p), the possible quantum numbers are

$$\ell_1 = 1, \ell_2 = 1 \Rightarrow L = \ell_1 \otimes \ell_2 = 2, 1, 0$$

$$s_1 = 1/2, s_2 = 1/2 \Rightarrow S = s_1 \otimes s_2 = 1, 0$$
$$\Rightarrow J = L \otimes S = 3, 2, 1, 0$$

Hence the configuration (2p)(3p) gives the possible terms

$$\boxed{^1S_0, ^1P_1, ^1D_2, ^3S_1, ^3P_{2,1,0}, ^3D_{3,2,1}}$$

## Configuration Quantum Numbers (3)

- For the configuration  $(2p)^2$ , there are additional restrictions due to identical particle statistics (the electrons are said to be *equivalent*) :

For the case  $S = 0$  :

- the spin wavefunction is *antisymmetric* :  $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$
- hence the spatial wavefunction,  $(\ell_1 = 1) \otimes (\ell_2 = 1)$ , must be *symmetric*
  - $\Rightarrow L = 2, 0$  only (slide 1.74)
  - $\Rightarrow J = 2, 0$  only

For the case  $S = 1$  :

- the spin wavefunction is *symmetric* :  $\uparrow\uparrow$ ,  $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ ,  $\downarrow\downarrow$
- hence the spatial  $1 \otimes 1$  wavefunction must be *antisymmetric*:
  - $\Rightarrow L = 1$  is the only possibility
  - $\Rightarrow J = 2, 1, 0$

- Hence, for  $(2p)^2$ , the possible spectroscopic terms are

$$^3P_{2,1,0}, ^1D_2, ^1S_0$$

a subset of those obtained for  $(2p)(3p)$

## Configuration Quantum Numbers (4)

- For full subshells, such as  $(2p)^6$ , we have already seen (slide 7.5) that the total angular momentum quantum numbers are  $J = L = S = 0$
- With one vacancy,  $(2p)^5$ , consistency with the Pauli exclusion principle requires that each of the five electrons occupies a different state :

1	2	3	4	5	$m_L$	$m_S$	$m_J$
$ +1\rangle \uparrow\rangle$	$ +1\rangle \downarrow\rangle$	$ 0\rangle \uparrow\rangle$	$ 0\rangle \downarrow\rangle$	$ {-1}\rangle \uparrow\rangle$	+1	$\uparrow$	+3/2
$ +1\rangle \uparrow\rangle$	$ +1\rangle \downarrow\rangle$	$ 0\rangle \uparrow\rangle$	$ 0\rangle \downarrow\rangle$	$ {-1}\rangle \downarrow\rangle$	+1	$\downarrow$	+1/2
$ +1\rangle \uparrow\rangle$	$ +1\rangle \downarrow\rangle$	$ 0\rangle \uparrow\rangle$	$ {-1}\rangle \uparrow\rangle$	$ {-1}\rangle \downarrow\rangle$	0	$\uparrow$	+1/2
$ +1\rangle \uparrow\rangle$	$ +1\rangle \downarrow\rangle$	$ 0\rangle \downarrow\rangle$	$ {-1}\rangle \uparrow\rangle$	$ {-1}\rangle \downarrow\rangle$	0	$\downarrow$	-1/2
$ +1\rangle \uparrow\rangle$	$ 0\rangle \uparrow\rangle$	$ 0\rangle \downarrow\rangle$	$ {-1}\rangle \uparrow\rangle$	$ {-1}\rangle \downarrow\rangle$	-1	$\uparrow$	-1/2
$ +1\rangle \downarrow\rangle$	$ 0\rangle \uparrow\rangle$	$ 0\rangle \downarrow\rangle$	$ {-1}\rangle \uparrow\rangle$	$ {-1}\rangle \downarrow\rangle$	-1	$\downarrow$	-3/2

- The allowed values of  $m_J$  consist of a set  $(+3/2, +1/2, -1/2, -3/2)$  corresponding to  $J = 3/2$ , plus a set  $(+1/2, -1/2)$  corresponding to  $J = 1/2$

The allowed values of  $m_L$  correspond to two sets of  $L = 1$

The allowed values of  $m_S$  correspond to three sets of  $S = 1/2$

## Configuration Quantum Numbers (5)

- Hence  $(2p)^5$ , with one “hole”, is the same as  $(2p)^1$ , with one real electron :

$$^2P_{3/2, 1/2}$$

- Similarly,  $(2p)^4$ , with two “holes”, is the same as  $(2p)^2$  :

$$^3P_{2,1,0}, \ ^1D_2, \ ^1S_0$$

This can be shown by counting states again, i.e. by tabulating the number of distinct ways of putting the four electrons into four distinct states

(left as an optional exercise : gives a table containing 15 rows)

- This just leaves  $(2p)^3$  : tabulating the number of distinct ways of putting the three electrons into three distinct states gives

$$^4S_{3/2}, \ ^2D_{5/2, 3/2}, \ ^2P_{3/2, 1/2}$$

(again left as an optional exercise : gives a table containing 20 rows)

## Configuration Quantum Numbers (6)

- It may not be necessary to evaluate *all* the above possibilities; we will see below that the case of maximal possible  $S$  is of particular interest  
e.g. for the  $(2p)^3$  ground state of nitrogen, only  $S = 3/2$  is needed

This case can be treated relatively straightforwardly ...

- Maximal spin,  $S = 3/2$ , includes the  $m_S = +3/2$  state  $|\uparrow\uparrow\uparrow\rangle$

Since all three electrons occupy identical spin states, they must all occupy *different*  $\ell = 1$  spatial states, i.e. they must have  $m_{\ell 1} \neq m_{\ell 2} \neq m_{\ell 3}$ :

$$\text{e.g. } m_{\ell 1} = +1, \quad m_{\ell 2} = 0, \quad m_{\ell 3} = -1$$

All such possibilities have

$$m_L = m_{\ell 1} + m_{\ell 2} + m_{\ell 3} = 0$$

Hence only  $L = 0$  is consistent with the Pauli exclusion principle

- Thus, for  $(2p)^3$  with  $S = 3/2$ , the only possibility is  $L = 0, J = 3/2$ :

$$^4S_{3/2}$$

## Configuration Quantum Numbers (7)

- This extends straightforwardly to any half-filled subshell with maximal  $S$  ; only  $L = 0$  is allowed :

$$(nd)^5 \rightarrow {}^6S_{5/2} ; \quad (nf)^7 \rightarrow {}^8S_{7/2} ; \quad \dots$$

- In summary, as we fill up the (2p) subshell, we obtain the possible terms

configuration	terms
(2p) <sup>1</sup> , (2p) <sup>5</sup>	<sup>2</sup> P <sub>3/2, 1/2</sub>
(2p) <sup>2</sup> , (2p) <sup>4</sup>	<sup>3</sup> P <sub>2, 1, 0</sub> , <sup>1</sup> D <sub>2</sub> , <sup>1</sup> S <sub>0</sub>
(2p) <sup>3</sup>	<sup>4</sup> S <sub>3/2</sub> , <sup>2</sup> D <sub>5/2, 3/2</sub> , <sup>2</sup> P <sub>3/2, 1/2</sub>
(2p) <sup>6</sup>	<sup>1</sup> S <sub>0</sub>

- In general, a given configuration leads to multiple possible terms ;
  - will see below how to order these possibilities by energy, and how to determine which of them corresponds to the ground state

# Coupling Schemes

- Everything we have done so far involves combining the electron angular momenta to form the total  $\mathbf{L}$ ,  $\mathbf{S}$  and  $\mathbf{J}$  of the atom as

$$\hat{\mathbf{L}} = \sum_{i=1}^N \hat{\mathbf{L}}_i ; \quad \hat{\mathbf{S}} = \sum_{i=1}^N \hat{\mathbf{S}}_i ; \quad \hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

→

***LS coupling***

(or *Russell-Saunders coupling*)

- Alternatively, we could first construct the total angular momentum of each electron separately as

$$\hat{\mathbf{J}}_i = \hat{\mathbf{L}}_i + \hat{\mathbf{S}}_i \quad \text{and then obtain } \mathbf{J} \text{ as} \quad \hat{\mathbf{J}} = \sum_{i=1}^N \hat{\mathbf{J}}_i$$

→

***jj coupling***

For example, for (2p)(3p), the quantum numbers for *jj* coupling would be

$$\left. \begin{array}{l} j_1 = \ell_1 \otimes s_1 = 1/2, 3/2 \\ j_2 = \ell_2 \otimes s_2 = 1/2, 3/2 \end{array} \right\} \Rightarrow J = j_1 \otimes j_2 = 0, 1, 2, 3$$

## Coupling Schemes (2)

- How do we know which (if either) set of quantum numbers provides the best description of atomic levels ?
  - we need to consider *spin-orbit* interactions ( $H_2$ ) also :

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2$$

$$\hat{H}_1 = \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} ; \quad \hat{H}_2 = \sum_{i=1}^N \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

- It was shown earlier (slide 4.33) that, for a single electron,

$$[\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i, \hat{\mathbf{L}}_i] \neq 0 , \quad [\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i, \hat{\mathbf{S}}_i] \neq 0$$

Hence

$$[\hat{H}_2, \hat{\mathbf{L}}_i] \neq 0 , \quad [\hat{H}_2, \hat{\mathbf{S}}_i] \neq 0 , \quad [\hat{H}_2, \hat{\mathbf{L}}] \neq 0 , \quad [\hat{H}_2, \hat{\mathbf{S}}] \neq 0$$

It was also shown that

$$[\hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i, \hat{\mathbf{J}}_i] = 0$$

Hence (as must be true from rotational symmetry)

$$[\hat{H}_2, \hat{\mathbf{J}}_i] = 0 , \quad [\hat{H}_2, \hat{\mathbf{J}}] = 0$$

## Coupling Schemes (3)

- A summary of what commutes with what :

	$\hat{\mathbf{L}}_i$	$\hat{\mathbf{L}}_i^2$	$\hat{\mathbf{S}}_i$	$\hat{\mathbf{S}}_i^2$	$\hat{\mathbf{J}}_i, \hat{\mathbf{J}}_i^2$	$\hat{\mathbf{L}}, \hat{\mathbf{L}}^2$	$\hat{\mathbf{S}}, \hat{\mathbf{S}}^2$	$\hat{\mathbf{J}}, \hat{\mathbf{J}}^2$
$\hat{H}_0$	✓	✓	✓	✓	✓	✓	✓	✓
$\hat{H}_1$	✗	✗	✓	✓	✗	✓	✓	✓
$\hat{H}_2$	✗	✓	✗	✓	✓	✗	✗	✓

