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Molecular Quantum Mechanics

3.1 (A) Quantum mechanics – theoretical methodology of investigation of the micro domain of nature.

To unveil the secrets of nature, physics has had two powerful theoretical instruments—Quantum Mechanics and Theory of Relativity. Quantum Mechanics and Theory of Relativity are the two most brilliant contributions of modern science to the human civilization. To day scientists describe the universe in terms of two basic partial theories—the general theory of relativity and quantum mechanics [1]. The general theory of relativity of Einstein describes the force of gravity and the large-scale structure of the universe and the quantum mechanics, on the other hand, deals with phenomenon on extremely small scale. The era of pre-1900 was the rule of classical physics in which space was fixed. Then relativity and quantum revolution changed every thing utterly. With the beginning of general relativity, space was combined with time in an integrated, but deformable, space-time range. Meanwhile, in quantum mechanics space-time remains fixed but matter becomes fuzzy, the whereabouts of particles can only be expressed in terms of probability clouds.

The first half of the present century has been one of the most fruitful periods in the development of modern physics and chemistry. The modern ideas of atoms, molecules and solids have evolved with the theories of relativity and quantum mechanics. The leading names to be attached to these twentieth century discoveries are Planck [2], Einstein [3,4] Rutherford [5], Bohr [6], de Broglie [7], Heisenberg [8], Schrödinger [9,10] and Dirac...
[11]. There are some vital dates to be remembered in connection with the progress of quantum theory

1. In 1900 Planck made the first suggestion of the Quantum Theory of radiation and sewed the seed of quantum mechanics.

2. In 1905 Einstein further extended the quantum theory of radiation of Planck to the effect that radiation is not a wave motion but a stream of energy particles and applied this idea to solve the problem of photoelectric effect and specific heat of atomic solid. All controversy regarding quantum theory of radiation was finally settled by the discovery of the phenomenon of Compton effect.

3. In 1913 Bohr applied the quantum theory of radiation to the atomic structure problem.

4. In 1924 Louis de Broglie put forward his hypothesis of matter-wave derived with the help of special theory of relativity. He generalized the attribute of wave-particle duality to matter.

5. Heisenberg introduced his uncertainty principle and introduced his matrix mechanics in 1925.

6. In 1926 Schrödinger discovered the wave equation for matter waves, now called the Schrödinger equation. This is the fundamental mathematical equation of quantum mechanics.

7. Max Born interpreted the de Broglie-Schrödinger waves as waves of probability. This was the wave mechanical version of quantum mechanics.
8. Dirac introduced his relativistic quantum mechanics of far reaching potentiality in 1928. Finally, he demonstrated that the two versions, matrix mechanics and wave mechanics, are equivalent.

All the great attainments of the bright present and the dazzling future of quantum mechanics were born in 20th century out of a small seed thrown, ninety nine years ago, into the fertile soil of scientific knowledge by Max Planck, and since carefully cultivated by a whole galaxy of brilliant scientists like Bohr, Born, Einstein, Schrödinger, Heisenberg, Feynman and Dirac.[9,12-18].

The applications of Quantum Mechanics can be grossly classified under the following heads:

1. Atomic and molecular structure
2. Nuclear structure and particle physics
3. Other fields of study of Nature.

1. *Atomic and Molecular structure*:

Quantum Chemistry is the quantum mechanics applied to the problems in chemistry. Quantitative information as to the way in which electrons are distributed in atoms is the most perennial quest of atomic physics. Quantitative information about the way in which electrons are shared between atoms to form the chemical bonds by which the atoms are held together in a molecule has revolutionized the science of chemistry giving forth a new borderline science known as chemical physics. Quantum mechanical detailed spectral analysis helps us in assigning experimental determination of molecular properties like the bond lengths, bond angles, dipole moments. The barriers
to internal rotation i.e., the energy differences between conformational isomers can be calculated accurately. We can also estimate the forces generated when a chemical bond is stretched and that govern the modes of normal vibration. It is applied to calculate molecular properties theoretically and to estimate relative stabilities of molecules. Under the frame work of Born-Oppenheimer approximation in which it is first assumed that the nuclei do not move at all and the electronic energy levels of such a system are then found to depend on the assumed distances of separation of the nuclei, the variation with nuclear co-ordinates of the electronic energy then can be used as the potential energy function that determines the equilibrium size and shape of the molecule. The computations involved in using Quantum Mechanics for molecular structure problems are exceedingly complex. Much use is made of automatic digital computers. But even so, in many cases the results so far have been only semi-quantitative. Nevertheless, the overall result has been to give a theoretical frame work for the correlation of many of the known facts of the chemistry.

2. Nuclear structure and particle physics

The major application of Quantum Mechanics to the nucleus is the barrier leakage interpretation of the natural radioactive decay of those elements that emit α particles or He nuclei. In Quantum Mechanics, however, the de Broglie waves have a small and calculable probability of penetrating such a barrier, which is totally impenetrable in classical mechanics. Quantum mechanical theory of β decay based on the idea of neutrino used some relatively new mathematical methods for treating processes of creation and
destruction of new particles in quantum transitions which led to the discovery of mathematical forms for processes, now called weak interaction.

3. Other applications

Going beyond the above application of Quantum Mechanics to molecular structure is its application (i) to the theory of matter in the solid state which is concerned with the forces that determine crystal structure, the behaviour of electrons in states that permit motion over large distances in a crystal (metals and semi-conductors), and the physical factors that determine magnetic properties. (ii) It has been widely applied to the study of electron–matter collision processes, i.e., of the details of the mechanics by which an electron collide with an atom can raise it to an excited quantum level or even knock free one or more of its electrons (ionized). (iii) Another major development is Quantum Electrodynamics. Initially it was assumed that electromagnetic field could be handled mainly by the classical methods of Maxwell. But it was soon realized that the equations of the electromagnetic field must be reformulated to take explicit account of quantum phenomena. (iv) The consequences of quantum electrodynamics is lasers – here light beams are produced that are millions times more intense than with any previously known light source. This is a consequence of a feature, first noted by Einstein in 1917, whereby atoms that are exposed to a coherent light beam are stimulated to emission at a greater rate that of their spontaneous emission.

Lastly, what amazing things are revealed to the explorer of this recently discovered world. What inspiring, truly fantastic horizons does this new science open up for technology,
industry, agriculture and medicine, nuclear power stations, radio active isotopes, solar batteries, to name a few.

3.2 Self-consistent field (SCF) theory

3.2.1 Schrödinger Equation

According to Feynman all problems in chemistry were solved when Schrödinger equation was solved. In other words, solution of all the problems is hidden into the Schrödinger equation [9, 10, 12] in an elegant simple form of the type:

\[ H\psi = E\psi \] \hspace{1cm} (3.1)

Here \( H \) is the quantum mechanical Hamiltonian operator for the system under study, which is represented by \( \psi \) – the wave function in its stationary state having energy \( E \). The operator \( H \), the total energy operator is obtained from the sum of the classical energy terms i.e., kinetic and potential energy etc. converted in to quantum mechanical operators. The function \( \psi \) depends on the spatial and spin coordinates of all the particles in the system under study. For a larger system, the complete Hamiltonian can be formulated as sum of kinetic energy operators for both the nuclei and the electrons together with the potential energy terms representing the various coulombic interactions. As for example, for system of \( N \) nuclei and \( n \) electrons, the many–particle Hamiltonian operator, \( H_{\text{total}} \), is of the form:

\[
H_{\text{total}}(1,2,\ldots;N;1,2,\ldots;n) = -(\frac{\hbar^2}{8\pi^2}) \sum_{A}^{N} M_{A}^{-1} \nabla_{A}^2 + \sum_{A < B} e^{2} Z_{A} Z_{B} r_{AB}^{-1}
\]

\[
-(\frac{\hbar^2}{8\pi m^2}) \sum_{p}^{n} \nabla_{p}^2 - \sum_{A}^{n} e^{2} Z_{A} r_{AP}^{-1} + \sum_{i < j} e^{2} r_{ij}^{-1} \] \hspace{1cm} (3.2)
Where $M_A$ is the mass of the nucleus A, $m$ and $e$ are the electronic mass and charge respectively, $Z_Ae$ and $Z_Be$ are the charges on nuclei A and B respectively and $r_{ij}$ is the distance between particles i and j.

