

How to deal with atoms beyond H ie periodic table?

→ Approximate the interactions of one electron with all the others as if the other electrons formed a static cloud of negative charge surrounding the nucleus [deaf physicist who invented this: Hartree? Fock]

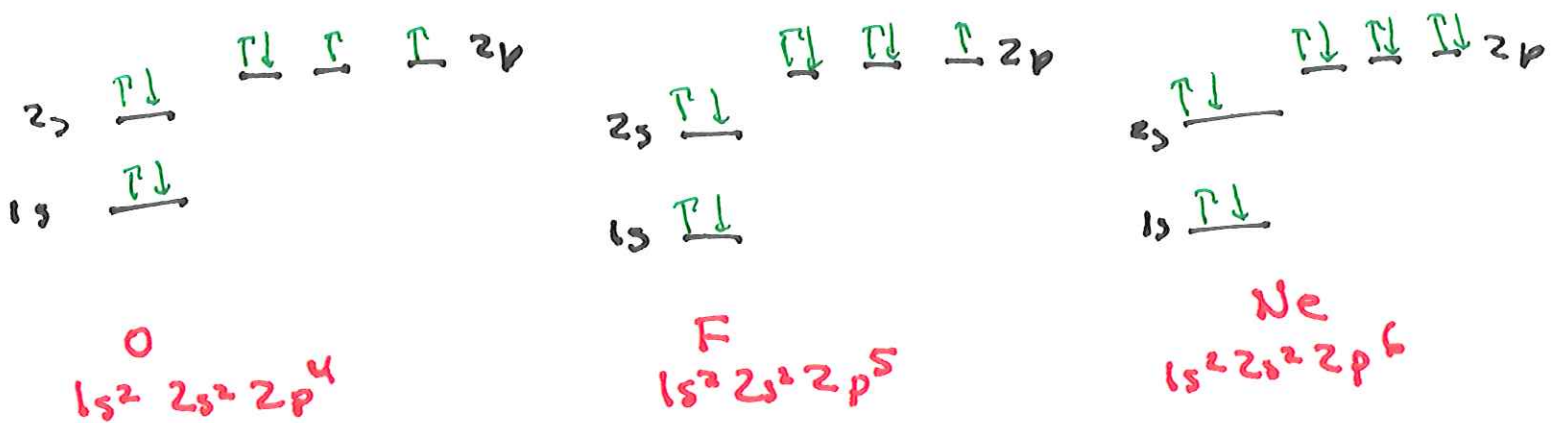
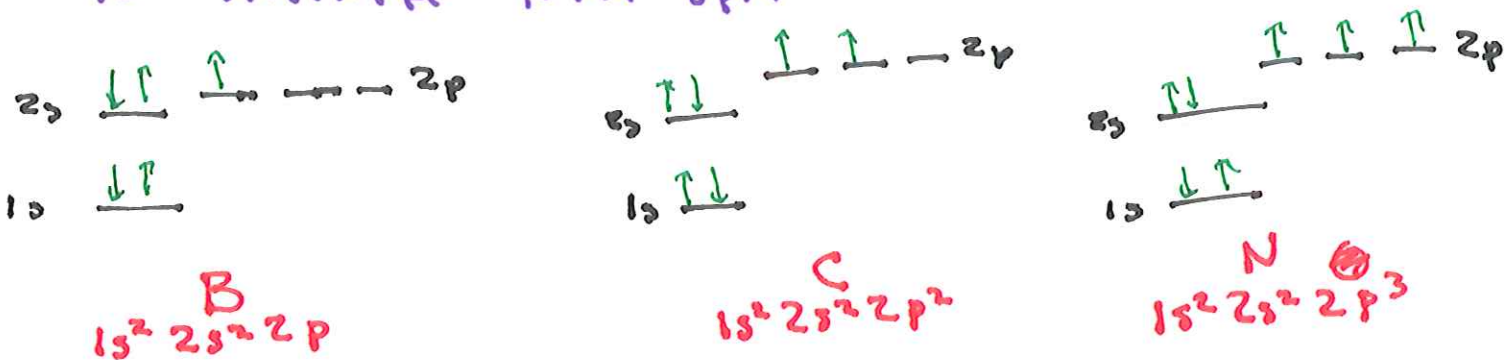
Result: the "l tilt" described previous lecture

Remarks: s, p, d →  $l = 0, 1, 2$   
with H atom:  $0 \leq l \leq n-1$

A state with angular momentum  $l$  is  $2l+1$  degenerate (not counting spin) ... eg in chemistry  $p_x, p_y, p_z$  but in real life:  $1117, 1107, 11-17$   
 $l \uparrow \quad m$

These are  $\psi_l^m(\theta, \phi)$  as wavefunctions

Simple chemist view: fill in these states - start with lowest available state. Follow Hund's rule to maximize total spin



the notation  $1s^2 2s^2 2p^3$  etc is called electron configuration

Note:  $4s$  is actually below  $3d$  so  $Ar = 1s^2 2s^2 2p^6 3s^2 3p^6$   
is followed by  $K = 1s^2 2s^2 2p^6 3s^2 3p^6 4s$

↳ this is a bit to write... abbreviate to  $[Ar]$

$Ca$  fills  $4s$  then  $Sc$  starts  $3d$  which finishes  $Zn$

"transition elements"

there is the big gap in the periodic table.

