

UNIT - IV

Atomic And Molecular Structure

Approximation in atomic structures - Central field approximation - Thomas fermi & statistical model - Hartree - fock equation - The method of self consistent field - Residual electrostatic and spin orbit interaction - Alkali atoms - Doublet separation - Coupling schemes - Hydrogen molecule - Covalent bond.

$$H = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right) + \sum_{i < j} \frac{e^2}{r_{ij}}$$

$$H\psi = E\psi$$

$$\psi = \sum_{i=1}^M c_i \phi_i$$

where r_i is the position of the i th electron from the nucleus $Z = 1, 2, \dots$

Equation (ii) cannot be solved by the method of separation of variables due to presence of interaction term. It is also cannot be solved by perturbation method.

In such a case we consider a modified field in which how all the electrons experience central symmetric field by superimposing the residual component of interaction between the electrons. The central interaction term

Central field approximation:-

The Hamiltonian for N electron atoms is given by,

$$H = H^0 + H^1 \rightarrow (1)$$

Where,

$$H^0 = \left[\sum_{i=1}^N \frac{p_i^2}{2m} - \sum_{i=1}^N \frac{ze^2}{r_i} \right]$$

$$H^0 = \sum_i H_i \rightarrow (2)$$

$$H^1 = \sum_{i>j} \frac{e^2}{r_{ij}} \rightarrow (3)$$

$$\therefore H = \left[\sum_{i=1}^N \left(\frac{p_i^2}{2m} - \frac{ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{r_{ij}} \right]$$

We know,

$$H\psi = E\psi$$
$$\left[\sum_{i=1}^N \left(\frac{p_i^2}{2m} - \frac{ze^2}{r_i} \right) + \sum_{i>j} \frac{e^2}{r_{ij}} \right] \psi = E\psi \rightarrow (4)$$

Where, r_i is the position of the i^{th} electron from the nucleus.

$$r_{ij} = |r_i - r_j|$$

Equation (4) cannot be solved by the method of separation of variables due to presence of interaction terms. It is also cannot be solved by Perturbation method.

In such a case we consider a modified field in which how all the electrons experience centrally symmetric field by superimposing the radial component of interaction between the electrons in the Coulomb interaction terms

$$\sum_{i=1}^N \left(\frac{-ze^2}{r_i} \right)$$

The remaining part of the interaction may be treated as small interaction term and it can be handled by perturbation theory.

Let the mutual repulsion term $\sum_{i \neq j} \frac{e^2}{r_{ij}}$ be divided into two parts.

i) $\sum_i S(r_i)$ directly away from the nucleus and

ii) Remainder $\sum_i R_i = \sum_{i > j} \frac{e^2}{r_{ij}} - \sum_i S(r_i) \rightarrow (5)$

\therefore The Central potential is

$$\sum_i \left[\frac{-Ze^2}{r_i} + S(r_i) \right] \rightarrow (6)$$

Now it is called screened potential.

Then the total Hamiltonian has expressed as

$$H = H^0 + H^1$$

Where,

H^0 is the Hamiltonian of the problem with Central potential.

i.e. $H^0 = \sum_i \left[\frac{p^2}{2m} - \frac{Ze^2}{r_i} + S(r_i) \right]$

(or)

$$H^0 = \sum_i \left[\frac{p^2}{2m} + V(r_i) \right] \rightarrow (7)$$

Where,

$$V(r_i) = -\frac{Ze^2}{r_i} + S(r_i) \rightarrow (8)$$

and

$$H^1 = \sum_{i > j} R_i$$

$$H^1 = \sum_{i > j} \frac{e^2}{r_{ij}} - \sum_i S(r_i)$$

(or)

$$H^1 = \sum_{i > j} \frac{e^2}{r_{ij}} - \sum_i \left[\frac{Ze^2}{r_i} + V(r_i) \right] \rightarrow (9)$$

(\therefore from eqn (8))

In zeroth order approximation the interaction term H' is negligibly small. So consider only the problem containing the central field and hence approximation method is called central field approximation.