$\nabla^2$ is the Laplacian operator used to denote the kinetic energy operator.

Summations involving indices A and B are over atomic nuclei and that of $p$, $i$ and $j$ are over electrons. In practice, the problem of finding the wave function consists of two parts. First part deals with the purely electronic problem for each set of nuclear positions under the framework of Born-Oppenheimer approximation [19] stating the separation off the nuclear coordinate from the electronic coordinate in the total wave function of the system, and ultimately leading to the separation of kinetic energy and nuclear–nuclear repulsion terms from the $H_{\text{total}}$, and considering only the part of the Hamiltonian which depends on the positions but not the momenta of the nuclei. This is the electronic Hamiltonian operator, $H_e$.

$$H_e = -(\frac{\hbar^2}{8\pi m^2}) \sum_p \nabla_p^2 - \sum_{AP} \sum_{e} e^2 Z_A \frac{1}{r_{AP}} + \sum_{p < q} e^2 r_{pq}^{-1} \ldots \ldots \ldots \ldots (3.3)$$

The second part deals with the electrostatic inter-nuclear repulsion energy for the fixed nuclear position. So the total energy, $E$, of the system is then given by the sum of the electronic energy, $\varepsilon$, and the electrostatic inter-nuclear repulsion energy.

$$E = \varepsilon + \sum_{A < B} e^2 Z_A Z_B \frac{1}{r_{AB}} \ldots \ldots \ldots \ldots (3.4)$$

Molecular orbital theory is concerned with electronic wave functions only. So superscript 'el' on the Hamiltonian operator is dropped and hence in terms of atomic units, the equation 3.3 reduces to:
\[ H = - \sum_{p} \frac{1}{2} V_p^2 - \sum_{A} Z_A \sum_{r_{pq}^{-1}} + \sum_{p < q} r_{pq}^{-1} \] 

Now an important step in the evolution of quantum theory is the introduction of self-consistency. The algebraic structure of quantum mechanics is that from the given situation each and every observable property of any system can be computed in terms of the wave function provided the wave function is known. Thus if the wave function of a system is known, all information about the system is known. The wave function of any system has to be known by solving the Schrödinger equation of the form shown in equations 1 & 2. But very soon it was realized that the wave function of many-electron / many-body systems cannot be known because the Schrödinger equation for many-electron / many-body system cannot be solved. It was found that such a situation of mathematical impasse was created out of the bottleneck in the exact solution of the many-electron Schrödinger equation because of the existence of the term \((r_{ij})^{-1}\) in the relevant Hamiltonians of the systems. The presence of these terms does not permit the many-dimensional differential equations to be separated into the individual electronic coordinates, and thus renders the exact solution of Schrödinger equation impossible. Many workers in this field suggested methods of obtaining approximate wave functions of atoms and molecules – the many electron systems, by setting the norm *apriori* that, within some limits of error, the approximate wave function should reproduce the known chemical and physical properties of the systems qualitatively and quantitatively. Since the inception of basic theory, a vast body of literature has evolved on various methods which have been developed to obtain approximate solutions of Schrödinger equation for many electron systems.
Mulliken [20] and Hund [21] sketched the qualitative conception of Molecular Orbital (MO) theory to understand its role of quantum mechanics in the interpretation of molecular spectra. This theory was cast in a firm mathematical form by Hartree, Fock and Slater who derived the equations to get solutions of the molecular orbitals envisioned by Mulliken and Hund. It became a practical molecular theory in the hands of Roothaan and Hall who solve the Hartree-Fock equations for a general polyatomic molecule by expanding the molecular orbitals in terms of atomic-like function. This was a monumental advance because it helps one to assess the quantitative accuracy of MO concept and dominate the computational chemistry landscape [22]. The accuracy of MO theory considering electron correlation has been further discussed by a group of scientists [23-25]

3.2.2 Hartree Method

In the year 1928, Hartree [26] first really made a successful attack on the problem. This method retains some of the simple features of the independent-particle model and yet introduces electron interactions in a systematic fashion. “The basic philosophy of the method is to decompose one many-electron problem into many one-electron problems”. As a first step towards this direction he introduced the idea of orbital approximation.

*Orbital approximation*

In a many-electron system, each and individual electron has its path or orbital. Orbital is a one-electron function. Each orbital depends on the coordinates of one electron only. According to the orbital approximation this very complicated function is approximated as a product of one-electron functions – orbitals – and written as

\[ \Psi (1,2,\ldots,n) = \prod_{i=1}^{n} \phi_i (i) \]  

\[(3.6)\]
Hartree's model was based on the assumption that each electron in a many electron system (atom, ion or molecule) moves under the potential field due to the average charge distribution of the other electrons that are assumed to remain spherically distributed smeared out frozen charge cloud. Instead of considering instantaneous electron-electron repulsion, he considered the two-body repulsive interaction between this charge cloud and the lone ith electron moving under the potential, $V_{i}^{\text{eff}}$, generated by smeared out charge cloud of the other electrons. Hartree equation is pseudo-one-electron system and the Hamiltonian for the ith electron may be written as

$$h_{i}(\phi_{i}) = \epsilon_{i}(\phi_{i})$$ ................................(3.7)

where

$$h_{i} = H_{i}^{(0)} + V_{i}^{\text{eff}}$$ ......................(3.8)

$H_{i}^{(0)}$ is the mono-electronic hamiltonian defined as

$$H_{i}^{(0)} = -(1/2) \nabla_{i}^{2} - Z / r_{i}$$ ..............................................(3.8a)

Which represents the kinetic energy of the ith electron plus the potential energy due to coulombic interaction with the nucleus.

The orbitals $\phi_{i}(i)$ may be used to define an effective one-electron potential, $V_{i}^{\text{eff}}$ of the form

$$V_{i}^{\text{eff}} = \sum_{j \neq i}^{n} \left\{ (\phi_{j}^{\ast}(j) \phi_{j}(j))/r_{ij} \right\} dv_{j} = \sum_{j \neq i}^{n} J_{j}(i) \quad .......(3.8b)$$

Thus potential is just an adaptation of the classical electrostatic expression for the interaction of the ith charged sphere with (n−1) other charged spheres. Here it is assumed
that the $i$ th electron is assumed to move in a potential field due to the average charge
distributions of the other $(n-1)$ electrons.

**Self-consistency**

From assumed set of $\phi_i^{(0)}(j)$, $V_{i\text{ eff}}$ is set up following the equation 8b and then
solution of equation 3.7 gives first-improved set of orbitals $\phi_i^{(1)}(i)$. The first-improved
orbitals are now used to define the first improved coulombic operator using the equation
8b leading to the second-improved set of orbitals $\phi_i^{(2)}(i)$. The process is repeated until
some set of coulombic operators $J_{ij}^{(n)}(i)$ leads to Hartree operators such that

$$H_i^{(n)} \approx H_i^{(n+1)} = H^{SCF} \text{...............(3.9a)}$$

$$\phi_i^{(n)}(i) \approx \phi_i^{(n+1)}(i) = \phi_i(i) \text{ ..........(3.9b)}$$

for all values of $i$. One then says that the electrons move in a self-consistent field. This
method is known as the Hartree self-consistent field (SCF) method. The final orbitals $\phi_i(i)$
are usually referred to as SCF AO’s (Self-consistent field atomic orbitals).

