

Hund's rules state that, to determine the  
(a)  $(S, L, J)$  ground state of an atom, we

- ① First, maximize  $S$ .
- ② Then, maximize  $L$ .
- ③ Finally, for more than half-filled shells, maximize  $J$ ; otherwise minimize  $J$ .

When applying Hund's rules, we need to take care to only consider valid states.

Applying Hund's rules to Li, B, N, Na, and K, we get

Element	$S$	$L$	$J$	term symbol
Li ( $Z=3$ )	$1/2$	$0$	$1/2$	$2S_{1/2}$
B ( $Z=5$ )	$1/2$	$1$	$1/2$	$2P_{1/2}$
N ( $Z=7$ )	$3/2$	$0$	$3/2$	$4S_{3/2}$
Na ( $Z=11$ )	$1/2$	$0$	$1/2$	$2S_{1/2}$
K ( $Z=19$ )	$1/2$	$0$	$1/2$	$2S_{1/2}$

Nitrogen is a little tricky.

It has three valence electrons in the 2p shell.

They have quantum numbers  $l_1, m_{l1}, m_{s1}, l_2, m_{l2}, m_{s2}, l_3, m_{l3}, m_{s3}$   
with  $l_1 = l_2 = l_3 = 1$ .

(a<sub>con</sub>) To maximize  $S$  to  $3/2$ , we need that

$$m_{s_1} = m_{s_2} = m_{s_3} = \pm 1/2,$$

in other words that all three electrons' spins are aligned.

So, in the  $|l_1 m_{l_1} m_{s_1}; l_2 m_{l_2} m_{s_2}; l_3 m_{l_3} m_{s_3}\rangle$  basis, we know that the ground state must satisfy

$$|1 m_{l_1} 1/2; 1 m_{l_2} 1/2; 1 m_{l_3} 1/2\rangle.$$

Since these are electrons, they are fermions and cannot occupy the same state.

Therefore,  $m_{l_1}, m_{l_2}, m_{l_3}$  must all be different.

Since  $m_{l_i} \in \{-1, 0, 1\}$  for  $l_i = 1$ , the only

possible state satisfying  $S = 3/2$  and  $l_1 = l_2 = l_3 = 1$

is the  $m_{l_1} = -1, m_{l_2} = 0, m_{l_3} = +1$  state:

$$|1 -1 1/2; 1 0 1/2; 1 1 1/2\rangle.$$

This state has  $M_L = 0$ , which implies that  $L = 0$ .

This means that the only possible  $J$  is  $J = 3/2$ .

(b) The lowest frequency line in the absorption spectrum of Na corresponds to an electron in the  $3s$  level absorbing a photon and being excited to a  $3p$  state. There are two such states, split by the spin-orbit effect. The splitting is given by

$$E_{so} \approx -\vec{\mu}_s \cdot \vec{B}$$

where  $\vec{\mu}_s = -g_s \mu_B \vec{S} / \hbar$  is the magnetic moment of the electron and  $\vec{B}$  is an effective magnetic field.

Semiclassically, we can think of the  $\vec{B}$  field as arising from a charged nucleus rotating around the electron:

$$\vec{B} \propto \frac{q\vec{v}}{c} \times \vec{E}. \quad (\text{related to Biot-Savart law})$$

The  $\vec{E}$  field is that of a point charge

$$\vec{E} \propto \frac{e}{r^2} \hat{r}.$$

So

$$\begin{aligned} \vec{B} &\propto \frac{qe}{cr^2} \vec{v} \times \hat{r} = \frac{qe}{cmr^2} (m\vec{v} \times \hat{r}) \quad (\vec{r} = r\hat{r}) \\ &= \frac{qe}{cmr^3} (m\vec{v} \times \vec{r}) = \frac{qe}{cmr^3} \vec{L}, \quad (\vec{L} = m\vec{v} \times \vec{r}) \end{aligned}$$