There are two approaches which have been employed to evaluate the central field.

- i) Thomas - Fermi statistical Model
- ii) Hartree's - self consistent field method.

Thomas - Fermi statistical - Model :-

The Thomas - Fermi model of the atom is a statistical one in which the electrons are treated as a gas obeying Fermi Dirac statistics.

As electrons are treated as a gas of fermions we can apply the concept of cells in phase - space to the states of individual electrons.

The volume of phase space occupied by electrons is $\frac{4}{3}\pi p^3 dv$.

The number of cells corresponding to this volume is $2 \times \frac{4}{3} \pi p^3 dv$.

Here the factor 2 is included to account for two possible spin states.

Thus the number of electrons per unit volume $n(r)$ is given by,

$$n(r) = \frac{8\pi p^3}{3h^3} \rightarrow \textcircled{1}$$

$$= \frac{8\pi p^3}{3h^3 8\pi^3}$$

$$n(r) = \frac{p^3}{3h^3 \pi^2} \rightarrow \textcircled{2}$$

$$\begin{aligned} \therefore h &= \frac{p}{2\pi} \\ h &= \frac{h 2\pi}{h} \\ h^3 8\pi^3 &= h^3 \end{aligned}$$

The maximum allowed kinetic energy at a distance 'r' from the nucleus is $-V(r)$

$$i, 0) \quad \frac{p^2}{2m} = -V(r)$$

$$p^2 = -2mV(r) \rightarrow (3)$$

Sub eqn (3) in (2), we get

$$n(r) = \frac{p^2 \cdot p}{3h^3 \pi^2} = \frac{[-2mV(r)] [-2mV(r)]^{1/2}}{3h^3 \pi^2}$$

$$n(r) = \frac{[-2mV(r)]^{3/2}}{3h^3 \pi^2} \rightarrow (4)$$

According to classical Poisson's equation

$$\nabla^2 \phi = -4\pi \rho \rightarrow (5)$$

Where,

ϕ is the electrostatic potential = $V(r)/e$

ρ is the charge density = $n(r)e$.

Equation (5) becomes,

$$\nabla^2 \left(\frac{V(r)}{e} \right) = -4\pi n(r)e \rightarrow (6)$$

(or)

$$\nabla^2 V(r) = -4\pi e^2 n(r)$$

Sub $n(r)$ value from eqn (4) we get

$$\nabla^2 V(r) = -4\pi e^2 \frac{[-2mV(r)]^{3/2}}{3h^3 \pi^2} \rightarrow (7)$$

The potential is spherically symmetric since the nucleus is at the origin and therefore,

$$\nabla^2 V = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr} \right) \rightarrow (8)$$

Comparing eqn (7) and (8), we get

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr} \right) = \frac{-4\pi e^2}{3h^3 \pi^2} [-2mV(r)]^{3/2}$$

$$\frac{d^2V}{dr^2} = \frac{-4\pi e^2}{3h^3 \pi^2} [-2mV(r)]^{3/2} \rightarrow (9)$$

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$$\text{Put } v(r) = \frac{-ze^2 \chi(r)}{r}$$

Therefore eqn (9) becomes

$$\frac{d^2 v}{dr^2} = \frac{-4\pi e^2}{8h^3 \pi^2} \left[-2m \left(\frac{-ze^2 \chi(r)}{r} \right) \right]^{3/2}$$

$$\frac{d^2}{dr^2} \left[\frac{-ze^2 \chi(r)}{r} \right] = \frac{-4\pi e^2}{3h^3 \pi^2} \left[2m \frac{ze^2 \chi(r)}{r} \right]^{3/2}$$

$$\frac{-ze^2}{r} \frac{d^2 \chi(r)}{dr^2} = \frac{-4\pi e^2}{3h^3 \pi^2} \left[\frac{2m ze^2 \chi(r)}{r} \right]^{3/2}$$