The total energy, $E$, of an $n$-electron atom in the Hartree SCF approximation is given
by

$$E = \sum_{i=1}^{n} \varepsilon_i^{(0)} + \sum_{i<j}^{n} J_{ij} \text{ .........................(3.10)}$$

$\varepsilon_i^{(0)}$ is the energy of a single electron $i$ described by the SCF AO $\phi_i$ and moving in the
field of the bare nucleus and is given by

$$\varepsilon_i^{(0)} = \int_{\phi_i(i)} H^{(0)}(i) \phi_i(i) \text{ d}v_i \text{ .........................(3.11)}$$
The coulomb integral \( J_{ij} \) represents the electrostatic energy due to interaction of the two charge clouds \( \phi(i) \phi(i)^2 \) and \( \phi(j) \phi(j)^2 \) and is given by
\[
J_{ij} = \int \int \phi_i^* \phi_j (1/r_{ij}) \phi_i \phi_j \, dv_i \, dv_j \cdots \cdots \cdots \cdot (3.12)
\]

But the Hartree's method suggested a form of product wave function, was not antisymmetric with respect to exchange of pair identical particles, i.e, such a form of wavefunction was found to be not satisfying the antisymmetry law of nature as well as Pauli principle.

3.2.3 The Laws of Symmetry and Antisymmetry of Nature

All 'bosons', i.e., the particles with zero and integral spins are described by symmetric wavefunctions, i.e., they do not change sign on interchange of a pair of identical 'bosons'. On the other hand, all 'Fermions', i.e., the particles with half-integral spin are described by the symmetric wavefunctions, which change sign on interchange of a pair of identical 'fermions'.

Electrons, being ‘fermions’ must follow the law of antisymmetry of nature.

Hartree equation incorporating antisymmetric nature of wave function was anticipated by Fock and Slater simultaneously and independently [27].

3.2.4 Slater Determinant

According to the law of antisymmetry of nature, many-electron wavefunction must change sign on interchange of a pair of identical fermions and thus, should follow the Pauli exclusion principle. Slater [28] pointed out that if the spin orbitals are arranged in the form of a determinant, the antisymmetry law (Pauli principle) is automatically satisfied. Such antisymetrized wavefunction is known as Slater determinant and is given as
\[ \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} S_1(1) & S_2(1) & \ldots & S_N(1) \\ S_1(2) & S_2(2) & \ldots & S_N(2) \\ S_1(3) & S_2(3) & \ldots & S_N(3) \\ \vdots & \vdots & \ddots & \vdots \\ S_1(N) & S_2(N) & \ldots & S_N(N) \end{vmatrix} \]  

(3.13)

Where, \( S_1, S_2, S_3, \ldots S_N \) are the spin orbitals having both space and spin parts, i.e.,

\[ S_i = \varphi_i \alpha \text{ or } \varphi_i \beta \]  

(3.14)

These spin-orbitals are assumed to be separately normalized. Expansion of this determinant leads to the \( N! \) number of terms of which half are with positive and half are with negative sign. The factor \( (1/N!)^{1/2} \) is the normalization factor and ensures that the wavefunction remains normalized. As, from the intrinsic property of determinant it follows that interchange of any pair of rows or columns of the determinant reverses its sign; this determinantal wavefunction spontaneously and automatically satisfies the Pauli exclusion principle.

### 3.2.5 Fock's extension of Hartree's Method

Fock [29], in the year 1930, replaced the simple Hartree product wave function by its anti-symmetric projection suitable for many Fermion systems. Also spin was included so that spin–orbital was taken into consideration. Fock, in fact, replaced the Hartree's method by a more rigorous treatment in which the resulting many electron wave function obeys Pauli’s principle and method has been known as Hartree–Fock method in literature. In this
method variational approach was exploited to obtain the approximate solutions of
Schrödinger equation for multi-electronic systems with closed shell electronic
configuration and according to this method, the energy expectation value, $<H>$, is given
by,

$$<H>_{av} = <\psi | H | \psi >$$ ................................(3.15)

Now under this method, variational approach to approximate solutions of Schrödinger
equation for a $2n$-electron molecule with closed shell configuration involves working with
the energy expectation value $<\psi | H | \psi >$. Where the determinantal wave function, $\psi$, can
be written in the form

$$\psi = A \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \mathcal{P} \{ \psi_1 (1) \alpha (1) \psi_1 (2) \beta (2) \ldots \ldots \ldots \ldots \ldots \psi_n (2n) \beta (2n) \}$$ ..........(3.16a)

with normalization constant $A = [(2n)!]^{-1/2}$ .......... ............(3.16b)

where $\mathcal{P}$ is a permutation of 1, 2, ......., 2n and $(-1)^{\mathcal{P}}$ is +1 or -1 for even or odd
permutations, respectively.

The hamiltonian operator may be separated into one and two-electron parts,

$$H = H_1 + H_2$$ ......................(3.17)

Where $H_1 = \sum_{\mathcal{P}} H^{\text{core}}_{\mathcal{P}}$ ..............(3.18)

with $H^{\text{core}}_{\mathcal{P}} = - (1/2) \nabla^2 + \sum_A Z_A r_{pA}^{-1}$ ..........(3.19)

And $H_2 = \sum_{\mathcal{P}} \sum_{p < q} r_{pq}^{-1}$ ..........(3.20)

The quantity $H^{\text{core}}$ is one-electron hamiltonian corresponding to motion of an electron in
the field of the bare nuclei, the charge of the nucleus $A$ being $Z_A$. Substituting equation 17
into the energy expectation value we have the expression in terms of the one-electron and
two-electron part,

\[ \langle \psi | H | \psi \rangle = \langle \psi | H_1 | \psi \rangle + \langle \psi | H_2 | \psi \rangle \quad \text{.........(3.21)} \]

For the one-electron part, from the equation 18 we have

\[ \langle \psi | H_1 | \psi \rangle = \sum_{p}^{2n} \langle \psi | H^{\text{core}} (p) | \psi \rangle \quad \text{...............(3.22)} \]

Since the electrons are indistinguishable and are treated on an equal footing in \( \psi \), the
expectation value of \( H^{\text{core}}(p) \) must be the same for all \( 2n \) values of \( p \). So equation 22 shows

\[ \langle \psi | H_1 | \psi \rangle = 2n < \psi | H^{\text{core}(1)} | \psi > \quad \text{...............(3.23)} \]

Now from eq. 3.16, and using the orthogonal behaviour of the orbitals, considering both
the spatial and spin functions describing all the electrons, eq. 3.23 gives

\[ \langle \psi | H_1 | \psi \rangle = 2 \sum_{i=1}^{n} H_{ii} \quad \text{...............(3.24)} \]

where \( H_{ii} \) is the expectation value of the one-electron core hamiltonian corresponding to
the molecular orbital and is given by

\[ H_{ii} = \int \psi_i^{(1)} \cdot H^{\text{core}} \psi_i^{(1)} \, d\tau \quad \text{...............(3.25)} \]

The evaluation of the expectation value of the two-electron hamiltonian \( H_2 \) can be divided
into two parts — in the first part, it follows the similar manner above where identical
permutation along with assignment of electrons 1 and 2 in different spatial molecular
orbitals \( \psi_i \) and \( \psi_j \), both may have \( \alpha \) or \( \beta \) spin, gives rise to the four contributions each equal to \( \frac{1}{2} J_{ij} \), where

\[
J_{ij} = \int \psi_i^*(1) \psi_j(2) \psi_i(1) \psi_j(2) \frac{1}{r_{12}} \ d\tau_1 \ d\tau_2 \quad \ldots \ldots \ldots (3.26)
\]

Again, assignment of electrons 1 and 2 having opposite spins in the same molecular orbital \( \psi_i \) contributes two \( \frac{1}{2} J_{ii} \) terms. So the total contribution is

\[
2 \sum \sum J_{ij} + \sum J_{ii} \quad \ldots \ldots \ldots (3.27)
\]

In the second part, where non-identical permutations differing one from another by a single interchange give rise to two contributions both being \( -\frac{1}{2} K_{ij} \) where

\[
K_{ij} = \int \psi_i^*(1) \psi_j(2) \psi_j(1) \psi_i(2) \frac{1}{r_{12}} \ d\tau_1 \ d\tau_2 \quad \ldots \ldots \ldots (3.28)
\]

Collecting all the terms, the final expression for the electronic energy is

\[
\epsilon = 2 \sum H_{ii} + \sum \sum \left( J_{ij} - K_{ij} \right) \quad \ldots \ldots \ldots (3.29)
\]

Noting that \( K_{ji} = J_{ij} \), this may be rearranged into the more compact form

\[
\epsilon = 2 \sum H_{ii} + \sum \sum \left( 2J_{ij} - K_{ij} \right) \quad \ldots \ldots \ldots (3.30)
\]

where \( J_{ij} \) and \( K_{ij} \) are known as Coulomb integrals and exchange integrals, respectively.