(b con) This then tells us that the spin-orbit splitting can also be written as

$$\begin{aligned}
 E_{SO} &= -\vec{\mu}_s \cdot \vec{B} \\
 &= -\left[ \frac{g_s m_B}{\hbar} \vec{S} \right] \cdot \left[ \frac{q_e}{4\pi\epsilon_0 r^3} \vec{L} \right] \\
 &= -\frac{g_s m_B q_e}{m c \hbar} \frac{1}{r^3} \vec{L} \cdot \vec{S} \\
 &\propto \vec{L} \cdot \vec{S} \cdot \frac{1}{r^3}
 \end{aligned}$$

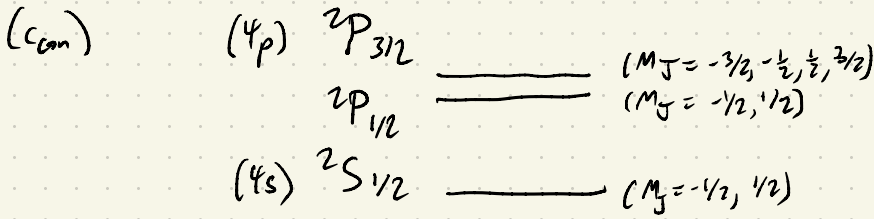
For the particular states considered,  $L$  and  $S$  are fixed and non-zero, so the splitting is proportional to  $\langle \frac{1}{r^3} \rangle$ .  $n = -3$ .

(c) For potassium  $K (Z=19)$ , there is one  $4s$  valence electron in the ground state. The term symbol corresponding to this  $(L=0, S=1/2, J=1/2)$  state is  $^2S_{1/2}$ .

The lowest single valence electron states are

$[Ar] 4s$	$^2S_{1/2}$	$(S, L, J) = (1/2, 0, 1/2)$
		<small>① max @ max @ min ← Hund's rules</small>
	$^2P_{1/2}$	$(1/2, 1, 1/2)$
$[Ar] 4p$	$^2P_{3/2}$	$(1/2, 1, 3/2)$

The energy levels look like



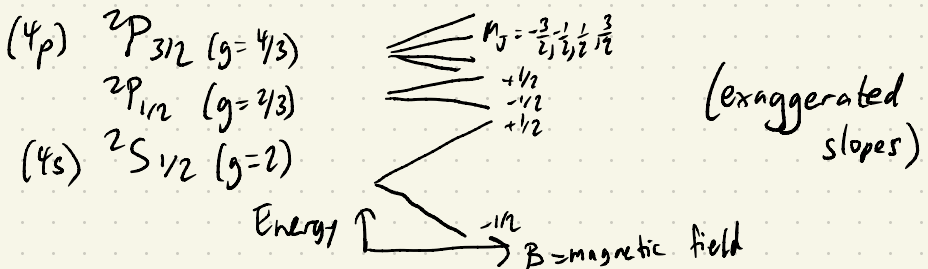
The energy of the electron's magnetic dipole in a magnetic field  $\vec{B} = B\hat{z}$  is

$$\hat{H}' = -\vec{\mu}_J \cdot \vec{B} = \frac{e}{2m} g \vec{J} \cdot \vec{B} = \frac{e}{2m} g J_z B \propto g M_J$$

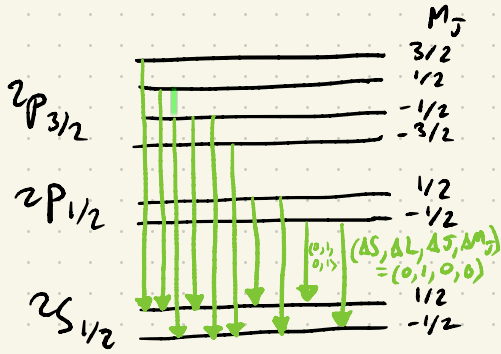
where  $\vec{\mu}_J = -\frac{e}{2m} g \vec{J}$  is the magnetic dipole of the electron in an  $(S, L, J)$  atomic state ( $g$  is the Landé- $g$  factor, which depends on  $S, L, J$ ).

So, larger  $g$  and  $M_J$  correspond to larger changes in energies due to magnetic fields.

The perturbed energy levels look like:



(d) All of the allowed E1 (dipole) transitions to the  $2S_{1/2}$  states are



which were determined by following the selection rules.