CHAPTER 2

2.1 INTRODUCTION

According to quantum mechanics, for the complete description of an arbitrary stationary state of a many electron system, e.g. a molecule, it is sufficient to know the solutions of the time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \quad \text{(2.1)}$$

These solutions, $\Psi$, are wavefunctions of the states (which depend upon the spatial and spin coordinates of all particles comprising the system) with eigenenergies $E$ (the energy relative to a state in which the constituent particles, i.e., the electrons and the nuclei, are infinitely separated and at rest) and $\hat{H}$ is the hamiltonian, a differential operator representing the total energy of the system. The hamiltonian is the sum of the kinetic energy operators for all particles and the potential energy operators for all interparticle interactions, given by equation 2.2.

$$\hat{H} = \hat{T}(R) + \hat{T}(r) + \hat{V}_{\text{nucl}} + \hat{V}_{\text{el}} + \hat{V}_{\text{el-nucl}} \quad \text{(2.2)}$$

where $\hat{T}(R)$ is the nuclear kinetic energy operator, $\hat{T}(r)$ the electronic kinetic energy operator and $\hat{V}_{\text{el}}, \hat{V}_{\text{nucl}}, \hat{V}_{\text{el-nucl}}$ the operators representing electron-electron, nuclear-nuclear and electron-nuclear interactions, respectively.
Although the Schrödinger equation can be written down for any arbitrary chemical system, be it an atom, an ion, a molecule, a transition state or an exciplex, the exact solutions for systems of chemical interest are known only for few systems. Even for a very simple molecular system, e.g. $\text{H}_2^+$, the analytical solution of the corresponding Schrödinger equation is impossible. It follows that approximate methods are necessary in molecular quantum chemistry. Many approximation methods are already known for simplifying the Schrödinger equation. Approximation methods known as ab initio methods are the most important. The theory underlying ab initio methods is given next.

2.2 Ab initio methods.

The term ab initio (means "from the beginning") is used to describe calculations in which the approximations are based on purely mathematical methods. Ab initio calculations do not use experimental data other than values of fundamental physical constants for the simplification of Schrödinger equation. The term ab initio should not be interpreted to mean hundred percent accurate nor even almost exact. An ab initio calculation uses a series of approximation methods to solve the Schrödinger equation. The first major step in simplifying the general molecular problem is the separation of nuclear and electronic motions, often referred to as Born-Oppenheimer approximation.\footnote{52}

The Born-Oppenheimer approximation is based on the fact that the nuclei, being much heavier than electrons, move slowly than electrons and hence, to a good approximation, one can consider the electrons in a molecule to be moving in the field of fixed nuclei. Therefore, the terms which represent the nuclear kinetic energy and the nuclear - nuclear repulsions can be excluded from the Hamiltonian and can be written as:

$$\hat{H}_{\text{el}} = \hat{T}_{\text{el}} + \hat{V}_{\text{el}} + \hat{V}_{\text{el-nucl}}$$  \hspace{1cm} (2.3)

As a consequence of the Born-Oppenheimer approximation, the molecular wavefunction can be expressed as the product of a nuclear wavefunction and an electronic wavefunction such that the latter depends on the nuclear co-ordinates parametrically.
Here, $R$ and $r$ denote the nuclear and electronic coordinates, respectively.

Quantitatively, the Born-Oppenheimer approximation may be formulated by writing down the Schrödinger equation for the electrons in the field of fixed nuclei as:

$$\hat{H}_{\text{elec}} \Psi_{\text{elec}}(R,r) = E_{\text{eff}}(R) \Psi_{\text{elec}}(R,r)$$  \hspace{1cm} (2.5)

It follows that the nuclear motion is characterised by potential energy $E_{\text{eff}}(R)$ which in turn represents the electronic energy at some fixed set of nuclear positions. This effective energy is then used as the potential energy for the subsequent study of nuclear motion. For a diatomic molecule, only the internuclear distance is required and $E_{\text{eff}}(R)$ is the potential curve for the molecule. For a polyatomic system, more relative coordinates are needed, and $E_{\text{eff}}(R)$ is termed as the potential surface for the molecule.

Although by the adoption of Born-Oppenheimer approximation, one can obtain highly accurate approximate wavefunctions for small molecules, such methods can hardly be extended and generalised to larger systems. Molecular orbital theory is an approach to molecular quantum mechanics which uses one electron functions or orbitals to approximate full wavefunctions of many-electron systems. A molecular orbital can be represented as a linear combination of atomic orbitals (LCAO). A one-electron function is a function of spatial and spin coordinates of a single electron and is known as a spin-orbital. Its square, $\psi^2$ (or absolute square, $|\psi|^2$, if $\psi$ is complex), is interpreted as the probability distribution of the electron in space.