$$\frac{d^2 \chi(r)}{dr^2} = \frac{4\pi e^2 r}{3h^3 \pi^2 ze^2} \left[\frac{2m ze^2 \chi(r)}{r} \right]^{3/2}$$

$$\frac{d^2 \chi(r)}{dr^2} = \frac{4\pi e^2 r}{3h^3 \pi^2 ze^2} \frac{(2m)^{3/2} (ze^2)^{3/2} (\chi(r))^{3/2}}{(r)^{3/2}}$$

$$= \frac{4}{3h^3 \pi} \frac{(2m)^{3/2} z^{3/2-1} e^3 [\chi(r)]^{3/2}}{r^{3/2-1}}$$

$$\frac{d^2 \chi(r)}{dr^2} = \frac{4 e^3 (2m)^{3/2} z^{1/2} [\chi(r)]^{3/2}}{3h^3 \pi r^{1/2}} \rightarrow (10)$$

Equation (10) can be expressed in a dimensionless form by writing

$$\frac{d^2 \chi}{d(bx)^2} = \frac{4 e^3 (2m)^{3/2} z^{1/2} \chi^{3/2}}{3h^3 \pi (bx)^{1/2}}$$

$$\frac{1}{b^2} \frac{d^2 \chi}{dx^2} = \frac{4 e^3 (2m)^{3/2} z^{1/2} \chi^{3/2}}{3\pi h^3 (b)^{1/2} (x)^{1/2}}$$

(or)

$$\frac{d^2 \chi}{dx^2} = \frac{b^2 4 e^3 (2m)^{3/2} z^{1/2} \chi^{3/2}}{3\pi h^3 (b)^{1/2} (x)^{1/2}}$$

$$\frac{d^2 \chi}{dx^2} = \frac{b^{3/2} 4 e^3 (2m)^{3/2} z^{1/2} \chi^{3/2}}{3\pi h^3 (x)^{1/2}} \rightarrow (11)$$

We select the value of 'b' in such a way that the Co-efficient of $\chi^{3/2} / x^{1/2}$ is unity

$$\text{i.e. } b^{3/2} = \frac{4 e^3 (2m)^{3/2} (z)^{1/2}}{3\pi h^3} = 1$$

$$(00) \quad b^{3/2} = \frac{3\pi \hbar^3}{4e^3 (2m)^{3/2} z^{1/2}}$$

$$b^{3/2 \times 2/3} = \frac{(3\pi)^{2/3} (\hbar^3)^{2/3}}{(4)^{2/3} (e^3)^{2/3} (2m)^{3/2 \times 2/3} (z)^{1/2 \times 2/3}}$$

$$b = \frac{(3\pi)^{2/3} \hbar^2}{4e^3 a_0 m z^{1/3}} = \frac{0.3853 a_0}{z^{1/3}}$$

sub 'b' value in eqn (11)

$$\frac{d^2 \chi}{dx^2} = \frac{\chi^{3/2}}{x^{1/2}} \rightarrow (12)$$

This equation is called the dimensionless Thomas - Fermi equation

Hartree's Equation (or) Hartree's Method of self consistent field :-

Consider an atom with 'z' electrons its Hamiltonian is

$$H = \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i) \right] + \sum_{i,j \neq 1} \frac{1}{2} \frac{ze^2}{r_{ij}} \rightarrow (1)$$

Where, $r_{ij} = |r_j - r_i|$

Put,

$$\left. \begin{aligned} H_i &= -\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i) \\ \text{and } V_{ij} &= \frac{ze^2}{r_{ij}} \end{aligned} \right\} \rightarrow (2)$$

sub eqn (2) in (1), we get

$$H = \sum_{i=1}^N H_i + \sum_{i,j \neq i} \frac{1}{2} V_{ij} \rightarrow (3)$$

The schrodinger equation to be solved is

$$H \psi(r_1, r_2, \dots, r_z) = E \psi(r_1, r_2, \dots, r_z) \rightarrow (4)$$

Hartree's followed a different procedure in which the variational method itself is used to select the trial wave function.

