

Chapter 11. Quantum states for many-electron atoms and atomic spectroscopy

Atomic spectra

H atom:

Not all transitions are allowed, due to conservation of angular momentum (photon has $1\hbar$ of angular momentum).

Selection rules:

$$\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1.$$

Example:

$1s \rightarrow 2s$, forbidden

$1s \rightarrow 2p_z$, allowed

$1s \rightarrow 3d_{z^2}$, forbidden

$3s \rightarrow 2p_y$, allowed

$3s \rightarrow 1s$, forbidden

For many-electron atoms, an electronic configuration may give rise to several states with different energies, because of the interaction between electrons (orbital-orbital, spin-spin, and spin-orbital)

Each state is represented by a term symbol:

$$^{2S+1}L_J$$

Total orbital angular momentum L of an atom

$$L = l_1 + l_2 + \dots \quad (\text{vector sum})$$

For a two-electron atom

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, l_1 + l_2 \quad (\text{Clebsch-Gordan series})$$

Code of L :

L :	0	1	2	3	4	...
	S	P	D	F	G	...

Example: L for $3p^1 3d^1$.

$$l_1 = 1 \text{ and } l_2 = 2.$$

so $L = 1, 2, 3$ or three terms P, D, F

Total spin angular momentum S of an atom

$$S = s_1 + s_2 + \dots$$

For a two-electron atom

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2$$

The multiplicity is $2S + 1$

Example: S for a two e^- atom.

$$s_1 = 1/2, s_2 = 1/2,$$

so $S = 0, 1$, or multiplicity = 1 (singlet), 3 (triplet).

Degeneracy can be removed by external field.

Since electrons are charged, their rotation and spin generate magnetic fields, and they interact with each other.

A closed shell has $L=0, S=0$. A p^n configuration is equivalent to p^{6-n} one.

Total angular momentum (Russell-Saunders coupling)

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

or

$$J = |L - S|, |L - S| + 1, \dots, L + S$$

Examples: He ($1s^2$)

$$\begin{array}{ll} l_1=l_2=0, & L=0 \\ s_1=s_2=1/2, & S=0 \text{ (1 violates Pauli's rule)} \end{array}$$

So, $J=0$. Term: 1S_0 . (close shell atom)

Ground and excited states of Na, $[\text{Ne}]3s^1$, $[\text{Ne}]3p^1$.

Single electron (ignore inner e^-), $l = 0, s = 1/2$,

$$L = 0, \quad S = 1/2 \text{ (} 2S+1 = 2 \text{)}, \quad J = 1/2$$

So the ground state term is $^2S_{1/2}$

$$L = 1, \quad S = 1/2 \text{ (} 2S+1 = 2 \text{)}, \quad J = 1/2, 3/2$$

So the terms are $^2P_{1/2}$ and $^2P_{3/2}$.

Excited state of Na splits to 2 sublevels because of the interaction between spin and orbital angular momenta (spin-orbit coupling, a relativistic effect)

Energy

$$E_{L,S,J} = (1/2)hcA[J(J+1) - L(L+1) - S(S+1)]$$

A is the coupling constant that increases with $\sim Z^4$, so spin-orbit coupling becomes more important for heavy atoms.

Splitting:

$$\begin{aligned} \Delta\tilde{\nu} &= \frac{\Delta E}{hc} = \frac{1}{2}A[J(J+1) - J'(J'+1)] \\ &= \frac{1}{2} \times 11.5 \text{ cm}^{-1} \left[\frac{3}{2} \left(\frac{3}{2} + 1 \right) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] = 17.25 \text{ cm}^{-1} \end{aligned}$$

Selection rules

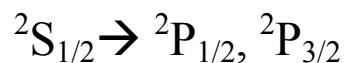
Not all transitions between energy levels are allowed.

$$\Delta S = 0$$

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

$$\Delta J = 0, \pm 1 \text{ but } J = 0 \text{ cannot combine with } J = 0$$

Fine structure of the Na D lines



$$\Delta S = 0, \Delta L = 1, \Delta J = 0, 1 \quad (\text{allowed})$$