- Apart from the relations  $[\hat{H}_2, \hat{\mathbf{L}}_i^2] = 0$ ,  $[\hat{H}_2, \hat{\mathbf{S}}_i^2] = 0$ , which follow from slide 4.9, the table above is a direct consequence of rotational symmetry :

For example, for the Coulomb term  $H_1$  (which is independent of spin) :

- the factor  $1/r_{ij}$  is not rotationally invariant (scalar) w.r.t.  $\mathbf{L}_i$  or  $\mathbf{L}_j$
- but it is scalar w.r.t. the *sum*  $\mathbf{L}_i + \mathbf{L}_j$ , and hence also w.r.t.  $\mathbf{L}$  and  $\mathbf{J}$

## Coupling Schemes (4)

- For “light” atoms, we have  $\langle H_1 \rangle \gg \langle H_2 \rangle$ , i.e.  $\langle \text{Coulomb} \rangle \gg \langle \mathbf{L} \cdot \mathbf{S} \rangle$   
(as has already been seen to be the case for helium)
  - large energy corrections from e-e repulsion and exchange forces
  - small energy corrections from fine structure (spin-orbit)

In this case, we can treat  $H_2$  as a perturbation

- The unperturbed Hamiltonian,  $H_0 + H_1$ , commutes with  $L, S, J$ , but not with  $J_i$ :

$$[\hat{H}_0 + \hat{H}_1, \hat{\mathbf{J}}_i] \neq 0$$

Hence  $L, S, J$  (but not  $j_i$ ) are good quantum numbers

- $LS$  coupling provides the better description of the atomic levels

## Coupling Schemes (5)

- The energy corrections from spin-orbit interactions grow approximately as

$$\langle \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \rangle \sim Z^4$$

→ eventually become larger than Coulomb repulsion effects

Thus, for “heavy” atoms, we have  $\langle H_2 \rangle \gg \langle H_1 \rangle$ , as electrons become more relativistic and spin-orbit interactions dominate

- The unperturbed Hamiltonian,  $H_0 + H_2$ , commutes with  $\mathbf{J}_i$  and  $\mathbf{J}$ , but not with  $\mathbf{L}$  or  $\mathbf{S}$ :

$$[\hat{H}_0 + \hat{H}_2, \hat{\mathbf{L}}] \neq 0 ; \quad [\hat{H}_0 + \hat{H}_2, \hat{\mathbf{S}}] \neq 0$$

Hence the  $j_i$  (but not  $L$  or  $S$ ) are good quantum numbers

→  $jj$  coupling provides the better description of the atomic levels

- In summary :

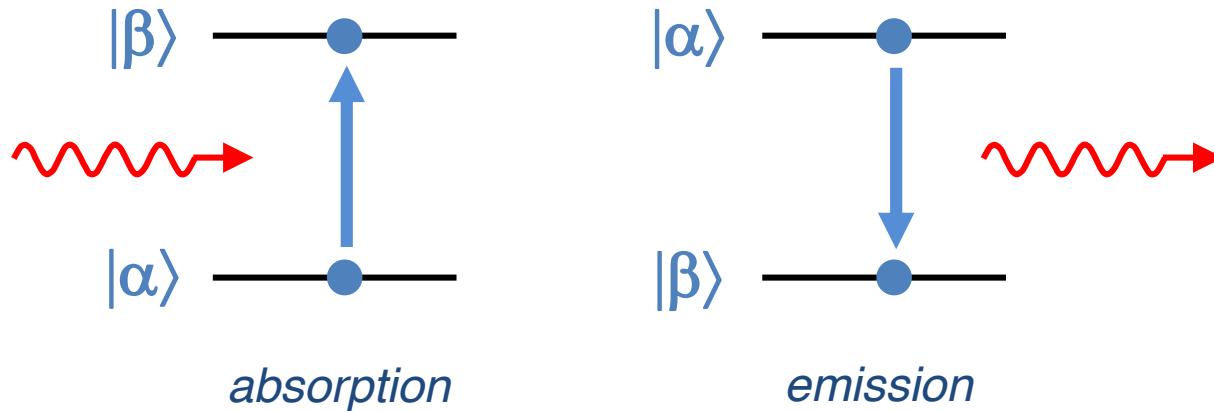
*low  $Z$  :  $\langle \mathbf{L} \cdot \mathbf{S} \rangle \ll \langle \text{Coulomb} \rangle \rightarrow LS \text{ coupling}$*

*high  $Z$  :  $\langle \mathbf{L} \cdot \mathbf{S} \rangle \gg \langle \text{Coulomb} \rangle \rightarrow jj \text{ coupling}$*

(though neither is ever a perfect description)

# Atomic Spectra

- The dominant electric dipole (E1) transitions for multi-electron atoms obey selection rules similar to those obtained earlier for hydrogen and helium



- For E1 transitions between atomic states  $|\alpha\rangle$  and  $|\beta\rangle$ , the transition rate is given by

$$\Gamma \propto \omega^3 |\langle \beta | \hat{\mathbf{d}} | \alpha \rangle|^2 ; \quad \hat{\mathbf{d}} = -e \sum_{i=1}^N \hat{\mathbf{r}}_i$$
$$\hbar\omega = |E_\alpha - E_\beta|$$

where the dipole operator  $\mathbf{d}$  now involves a sum over all  $N$  electrons

## Atomic spectra : selection rules

- From the Wigner-Eckart theorem, E1 transitions can only occur provided

$$\boxed{\Delta J = 0, \pm 1 ; \quad J_\alpha + J_\beta \geq 1 ; \quad \Delta m_J = 0, \pm 1}$$

- Also, under a parity transformation, the dipole operator  $\hat{d}$  changes sign :

$$\hat{r}_i \rightarrow -\hat{r}_i \quad \Rightarrow \quad \hat{d} \rightarrow -\hat{d}$$

Hence (slide 5.49), for an electric dipole transition to occur, the initial and final states must also have opposite parity :

$$\boxed{P_\beta = -P_\alpha}$$

- The selection rules above are exact ;  
they are derived from rotational and parity invariance, and apply to any electric dipole transition
- In the approximation that  $LS$  coupling applies, i.e. that  $L$  and  $S$  are good quantum numbers, we obtain additional selection rules ...

## Atomic spectra : selection rules (2)

- Since the dipole operator  $d$  does not depend on spin, the spin state of the atom is unchanged in an electric dipole transition

Thus (as for helium) we obtain the additional selection rule

$$\Delta S = 0 ; \quad \Delta m_S = 0$$

- Combined with the  $\Delta J$  selection rules, we then also have (for  $LS$  coupling)

$$\Delta L = 0, \pm 1 ; \quad L_\alpha + L_\beta \geq 1 ; \quad \Delta m_L = 0, \pm 1$$

- Almost all electric dipole transitions are single-electron transitions (similar to the case for helium), in which only one electron changes state

The selection rules obtained earlier for hydrogen and helium carry over directly to the single electron involved in the transition :

$$\Delta \ell = \pm 1 ; \quad \Delta m_\ell = 0, \pm 1$$

## Summary of electric dipole ( $E1$ ) selection rules

*For any  $E1$  transition :*

$$\Delta J = 0, \pm 1 ; \quad J_\alpha + J_\beta \geq 1 ; \quad \Delta m_J = 0, \pm 1$$
$$P_\beta = -P_\alpha$$

