

Lecture 13

L-S Coupling

Let's consider the non-central part of e^2/r_{ij} term as perturbation.

As the different configurations are far apart, in the perturbative approach to begin with we take the Slater det. of spin orbitals corresponding to same config.

e.g. He atom

Consider (1s, 2s) configuration

The degenerate central field Slater states

$$1s^+ 2s^- : |\phi_1\rangle$$

$$1s^- 2s^+ : |\phi_2\rangle$$

$$1s^+ 2s^+ : |\phi_3\rangle$$

$$1s^- 2s^- : |\phi_4\rangle$$

$$H = \sum_i h_i + \sum_{i>j} g_{ij}$$

$$\therefore \langle \phi_i | H | \phi_i \rangle = \sum_{\lambda} \langle \lambda | h | \lambda \rangle + \frac{1}{2} \sum_{\lambda \mu} \{ \langle \lambda \mu | g_{12} | \lambda \mu \rangle - \langle \lambda \mu | g_{12} | \mu \lambda \rangle \}$$

If $|\phi_i\rangle$ is $\{ab\}$ then

$$\langle \phi_i | H | \phi_i \rangle = \langle a | h | a \rangle + \langle b | h | b \rangle + \frac{1}{2} \{$$

$$\begin{aligned} & \langle aa | g | aa \rangle + \langle ab | g | ab \rangle \\ & + \langle ba | g | ba \rangle + \langle bb | g | bb \rangle \} \end{aligned}$$

$$= h_a + h_b + \langle ab | g | ab \rangle - \langle ab | g | ba \rangle$$

$$= h_a + h_b + J - K \delta_{m_s a m_s b}$$

$$\therefore \langle \phi_1 | H | \phi_1 \rangle = \langle \phi_2 | H | \phi_2 \rangle = h_{1s} + h_{2s} + J$$

$$\langle \phi_3 | H | \phi_3 \rangle = \langle \phi_4 | H | \phi_4 \rangle = h_{1s} + h_{2s} + J - K$$

$$\langle \phi_1 | H | \phi_2 \rangle = -K$$

$$\langle \phi_2 | H | \phi_1 \rangle = -K$$

$$\langle \phi_3 | H | \phi_4 \rangle = \langle \phi_4 | H | \phi_3 \rangle$$

$$= \langle \phi_1 | H | \phi_3 \rangle = \langle \phi_1 | H | \phi_4 \rangle$$

$$= \langle \phi_2 | H | \phi_4 \rangle = \langle \phi_2 | H | \phi_3 \rangle$$

$$= 0$$

$$\therefore [H] = (h_{1s} + h_{2s}) + \begin{bmatrix} J & -K & 0 & 0 \\ -K & J & 0 & 0 \\ 0 & 0 & J-K & 0 \\ 0 & 0 & 0 & J-K \end{bmatrix}$$

The eigenvalues are

$|J-K\rangle$: 3 states which are degenerate.
 & $|J+K\rangle$: 1 state

$|J-K\rangle$: Triplet
 $|J+K\rangle$: Singlet.

\therefore For these states total angular mom. (orb)

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

\therefore The states are $3S, ^1S$

We allowed $\frac{e^2}{r_{ij}}$ to mix only central field

states within a given configuration

For example,

He ground state

Under configuration with central field the He ground state is

$$|\gamma^1s\rangle = |\gamma^1s\rangle_c$$

↑ All other quantum nos.

If we bring other configurations μ such that

$$|\gamma^1s\rangle = |\gamma^1s\rangle_c + \sum_{\mu} a_{\mu} |\mu^1s\rangle_c$$

This is called configuration mixing.

It correlates position of e's. The mixing usually happens with configurations leading to same multiplicity. as $\frac{e^2}{r_{ij}}$ is diagonal for eigen states of \vec{L} & \vec{S} .

Autoionization

The state $(1s, nl)$ for He converge as $n \rightarrow \infty$ on 1st I.P. which corresponds to $\text{He}^+(1s)$. The excited electron will have +ve energy E further if excited by more energy.