To apply the Variational procedure we shall assume that the trial wave function is of the form.

$$\psi(r_1, r_2, \dots, r_z) = u_1(r_1) u_2(r_2) \dots u_z(r_z) \rightarrow (5)$$

Where,

$u_1(r_1) u_2(r_2) \dots$ are normalised single particle wave function.

$$(e) \int u_i^* u_i d\tau_i = 1 \rightarrow (6)$$

where,

$$i = 1, 2, 3, \dots, z$$

Using eqn (6), eqn (3) can be written as

$$\langle H \rangle = \int u_1^* u_2^* \dots u_z^* \left[\sum_{i=1}^z H_i + \frac{1}{2} \sum_{i,j \neq 1} V_{ij} \right] u_1 u_2 \dots u_z d\tau \rightarrow (7)$$

Where,

$$d\tau = d\tau_1 d\tau_2 \dots d\tau_z$$

~~As~~ H_i operates only the Co-ordinates of i th electron and V_{ij} operates on the Co-ordinates of i and j electron.

$$\langle H \rangle = \sum_i \int u_i^* \left(H_i + \frac{1}{2} \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right) u_i d\tau_i \rightarrow (8)$$

minimisation w.r. to u_i^* we gives

$$\langle H \rangle = \sum_i \int \delta u_i^* \left[H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right] u_i d\tau_i = 0 \rightarrow (9)$$

To use the method of Lagrangian multipliers multiply by the multipliers E_i , we have

$$\sum_i \int \delta u_i^* \left[H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j - E_i \right] u_i d\tau_i = 0 \rightarrow (10)$$

As the variations δu_i^* are independent therefore eqn (10) becomes,

$$\left[H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j - E_i \right] u_i d\tau_i = 0$$

(or)

$$\left[H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right] u_i d\tau_i = E_i u_i d\tau_i$$

$$\left[H_i + \sum_{j \neq i} \int u_j^* V_{ij} u_j d\tau_j \right] u_i = \epsilon_i u_i$$

But,

$$\int u_j^* V_{ij} u_j d\tau_j = \int V_{ij} |u_j(r_j)|^2 d\tau_j$$

$$\left[H_i + \sum_{j \neq i} \int V_{ij} |u_j(r_j)|^2 d\tau_j \right] u_i(r_i) = \epsilon_i u_i(r_i)$$

Sub H_i and V_{ij} value.

$$\left[-\frac{\hbar^2}{8m} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i} \int \frac{1}{r_{ij}} |u_j(r_j)|^2 d\tau_j \right] = \epsilon_i u_i(r_i)$$

$$\left(\because V(r_i) = -\frac{Ze^2}{r_i} \right)$$

This integral-differential equation is called the Hartree's equation.

The second term is the attractive Coulomb potential due to nuclear charge Ze and third term is a repulsive contribution due to the charge density of all other electrons.

The j^{th} electron is described by normalised wave function which has been made self-consistent.

Thus each electron in the system is being considered as moving in the self consistent field due to the nucleus together with all the other electrons.

Hartree's - fock equation :-

In the Hartree method, the ~~many~~ many electron wave function is a product of one electron wave function. This is not acceptable when the particles are indistinguishable.

In this theory, fock used an Anti-symmetrised trial wave function for the variational calculations.

Therefore the wavefunction to take the form of a Slater's determinant is given by,

$$\psi(x_1, x_2, \dots, x_z) = \frac{1}{\sqrt{z!}} \begin{vmatrix} u_1(x_1) & u_1(x_2) & \dots & u_1(x_z) \\ u_2(x_1) & u_2(x_2) & \dots & u_2(x_z) \\ \vdots & \vdots & \ddots & \vdots \\ u_z(x_1) & u_z(x_2) & \dots & u_z(x_z) \end{vmatrix}$$