*For a single-electron transition, we also have :*

$$\Delta \ell = \pm 1 ; \quad \Delta m_\ell = 0, \pm 1$$

*If LS coupling is exact, we also have :*

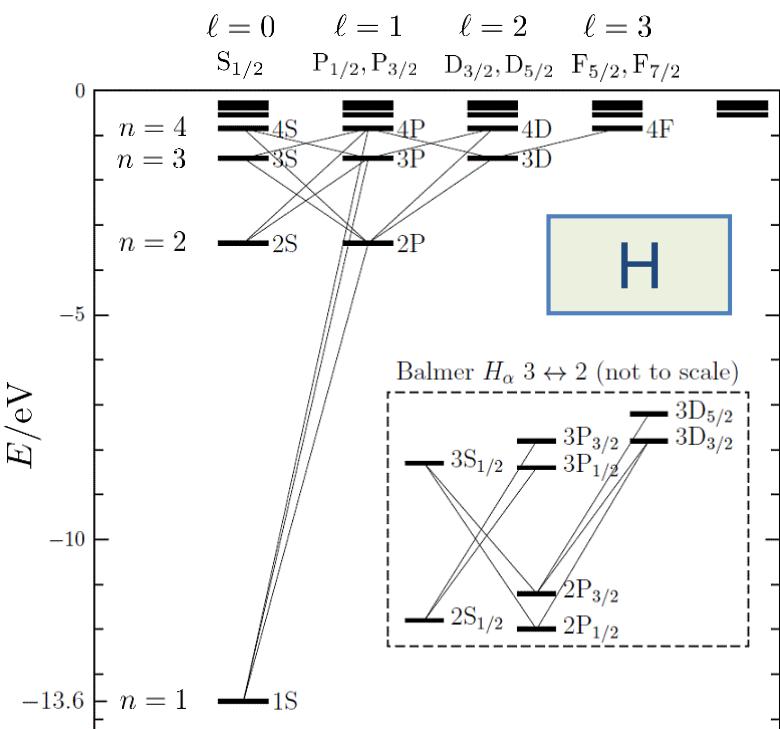
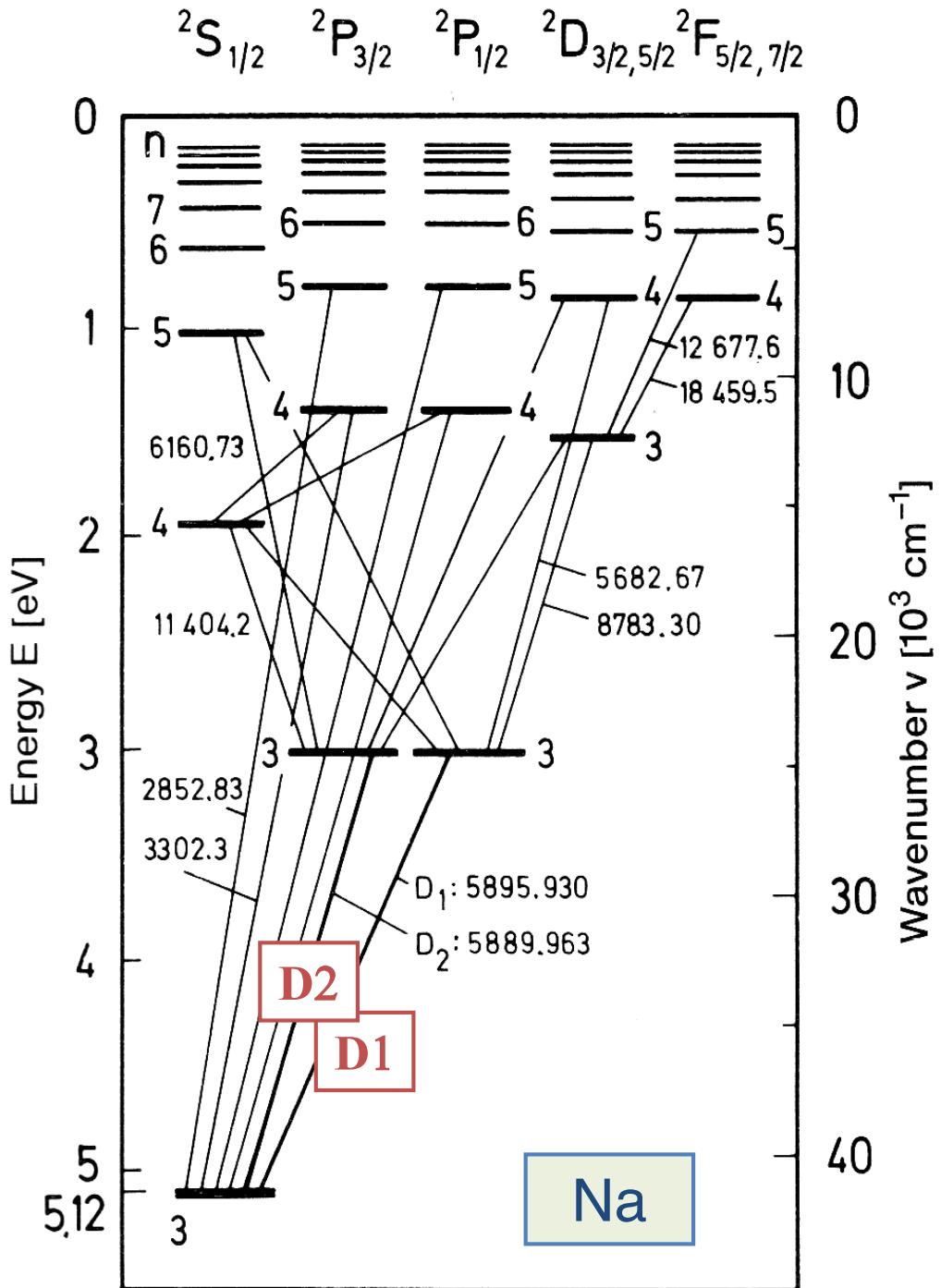
$$\Delta S = 0 ; \quad \Delta m_S = 0$$
$$\Delta L = 0, \pm 1 ; \quad L_\alpha + L_\beta \geq 1 ; \quad \Delta m_L = 0, \pm 1$$

- The topmost set of selection rules are a consequence of rotational symmetry and parity invariance, and are *exact* ;

The remainder apply in the approximation that *LS* coupling provides a good description, so that *L* and *S* are good quantum numbers

## Single Electron Atoms

- Consider atoms with a ground state of one s-state electron lying outside a core of closed shells : Li (2s)<sup>1</sup>, Na (3s)<sup>1</sup>, K (4s)<sup>1</sup>, Rb (5s)<sup>1</sup>, Cs (6s)<sup>1</sup>, ....  
→ similar spectra to hydrogen, (1s)<sup>1</sup>, but with significant differences
- For example, consider sodium (Na,  $Z = 11$ ) :
  - The ground state ionisation energy is only 5.1 eV (cf: 13.6 eV for H)  
(the 3s valence electron in Na is easier to remove than the 1s in H)
  - States with different  $\ell$  are no longer approximately degenerate  
e.g. the  $n = 3$  levels in Na have a spread in energies  $\sim 3.5$  eV  
→ transitions within  $n = 3$  now have a high rate (unlike slide 5.63)
  - Sodium starts with  $n = 3$ , not  $n = 1$   
→ unlike H, there are no metastable states  
(e.g. unlike 2s in H, the 4s state in sodium can decay as 4s → 3p)
- As  $n$  increases, the nuclear charge is more effectively screened, and the energy levels approach those for hydrogen

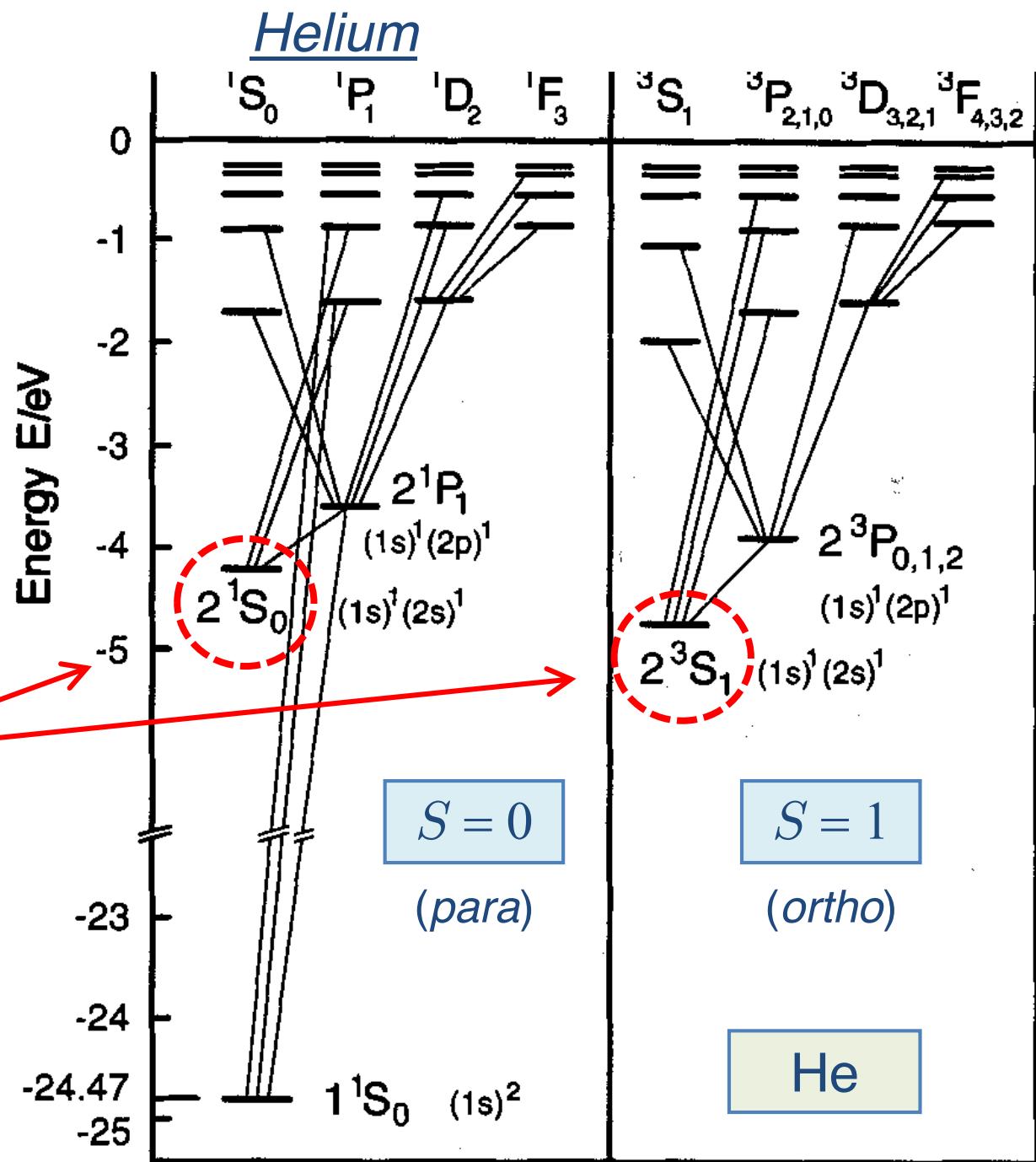


The fine structure splittings for sodium are larger than for hydrogen ...

(the spin-orbit interaction grows as  $Z^4$ )

... but they are still too small to be visible on the scale of the diagram

(see slide 6.59)