Now extend HF central field states to include $|1s, l, m_l, m_s\rangle$

↑ free e^- with angular mom. l
spin comp. m_s & k.E. E .

Consider doubly excited state of He
 $(2s)^2 : ^1S$

It is deg. with $|1s, E\rangle$ continuum state.
In central field they are orthogonal but they can be coupled by the non central part

$$\propto \frac{e^2}{r_{ij}} \quad (\text{config. mix})$$

By Fermi's Golden Rule, the population of discrete level decays into continuum of same energy by rate

$$\Gamma_k = \frac{2\pi}{\hbar} \left| \langle (ls)^2 {}^1S | \frac{e^2}{r_{12}} | (1s l_2) {}^1S \rangle \right|^2 \rho(E)$$

where $\rho(E)$ is density of states

$\Rightarrow e^-e^-$ correlation causes ejection of e^- with spin opp to that of He^+ left. This is accompanied with deexcitation of other electron. This is called "Autoionization".

The outgoing electron has $l=0$ making it a 's-wave' electron. This provides a finite width to the autoionizing states which correspond to their lifetime against such autoionization. These states are observed in ionization signal.

The outgoing e^- has a specified \uparrow or \downarrow (m_s)
Knowing or measuring it we can know the spin of left one e^- . A simple example of entangled state!

Coming back to LS coupling!

In central field approximation

$$H_c = \sum_i h_i$$

The two main corrections are

H_1 : non central part

H_2 : LS coupling.

$$H_2 = \sum_i \eta_i \vec{L}_i \cdot \vec{S}_i$$

$$\eta_i(r_i) = \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{dV(r_i)}{dr_i}$$

(Total Parity & Total angular momentum J are conserved)

If $H_1 \gg H_2$ L-S coupling!

that means all l s couple to give total orbital angular momentum & all s s couple to give total spin angular momentum. & then L & S couple through H_2

If $H_2 \gg H_1$ j-j coupling

Individual l s and s s couple giving j s as good Q. No. & then these j s couple through H_1 .

Most lighter atoms show L-S coupling scheme whereas heavy ions are good candidates for j-j coupling.

Determining possible terms under LS coupling

1. Equivalent electrons: (e^- s belonging to same subshell)

$$nsns \quad l_1 = l_2 = 0 \quad L = 0$$

$$s_1 = s_2 = 1/2 \quad S = 1, 0$$

but $S = 1$ & $L = 0$ not possible due to Pauli's principle.

$$M_L = 0 \quad M_S = 0 \quad \text{the term: } {}^1S$$

This is true for all closed subshells.

$$\begin{aligned} npnp : \quad l_1 = 1, l_2 = 1 \\ (np)^2 \quad m_{l_1} = 0, \pm 1 \quad m_{l_2} = 0, \pm 1 \\ m_{s_1} = \pm 1/2 \quad m_{s_2} = \pm 1/2 \end{aligned}$$

$$\text{Degeneracy} : = \frac{6 \times 5}{2} = 15 \quad \begin{array}{l} 6 \text{ ways for 1st } e^- \\ 5 \text{ ways for 2nd } e^- \\ 1/2 \text{ indistinguishable} \end{array}$$

$$\begin{aligned} \text{Possible } L &= 2, 1, 0 \\ S &= 1, 0 \end{aligned}$$

Possible terms: ${}^3D, {}^1D, {}^3P, {}^1P, {}^3S, {}^1S$

3D not possible as $m_{l_1} = m_{l_2} = \pm 1$ & $m_{s_1} = m_{s_2} = \pm 1/2$

3S not possible as $m_{l_1} = m_{l_2} = 0$ $m_{s_1} = m_{s_2} = \pm 1/2$

1P not possible as $L = 1$ is antisymmetric for 2 p electrons & singlet is also anti sym making wave f² symm.