Because of the fermion character of electrons, it is required that the total many electron wave-function $\Psi$ should be antisymmetric upon exchange of indices of a pair of electrons (Pauli exclusion principle).

An important property of the molecular orbitals is that they are orthonormal.
With these features, the full many electron wavefunction for the closed shell ground state of a molecule with \( n \) (even) electrons, doubly occupying \( n/2 \) orbitals is:

\[
S_{ij} = \int \psi_i^* \psi_j \, dx \, dy \, dz = 0 \text{ for } i \neq j
\]

\[
S_{ii} = \int \psi_i^* \psi_i \, dx \, dy \, dz = 1.
\]

(2.6) \hspace{2cm} (2.7)

The problem of determining the optimal form of the many-electron wavefunction defined in terms of spin orbitals becomes automatically the problem of splitting the Hamiltonian into one electron Hamiltonians. Although the one electron wavefunction is introduced, the Hamiltonian yet cannot be written as the sum of one
electron hamiltonians because of interelectronic interactions. A practical solution to this problem is offered by the Hartree-Fock scheme, which is described next.

Hartree-Fock approach is based on the variational method in quantum mechanics. The application of variational condition with the LCAO-MO approximation leads to a set of algebraic equations for MO coefficients, which in matrix form may be written as:

\[ F'C = SCE \]  \hspace{1cm} (2.10)

where \( F' \) is the Fock matrix and \( S \) is the overlap matrix. Equation 2.10 are known as Roothaan-Hall equations. The elements of Fock matrix and overlap matrix are given by:

\[ F_{\mu\nu} = S^{\text{core}}_{\mu\nu} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} F'_{\lambda\sigma} \left[ \langle \mu \nu | \lambda \sigma \rangle - 1/2 \langle \mu \lambda | \nu \sigma \rangle \right] \]  \hspace{1cm} (2.11)

\[ S_{\mu\nu} = \int \phi^*(\mu) \phi(\nu) \, dx_1 \, dy_1 \, dz_1 \]  \hspace{1cm} (2.12)

In the above equations, \( H^{\text{core}}_{\mu\nu} \) is a matrix representing the energy of a single electron in the field of "bare" nuclei. Its elements are:

\[ S^{\text{core}}_{\mu\nu} = \int \phi^*(\mu) \phi(\nu) \, dx_1 \, dy_1 \, dz_1 \]  \hspace{1cm} (2.13)

\[ \mathcal{H}^{\text{core}} (1) = -1/2 \nabla^2 - \sum_{\Lambda=1}^{M} \frac{Z_{\Lambda}}{r_{1\Lambda}} \]  \hspace{1cm} (2.14)

Here \( Z_{\Lambda} \) is the atomic number of atom \( \Lambda \), and summation is carried out over all atoms. The quantities \( \langle \mu \nu | \lambda \sigma \rangle \) shown in equation 2.10 are two-electron integrals.
The elements of one electron density matrix in equation 2.10 are given by:

\[
\rho'_{\lambda\sigma} = 2 \sum_{i=1}^{\text{occ}} c_{\lambda i}^* c_{\sigma i}
\]  

(2.16)

The summation is over occupied molecular orbitals only. The factor of two indicates that two electrons occupy each molecular orbital.

The total energy is the sum of the electronic energy \( E_{ee} \) and the energy of internuclear repulsion \( E_{nr} \), which may be represented as:

\[
E_{ee} = \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} P_{\mu\nu} \left( F_{\mu\nu} + \phi_{\mu\nu}^{\text{occ}} \right)
\]

\[
E_{nr} = \sum_{\Lambda < B} \frac{Z_{\Lambda} Z_{B}}{R_{\Lambda B}}
\]

(2.17)  

(2.18)

Roothaan-Hall equations 2.10 are not linear since the Fock matrix \( F_{mn} \) depends upon the molecular orbital coefficients \( c_{\mu i} \) through the density matrix expression 2.16. The solution of Hartree-Fock equation necessarily involves an iterative process. Since the resulting molecular orbitals are derived from their own effective potential, the technique is frequently called self-consistent field theory.

The starting point of a typical energy calculation is the specification of molecular geometry and the basis set needed. The necessary one and two electron integrals are evaluated and stored in a well defined manner. An initial guess of the MO coefficients or density matrix elements is made (either by diagonalising the core Hamiltonian or from an extended Hückel calculation on the molecule). Then the iterative solution of the molecular orbital coefficients, the associated orbital energies and the total energy is carried out till the self-consistent solution is obtained.
So far we were discussing about the theory behind ab initio methods. There are a number of advantages and also disadvantages of ab initio theory. Ab initio calculations give very good qualitative results and can give increasingly accurate quantitative results faster as the molecules in question become smaller.