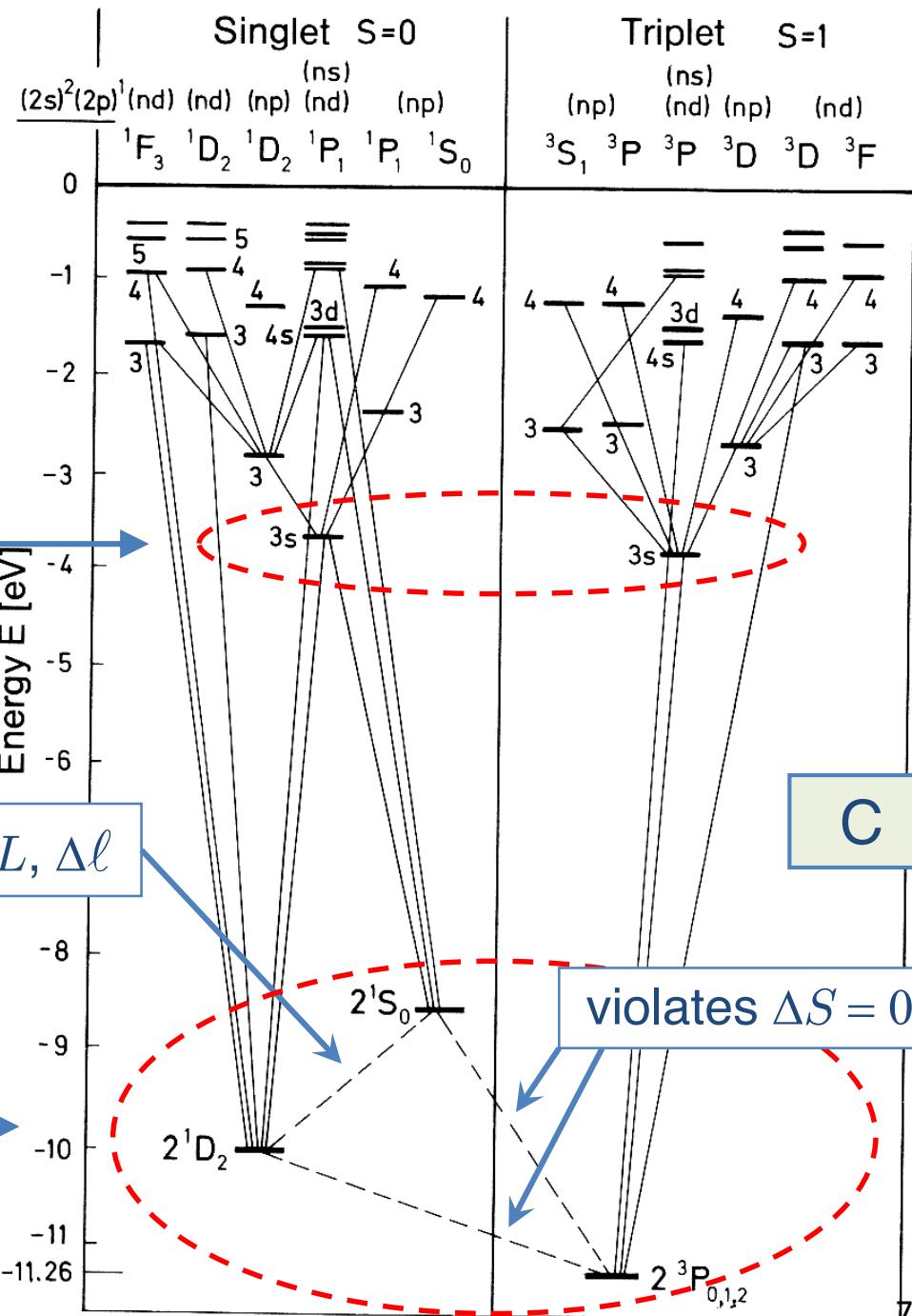
## Alkaline Earths

- The alkaline earths all have two valence s-state electrons lying outside a closed shell :      Be (2s)<sup>2</sup>, Mg (3s)<sup>2</sup>, Ca (4s)<sup>2</sup>, .... , Hg (6s)<sup>2</sup>, ...  
Similar to helium, (2s)<sup>1</sup>, they possess two approximately separate spectroscopic systems (due to the  $\Delta S = 0$  selection rule)
- For calcium ( $Z = 20$ ) for example :
  - the ground state, (4s)(4s), belongs to  $S = 0$
  - the lowest lying state with  $S = 1$  is (4s)(4p), and is metastable
  - but faint emission due to the transition to the ground state is seen, violating the  $\Delta S = 0$  rule :       $^3P_1 \rightarrow ^1S_0$  ;      (4s)(4p)  $\rightarrow$  (4s)<sup>2</sup>  
 $\Rightarrow$  LS coupling is not as good in this case
- A more extreme case is mercury ( $Z = 80$ ) :
  - the ‘forbidden’  $\Delta S = 1$  transition to the ground state is a prominent feature of the emission spectrum :     $^3P_1 \rightarrow ^1S_0$  ;    (6s)(6p)  $\rightarrow$  (6s)<sup>2</sup>  
 $\Rightarrow$  LS coupling is not a good approximation at all

## Carbon, nitrogen and oxygen

- Carbon ( $Z = 6$ )
  - the ground state is  $(2s)^2(2p)^2$ , with terms  ${}^3P_{2,1,0}$ ,  ${}^1D_2$ ,  ${}^1S_0$  (slide 7.27)
  - excited states are mainly  $(2s)^2(2p)^1(n\ell)^1$ , but  $(2s)^1(2p)^3$  also seen;  
i.e. can excite *two* electrons out of the ground state
  - separates into two spectroscopic systems :  $S = \frac{1}{2} \otimes \frac{1}{2} = 0, 1$
- Nitrogen ( $Z = 7$ )
  - the ground state is  $(2s)^2(2p)^3$ , with three unpaired electrons
  - separates into  $S = 1/2$  and  $S = 3/2$ :  $S = \frac{1}{2} \otimes \frac{1}{2} \otimes \frac{1}{2} = \frac{1}{2}, \frac{3}{2}$
- Oxygen ( $Z = 8$ )
  - the ground state is  $(2s)^2(2p)^4$ , with two (2p) “holes”
  - many features similar to carbon (two holes instead of two electrons)

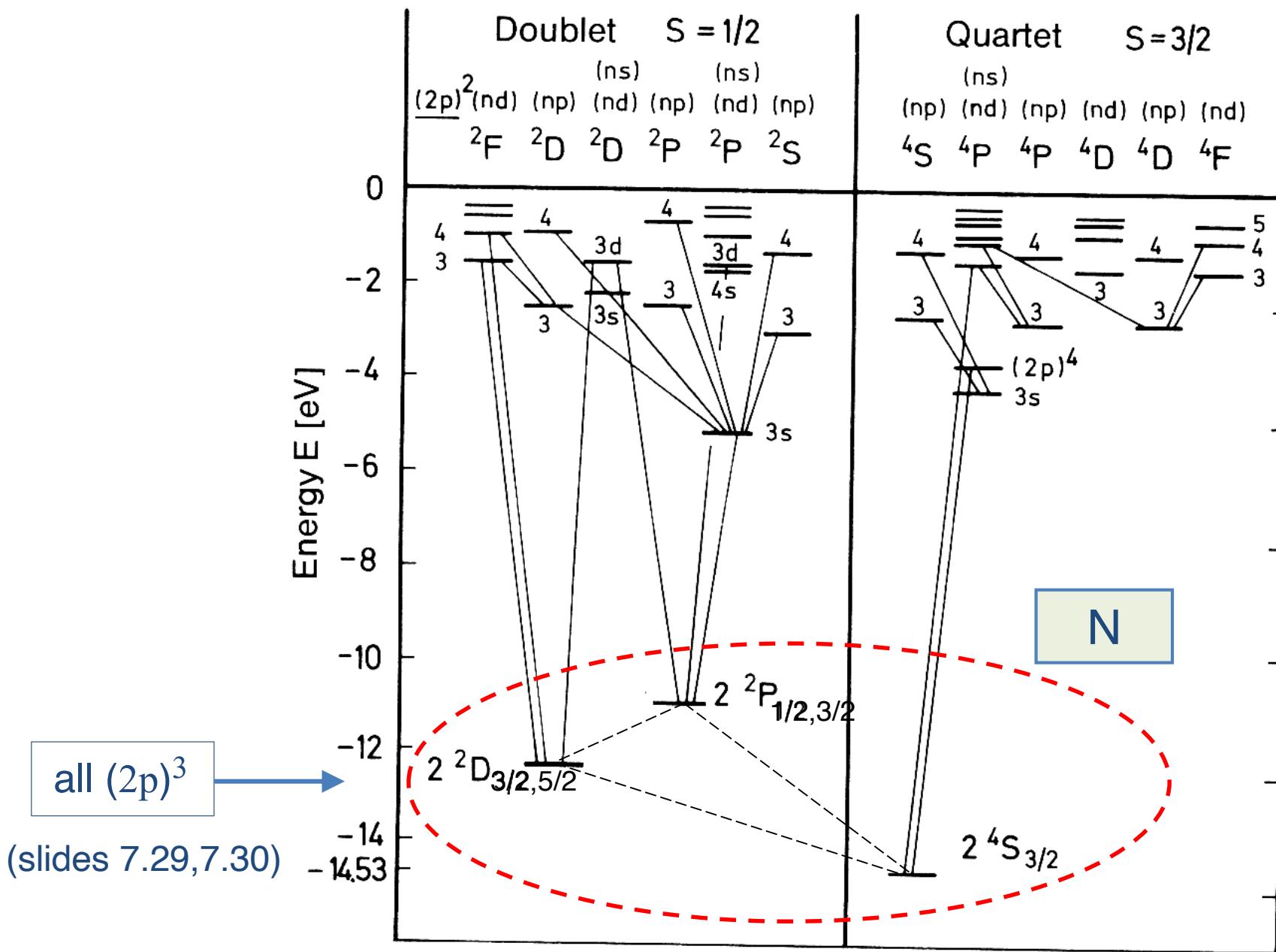
# Carbon



*ground state multiplet  
all with configuration (2p) $^2$*

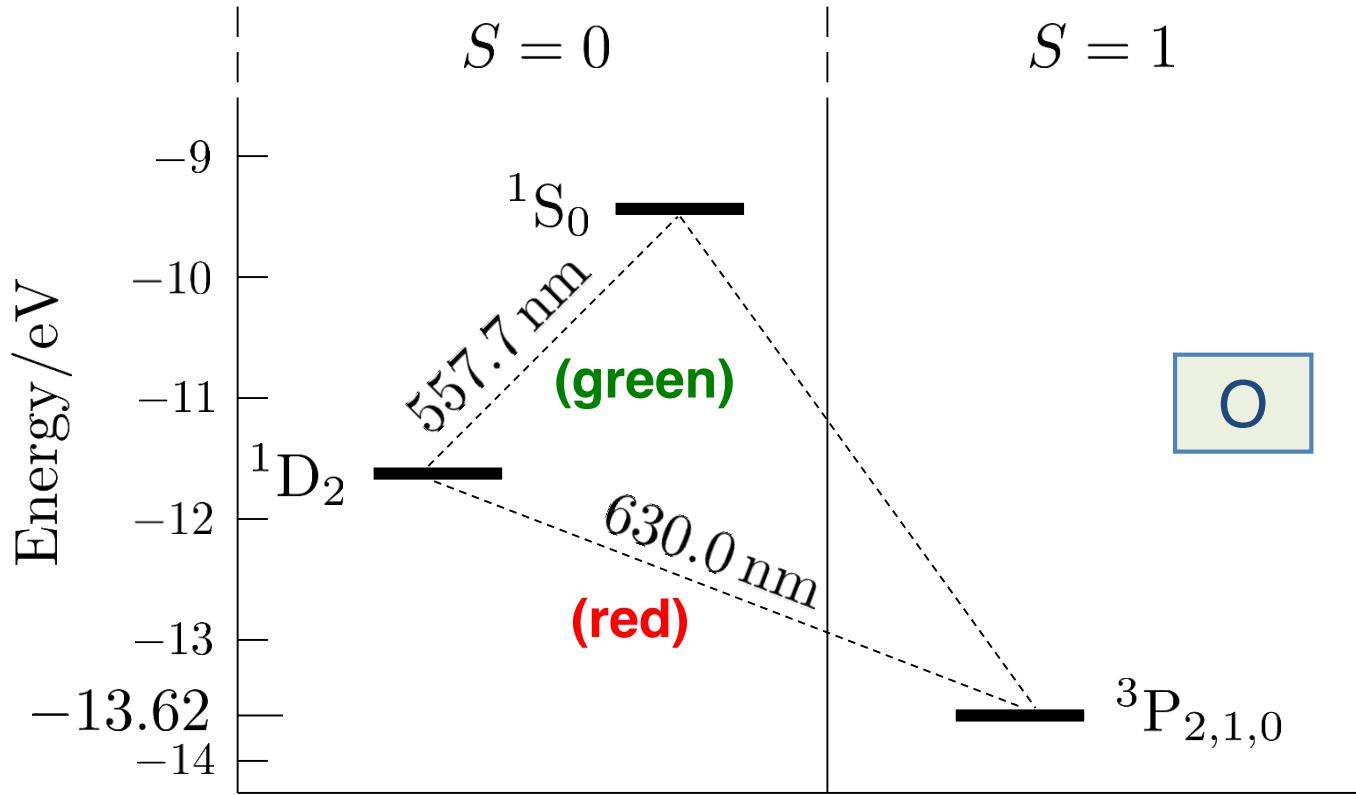
(slide 7.27)

