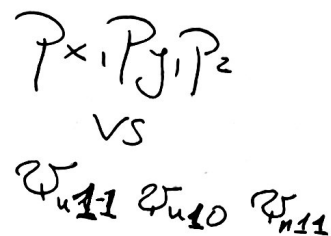
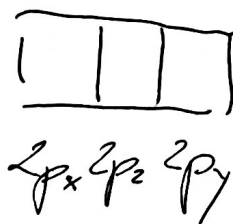


# Multielectron Atoms - Atomic Terms

## Motivation

C:



Atomic Term:

$$2s+1$$
  
 $L$

S: Total spin angular momentum  
 L: Total orbital angular momentum  
 J: "Total angular momentum"

Vector Addition:

$$\vec{L} = \sum_i \vec{L}_i$$

$$\vec{S} = \sum_i \vec{S}_i$$

$$\hat{L}^2 \psi_{ulm} = \hbar^2 l(l+1) \psi_{ulm} \quad \hat{S}^2 \alpha = \hbar^2 \frac{1}{2}(\frac{1}{2}+1) \alpha$$

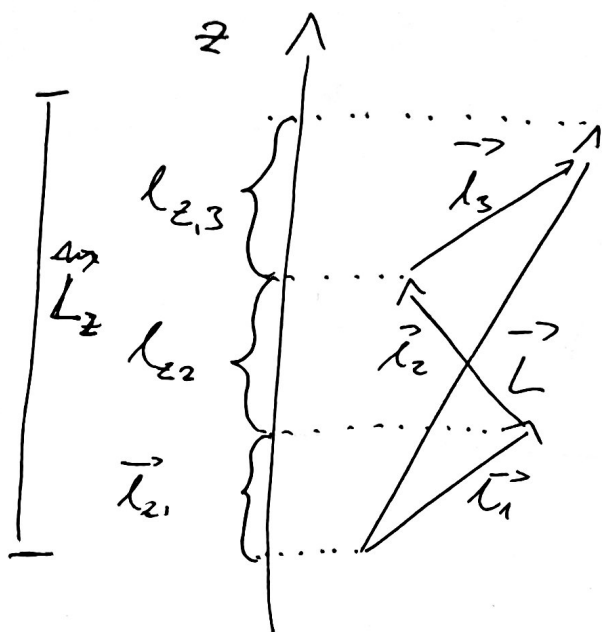
Instead: the z component of  $\vec{L}$  and  $\vec{S}$

$$L_z = \sum_i L_{iz} = \sum_i m_{li}$$

$$S_z = \sum_i S_{iz} = \sum_i m_{si}$$

$$M_L =$$

$$M_S =$$



1. The order/permutation does not matter

2.  $\vec{L}$  vs  $[l_x, l_y]$

$2S+1$   $L: 0 1 2 3 4 5$

$L \rightarrow$

$2S+1 \rightarrow$  multiplicity

1  $\rightarrow$  singlet  $(\uparrow\downarrow) S=0$

2  $\rightarrow$  Doublet

3  $\rightarrow$  Triplet

$(\uparrow\downarrow) S=\frac{1}{2}$

$S=1$

$\vec{J} = \vec{L} + \vec{S}$  / spin-orbit coupling.

Helium atom

$1s^2$



Lithium atom

$1s^2 2s^1$



Neon atom

$2s^2 2p^6 \rightarrow$

Zn atom

$4s^2 3d^{10} \rightarrow$

Excited Helium atom

$1s^* 2s^1$



microstate vs macrostate

$^3S_1$  and  $^1S_0$

Triple  
degeneracy  
( $2S+1$ )

non-  
degeneracy

3-microstates

1-microstate

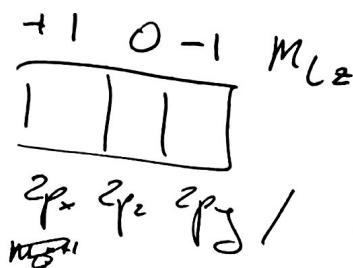
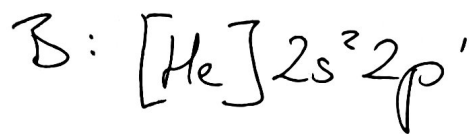
$\uparrow_{1s} \uparrow_{2s}$