The problem is now to find the best antisymmetric product for which the energy reaches its absolute minimum. So we have to minimize the expression 30 by varying the MO's within the limits permitted by the requirement they form an orthonormal set expressed as follows

\[
S_{ij} = \psi_i^{(1)} \psi_j^{(2)} \ d\tau \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.31)
\]
This type of problem is handled mathematically by invoking the calculus of variations, using the method of undetermined multipliers. This involves minimizing the function

\[ G = \varepsilon - 2 \sum_i \sum_j (\varepsilon_{ij} S_{ij}) \]

\[ = 2 \sum_i H_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) - \sum_i \sum_j \varepsilon_{ij} S_{ij} \] .............................(3.32)

Where \( \varepsilon_{ij} \)'s are undetermined constants.

A stationary point of the function \( G \) is such that the variation in \( G \), \( \delta G \), is zero to first order,

\[ \delta G = 0 \] .................................(3.33)

Which leads directly to the differential equations

\[ F \psi_i = \sum_j \varepsilon_{ij} \psi_j \] ......................................(3.34)

With Fock Hamiltonian operator, \( F \), given by

\[ F = [H^{\text{core}} + \sum_j (2J_{ij} - K_{ij})] \] ......................................(3.35)

From eq. 3.34 it is clear that Hartree–Fock orbitals are not unique. So it turns out that eqs. 3.34 are not particularly suitable for the description of many-electron systems in terms of the orbitals associated with definite energy values.

Now since \( \varepsilon_{ij} \) are the elements of Hermitian matrix, so there exits a unitary matrix giving rise to survive the diagonal elements only, that is, all \( \varepsilon_{ij} = 0 \) unless \( i = j \). So there is no loss of generality if we assume that our set of best MO's satisfies the simpler equations of the form

\[ F \psi_i = \varepsilon_i \psi_i \] ..................................................(3.36)
These are commonly known as the Hartree–Fock equations. \( F \) is Fock operator.

The general procedure for solving the Hartree–Fock equations is essentially a trial-and-error process, first assuming a set of trial solutions \( \psi_1', \psi_2', \ldots \) which allows computation of the Coulomb and exchange operators and thus the calculation of a first approximation to Hartree–Fock Hamiltonian operator. The eigenfunctions \( \psi_1'', \psi_2'' \) of this operator constitute a second set of trial functions, and the entire procedure is continued until the orbital along with the energy of the system no longer changes (within a certain tolerance) on further iteration. This method for solving Fock's equation is called Hartree–Fock self-consistent field (SCF) method.

### 3.2.6 Roothaan's Equation

For molecular systems of any size, however, direct solution of Hartree–Fock equations is impractical and more approximate methods are required. The most rewarding approach was from Roothaan [30] who, in 1951, developed an analytical method for obtaining solutions to Hartree–Fock equations by expanding each Hartree–Fock orbital in terms of some complete set of single particle functions used to form the basis set constituted by atomic orbitals of the atoms forming the molecule and thus eliminating the tedious numerical procedure previously inherent in the Hartree–Fock method. The Hartree–Fock equations along with the introduction of LCAO approximation are known as Roothaan equations.

In this approach, each molecular orbital is considered in the form

\[
\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}
\]

(3.37)
where the $\phi_\mu$ are real atomic functions. The suffixes greek and roman letters are reserved for denoting the atomic and molecular orbitals respectively.

The total electronic energy can also be written in terms of integrals over atomic orbitals if we substitute the linear expansion (3.37) in the molecular integrals. Thus

$$H_{\mu} = \sum_{\nu} C^*_\mu C_\nu H_{\mu\nu} \quad \text{(3.38)}$$

Where $H_{\mu\nu}$ is the matrix elements of the core–hamiltonian with respect to atomic orbitals and is given by

$$H_{\mu\nu} = \int \phi^{*}_\mu (1) H^{core} \phi_\nu (1) \, d\tau_1 \quad \text{(3.39)}$$

Similarly, we may write

$$J_{ij} = \sum_{\mu, \lambda, \nu} C_{\mu i}^{*} C_{\lambda j}^{*} C_{\nu i} C_{\sigma j} \quad \text{ (3.40)}$$

$$K_{ij} = \sum_{\mu, \lambda, \nu} C_{\mu i}^{*} C_{\lambda j}^{*} C_{\nu i} C_{\sigma j} \quad \text{ (3.41)}$$

Where $(\mu \nu| \lambda \sigma)$ is the general two electron interaction integral over atomic orbitals and is given by

$$(\mu \nu| \lambda \sigma) = \int \phi^{*}_\mu (1) \phi_\nu (1) (1/\tau_{12}) \phi_\lambda (2) \phi_\sigma (2) \, d\tau_1 \, d\tau_2 \quad \text{(3.42)}$$

Substituting the equations 3.38, 3.40 and 3.41 into the expression for total electronic energy, eq. 3.30, we get the equation of the form

$$\varepsilon = \sum_{\mu \nu} P_{\mu \nu} H_{\mu \nu} + (1/2) \sum_{\mu \lambda \nu \sigma} P_{\mu \lambda \nu \sigma} \left[ (\mu \nu| \lambda \sigma) - 1/2 (\mu \lambda| \nu \sigma) \right] \quad \text{(3.43)}$$

Where

$$P_{\mu \nu} = \sum_{\nu} C^{*}_{\mu i} C_{\nu i} \quad \text{(3.44)}$$
Now the important step is to find out the optimum values of the coefficients $c_{\mu i}$, leading to a set of LCAO self-consistent field (SCF) molecular orbitals. Using the criterion of lowest calculated energy, such orbitals will be the best for any particular set of basis functions $\phi_{\mu}$.

This can be carried out by invoking the principle of calculus of variation as in the previous Hartree–Fock method. The small variation of the molecular orbital $\psi_i$ is now given as

$$\delta \psi_i = \sum_{\mu} \delta C_{\mu i} \phi_{\mu}$$ ......................................(3.45)

Now under the framework of calculus of variation the condition for a stationary point in the function given by

$$G = \varepsilon - 2 \sum_i \sum_j (\epsilon_{ij} S_{ij})$$

$$= 2 \sum_i H_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) - \sum_i \sum_j \epsilon_{ij} S_{ij}$$ .................(3.46)

ultimately leads to the expression of the form

$$\sum_v F_{\mu v} C_{vj} = \sum_j \epsilon_{ij} \sum_v S_{\mu v} C_{vj}$$ ......................(3.47)

where $F_{\mu v}$ is given by

$$F_{\mu v} = H_{\mu v} + \sum_{\lambda \sigma} P_{\lambda \sigma} \left[ (\mu \nu / \lambda \sigma) - 1/2(\mu \lambda / \nu \sigma) \right]$$ ......................(3.48)

Like Hartree–Fock method unique specification of molecular orbitals is obtained from unitary transformation so that the elements of the Hermitian matrix, $\epsilon_{ij}$, follows the relation

$$\epsilon_{ij} = 0, \text{ if } i \neq j$$ ..................................................(3.49)

So equation 3.47 now reduces to
\[ \sum_{\nu} F_{\mu \nu} C_{\nu i} = \sum_{i} \epsilon_{i} \sum_{\nu} S_{\mu \nu} C_{\nu i} \] \hspace{2cm} (3.50)

Or, \[ \sum_{\nu} (F_{\mu \nu} - \epsilon_{i} S_{\mu \nu}) C_{\nu i} = 0 \] \hspace{2cm} (3.51)

The equations (3.51 with \( F_{\mu \nu} \) given by equation 3.48) are independently set forth by Hall [31] and Roothan, now generally known as Roothaan equations. The above equations is self-consistent with respect to \( C_{\nu i} \) matrix.