# Nitrogen



## Oxygen

- The  $(2p)^4$  ground state multiplet of oxygen is similar to carbon :



- No E1 transitions are allowed (only lower rate M1, E2 transitions)
  - the  $^1S_0$  and  $^1D_2$  excited states have long lifetimes ( $\sim 1$  s,  $\sim 3$  mins)

## Oxygen : Aurora

- Under “normal” conditions, atomic collisions disrupt this relative stability and lead to rapid decay of the  $^1S_0$  and  $^1D_2$  states

But for the low pressures found in the upper atmosphere, excited states can survive disruption from collisions, and are long-lived

- *aurora borealis*
- *aurora australis*

<https://aurorawatch.lancs.ac.uk/>

- Highest altitudes :

- atomic oxygen  
 $\lambda = 630 \text{ nm (red)}$

Lower altitudes :

- atomic oxygen  
 $\lambda = 557.7 \text{ nm (green)}$

Even lower altitudes :

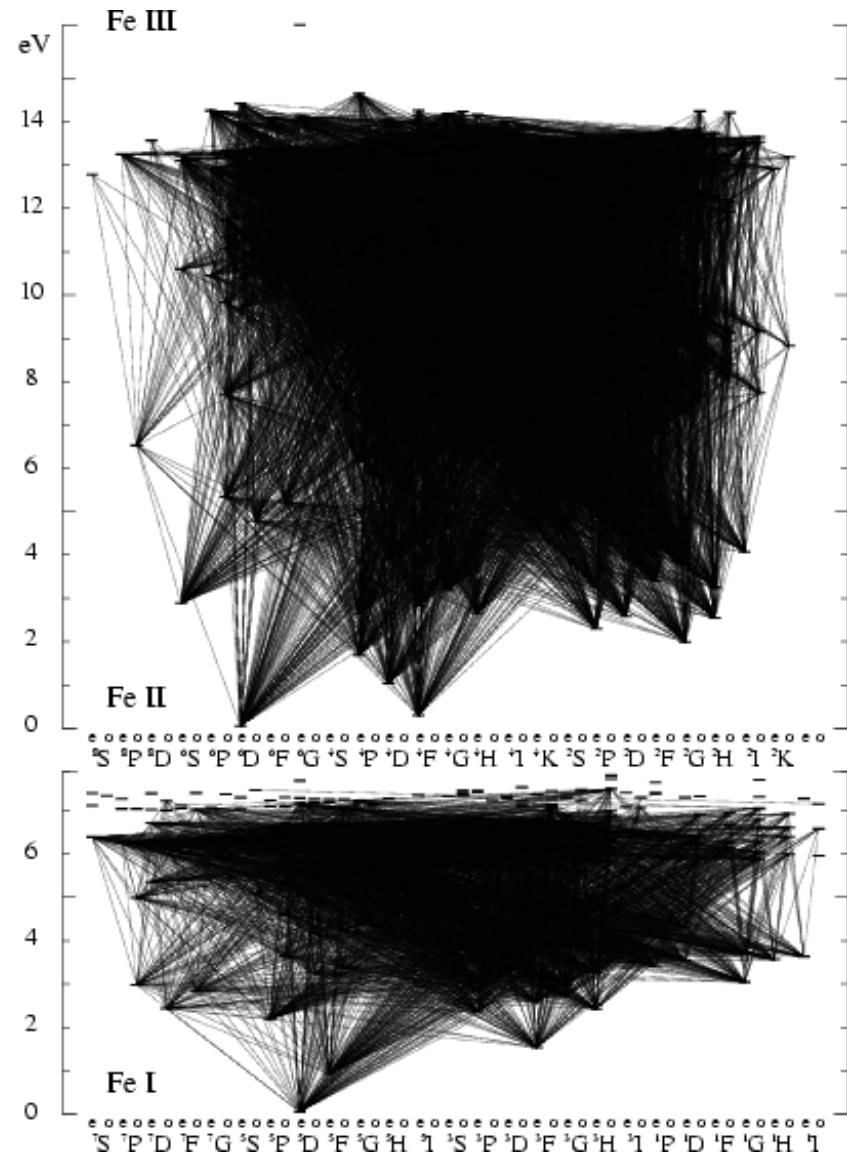
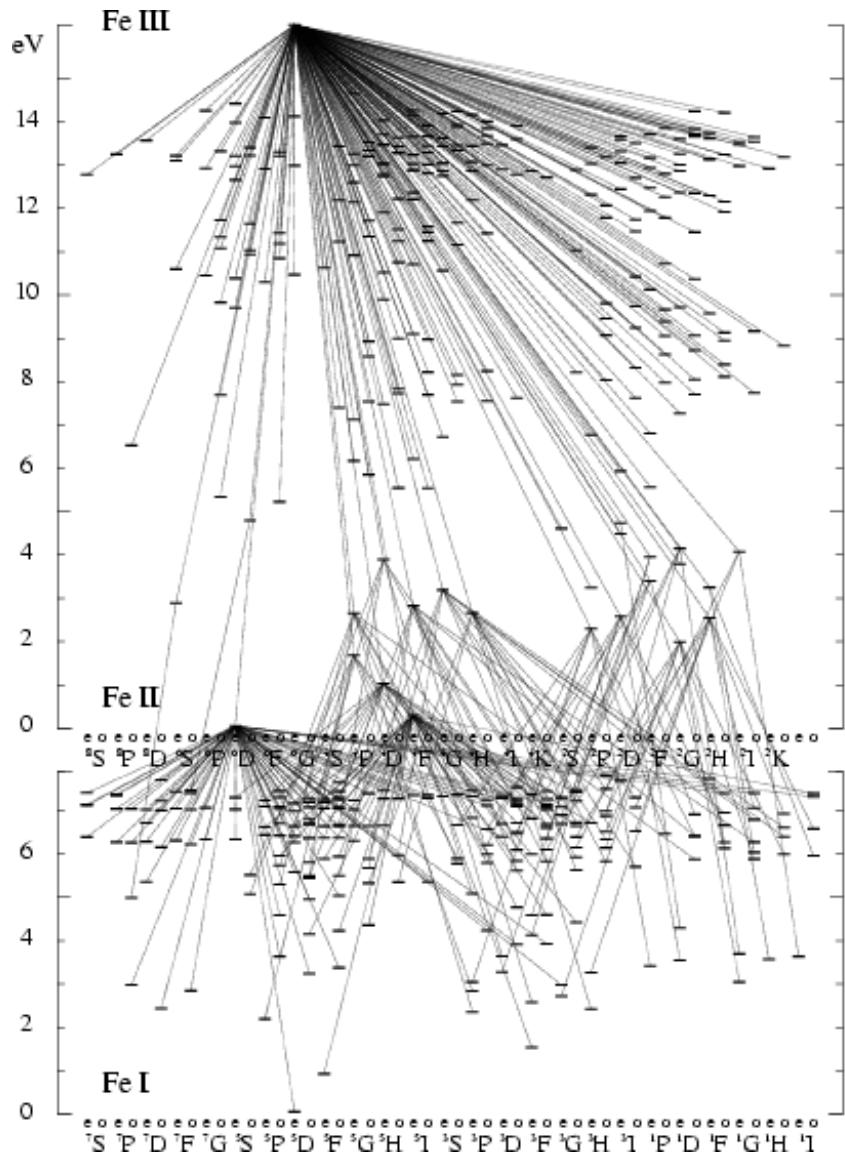
- molecular  $N_2$  and ionised  $N_2$  (blue or red)



<https://apod.nasa.gov/apod/ap180501.html>

<https://en.wikipedia.org/wiki/Aurora/>

# The mother of all Grotrian diagrams ?



## Examples of emission spectra

H :



He :



Na :



C :