Where, x_1, x_2, \dots represents the co-ordinates for both space and spin

The Hamiltonian of a system having z interacting electrons can be written as

$$H = \sum_i H_i(r_i) + \frac{1}{2} \sum_{i \neq j} V(r_i, r_j) \rightarrow (2)$$

The Schrödinger equation to be solved

$$H\psi(x_1, x_2, \dots, x_z) = E\psi(x_1, x_2, \dots, x_z) \rightarrow (3)$$

Rewrite the Hamiltonian of equation (2) is,

$$H = \sum_i [H_i(r_i) + F(r_i)] + \left[\frac{1}{2} \sum_{i \neq j} V(r_i, r_j) - \sum_i F(r_i) \right] \rightarrow (4)$$

Now we take the modified z^{th} order determinant of one electron function of the equation,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) + F(r) \right] \phi(r) = \epsilon \phi(r) \rightarrow (5)$$

Use of a single determinant these function as the ground state wave function is known as Hartree Fock method.

The value of F in accordance with the variational principle is given by

$$\langle n | F | m \rangle = \sum_i \left[\langle n | v | i m \rangle - \langle n | v | i m \rangle \right] \rightarrow (6)$$

To get explicit form of the Hartree Fock equation, writing eqn (6) in the integral form

$$\int u_n^*(x_1) F(x) u_m(x_2) dx = \sum_i \iint u_i^*(x_1) u_n^*(x_2) v(x_1, x_2) u_i(x_1) u_m(x_2) dx_1 dx_2$$

(Or)

$$\int u_n^*(x) F(x) u_m(x) dx = \sum_i \int u_n^*(x_2) \left[\int u_i^*(x_1) v(x_1, x_2) u_i(x_1) dx_1 \right] u_m(x_2) dx_2$$

(Or)

$$\int u_n^*(x) F(x) u_m(x) dx = \sum_i \int u_n^*(x_2) \left[\int |u_i(x_1)|^2 v(x_1, x_2) dx_1 \right] u_m(x_2) dx_2$$

→ (7)

We have interchanged x_1 and x_2 in the second integral of R.H.S which is possible as the value of the definite integral does not depend on the variable of integration.

Under the same rule replacing the variable x_2 by x , we get and x_1 by x , we get

$$\int u_n^*(x) F(x) u_m(x) dx = \int u_n^*(x) \left[\int |u_i(x_1)|^2 v(x, x_1) dx_1 \right] u_m(x) dx$$

$$\int u_n^*(x) F(x) u_m(x) dx = \int u_n^*(x) \left[\sum_i \left(\int |u_i(x_1)|^2 v(x, x_1) dx_1 \right) u_m(x) \right] dx \rightarrow (9)$$

Comparing L.H.S and R.H.S values of eqn 9, we get

$$F(x) u_m(x) = \sum_i \left[\int |u_i(x_1)|^2 v(x, x_1) u_m(x) \right] u_i(x)$$

→ (10)

As $u(r)$ is the product of orbital path $\phi(r)$ and spin function.

Eqn (10) becomes,

$$E(r) \phi_m(r) = \sum_i \int |\phi_i(r_i)|^2 v(r_i, r) \phi_m(r) dr_i - \sum_i \int \phi_i^*(r_i)$$

$$\phi_m(r_i) v(r_i, r) \phi_i(r_i) dr_i \rightarrow (11)$$

In non ferromagnetic system, the number of electrons with opposite spin are equal and therefore eqn (11) becomes,

$$E(r) \phi_m(r) = 2 \sum_i^{Z/2} \int |\phi_i(r_i)|^2 v(r_i, r) \phi_m(r) dr_i - \sum_i^{Z/2} \int \phi_i^*(r_i)$$

$$\phi_m(r_i) v(r_i, r) \phi_i^*(r_i) dr_i \rightarrow (12)$$

Now Hartree like equation to the function for $\phi(r)$ becomes. (from eqn 5)

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \phi_m(r) + 2 \sum_i^{Z/2} \int [|\phi_i(r_i)|^2 v(r_i, r) dr_i$$

$$\phi_m(r) - \sum_{i=1}^{Z/2} \int \phi_i^*(r_i) \phi_m(r_i) v(r_i, r) \phi_i(r_i) dr_i = E_m \phi_m(r)$$

↳ (13)

The ~~third~~ term on LHS of eqn (13) is called the exchange term without this term the eqn would reduce to Hartree equation in which the ground state wavefunction consists of a simple product of one electron function.