### 3.3 Non-empirical Vs. Semi-empirical

In the previous description of this chapter, it has been pointed out that Quantum Mechanics is a powerful methodology of investigation into the problems of electronic structure of matter: atoms, molecules and crystals. The theoretical model for the molecules, the Molecular Quantum Mechanics, is essentially the Hartree–Fock–Roothaan LCAO–MO theory. Mainly the MO method is used to investigate the accurate electronic wave functions of polyatomic molecules. A detailed and vivid theoretical treatment of polyatomic molecule involves calculations of electronic wave function using correct hamiltonian. Such a Hartree–Fock calculation seeking the antisymmetrized product of one electronic functions that minimize the total energy using true hamiltonian is classified as ab initio—"from the beginning" method which indicates a calculation based on fundamental principles and solve molecular electronic Schrödinger equation with chemical accuracy.

When the labour of self-consistent field molecular orbital calculation appears too great, approximations are introduced in a more or less rational fashion and integrals are estimated from empirical data. Such methods are known as semiempirical technique in molecular orbital theory [32]. In fact quantum chemistry was started with the idea of approximation.
If we are accurate in solution, vacuum (no body) is many body. Still to day, very accurate calculation is feasible for very small systems only.

Molecular Quantum Mechanical methods are classified as either ab initio (non-empirical) or semi-empirical. Semi-empirical methods despairs the complexity of such calculations and use a simpler hamiltonian than the correct molecular hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of ab initio calculations.

However, Freed [33] tried to find out a bridging hamiltonian operator between ab initio and semi-empirical theories of valence.

3.4 Necessity of approximate methods:
The self-consistent-field theory attempts to calculate atomic or molecular orbitals using the full many-electron hamiltonian and a single determinantal wave function. Optimization of the orbitals using the variational principle leads to a set of differential equations [30, 34] which are normally intractable, so most applications of the theory have used linear combinations of atomic orbitals (LCAO). If the coefficients in the LCAO orbitals are chosen to minimize the total energy, one obtains LCAO–SCF orbitals, the best LCAO approximations to the self-consistent functions, for which equations were first given by Hall [31] and by Roothaan [30]. Accurate calculations using this technique have since been made for many small systems. However, the use of the LCAO–SCF method without further approximation is limited by computational difficulties, particularly, in the electron repulsion integrals— their number and nature. The number of repulsion integrals varies as
the fourth power of the number of orbitals in the basis set. The repulsion integrals can be divided into four categories, viz.

1. one-center integrals
2. two-center integrals
3. three-center integrals
4. four-center integrals

The evaluations of the three and four center integrals are exceedingly difficult. So there remains a need for simpler methods which retain the principal features determining the electron distribution but are sufficiently tractable to be applied to large molecules. It is not surprising that the methods have been suggested to simplify the procedure by reducing the number and nature of the electron repulsion integrals.

3.5 Semi-empirical methods:

Because of the difficulties in applying ab initio methods to medium and large molecules, many semi-empirical methods have been developed to treat such molecules. The methods can be classified grossly into two categories, viz.

1. The \( \pi \)-electron semi-empirical MO methods for planar conjugated molecules.

Where the Roothaan LCAOSCF equations have been simplified by the neglect of differential overlap approximation [35-36] which deals with the neglect of the product of pairs of different atomic orbitals in certain electron interaction integrals. There is also known kind of treatment [37] which is intermediate in full LCAOSCF calculations for \( \pi \)-electrons and the very simple Hückel approach not handling with electron interaction in any explicit manner, and this treatment was done by combining the above approximation
with semi-empirical approach to correlate many physical properties of aromatic molecules. Full treatment of σ and π-electrons in planar molecules is done for increased value of MO calculation and hence is extended to all valence electrons. This approach is already been made with "extended Hückel methods" treating electrons independently[38-41].

2. The general semi-empirical MO methods applicable to planar as well as non-planar including all the valence electrons of the molecules.

The number of semi-empirical methods is quite large and the new methods are being suggested everyday. We have not set out the enumerating semi-empirical methods. We make references to the particular method which has been found to be quite effective in computing molecular geometries and reliable wave function and to be used in the present work. The semi-empirical method to be mentioned is the CNDO, complete neglect of differential overlap, method of Pople, Santry and Segal [42-43]. Now within the framework of CNDO method we shall proceed towards the self-consistent method based on neglect of differential overlap for all valence orbitals. This procedure leads to simplified LCAOSCF equations which is quite tractable for quite large systems. Now I can be discussed as various levels at which such approximations can be made systematically and the general method to be used for closed-shell molecules.

Now we wish to simplify the Roothaan equations. In order to reduce the number of electron repulsion integrals, scientists were looking forward to some approximate methods which are sufficiently reliable to reproduce electronic structure and geometry of molecules and suggested a ZDO method. In fact approximate theories were prevailing in the field of quantum mechanics before the advent of high speed digital computer. The approximate
methods were of two fundamental types – naive \( \pi \)-electron theory where only the \( \pi \)-electrons are considered and the \( \sigma \)-electrons are in static framework; other is all valence electron semi-empirical theory by generalization of zero differential overlap, ZDO principle. Within this framework, it transpires that there are two degrees of approximation which retain this type of invariance — (i) Complete Neglect of Differential Overlap (CNDO) and (ii) Neglect of Di-atomic Differential Overlap (NDDO). A very short discussion of the CNDO method is furnished in view of the fact the the method has been used to calculate the geometric and other parameters by invoking the CNDO formalism.

3.6 Theory with Complete Neglect of Differential Overlap (CNDO):

Here the assumption of neglect of differential overlap is invoked to reduce the the number and type for the two electron repulsion integrals. In his original derivation, Pople solved the problem of three-and four-center integrals in the Roothaan treatment by the cavalier procedure of simply ignoring them. In mathematical terms the Pople method rests on the assumption that the AO’s \( \phi_\mu \) nowhere overlap in space, i.e. if \( \phi_\mu \) and \( \phi_\nu \) are two different AO’s, then

\[
\phi_\mu \phi_\nu \, d\tau = 0 \quad \text{..................(3.52)}
\]

for all volume elements \( d\tau \).

With this assumption, the integrals \( \langle \mu \nu | \lambda \sigma \rangle \) clearly vanishes unless \( \mu = \nu \) and \( \lambda = \sigma \) and hence equations of three- and four-center integrals reduce to two center integrals \( \langle \mu \mu | \nu \nu \rangle \) which is much easier to evaluate. The approximation, eq. 3.52, is known as neglecting differential overlap or zero differential overlap (ZDO).
Now consider the simplest version of the theory involving the complete neglect of differential overlap between atomic orbitals on the same atom. The approximations used are as follows:

**Approximation 1**

The \( \phi_\mu \) are treated as if they form an orthonormal set; that is, the overlap integrals \( S_{\mu \nu} \) are put equal to zero unless \( \mu = \nu \), in which case they are unity. So it can be written as below.

\[
S_{\mu \nu} = \delta_{\mu \nu} \quad \ldots \ldots \quad (3.53)
\]

The coefficients \( C_\mu \) then form an orthogonal matrix and the orthonormality condition for \( \psi_i \) becomes

\[
\sum_{\mu} C_{\mu} C^*_{\mu} = \delta_{ij} \quad \ldots \ldots \quad (3.54)
\]

where \( \delta_{ij} \) is unity if \( i = j \) and zero otherwise. For different orbitals on the same atom, the overlap integral \( S_{\mu \nu} \) is already zero; for orbitals on different atoms, the approximation is not quantitatively accurate, but it does simplify much of the subsequent analysis and permits extensive application of the method.

**Approximation 2**

All two-electron integrals which depend on the overlapping of charge densities of different basis orbitals are neglected so that

\[
(\mu \nu | \lambda \sigma) = \delta_{\mu \nu} \delta_{\lambda \sigma} (\mu \mu | \lambda \lambda) \quad \ldots \ldots \quad (3.55)
\]

This means that \( (\mu \nu | \lambda \sigma) \) is zero unless \( \mu = \nu \) and \( \lambda = \delta \). The non-zero values can be written \( \gamma_{\lambda \mu} \) where

\[
\gamma_{\lambda \mu} = (\lambda \lambda | \mu \mu) \quad \ldots \ldots \quad (3.56)
\]
At this point, the theory is not invariant under a rotation of local axes or under hybridization. So further approximations must be made to restore invariance.