Ab initio method uses a single determinant for describing the wavefunction of the chemical system in question, and the wavefunction is said to have little flexibility. This inflexibility of wavefunction introduces an error known as correlation error to the total energy of the system. This error can be avoided by including additional determinants via a configuration interaction method or by appealing to perturbation theory. These techniques are outlined in section 2.3.

Theoretically the expansion of molecular orbitals in terms of atomic orbitals needs infinite number of basis functions, which is impossible practically. For computational work a small number of basis functions are used in order to define a molecular orbital, which necessarily introduces an error to the total energy calculated. A brief discussion on the widely used basis sets is entailed in the following section.

2.2.1 BASIS SETS

The choice of the basis set is dependent upon a number of factors. The most important factor which determines the selection of the basis set is that the final wavefunction and the associated bonding should be easily interpretable. Therefore, it is preferable to choose atom centred functions. Functions which represent the atomic orbitals are preferred. Nevertheless, the integrals involved in the ab initio calculations should be readily computable. Two types of basis functions are frequently employed in molecular orbital calculations, Slater-type orbitals (STO) and Gaussian type orbitals (GTO). Slater-type atomic orbitals (STO's) have exponential radial parts. The gaussian-type atomic functions are represented as powers of \( x, y, z \) multiplied by \( \exp (-\alpha r^2) \), \( \alpha \) being a constant determining the size, that is, radial extent, of the function.

While Slater type orbitals (STO's) are closer to real atomic orbitals, Gaussian functions lead to simple integral formulae. Because of the analytical form, gaussian basis functions are suited for computational work. This may be a primitive gaussian function (single function to define a basis function) or contracted gaussian (linear combination of primitive gaussians to represent a basis function).
Once the form of the basis functions are chosen, there can be question about the number of functions per atom as well as the precise exponents and contraction coefficients, since the final results depend critically on them. A number of basis sets of varying complexity have already been formulated, which have been tested for various chemical problems. In the literature, a fair amount of reference data is available, and so comparisons can easily be made.

A limiting Hartree-Fock treatment would involve an infinite set of basis functions, which is clearly impractical since the computational time is directly proportional to the fourth power of the total number of basis functions. The ultimate choice of the basis set size depends on the compromise between accuracy and efficiency.

The simplest of all basis sets is the minimal basis set. For a minimal basis set the number of basis functions on each atom is just enough to accommodate all the electrons and still maintain the spherical symmetry. As a consequence, the molecular orbitals have only limited flexibility. The widely used series of minimal basis sets, the STO-KG,\( ^{56} \) consists of expansion of Slater type atomic orbitals in terms of \( K \) gaussian functions. For STO-KG basis sets 2s, 3s, 4s and 5s functions are expanded in terms of zero order 's' gaussians; 3p, 4p and 5p functions are expressed in terms of first order 'p' gaussian functions. 4d are expressed in terms of second order 'd' gaussian primitives. Atomic functions of given principal quantum number '\( n \)' often share a common set of gaussian exponents.

Minimal basis sets such as STO-3G have several inherent inadequacies: basis functions are not apportioned according to electron count; fixed gaussian exponents are unable to expand and contract in response to differing molecular environments; another drawback is the inability to describe adequately the non-spherical anisotropic effects of molecular charge distributions. This is because a minimal basis set contains only a single valence function of each particular symmetry type.

In principle, the first two deficiencies may be alleviated by allowing for more than a single valence electron function of each symmetry type in the basis set description and the third by using either an anisotropic minimal basis set\(^{57} \) or by more than a single set of valence \( p \) and/or \( d \) type functions.
A double zeta basis results by replacing each STO of minimal basis set by two Slater type orbitals which differ in their orbital exponents. An even simpler extension of a minimal basis set is to double only the number of basis functions representing the valence region. While the inner-shell electrons are not important with regard to the total energy, their effect on molecular bonding is of little consequence. The 3-21G basis set, a split valence basis one, uses a combination of three gaussian primitives to describe the core orbitals while valence orbitals are described by two sets of functions: the inner function by two gaussians and the outer by a single gaussian.58

Larger split-valence representations like the 4-31G59 and 6-31G60 basis set comprises inner-shell functions, each written in terms of a linear combination of four and six gaussians, respectively, and two valence shells represented by three and one gaussian primitives.