Residual Electrostatic and spin orbit interaction (or) Correction to the Central field approximation:

The two interaction terms are neglected in the central field approximation. They are

i) Residual electrostatic interaction.

ii) spin orbit interaction.

The residual interaction is given by,

$$V_{res} = \sum_{i \neq j} \frac{e^2}{r_{ij}} = \left\langle \sum_{i \neq j} \frac{e^2}{r_{ij}} \right\rangle \rightarrow (1)$$

and spin orbit interaction for a single electron is,

$$V_{so} = a(r_i) l_i \cdot s_i \rightarrow (2)$$

Eqn (1) and (2) gives rise to two coupling schemes.

i) Russell-Saunders (or) L-S coupling scheme

When $V_{res} \gg V_{so}$

ii) j-j coupling scheme When $V_{so} \gg V_{res}$.

L-S Coupling scheme :-

In this case H is given by

$$H = \sum_i H_i^0 + H' \rightarrow (1)$$

(or)

$$H = H_0 + H'_{res} \rightarrow (2)$$

Where,

$$H'_{res} = H' - [H']_{av} \rightarrow (3)$$

For this Hamiltonian L, S and J are constants of motion.

The L-S Coupling scheme is defined as,

$$\left. \begin{aligned} L &= \sum_i l_i \\ S &= \sum_i s_i \\ J &= L + S \end{aligned} \right\} \rightarrow (4)$$

In this scheme one can represent a state as $|L, S, M_L, M_S\rangle$ (or) $|L, S, J, M_J\rangle$.

The eigen values of H_0 are easily found,

$$E_0 = \sum_i E_i^0$$

$$E_0 = \sum_i E_{n_i, l_i} \rightarrow (5)$$

Then,

E_{res} is the solution of the secular equation

$$\left| E_{res} \cdot S_{mn} - (H_{res})_{mn} \right| = 0 \rightarrow (6)$$

$$S_{mn} = \langle \psi_m | \psi_n \rangle \rightarrow (7)$$

$$(H_{res})_{mn} = \langle \psi_m | H_{res} | \psi_n \rangle \rightarrow (8)$$

Where,

ψ 's are normalised determinant type wave functions.

In the L-S scheme, the three empirical Hund's rules are possible.

The lowest energy corresponds to

- i) The state with the lowest value of 'S'
- ii) The state with the largest value of 'L'
- iii) The ground state with

$J_{min} = |L-S|$ if the shell is less than half - full

$J_{max} = L+S$ if the shell is more than half - full.

j-j Coupling scheme:

In some heavy atoms and in atoms with nearly full shells j-j Coupling scheme may happen that $V_{so} > V_{res}$.

If V_{res} is neglected, the total quantum number.

$$J = \sum_i j_i \quad \left. \begin{array}{l} \rightarrow (9) \\ j_i = l_i + s_i \end{array} \right\}$$

This defines the j-j coupling scheme

Here the interaction between the l and s of a single electron is higher than the interaction between l's of different electrons (or) the s's of different electrons.

Therefore it is appropriate to add l and s of each electron to form j and then to couple the j 's of various electron from J .

Some important features of optical spectra are

i) The electron in the highest energy shell of the atom in ground state are called optical electrons.

ii) The atom in the quasi stationary excited state makes a transition to the ground state, emitting one photon (or) several photons.

pure L-S (or) $j-j$ Coupling spectra are rare. As Z increases there is a continuous change from L-S to $j-j$ Coupling.