∴ possible terms $1D, 3P, 1S$

$M_L \backslash M_S$	+1	<u>OR</u>	0	-1
+2	(1,1)		(1,1̄)	(1̄,1̄)
+1	(1,0)		(1,0̄)(1̄,0)	(1̄,0̄)
0	(1,-1)		(1,-1̄)(1̄,-1)(0,0̄)	(1̄,-1̄)
-1	(-1,0)		(-1,0̄)(-1̄,0)	(-1̄,0̄)
-2	(-1,-1)		(-1,-1̄)	(-1̄,-1̄)

Possible comb. of M_L & M_S are

1. $M_L = \pm 2, \pm 1, 0$ & $M_S = 0 \Rightarrow L=2, S=0 \Rightarrow 1D$

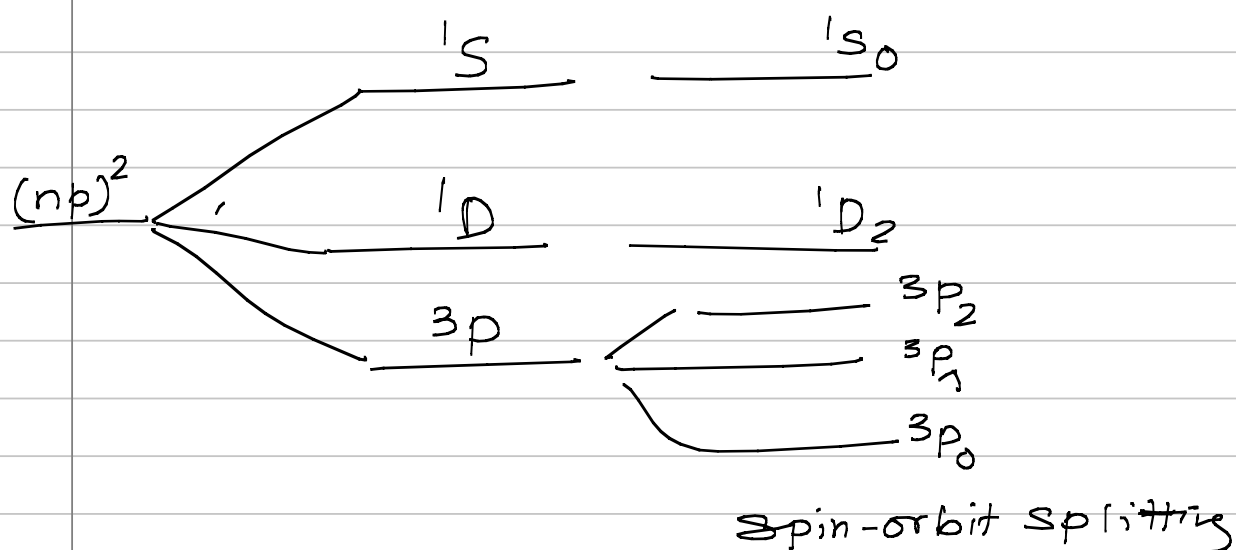
2. $M_L = \pm 1, 0$ & $M_S = \pm 1, 0 \Rightarrow L=1, S=1 \Rightarrow 3P$
(5)
(9)

3. $M_L = 0$, & $M_S = 0 \Rightarrow L=0, S=0 \Rightarrow 1S$
(1)
(15)

By Hund's Rule

1. Largest S has lowest energy
2. If more than one term has same S then lowest L has largest energy.

∴ $3P < 1D < 1S$



Normal multiplets.

$$\begin{aligned}
 \langle LSJM_J | H_2 | LSJM_J \rangle &= \langle LSJM_J | \vec{L} \cdot \vec{S} | LSJM_J \rangle \\
 &= \frac{1}{2} A \langle J^2 - L^2 - S^2 \rangle \\
 &= \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)]
 \end{aligned}$$

$A < 0$ if subshell is more than half filled

$A > 0$ if subshell is less than half filled.