All the above mentioned basis sets do not incorporate functions with significant long range amplitude and hence are incapable of describing electron rich systems. Diffuse orbitals are useful for calculations of molecular systems with lone pair of electrons and anions.61 The 3-21+G62 basis set includes one diffuse function for all atoms except hydrogen.

All these basis sets comprise functions constrained to be centered at the nuclear positions. Evidence suggests that the description of highly polar molecules, and systems incorporating small strained rings require that some allowance must be made for the possible displacement of charge away from the nucleus. The shape of an orbital can be changed by adding orbitals of higher angular momentum, which introduces non-uniformity in charge distribution in the orbital. Such a representation is termed as a polarization basis set.63 The polarized basis set 6-31G*, formed by addition of a set of six second order (d type) gaussian primitives to the split valence 6-31G basis set of each heavy atom (non-hydrogen) has become the common standard for calculations on medium-sized systems.

The 6-31G** basis set is identical to 6-31G* except for the addition of a single set of gaussian p type functions to each hydrogen and helium. This basis set is proved to be good for calculations on hypervalent molecules and molecules which have
unusual geometries. In the present investigation the 6-31G** basis set is extensively used.

Basis sets like 6-311G** have more flexibility than 6-31G* and 6-31G** basis sets. The special feature of 6-311G** basis set is that gaussian exponents and expansion coefficients can be chosen so as to minimize the atomic ground state at second order Møller-Plesset perturbation level, rather than at the Hartree-Fock level. This allows for the possibility of specific basis functions contributing to electron correlation within the atomic valence region.

The smaller basis sets have limited flexibility. The choice of a larger basis set increases the number of adjustable coefficients in the variational procedure, and hence an improved description of molecular orbitals is achieved. A major factor in selecting a suitable basis set for a particular application is the availability of computational resources. The computational time increases drastically with the increase in the size of basis functions. Therefore, the choice of basis set is a compromise between the computational time and the number of functions used.

Up to this point, the theory has been developed in terms of single-determinant wavefunctions. Nevertheless, it must be recognised that the exact wavefunctions cannot generally be expressed as single determinants. There is a need for further refinement of theory to estimate errors implicit in the Hartree-Fock approximation.

### 2.3 Electron Correlation Methods

The primary deficiency of Hartree-Fock theory is the inadequate treatment of the correlation between motion of electrons. In particular, single determinant wavefunctions take no account of correlation between electrons with opposite spin. Correlation of the motions of electrons with the same spin is practically, but not completely, accounted for by virtue of the determinantal form of the wavefunction. These limitations lead to calculated (Hartree-Fock) energies that are above the exact values. The difference between the exact nonrelativistic energy and the Hartree-Fock energy is known as correlation energy.
The neglect of correlation between electrons of opposite spin leads to a number of qualitative deficiencies in the description of electronic structure. The most important consequence is that the closed shell Hartree-Fock function often does not dissociate correctly when nuclei are moved to infinite separation. The single determinant wavefunction may not always have the full symmetry of the exact wavefunction.

Configuration interaction is one of the widely used methods for getting correlation energy. The method is based on the idea that the exact wavefunction can be represented as a linear combination of N-electron trial wavefunctions and it uses the linear variation method.\textsuperscript{64} If the basis sets are complete, one would obtain the exact energies not only of the ground state but also of all excited states of the system. In principle, this method provides an exact solution of the many electron problem.

Practical models incorporating electron correlation do not usually satisfy all the requirements of a theoretical model. As with basis set selection, choice of the electron correlation method may ultimately be governed primarily by practical considerations. The most straightforward way of limiting the length of CI expansion is to truncate the wavefunction at a given level of substitution. Another approach of adding higher excitations to Hartree-Fock functions is the Møller-Plesset theory, which is outlined below.

The perturbation theory of Møller-Plesset,\textsuperscript{65} closely related to many body perturbation theory, is an alternative approach to the correlation problem. These methods treat the complete hamiltonian as the sum of two parts, the non-Hartree-Fock part being treated as a perturbation on the Hartree-Fock part. The energy expression may be terminated at any desired order, although practical implementations are presently limited to the fourth order. These energies have the property of size consistency, but do not represent rigorous upper bounds to the true energy. The complexity and the cost of computing the energy terms in this expansion increase rapidly with the order.

The energy correct to the first order in Møller-Plesset (MP) expansion is identical to the Hartree-Fock energy. The simplest approximation to the energy correction due to correlation is the second order quantity. If the expansion is terminated
here, the model may be described as MP2. The third and fourth order methods may be denoted by MP3 and MP4, respectively.