Alkali atoms :-

The ground state configuration of an alkali atom [Li, Na, K, Rb, Cs, Fr] consists of a series of full shells followed by a single s -electron and S_0 is $2S_{1/2}$.

Thus the alkali's can be treated to a good approximation in terms of a model in which electron moves in a ^{spherically} symmetric non-Coulomb potential energy $V(r)$.

Doublet separation :-

The configuration of an alkali atom can be specified by a single pair of quantum numbers ' n ', ' l '.

Since there is only one electron the perturbing electrostatic term does not appear.

In the absence of external field the Hamiltonian including spin orbit energy,

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) + \zeta(r) L \cdot S \rightarrow (1)$$

Where,

$$\zeta(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \rightarrow (2)$$

The total angular momentum $J = L + S$ of the valence electron is a constant of motion so that the states can be designated by J, m .

$$\text{i.e.) } J^2 = j(j+1)\hbar^2$$

$$\text{and } J_z = m\hbar$$

The difference in energy between states of different 'j' is due to the L-S term and can be found from its expectation value.

We have the operator relation

$$J^2 = (L+S)^2 = L^2 + S^2 + 2L \cdot S \rightarrow (3)$$

Eqn (3) can be solved for the diagonal matrix element L-S.

$$\langle l_j | L \cdot S | l_j \rangle = \frac{1}{2} [j(j+1) - l(l+1) - \frac{3}{4} J^2] \hbar^2 \rightarrow (4)$$

Now, if 'l' is different from zero 'j' can be either $(l + \frac{1}{2})$ (or) $(l - \frac{1}{2})$

Thus the first order perturbation arising from $\zeta(r) L \cdot S$ is,

$$\left. \begin{aligned} &\frac{1}{2} \zeta_{nl} \quad \text{if } j = l + \frac{1}{2} \\ &-\frac{1}{2} \zeta_{nl} \quad \text{if } j = l - \frac{1}{2} \end{aligned} \right\} \rightarrow (5)$$

Here,

$$\zeta_{nl} = \hbar^2 \int_0^\infty |R_{nl}(r)|^2 \zeta(r) r^2 dr \rightarrow (6)$$

Where, $R_{nl}(r)$ is the normalised radial part of the unperturbed eigen function associated with the nl configuration

χ - chi
 ψ - psi
 ξ - xi

ζ - zeta



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The value of $\zeta(r)$ is positive because $v(r)$ in eqn (2) represents the attractive potential energy and therefore ζ is positive.

Thus eqn (5) shows that the state with higher j has the eigen energy. The pair of states is called doublet.

The doublet separation can be calculated from eqn (6),

$$\zeta_{nl} = \hbar^2 \int_0^{\infty} |R_{nl}(r)|^2 \zeta(r) r^2 dr.$$

Sub $\zeta(r)$ value,

$$i, e) \quad \zeta(r) = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dv}{dr}$$

$$\text{Here, } \frac{dv}{dr} = \frac{-ze^2}{r}$$

The above eqn becomes

$$\zeta_{nl} = \hbar^2 \int_0^{\infty} |R_{nl}(r)|^2 \frac{1}{2m^2c^2} \frac{1}{r} \left(\frac{-ze^2}{r} \right) r^2 dr$$

$$\zeta_{nl} = \frac{-\hbar^2 ze^2}{2m^2c^2} \int_0^{\infty} |R_{nl}(r)|^2 dr.$$

(or)

$$\zeta_{nl} = \frac{\hbar^2 z^4 e^2}{z m^2 c^2 a_0^3 n^3 (l + \frac{1}{2}) (l+1)} \rightarrow (7)$$

Where,

$$\int_0^{\infty} |R_{nl}(r)|^2 dr = - \left(\frac{z}{a_0 n} \right)^3 \frac{1}{(l + \frac{1}{2}) (l+1)}$$

This expression is valid only for $l > 0$ from eqn (6) and (7) shows that the doublet separation is proportional to n^{-3} and this is in full agreement with observation.