$\downarrow_{1s} \downarrow_{2s}$

$\uparrow_{1s} \downarrow_{2s}$

$\uparrow_{1s} \uparrow_{2s}$

Boron atom  
B:  $[He] 2s^2 2p^1$



$$M_L =$$

$$M_s =$$

$$\vdash \Rightarrow$$

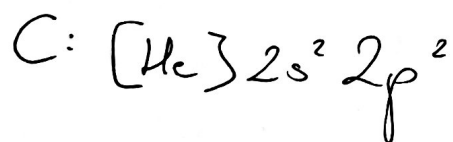
$\Rightarrow$

$M_{L_2}$	$M_S$
1	
0	
-1	

$$\vec{J} = \vec{L} + \vec{S}$$

$$J = L + s, L + s - 1, \dots, L - s$$

Carbon atom



A hand-drawn diagram consisting of a horizontal line and a vertical line intersecting. The label  $M_L$  is positioned in the top-left quadrant, and the label  $M_S$  is positioned in the top-right quadrant. The lines are drawn with a black pen on a white background.

$$\text{Total: } \frac{6!}{2!4!} = 15$$

Resulting terms:

$$J = {}^3P \quad {}^1D \quad {}^1S$$

In effect:

Microstates:

$$\underbrace{(5 + 3 + 1)}_{{}^3P \quad (3 \times 3)} + \underbrace{5}_{{}^1D \quad (5 \times 1)} + \underbrace{1}_{{}^1S \quad (1 \times 1)}$$

Energy ordering: Hund's Rules.

- ① The largest value of  $S$  (multiplicity)
- ② For the same  $S$ , the largest value of  $L$
- ③ if filled less than half: smallest  $J$   
if filled more than half: largest  $J$  ⑤

For Hydrogen Atom:  
(Table 8.5)

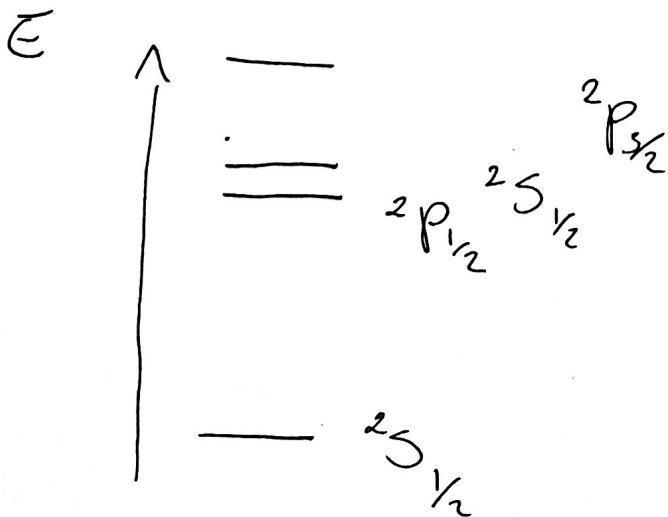
		$E: (eV)$
1s	$1s^2S_{1/2}$	0.00
2p	$2p^2P_{1/2}$	82258.317
2s	$2s^2S_{1/2}$	82258.942
2p	$2p^2P_{3/2}$	82259.272

What does the difference come from?

# Rydberg formula  
 $109677.5(1 - \frac{1}{n^2})$   
is "satisfied"

Spin-Orbit coupling

$$\hat{H} = \underbrace{-\frac{\nabla^2}{2} - \frac{1}{r}}_{\hat{H}_0} + \underbrace{\frac{1}{2} \hbar^{-1} \vec{r} \cdot \vec{l} \cdot \vec{s}}_{\hat{H}_{SO}}$$



Selection Rules

$$\Delta S = 0$$

$$\Delta L = \pm 1$$

$$\Delta J = 0, \pm 1$$

(except  $0 \rightarrow 0$ )

Example 8.3

⑥