$$E_J - E_{J-1} = AJ > 0 \quad \text{Normal multiplets}$$

Lande Interval Rule

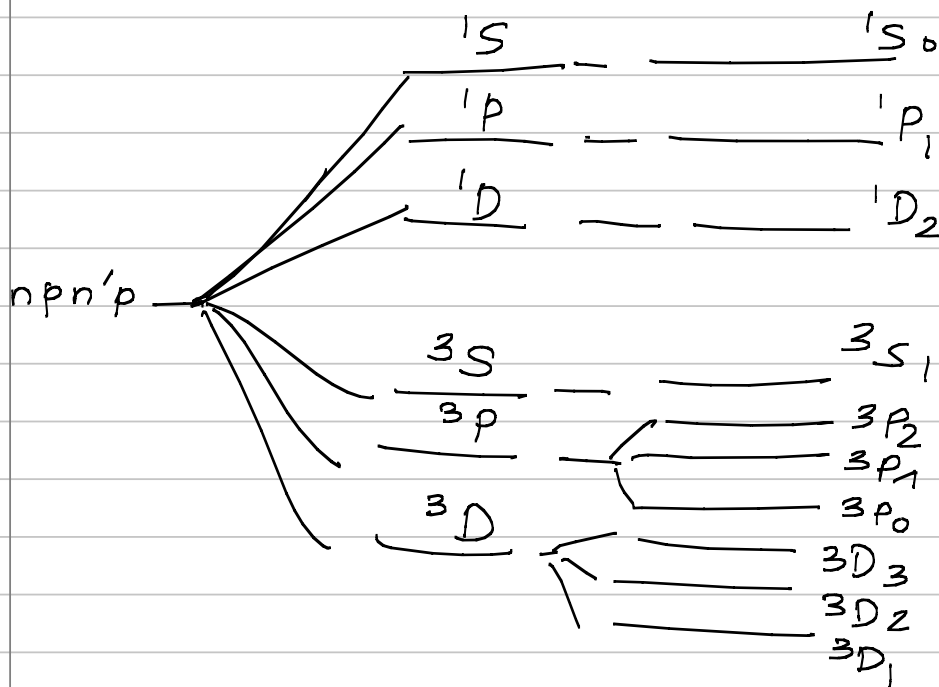
Non equivalent electrons

$(np)(n'p)$: All terms

$^3D, ^1D, ^3P, ^1P, ^3F, ^1S$ are possible.

$$\text{Deg.} = 6 \times 6 = 36$$

$$15 + 5 + 9 + 3 + 3 + 1 = 36$$



J-j coupling

$$H_2 \gg H_1$$

degeneracy for $\ell + 1/2 = j$ is $2\ell + 2$

degeneracy for $\ell - 1/2 = j$ is 2ℓ

$$H_0 = H_c + H_2 = \sum_i h_i + \sum_i \eta(r_i) \vec{\ell}_i \cdot \vec{S}_i$$

ns ns

$$j_1 = 1/2, j_2 = 1/2 \quad J = 0$$

$$\therefore \text{Term } (1/2, 1/2)_0 \quad \text{Notation } (j_1, j_2)_J$$

ns np

$$j_1 = 1/2, j_2 = 3/2, 1/2$$

$$j_1 = 1/2, j_2 = 1/2$$

$$J = 0, 1$$

$$(1/2, 1/2)_0, (1/2, 1/2)_1$$

$$j_1 = 1/2, j_2 = 3/2 \quad J = 1, 2$$

$$(1/2, 3/2)_1, (1/2, 3/2)_2$$

ns np

$\underbrace{j_1 = 1/2, j_2 = 3/2}_{J=2}$

$\underbrace{j_1 = 1/2, j_2 = 1/2}_{J=1}$

$\underbrace{j_1 = 1/2, j_2 = 1/2}_{J=0}$

For more than 2 electrons either in LS coupling or in JJ coupling the procedure can be repeated for every pair of 2 electrons and the subsequent the final terms can be evaluated. Also for subshell which is less than half filled and that more than half filled the terms would be same if no. of e^- in 1st case are same as no. of holes in second.

eg. $(p)^2$ is equivalent to $(p)^4$