**Approximation 3**

The electron–interaction integrals $\gamma_{\mu\nu}$ are assumed to depend only on the atoms to which the orbitals $\phi_\mu$ and $\phi_\nu$ belong and not to the actual type of orbital. This means that there remains only a set of atomic electron–interaction integrals $\gamma_{AB}$. That is

$$(\mu\mu|\lambda\lambda) = \gamma_{\mu\lambda} = \gamma_{AB} \quad \ldots \ldots \ldots (3.57)$$

where the orbitals $\mu$ is on atom A and $\lambda$ on atom B. This, in effect, introduces a single coulomb integral between each atom pair $\gamma_{AB}$ and for each atom $\gamma_{AA}$. These integrals are then calculated using the S–type atomic orbital from the valence level of each atom. Using approximation 1 and 2, the matrix elements $F_{\mu\nu}$ become

$$F_{\mu\nu} = H_{\mu\nu} + \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} + \sum_{\sigma\mu} P_{\sigma\sigma} \gamma_{\mu\sigma} \ldots \ldots \ldots (3.58)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \ldots \ldots \ldots (3.59)$$

With the addition of approximation 3, $F_{\mu\nu}$ can be rewritten

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} + P_{\lambda\lambda} \gamma_{\lambda\mu} + \sum_{B=A} P_{BB} \gamma_{AB} \ldots \ldots \ldots (3.60)$$

Where $\mu$ belongs to atom A and $P_{BB}$ is the total valence electron density on atom B.

$$P_{BB} = \sum_{B=\nu} P_{\nu\nu} \ldots \ldots \ldots (3.61)$$
The diagonal core matrix elements, $H_{\mu \mu}$, include the interaction of an electron in the atomic orbital $\phi_\mu$ with the core of a given atom along with the interaction with the cores of other atoms. So we can write

$$H_{\mu \mu} = \{ \mu/(-1/2V^2 - V_A)/\mu \} + \sum_{B(xA)} (\mu/V_B/\mu)$$

$$= U_{\mu \mu} - \sum_{B(xA)} (\mu/V_B/\mu)...........................(3.62)$$

where $U_{\mu \mu}$ is the diagonal matrix element of $\phi_\mu$ with respect to the one-electron hamiltonian containing only the core of its own atom. $U_{\mu \mu}$ is an essentially atomic quantity which measures the energy of the atomic orbital. It may either be evaluated from approximate atomic orbitals or chosen semi-empirically from experimental data on atomic energy levels or possibly even used as a purely empirical parameter in molecular calculations. The remaining terms in eq. 3.62 give the interaction of an electron in $\phi_\mu$ with the cores of other atoms $B$. In case of off-diagonal core matrix elements $H_{\mu \nu}$, it is convenient to distinguish cases where $\phi_\mu$ and $\phi_\nu$ are on the same or different atoms. If both belong to the same atom, $H_{\mu \nu}$ may be written analogously to eq. 3.62 as follows:

$$H_{\mu \nu} = U_{\mu \nu} - \sum_{B(xA)} (\mu/V_B/\nu)...........................(3.63)$$

Where again $U_{\mu \nu}$ is the one-electron matrix element using the local core hamiltonian. For s, p, d functions, this is zero by symmetry. The remaining terms in eq. 3.63 represent the interaction of the distribution $\phi_\mu \phi_\nu$ with cores of other atoms. Now the neglect of differential overlap is consistent to neglect these contributions and leads to the further approximation.
Approximation 4

Neglecting monatomic overlap in an invariant manner in the interaction integrals involving the cores of other atoms the integral $\langle \mu | V_B | \nu \rangle$ assumes to be of the form

$$\langle \mu | V_B | \nu \rangle = \delta_{\mu\nu} V_{AB} \quad \cdots \cdots (3.64)$$

That means integrals $\langle \mu | V_B | \nu \rangle$ where $\phi_\mu$ and $\phi_\nu$ belong to atom A are put equal zero if $\mu \neq \nu$. Further, if $\mu = \nu$, the integral is taken to be the same for all valence atomic orbitals on atom A and we can write it as below.

$$\langle \mu | V_B | \mu \rangle = V_{AB} \quad \cdots \cdots (3.65)$$

In consequence, for s, p, d ... basis functions, using the equations 3.65 and 3.64, the diagonal and off-diagonal core matrix elements reduce to the forms given below.

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B(A)} V_{AB} (\mu \text{ on atom A}) \quad \cdots \cdots \cdots \cdots (3.66)$$

$$H_{\mu\nu} = 0 \quad (\mu \neq \nu, \text{ but both on the same atom}) \quad \cdots \cdots \cdots \cdots (3.67)$$

Now consider the matrix elements $H_{\mu\nu}$ where $\phi_\mu$ and $\phi_\nu$ are on different atoms. Here again the interaction of the distribution $\phi_\mu \phi_\nu$ with distant cores is neglected and supposed that $H_{\mu\nu}$ depends on the local environment between the two atoms. It is then a measure of the possible lowering of energy levels by being in the electrostatic field of the two atoms simultaneously, referred as the "resonance integral", and is denoted by the symbol $\beta_{\mu\nu}$. To estimate it further approximation is adopted.

Approximation 5

Off-diagonal core matrix elements between atomic orbitals on different atoms are estimated by a formula given by
\[ H_{\mu\nu} = \beta_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} \quad \ldots \ldots \ldots (3.68) \]

Where \( S_{\mu\nu} \) is the overlap integral and \( \beta^0_{AB} \) is a parameter depending only on the nature of the atoms A and B. However, the proportionality factor between \( H_{\mu\nu} \) and \( S_{\mu\nu} \) must be taken the same for all atomic orbitals on two given atoms for calculations to be invariant under transformation of the atomic basis sets. Empirical values are chosen either to fit experimental data or to reproduce results already obtained by complete a priori calculations.

The \( F_{\mu\nu} \) diagonal matrix elements of eq.3.60 now reduce to the form (\( \phi_n \) belonging to atom A and \( \phi_v \) to atom B) by using the eq.3.66 given by

\[
F_{\mu\mu} = U_{\mu\mu} - (P_{AA} - 1/2 P_{\mu\mu}) \gamma_{AA} + \sum_{B \neq A} (P_{BB} \gamma_{AB} - V_{AB}) \ldots \ldots \ldots \ldots (3.69)
\]

And \( F_{\mu\nu} \) off–diagonal matrix elements of eq.3.59 reduces to the form by using approximation 3 and eq.3.68 given by

\[
F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - 1/2 P_{\mu\nu} \gamma_{AB}, \mu \neq \nu \ldots \ldots \ldots (3.70)
\]

where for the same atom \( S_{\mu\nu} = 0 \) and \( \gamma_{AB} \) is replaced by \( \gamma_{AA} \). Again, from the eq. 3.43 and 3.48 total electronic energy can be written as below

\[
\varepsilon = 1/2 \sum_{\mu \nu} \left( H_{\mu\nu} + F_{\mu\nu} \right) \ldots \ldots \ldots \ldots (3.71)
\]

So the total energy takes the expression of the form given by

\[
\varepsilon_{\text{total}} = 1/2 \sum_{\mu \nu} \left( H_{\mu\nu} + F_{\mu\nu} \right) + \sum_{A < B} Z_A Z_B R^{-1}_{AB} \ldots \ldots \ldots (3.72)
\]

where \( Z_A \) and \( Z_B \) are nuclear charges on atoms A and B respectively with complete shielding by 1s electrons. The second part of the right hand side expression denotes the nuclear–nuclear repulsion sum.
Self-consistency:

Once a set of CNDO coefficients $C_\mu$ is obtained, the corresponding density matrix elements, $P_\mu^\nu$, are calculated and so corresponding $F$-matrix is obtained and hence total energy can be computed from the equation 3.72. Now diagonalization of the formed $F$-matrix gives rise to a new set of eigenvectors corresponding to a new set of MO's. These are used to construct a new set of $P_\mu^\nu$ and so a new $F$-matrix. Again total energy is obtained from the equation 3.72. The cycle is repeated until the $P_\mu^\nu$, the eigenvalues and eigenvectors of the $F$-matrix and also the total energy of the system converge to a limit within the paradigm of Born–Oppenheimer approximation.