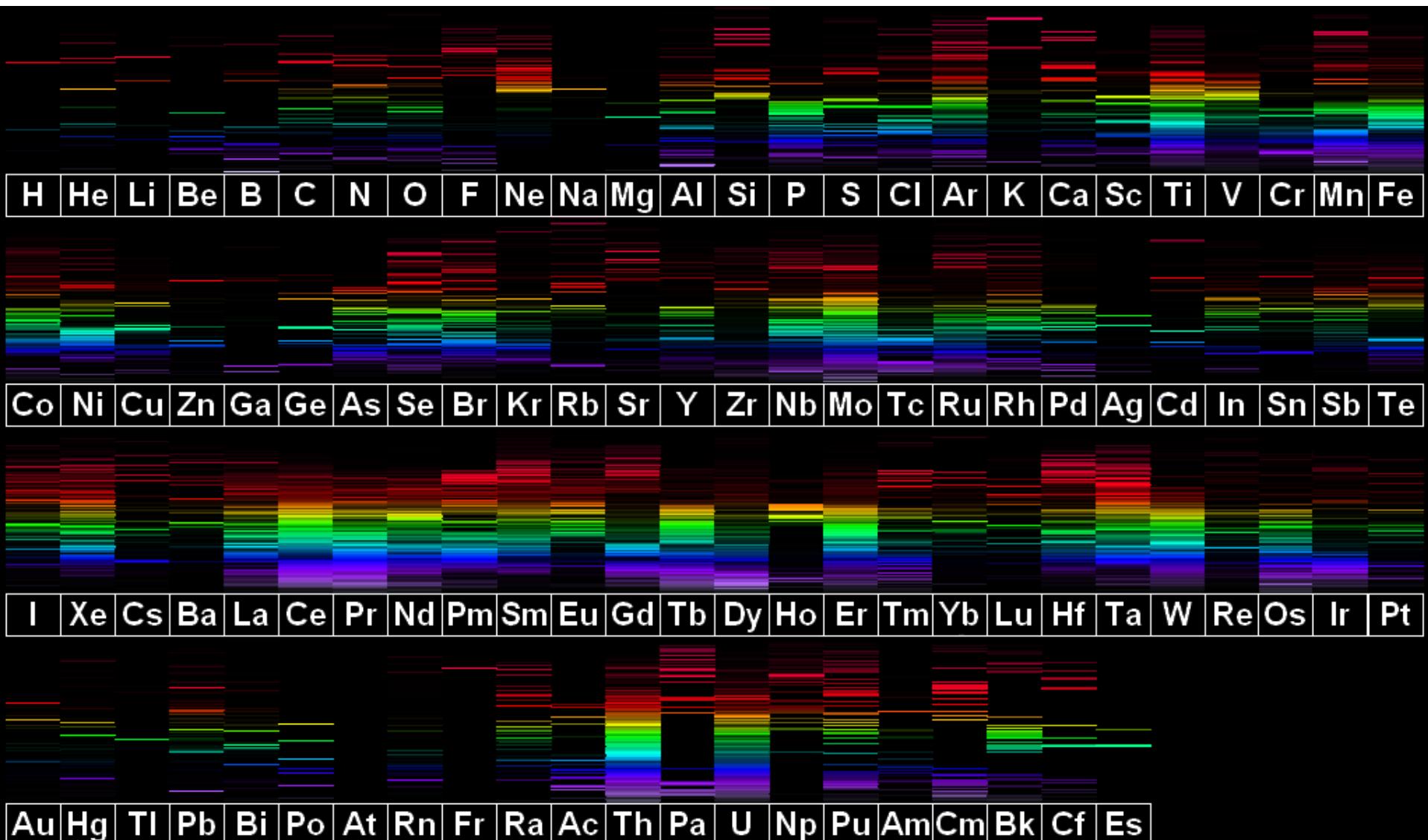
N :



O :



# A periodic table of emission spectra



# Emission and Absorption

- In *emission*, atoms are excited into all levels (e.g. by electrical discharge), and decay back to lower energy levels, emitting one or more photons
  - all possible transitions can (in principle) be seen
  - the observed spectrum consists of many isolated bright lines (as on the two previous slides)

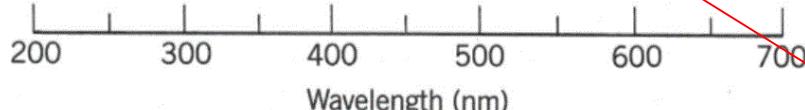
*Emission*

Hg



Ultraviolet      Visible

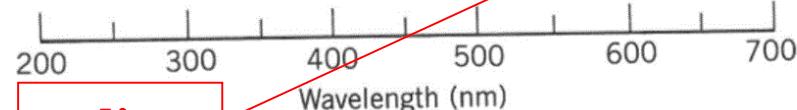
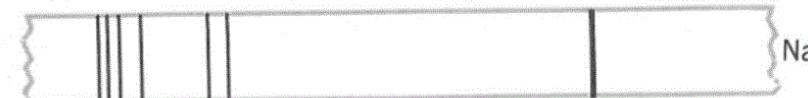
Na



*Absorption*



Ultraviolet      Visible



sodium  
D-lines

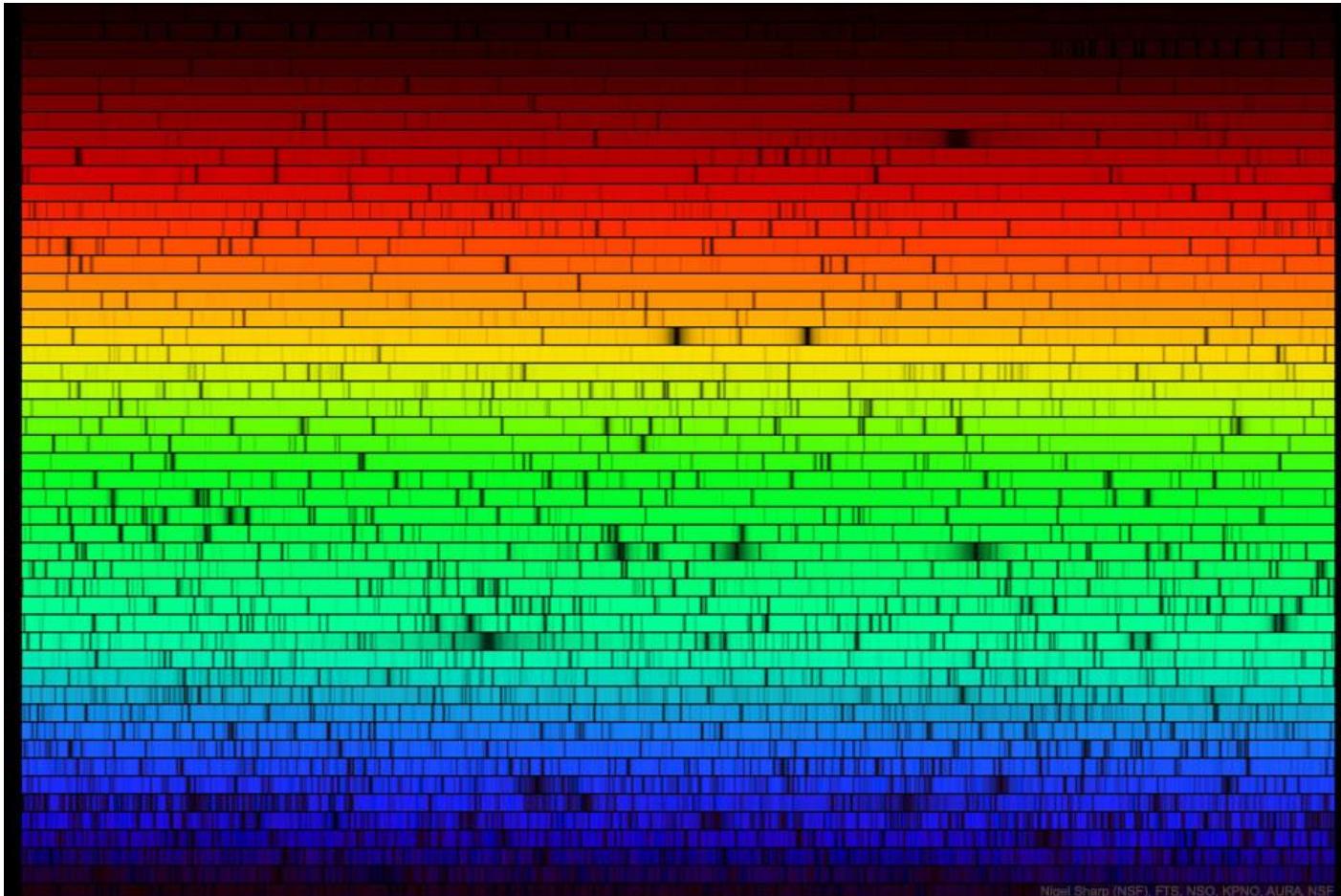
## Emission and Absorption (2)

- In *absorption*, atoms in their ground state are irradiated with a broad continuum of wavelengths
  - the observed spectrum contains dark lines due to transitions from the ground state to an excited state (absorbing a photon)
  - not all lines are seen in absorption (only those which involve the ground state)
- e.g. for sodium, only  $(3s) \leftrightarrow (np)$  lines are seen (including the D-lines)  
Absorption lines can also be seen due to transitions from metastable states  
e.g. for helium, absorption lines from  $(1s)(2s) \leftrightarrow (1s)(2p)$  can be seen
- Comparing emission and absorption spectra helps to distinguish which spectral lines are associated to which atomic states

## Absorption spectra : the Sun

- The element helium was discovered (1870) from its solar absorption lines

Nigel Sharp, NSF <https://apod.nasa.gov/apod/ap180926.html>



Nigel Sharp (NSF), FTS, NSO, KPNO, AURA, NSF

(not all the lines have yet been identified)

## Hund's Rules

- Can we explain the observed *ordering* of levels within each configuration ?
  - e.g. how are the  $2^3P_{2,1,0}$ ,  $2^1D_2$ ,  $2^1S_0$  levels within the carbon ground state  $(2p)^2$  multiplet (slide 7.46) ordered in energy ?
- If  $LS$  coupling applies, the ordering is given by *Hund's Rules* :

- (1) The largest permitted value of  $S$  lies lowest in energy
- (2) For a given value of  $S$ , the largest value of  $L$  lies lowest in energy
- (3) For given values of  $L$  and  $S$  :  
If the subshell is less (more) than half full, the smallest (largest) value of  $J$  lies lowest in energy

- Hund's rules are empirical – they don't always work (but see below)

## Hund's Rules (2)

- At some level, we can understand the physical origin of Hund's Rules :
  - (1) Maximising  $S$  makes the spin wavefunction as symmetric as possible, which tends to make the spatial wavefunction antisymmetric  
An antisymmetric spatial wavefunction vanishes for two  $e^-$  at the same position, keeping them apart and reducing the Coulomb energy
  - (2) Maximising  $L$  similarly tends to keep the electrons apart
  - (3) The ordering of states of different  $J$  arises from treating the spin-orbit term as a perturbation (fine structure)
- Up to at least xenon ( $Xe$ ,  $Z = 54$ ) , Hund's rules
  - correctly predict the quantum numbers of all ground states
  - correctly predict the  $J$  ordering of the fine structure levels for all ground states except He ( $Z = 2$ , see below) and Te ( $Z = 52$ )
  - correctly predict the ordering of terms within the ground state multiplet except for  $d^2$  (Ti, Zr) and  $d^8$  (Ni)

## The Landé Interval Rule

- Using the Wigner-Eckart theorem, it can be shown that

$$\langle Jm_JLS | \sum_i \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i | Jm_JLS \rangle = \zeta(L, S) \langle Jm_JLS | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | Jm_JLS \rangle$$

where  $\zeta(L, S)$  changes sign according to whether the subshell is more than, or less than, half filled

- Setting

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} (\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$$

$$\Rightarrow \langle Jm_JLS | \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | Jm_JLS \rangle = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \hbar^2$$