The  $4f$  states get filled following  $n=6$   $Rn$

$$\begin{aligned} &\uparrow \\ &l=3 \\ &2l+1=7 \end{aligned}$$

"Rare Earths" & Actinide series  
of 14 elements

$$2 \times 7 = 14$$

Note: particularly in the bottom half of periodic table (ie large  $Z$ ) the energy levels get close together so exceptions are not uncommon.

Grown up version - a filled orbital (eg  $2s^2$ )  
is spherically symmetric & antisymmetric under exchange  
and so it can largely be ignored. Focus on  
the electrons in the unfilled orbital (eg for  $C - 2p^2$ )  
we need to make wavefunctions that are antisymmetric  
under exchange. The radial wavefunction that is  
this orbital ( $R_{21}(r)$  for  $C$ ) will be identical  
for those remaining electrons and hence symmetric  
under exchange. we need to mix angle & spin to  
make something antisymmetric under exchange.

LS (or Russell-Saunders) coupling - combine all the orbital angular momentum; combine all the spin angular momentum. Combine so as to make something with overall antisymmetric symmetry.

Eg for Carbon:  $p \Rightarrow l=1 \rightarrow \overline{1+1} = 0, 1, 2 = L$   
 electrons are spin  $\frac{1}{2}$ :  $\overline{\frac{1}{2} + \frac{1}{2}} = 0, 1 = S$

3 ways to make antisymmetric:

- ①  $S=1 \rightarrow 3P$       ②  $S=0 \rightarrow 1D$       ③  $S=0 \rightarrow 1S$   
 $L=1$                        $L=2$                        $L=0$

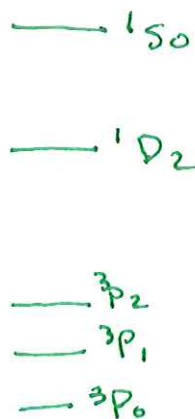
Hund's rule #2: the one with the largest S has lowest energy

Now combine total L & total S to make total J

For the singlets that's easy:  $1D \rightarrow 1D_2$        $1S \rightarrow 1S_0$   
 $\uparrow$  J value

For  $3P$ :  $\overline{1+1} = 0, 1, 2: 3P_0, 3P_1, 3P_2$

Hund's rule #3: For  $\frac{1}{2}$  or less filled orbitals small J has least energy. For  $> \frac{1}{2}$  filled max J has least energy



Note: all of these states are  $2p^2$  i.e. the electrons have same orbital  
 The difference in energy is a result of how angular momentum are combined to reduce the  $\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$  electron-electron interaction energy

carbon

Table II in handout says for  $N = (2p)^3$  the possible combinations are  $2P, 2D, 4S$

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

$S = \frac{3}{2}, L = 0$   
 $S = \frac{1}{2}, L = 2$

The ground state is  $4S_{3/2}$

$O = (2p)^4$  is just like Carbon except  $> \frac{1}{2}$  filled  
 so ground state is  $3P_2$

more complex case:  $Ti = (3d)^2$

$2p \uparrow \downarrow \uparrow \downarrow$   
 $l = 2$ ;  $\overline{2+2} = 0, 1, 2, 3, 4$   
 $\overline{\frac{1}{2} + \frac{1}{2}} = 0, 1$

mix/match for overall antisymmetry:

$L=4$	$L=3$	$L=2$	$L=1$	$L=0$
$S=0$	$S=1$	$S=0$	$S=1$	$S=0$
↓	↓	↓	↓	↓
$1G$	$3F$	$1D$	$3P$	$1S$

ground state  $3F_2$  ✓ table p217 text

using table II in handout ground state  $V = (3d)^3$

is  $4F_{3/2}$   $L=3$   $S=3/2$

From text p217 see Cr actually anomalous but if it were  $Cr = (3d)^4$  from table II in handout

$5D_0$   $L=2$   $S=2$

$Mn = (3d)^5 \rightarrow 6S_{5/2}$

Notation:  $2S+1$   
 $L$   
 $J$

Note: not all transitions are "allowed" - the rules are on the handout - we will touch on those rules at the end of this course. For the time being note that the  $l$ 's of the electrons must change by an odd number ("parity" change) so for the low levels we've been discussing are not connected by transitions. However as Fig 58 on handout shows "forbidden" transitions do occur particularly in very low density gases w/o walls - i.e. in space

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### Solid State Physics - electrons in solids

Start with a super simple model - replace nuclei with a uniform "jelly" of positive charge and ignore electron-electron interactions. This is motion in a homogeneous space - "free" particles or particle in a box

if we make box = cube with sides  $l_x, l_y, l_z$

$$\rightarrow \psi = \sqrt{\frac{8}{l_x l_y l_z}} \sin\left(\frac{n_x \pi}{l_x} x\right) \sin\left(\frac{n_y \pi}{l_y} y\right) \sin\left(\frac{n_z \pi}{l_z} z\right)$$

where we've required  $\psi = 0$  at box edge

Remark: a better choice is:  $e^{i\vec{k}\cdot\vec{r}}$

where  $\vec{k} = \left(\frac{2\pi}{l_x} n_x, \frac{2\pi}{l_y} n_y, \frac{2\pi}{l_z} n_z\right)$

This is what you did p 59 for free particles

Here  $\psi(x) = \psi(x+L)$  "periodic boundary conditions"

You will do this in Stat Mech next semester.