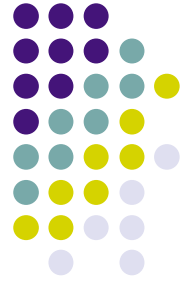# Chapter 4. Atomic Spectroscopy

Hartree Approximation (mean field approximation) - electron-electron repulsion is replaced with average mean field potential. Many electron system is described in terms of hydrogen-like single electron states.

n : principal quantum number (shell)

l, m, s : angular momentum, magnetic momentum (z-component of l), and spin quantum numbers of a single electron
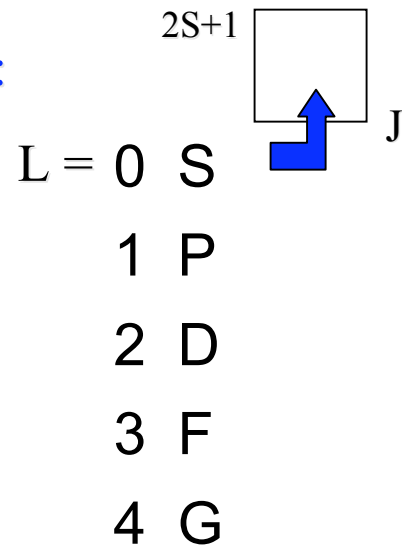
Orbital: specified by n and l

Configuration - Assignment of electrons to orbitals
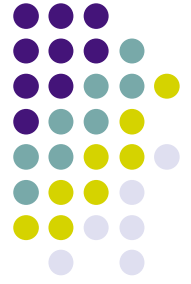
L, M, S : quantum numbers for sum over all the electrons

For l_1 and l_2

$$l = |l_1 - l_2|, \ldots, l_1 + l_2$$

Term Symbol:

$$^{2S+1}\boxed{}_J$$

L = 0 S

1 P

2 D

3 F

4 G

J: Quantum number for sum of L and S

Possible combinations of angular momenta and term symbols for two equivalent p electrons.

L	S	J	Term Symbols
2	0	2	$^1D_2$
1	1	2,1,0	$^3P_2,\ ^3P_1,\ ^3P_0$
0	0	0	$^1S_0$

Hund's rules

(i) Of the terms arising from equivalent electrons, those with the highest multiplicity lie the lowest in energy.

(ii) Of these, the lowest is that with the highest value of L.

Lande's interval rule

For less than half-filled orbitals, smaller J has lower energy.
For more than half-filled orbitals, larger J has lower energy.

Selection rules

$$\Delta S = 0$$

$$\Delta L = \begin{cases} \pm 1, 0 & \text{if } L' \neq 0 \\ 1 & \text{if } L' = 0 \end{cases}$$

$$\Delta J = 0, \pm 1 \ (\text{ no } 0 \leftrightarrow 0 \text{ transition})$$

Laporte's Rule $\qquad \sum_i l_i :$ even $\leftrightarrow$ odd

This is due to the fact that the transition dipole vector has odd inversion symmetry and that the sum of l_i dtermines the inversion symmetry of the eigenstate.
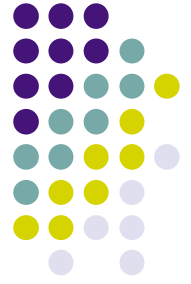
Examples of Atomic Spectra

1. Alkali metal atoms (Li,Na, K, Rb, Cs) - (Closed shell)ns^1

Emission has at least three series in the visible region.

$$\Delta n : \text{unrestricted}$$

$$\Delta l = \pm 1 \quad (\ \Delta l = 0 \text{ is forbidden because of Laporte's rule})$$
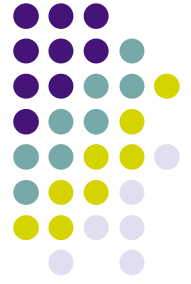
$$\Delta J = 0, \pm 1 \text{ except } J = 0 \nleftrightarrow J = 0$$

$$S : s \rightarrow p$$
$$P : p \rightarrow s$$
$$D : d \rightarrow p$$
$$F : f \rightarrow d$$

The principal series in the sodium atom (Na)

$$n\,^2P_{1/2} \to 3\,^2S_{1/2}$$
$$n\,^2P_{3/2} \to 3\,^2S_{1/2}$$

$$n \geq 3$$

n=3: Sodium D lines: 589.592 nm, 588.995 nm

Hydrogen atom

Ground state ($^2S_{1/2}$) : $n = 1, l = 0, s = 1/2$

Excited states ($^2P_{3/2},\ ^2P_{1/2},\ ^2S_{1/2}$): $n = 2, l = 1, s = 1/2$

Helium atom

Ground state configuration: $1s^2$ Ground state term: $1\,^1S_0$

Excited state configurations: $1s^1np^1, 1s^1nd^1, \ldots$

Excited state terms: $n\,^1S_0,\ ^1P_1,\ ^1D_1$ Singlets

$n\,^3S_1,\ ^3P,\ ^3D$ Triplets