- Hence, for given  $L$  and  $S$ , the separation between neighbouring levels is

$$E_J - E_{J-1} \propto J(J+1) - (J-1)J = 2J$$

We thus obtain the *Landé interval rule* :

$$(E_J - E_{J-1}) \propto J$$

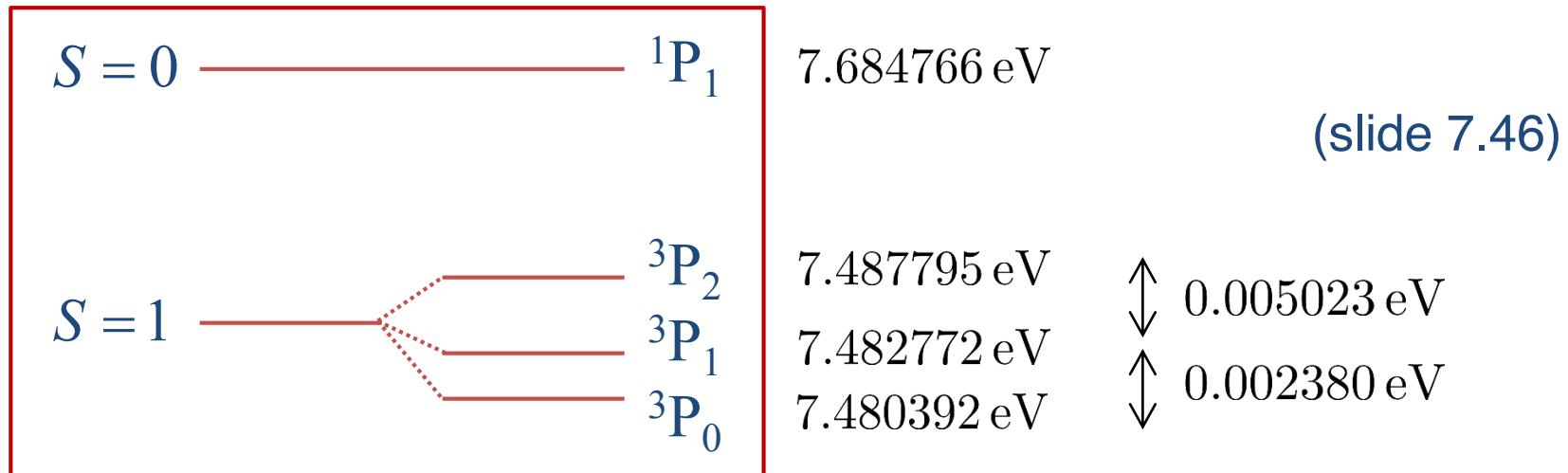
- ⇒ the separation between adjacent levels in a fine structure multiplet is proportional to the larger of the two  $J$  values

## Example: $(2p)^1(3s)^1$ excited state of carbon

$$\ell_1 = 1, \quad \ell_2 = 0, \quad s_1 = s_2 = 1/2$$

- Hund (1) : the total spin can be  $S = 1, 0$  ; predict  $S = 1$  lies lowest
- Hund (2) : the only possibility is  $L = 1$
- Hund (3) : for  $S = 0$ , the only possibility is  $J = 1$   
for  $S = 1$ , we can have  $J = 2, 1, 0$  ; predict  $J = 0$  lies lowest

The predictions agree with observation :

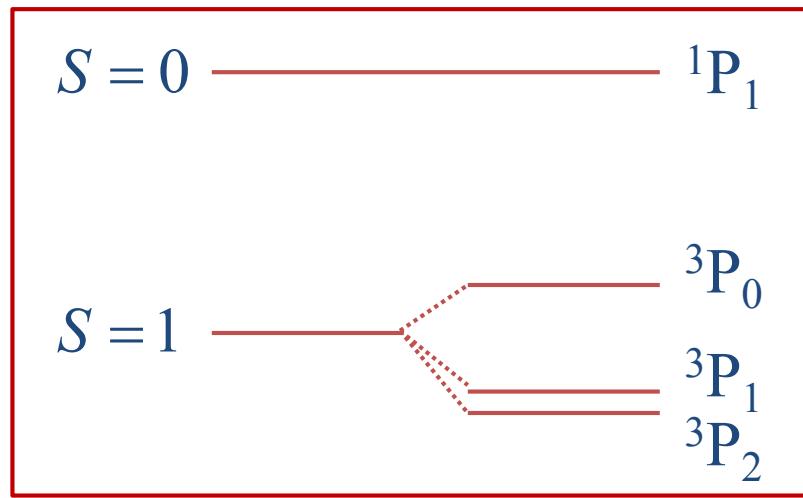


- The Landé interval rule predicts a fine structure splitting in the ratio 2:1, which is approximately obeyed

## Example: $(1s)^1(2p)^1$ excited state of helium

$$\ell_1 = 0, \quad \ell_2 = 1, \quad s_1 = s_2 = 1/2$$

- Hund's Rules give the same prediction as for  $(2p)^1(3s)^1$  on the previous slide; however, for helium, the predicted  $J$  ordering *disagrees* with data :  
the  $J=2$  level is found to lie lowest (not  $J=0$ )



21.2180228438 eV

(slide 7.43)

20.96421899233 eV

↑  $(1.2 \times 10^{-4})$  eV

20.96409650646 eV  
20.96408703092 eV

↑  $(9.5 \times 10^{-6})$  eV

- In helium, not only spin-orbit interactions for each electron are important,

$$\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{S}}_1, \quad \hat{\mathbf{L}}_2 \cdot \hat{\mathbf{S}}_2$$

but also “spin-other-orbit”, “spin-other-spin”, relativistic corrections, ...

$$\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{S}}_2, \quad \hat{\mathbf{L}}_2 \cdot \hat{\mathbf{S}}_1, \quad \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \quad \dots$$

## Example: $(2p)^2$ ground state of carbon

$$\ell_1 = \ell_2 = 1, \quad s_1 = s_2 = 1/2$$

- We now have two *equivalent electrons* in the partially filled (2p) subshell; the possible terms were worked out on slide 7.27

Hund (1) : can have  $S = 1, 0$  ; predict  $S = 1$  lies lowest

Hund (2) : for  $S = 0$  : can have  $L = 2, 0$  ;  $L = 2$  lies lower than  $L = 0$   
for  $S = 1$  :  $L = 1$  is the only possibility

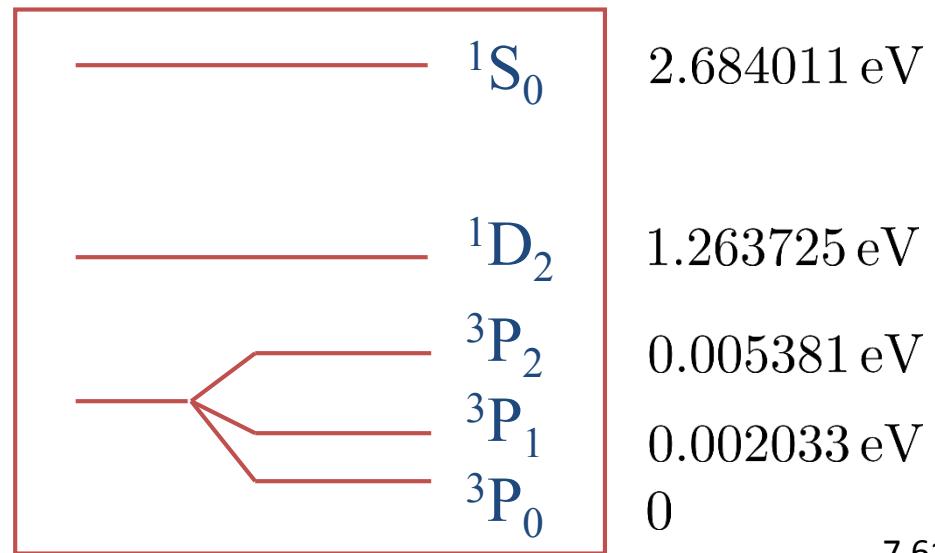
Hund (3) : the (2p) subshell is less than half full :  $J = 0$  lies lowest

- Hence, in order of increasing energy, Hund's Rules predict

$^3P_{0,1,2}, \ ^1D_2, \ ^1S_0$

(as observed, slide 7.46)

- The Landé interval rule is approximately obeyed



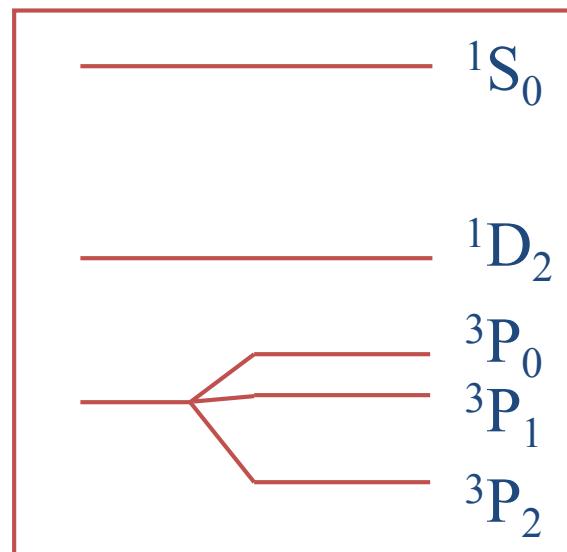
## Example: $(2p)^4$ ground state of oxygen

$$\ell_1 = \ell_2 = \ell_3 = \ell_4 = 1, \quad s_1 = s_2 = s_3 = s_4 = 1/2$$

- The possible values of  $S$ ,  $L$ ,  $J$  for  $(2p)^4$  are the same as for  $(2p)^2$ , but the subshell is now *more* than half full
  - ⇒ the *largest* possible value,  $J=2$ , lies lowest
- Hence the ground state of oxygen is predicted to be the same as for carbon, except that the fine structure ( $J$  ordering) is inverted :

$^3P_{2,1,0}, \ ^1D_2, \ ^1S_0$

(as observed, slide 7.48)



- The Landé interval rule is again approximately obeyed

## Example: $(2p)^3$ ground state of nitrogen

$$\ell_1 = \ell_2 = \ell_3 = 1; \quad s_1 = s_2 = s_3 = 1/2$$

- We now have *three equivalent electrons* in the unfilled subshell; the possible terms were worked out on slide 7.29

Hund (1) : can have  $S = 1/2, 3/2$ ;  $S = 3/2$  lies lowest

Hund (2) : for  $S = 3/2$ :  $L = 0$  is the only possibility

for  $S = 1/2$ : can have  $L = 2, 1$ ;  $L = 2$  lies lower than  $L = 1$

Hund (3) : for  $S = 3/2$ : the only possible value of  $J$  is  $J = 3/2$

for  $S = 1/2$ : there are multiple possible values of  $J$  ...

