Multi-electron atoms (L-S coupling)

The Hamiltonian is

$$H = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j>i} \frac{e^2}{r_{ji}} \right\}$$

Central-field approximation:

Assume that the repulsion (last term, RHS) be replaced by a radially smooth potential, $S(r)$

$$V_{CF}(r) = -\frac{Ze^2}{r} + S(r)$$

$$H_{CF} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m_e}\nabla_i^2 + V_{CF}(r_i) \right\}$$

We construct

$$\Psi = \psi_1(r_1)\,\psi_2(r_2)\ldots\psi_N(r_N)$$

$$\left[\frac{-\hbar^2}{2m_e}\nabla_i^2 + V_{CF}(r_i) \right] = E_i \psi_i$$

The total energy of the atom is $\sum_{i=1}^{N} E_i$

Since the potential is radially symmetric, as with hydrogen, the Schrodinger equation, splits into, radial and (θ, ϕ), differential equations. The latter are spherical harmonics, as before.

$$\psi_i = R(r_i)\, Y_{l_i, m_i}(\theta, \phi)$$

The radial equation is (cf. Hydrogen)

$$\left[\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + V_{CF}(r) + \frac{\hbar^2 l(l+1)}{2m_e r^2} \right] P(r) = E P(r)$$

where $P(r) = rR(r)$

Note since the potential is radial <u>angular momentum is conserved</u>.

In practice:

1) Use spin-orbitals which are anti-symmetric

2a) Start with a guess $V(r)$

$$V(r) \to -\frac{Z}{r} \quad \text{small } r$$

$$V(r) \to -\frac{1}{r} \quad \text{large } r$$

Slater determinants

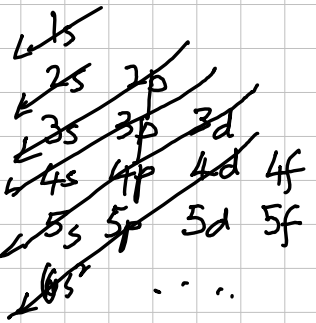
$$\Psi = \frac{1}{\sqrt{N}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \cdots & \psi_a(N) \\ \psi_b(2) & & & \\ \vdots & & & \\ \psi_x(1) & \psi_x(2) & & \psi_x(N) \end{vmatrix}$$

$a, b, c, d, \ldots$ possible sets of quantum numbers of individual electrons (including spin and space).

This determinant ensures that no two electrons have the same set of quantum numbers

$\Rightarrow$ Periodic Table

$1s^2$
$1s^2 2s^2$
$1s^2\ 2s^2\ 2p^6$
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$



L-S coupling

- In central-field approximation, $V_{CF}(r)$, angular momentum, $\vec{L}$ is conserved. So, M_L is a good quantum number.
- Spin is conserved. So M_S is a good quantum number.
- The spin-part of the wave function leads to singlet, doublets, triplets families
- The L.S interaction results in small corrections
  $\Rightarrow$ So, we can take perturbation analysis
- The spatial part of the wave-function is

$$\Phi = \psi_{n_1, l_1, m_{l_1}} \psi^{*}_{n_2, l_2, m_{l_2}}$$

$$E^{1} = \langle \Phi | H' | \Phi^{*} \rangle$$

- Clebsh-Gordon:
  Allows products of spherical harmonics
  $\Rightarrow$ L-S coupling

Combination of valence electrons

There are two types of combinations.

- electrons with different n
- electrons with same n

For the former we use the designation $s \cdot s$

For the latter we use the designation s^2

$s \cdot s$ $\quad s_1 = \frac{1}{2}$ $\quad s_2 = \frac{1}{2}$ $\quad l_1 = 0$ $\quad l_2 = 0$

$S = s_1 \pm s_2 \quad L = l_1 \pm l_2$

(negative not allowed)

$S = 0, 1 \quad L = 0$

$\Rightarrow$

s_0: $\quad {}^1S_0 \quad {}^3S_1$

In contrast:

$1s^2$ (Helium) we get only ${}^1S_0$

Useful rule: For such case select only terms for which $S+L =$ even

Different electrons: ex. $2p\,3p$ "p·p"

$\ell_1 = 1 \quad \ell_2 = 1 \quad s_1 = \frac{1}{2} \quad s_2 = \frac{1}{2}$

$L = 0, 1, 2 \quad S = 0, 1$

$\Rightarrow \quad {}^1S \;\; {}^1P \;\; {}^1D$

$\quad\quad\;\; {}^3S \;\; {}^3P \;\; {}^3D$

Identical electrons: p^2 (e.g. CI, $1s^2 2s^2 2p^2$)

Index	(m_ℓ, m_s)
a	$(1, 1/2)$
b	$(0, 1/2)$
c	$(-1, 1/2)$
d	$(1, -1/2)$
e	$(0, -1/2)$
f	$(-1, -1/2)$

Thus there are six possible states for each p electron.

	a	b	c	d	e	f
a	✗	o	o	o	o	o
b	·	✗	o	o	o	o
c	·	·	✗	o	o	o
d	·	·	·	✗	o	o
e	·	·	·	·	✗	o
f	·	·	·	·	·	✗

← allowed

↖ indistinguishable

$\ell_1 = 1 \quad \ell_2 = 1 \quad s_1 = \frac{1}{2} \quad s_2 = \frac{1}{2}$

$L = 0, 1, 2 \quad S = 0, 1$

${}^1S \;\; {}^1P \;\; {}^1D$

${}^3S \;\; {}^3P \;\; {}^3D$

Pauli forbidden

$M_L = m_{l_1} + m_{l_2}$

$M_S = m_{s_1} + m_{s_2}$

	Combination	M_L	M_S			
1	ab	1	1		P ← ②	
2	ac	0	1		P	
3	bc	-1	1		P	
4	de	1	-1		P	
5	df	0	-1		P	
6	ef	-1	-1		P	
7	ad	2	0	D ← ①		
8	ae	1	0	D		
9	af	0	0	D		
10	bd	1	0		P	
11	be	0	0		P	
12	bf	-1	0	D		
13	cd	0	0			S ← ③
14	ce	-1	0		P	
15	cf	-2	0	D		
				5	9	1

$^1S_0 \quad ^3P \quad ^1D$ Answer

Trick: It is easy to work out the terms for non-identical electrons. For identical electrons the allowed terms are those with S+L = even

Exercise: Apply this to p^2.

For p^3 similar exercise (see SRK Unix program)

^2D, ^2P, ^4S

Hund's rule (ground state)

The lowest energy term is:

- highest spin multiplicity (bus rule)
- within which highest L

For a given term, lowest energy is lowest J
(unless shell is more than half filled)