In the first place, the CNDO method should be regarded as an approximation to a full LCAO–SCF calculation using a minimal basis set (i.e., a basis set consisting only of inner–shell and valence–shell atomic orbitals). So it should be emphasized, however, that the CNDO method attempts to reproduce the results of full minimal–basis LCAO–SCF calculations, which may not themselves, give satisfactory agreement with experimental data. It is possible that further semi–empirical modification of the CNDO method can correct some of the inadequacies of a priori calculations using a minimal basis set.

Following this line of attack, the method of calculation is specified in full by invoking certain semi–empirical parameter ($\beta_\mu$) being determined by detailed comparison with full LCAO–SCF treatments of diatomic at equilibrium separations as below.

3.7 Method of calculation and choice of parameters:

To specify the calculation in full, it is necessary to choose values for the overlap integrals, $S_{\mu\nu}$, the core hamiltonian elements, $U_{\mu\mu}$, $V_{AB}$, the electron repulsion integrals $\gamma_{AB}$
and the bonding parameters $P^0_{ab}$. Two procedures for obtaining these have been proposed which will be referred to as CNDO/1 and CNDO/2. Now some features of CNDO/1, which is retained in the second version, are first considered. The basis set $\phi_\mu$ consists of Slater-type atomic orbitals for the valence shell (1s for hydrogen and 2s, 2px, 2py, 2pz for lithium to fluorine). The overlap integrals $S_{\mu\nu}$ are calculated explicitly using formulas. The electron repulsion integral $\gamma_{AB}$, which represents an average interaction between electrons in valence atomic orbitals on atoms A and B, is calculated as the two-center coulomb integral involving valence $s$ functions,

$$\gamma_{AB} = \int S_A^2(1) S_B^2(2) d\tau_1 d\tau_2 \quad \text{(3.73)}$$

These are also evaluated using the explicit formulas.

Now to reduce the amount of empirical parameterization, the bonding parameters $P^0_{AB}$ are assumed to have the form

$$P^0_{AB} = \frac{1}{2}(\beta^0_A + \beta^0_B) \quad \text{(3.74)}$$

Where $\beta^0_A$ depends only on the nature of the atom A, so only a single semi-empirical parameter is selected for each element.

As the second version of CNDO method is rather more successful and has been more widely applied in respect of dealing with penetration integrals and the one-center atomic core integrals, direct translation to the CNDO/2 method is done now.

In the penetration effect electrons in an orbital on one atom penetrate the shell of another leading to a net attraction. Mathematically this is described by the penetration integrals ($Z_B \gamma_{AB} - V_{AB}$). These penetration terms give rise to calculated bonding energies even when the bond orders connecting two atoms are zero. This over emphasize on the
interaction energy is avoided in CNDO/2 method by neglecting the penetration integrals. Thus the electron–core potential integrals $V_{ab}$ are no longer evaluated separately but are related to the electron repulsion integrals by

$$V_{ab} = Z_B Y_{ab} \ldots \ldots \ldots (3.75)$$

No really satisfactory theoretical justification for this neglect of penetration can be given, but it does appear to compensate errors of the opposite sign introduced by the neglect of overlap integrals.

The second change in CNDO/2 concerns the way that the local core matrix element $U_{\mu\mu}$ is estimated from atomic data. In CNDO/1, this was obtained from the ionization potential $I_{\mu}$ of the appropriate average atomic state by the relation

$$-I_{\mu} = U_{\mu\mu} + (Z_A - 1) Y_{\mu\mu} \ldots \ldots \ldots (3.76)$$

the atomic orbital $\phi_{\mu}$ belonging to atom A. An alternative procedure would have been to use atomic electron affinities $A_{\mu}$ for which the corresponding relation is

$$-A_{\mu} = U_{\mu\mu} + Z_A Y_{\mu\mu} \ldots \ldots (3.77)$$

In a comprehensive molecular orbital theory, to account satisfactorily for the tendency of an atomic orbital to acquire and lose electrons, new procedure adopted in CNDO/2 is to use the average of eqs. 3.76 and 3.77.

$$-1/2(I_{\mu} + A_{\mu}) = U_{\mu\mu} + (Z_A - 1/2) Y_{\mu\mu} \ldots \ldots (3.78)$$

Rearrange of eq. 3.78 gives the expression of $U_{\mu\mu}$ and is given by

$$U_{\mu\mu} = -1/2 (I_{\mu} + A_{\mu}) - (Z_A - 1/2) Y_{\mu\mu} \ldots \ldots (3.79)$$
Now using eqns. 3.75 and 3.79, equn. 3.66 for diagonal core matrix elements become of the form

\[ H_{\mu \mu} = -\frac{1}{2}(1+\mu) - \left( Z_A - \frac{1}{2} \right) \gamma_{AB} - \sum_{B(A)} Z_B \gamma_{AB} \] ..........(3.80)

Also diagonal Fock matrix elements become

\[ F_{\mu \mu} = H_{\mu \mu} - \frac{1}{2} P_{\mu \mu} \gamma_{AA} + \sum_{B} P_{BB} \gamma_{AB} \] ..........(3.80)

Where there is no restriction on atoms A and B, i.e., A may be B.

*Self-consistency:*

Given a complete set of parameters specified in this way, the LCAOSCF equations may be solved by a series of steps.

1. An initial guess is made at the molecular orbital coefficients. This is best done by Hückel-type approximation to the Fock matrix with diagonal elements formed from \(-\frac{1}{2}(1+\mu)\) and off-diagonal elements formed from \(\beta_{\mu} \gamma_{AB} \).

2. Electrons are assigned in pairs to the molecular orbitals with lowest energies (lowest eigenvalues of \(F_{\mu \nu}\)).

3. The density matrix \(P_{\mu \nu}\) is calculated from the coefficients of the occupied molecular orbitals and then used to form a new Fock matrix.

4. Diagonalization of the \(F_{\mu \nu}\) matrix then leads to a new set of coefficients \(C_{\mu \nu}\).

5. Steps 2, 3 and 4 are repeated until self-consistency is achieved i.e. the \(P_{\mu \nu}\), the eigenvalues and eigenvectors of the \(F\)-matrix and also the total energy of the system converge to a limit.
The status of CNDO method has been argued by Löwdin as a full SCF method i.e. an \textit{ab-initio} SCF method with orthogonalized basis set. Under the assumption of neglect of overlap, the original Roothaan equation
\[ F'C' = SC'E' \quad \text{(3.82)} \]
Becomes
\[ FC = CE \quad \text{(3.83)} \]
Which is the form used in CNDO treatment. The full equations become comparable to equation 3.82, however, if the transformation
\[ C = S^{1/2} C' \quad \text{(3.84)} \]
is applied equation 3.82 then becomes, after pre-multiplication by $S^{-1/2}$,
\[ (S^{-1/2} F S^{-1/2}) C = CE \quad \text{(3.85)} \]
The transformation given in equation 3.84 is equivalent to replacing the original basis of atomic orbital $\phi'$ by a set of orbitals $\phi$ orthogonalized by procedure first proposed for molecules by Löwdin.
Thus \[ \phi = \phi' S^{-1/2} \quad \text{(3.86)} \]
As $\phi$ is the closest set of orthogonal orbitals to the original atomic orbitals $\phi'$.
However, the CNDO, C matrix or density matrix P can be retransferred back to the original basis by
\[ P \text{ (original)} = S^{-1/2} P S^{-1/2} \quad \text{(3.87)} \]
\[ C \text{ (original)} = S^{-1/2} C \quad \text{(3.88)} \]
Such method is rightly labeled as CNDO/2D where the deorthogonalization technique developed by Löwdin, is incorporated into CNDO/2 program [44-47]
(B) 3.8 Configuration interaction:

For the detailed study of the electronic structure of the molecular complexes, there have been extensive studies from both experimental and theoretical viewpoint [48]. In the theoretical ground, Mulliken originally proposed the intermolecular charge-transfer theory and elucidated the force of complex formation and the spectra [49]. After this theory, some MO perturbation theories have been proposed to find out the detailed mechanism of chemical interaction of two systems [50-54] and also numerical calculations were carried out on the interaction energies and their components (Coulomb, charge transfer, dispersion energy, etc.) [55-57]. Thus the dominant role of the charge-transfer effect has been emphasized to interpret the characteristic nature of molecular complexes, and these theories give the acceptable present day routine chemical concept of donor-acceptor interaction. Such treatments, however, have a defect that they cannot be applied with a sufficient accuracy to the case of strong complexes, for the interaction between two species is too strong to be dealt with as a perturbation. Although molecular orbital (MO) calculations, of which ab initio MO calculations [58] have been reliable, were performed to investigate the stability of molecular complexes taking the two molecules of the complex as an entity from the point of view of energy and charge distribution, the pictures, however, are often ambiguous for understanding the chemical features of complex formation, i.e., the conceptual aspects of donor-acceptor interaction.