... but the subshell is *exactly* half-full ... quoi faire ???

- Modulo the  $J$  ordering, these predictions agree with observation: in order of increasing energy, the nitrogen ground state multiplet has terms

$$^4S_{3/2}, \ ^2D_{5/2, 3/2}, \ ^2P_{1/2, 3/2}$$

## Example: $(2p)^3$ ground state of nitrogen (2)

—	$^2P_{3/2}$	3.5756182 eV
—	$^2P_{1/2}$	3.5755703 eV
—	$^2D_{3/2}$	2.3846100 eV
—	$^2D_{5/2}$	2.3835297 eV
—	$^4S_{3/2}$	0

(slide 7.47)

- The *ground state* can be determined using Hund (1) alone  
The argument presented on slide 7.30 then gives the (correct) prediction
- $^4S_{3/2}$
- For the *excited states*, the ordering in  $J$  is not predicted (because the shell is half full), and  $^2D$  and  $^2P$  above are seen to have *opposite* ordering

# *jj Coupling*

( *non-examinable* )

- The spin-orbit interaction grows approximately as  $Z^4$ , while the electron-electron repulsion grows more slowly
  - ⇒ for heavy atoms, it is more appropriate to treat the e-e repulsion, rather than the spin-orbit interaction, as a perturbation :

$$\langle \hat{H}_2 \rangle \gg \langle \hat{H}_1 \rangle$$

- In *jj* coupling, the unperturbed Hamiltonian is taken to be

$$\hat{H}_0 + \hat{H}_2 = \hat{H}_0 + \sum_{i=1}^N \xi_i(r_i) \hat{\mathbf{L}}_i \cdot \hat{\mathbf{S}}_i$$

- $H_0 + H_2$  is a sum of  $N$  independent single-electron Hamiltonians, with
  - $[\hat{H}_0 + \hat{H}_2, \hat{\mathbf{J}}_i^2] = [\hat{H}_0 + \hat{H}_2, \hat{\mathbf{J}}^2] = 0$
  - ⇒ the unperturbed energy eigenstates are eigenstates of  $\mathbf{J}^2$ , and of  $\mathbf{J}_i^2$  for each electron

## *jj Coupling (2)*

- For  $jj$  coupling, the coupling procedure is
  - Combine  $\ell$  and  $s$  for each electron to find the allowed values of  $j$  :
$$j_i = \ell_i \otimes s_i = \ell_i \otimes 1/2 = \ell_i \pm (1/2)$$
  - Combine the values of  $j$  for each electron to find the allowed values of total  $J$  :
$$J = j_1 \otimes j_2 \otimes \dots \otimes j_N$$
- The effect of electron-electron repulsion (switching on  $H_1$  as a perturbation) is to split the  $J$  values for a given set of values of  $j$   
There are no simple rules like Hund's Rules to give the ordering in energy
- A prime example of  $jj$  coupling is to be found in *nuclear physics* :
  - the ***shell model of nuclear structure*** (see next term's Particle and Nuclear course) is an atomic-like model based on  $jj$  coupling

## Example: $(np)^2$ in $jj$ coupling

- Consider again  $(2p)^2$  of slide 7.61, but now for  $jj$  coupling rather than for  $LS$  coupling :  $\ell_1 = \ell_2 = 1, s_1 = s_2 = 1/2$

Each electron can have either  $j = 1/2$  or  $j = 3/2$

- If both electrons have the *same* value of  $j$ , they are equivalent, and the two-electron state must be *antisymmetric* :

$$j_1 = j_2 = 3/2 \Rightarrow J = 3, 2, 1, 0 ; \quad J = 2, 0 \text{ are antisymmetric}$$

$$j_1 = j_2 = 1/2 \Rightarrow J = 1, 0 ; \quad J = 0 \text{ is antisymmetric}$$

Hence the possible quantum numbers are

$$(j_1, j_2)_J = (3/2, 3/2)_0, (3/2, 3/2)_2, (1/2, 1/2)_0$$

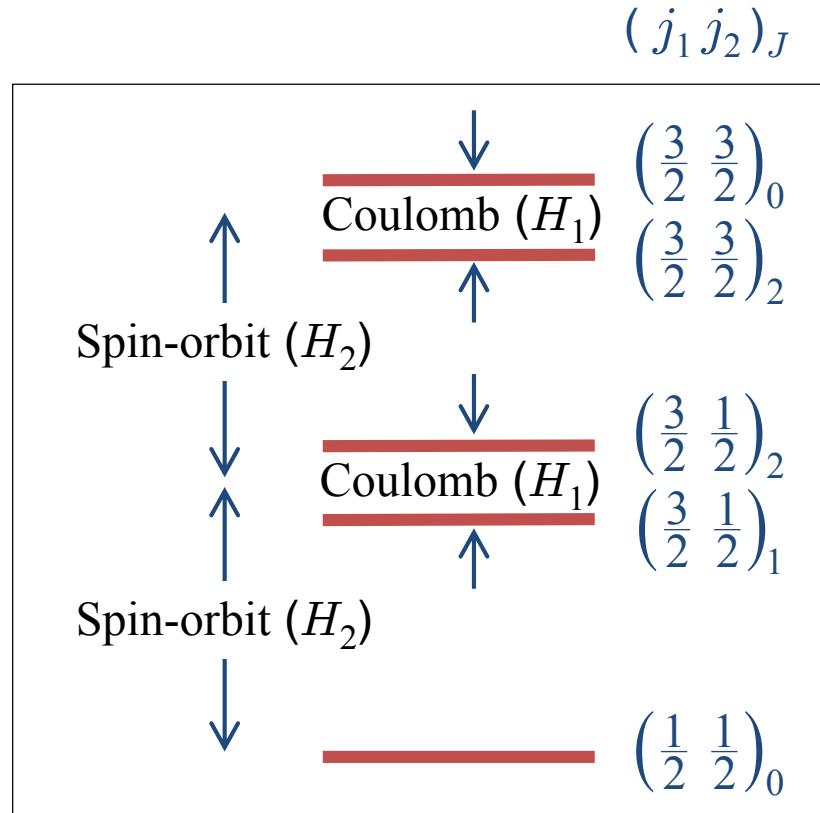
- If the two electrons have *different* values of  $j$ , there are no constraints on the value of  $J$  :

$$j_1 = 3/2, j_2 = 1/2 \Rightarrow J = 2, 1$$

$$(j_1, j_2)_J = (3/2, 1/2)_2, (3/2, 1/2)_1$$

## Example: $(np)^2$ in $jj$ coupling

- $LS$  and  $jj$  coupling lead to the same values of  $J$

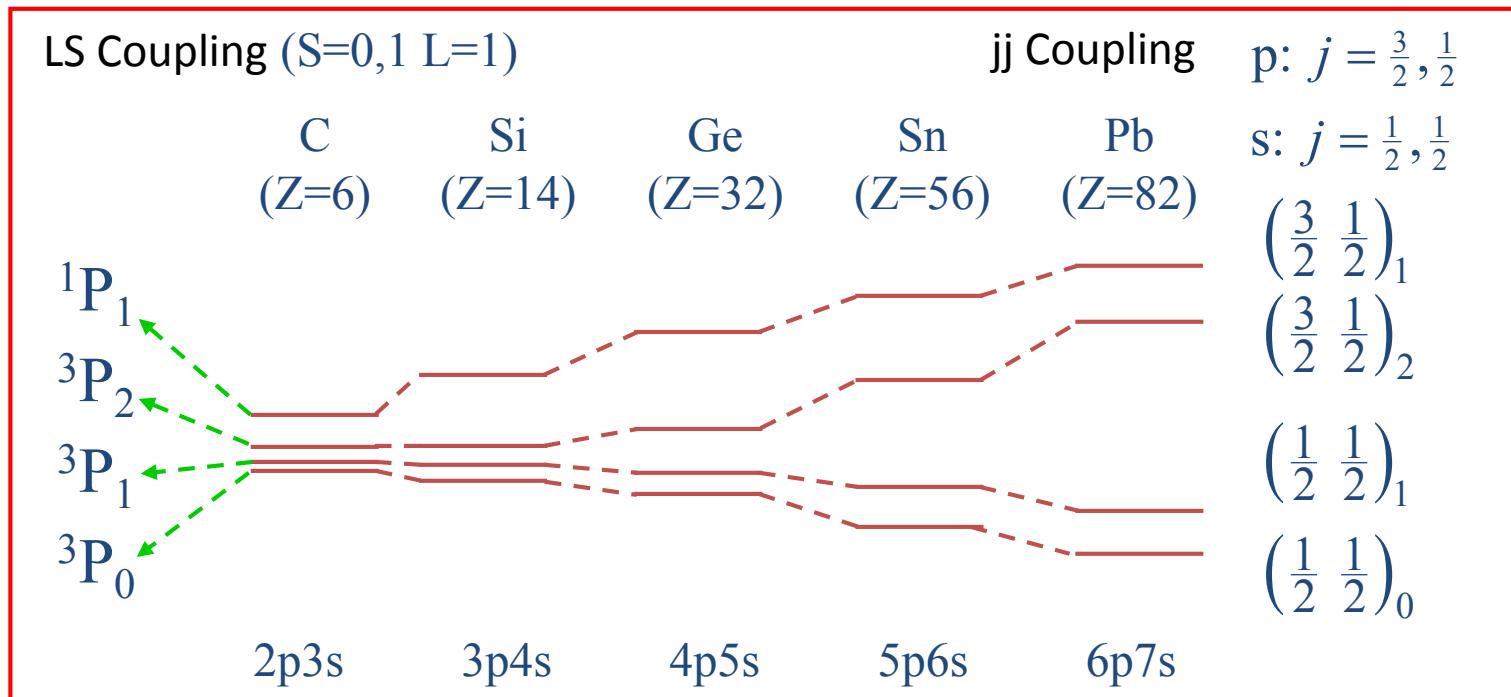


$$\langle \hat{H}_2 \rangle \gg \langle \hat{H}_1 \rangle$$

- The energy ordering above assumes that the  $J$  ordering for  $jj$  coupling is the same as found earlier (slide 7.61) for  $LS$  coupling

## Evolution from LS to jj coupling

- A classic example of the transition from *LS* to *jj* coupling is seen in a sequence of C-Si-Ge-Sn-Pb excited states :  $(2p)(3s)$ , ... ,  $(6p)(7s)$



- *LS* and *jj* states are linear combinations of each other ;  
real physical states are slightly different from either