Kenichi Fukui [59,60] developed a method of analysis of the molecular electronic structure of donor-acceptor complexes in a chemically graspmable form. In this method of analysis
the origin of transfer of charge and the mechanism of formation of bond between the interacting donor and acceptor species are straightforward.

Now the most satisfactory method consists of expanding the MO's of the addition compound in terms of the MO's of the donor and the acceptor in isolated state and then calculating the changes in the occupation number of the various MO's of the fragmental parts due to chemical interaction. The original procedure [61] in this respect is adapted in a simpler way and cast in matrix form [47] to straightway arrive at the appropriate equations.

Now brief description of the theoretical aspect of the donor-acceptor interaction is given here.

Let A, B and AB be the acceptor, the donor and the adduct respectively with closed shell structures. The MO's of each system are the linear combination of atomic orbitals (LCAO).

Let \( \Phi, [I] \) and \( \Psi \) be the row vectors including both the ground state (or occupied) as well as virtual SCF molecular orbitals having \( n \), \( m \) and \( n + m \) orthonormal sets respectively and are given as follows:

\[
\Phi = (\varphi_1 \varphi_2 \varphi_3 \ldots \varphi_n) \\
[I] = (\chi_1 \chi_2 \chi_3 \ldots \chi_m) \\
\Psi = (\psi_1 \psi_2 \psi_3 \ldots \psi_{n+m})
\]

where \( \varphi \)'s, \( \chi \)'s and \( \psi \)'s are the MO's of A, B and AB respectively. A and B are in the same nuclear configuration as in the adduct so that as such they are removed adiabatically from the adduct. The LCAO expansion of the row vectors can be written of the form given as follows:

\[
\Phi = F_A C_A
\]
\[ |l| = F_B C_B \] ........................................(3.93)
\[ \Psi = F_{AB} C_{AB} \] ..........................................(3.94)

where \( F_A \) and \( F_B \) are the row vectors of the AO's of A and B and are given by

\[ F_A = (f_1^a f_2^a f_3^a \ldots | f_n^a) \] .................(3.95)
\[ F_B = (f_1^b f_2^b f_3^b \ldots | f_m^b) \] .................(3.96)
\[ F_{AB} = (f_1^a f_2^a f_3^a \ldots | f_n^a | f_1^b f_2^b f_3^b \ldots | f_m^b) \]
\[ = (F_A \mid F_B) \] .............................................(3.97)

\( C_A \), \( C_B \) and \( C_{AB} \) are \( n \times n \), \( m \times m \) and \( (n + m) \times (n + m) \) coefficient matrix of such LCAO expansion.

Now MO's of the AB are expanded in terms of the MO's of the A and B and are given by the expression below:

\[ \Psi' = \chi' D \] ..................................................(3.98)

where \( \chi' \) is the row vector of the MO's of A and B and is shown below.

\[ \chi' = (\phi_1 \phi_2 \phi_3 \ldots | \phi_n \chi_1 \chi_2 \chi_3 \ldots | \chi_m) \] ..................................................(3.99)

Now the expansion of \( \chi' \) in terms of the original AO basis leads to the expression given by

\[ \Psi = F_{AB} A D \] ..........................................................(3.100)

where A shows the expression of the form

\[ A = \begin{bmatrix} C_A & 0 \\ 0 & C_B \end{bmatrix} \] ............................................(3.101)

Now comparing equations 3.94 and 3.100, we have

\[ D = A^{-1} C_{AB} \] .............................................(3.102)
So the expected matrix for the expansion of the MO's of AB in terms of the MO's of A and B is obtained. As matrices A and C\textsubscript{AB} are known, D can be easily calculated. The occupation numbers of the MO's of the fragmental parts after chemical interaction are calculated through the elements of D matrix. The occupation number \( v_i \) for a MO \( \phi_i \) of A is given by

\[
\nu_i = 2 \sum_{g=1}^{\text{occ m}} (d_i^{(g)})^2 + 2 \sum_{g=1}^{\text{occ m}} d_i^{(g)} d_k^{(g)} S_{ik} \tag{3.103}
\]

where \( d_i \)'s are the elements of D matrix and \( g \) runs through all the occupied MO's of AB and \( k \) runs through all the MO's of B, and \( S_{ik} \) is the overlap integral between the MO's \( \phi_i \) and \( \chi_k \)

\[
S_{ik} = \int \phi_i^{(1)} \chi_k^{(1)} dv \tag{3.104}
\]

The first part of the eq. 3.103 without overlap is called valence inactive part and the second part including overlap is called the valence active part [62]. The method, which is silent about overlap, accounts for the occupation number with the expression

\[
\nu_i = 2 \sum_{g=1}^{\text{occ m}} (d_i^{(g)})^2 \tag{3.105}
\]

\( C_A, C_B \) and \( C_{AB} \) are the eigen vector matrices for the acceptor(A), donor(B) and the adduct(AB) generated through the CNDO/2 method of Pople and Co-workers [63]. After this, these unitary matrices are deorthogonalized under L\öwdin's recipe [64].

\[
C' = S'^{-1/2} C \tag{3.106}
\]
Where \( C \) = eigenvectors over orthogonal atomic AO's, \( C' \) = eigenvectors over deorthogonalized atomic orbitals and \( S \) is the overlap matrix over Slater orbitals, and then computation of \( D \) gives the occupation number according to the eq. 3.103.

### 3.9 Computation steps

(i) \textit{Parameters used}

(a) Bonding parameters\( (\beta^b) \); (b) The atomic data (\( U \)), The orbital exponent parameter (\( \zeta \)) connected with Slater's effective nuclear charge

Their values for present work are given below

<table>
<thead>
<tr>
<th>Atoms</th>
<th>( U ) (eV)</th>
<th>( \beta^b ) (eV)</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s</td>
<td>2( s )</td>
<td>2( p )</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>9.594</td>
<td>4.001</td>
</tr>
<tr>
<td>F</td>
<td>-</td>
<td>32.272</td>
<td>11.080</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>19.316</td>
<td>7.275</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>14.051</td>
<td>5.572</td>
</tr>
<tr>
<td>H</td>
<td>7.176</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

{All standard parameters given here are taken from textual reference [63]}

(ii) \textit{Computation of overlap (S) and Coulomb (\( \gamma \)) integrals}

The overlap (\( S \)) and Coulomb (\( \gamma \)) integrals are computed through the explicit formulae laid down by Roothaan.

(iii) \textit{Steps of iteration}

Bond lengths and bond angles are varied by 0.001 \( \text{Å} \) and 0.1\(^{\circ} \) respectively till the systems attain minima in its total energy value when the energy difference between two successive iterations are \( \leq 0.00001 \).
(iv) *Coordinate calculation*

The B–L bond is made to coincide with Z (C₃) axis of the coordinate system. B atom is placed at the origin of the coordinate system and the then coordinates of other atoms are calculated by the help of translation and rotation of axes without shifting origin, using simple trigonometric and algebraic concept.

(v) *Program*

The necessary computer program for the work was made available to me by my supervisor Prof. D.C. Ghosh who partly adapted and partly developed the program of this work.

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