Chapter I

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Chapter I

1.1 Molecular Orbital Theory

1.1.1. Introduction

Modern molecular physics includes the quantum mechanical explanation of the several kinds of chemical bonding between the atoms in a molecule, the polarizability of the molecules, the quantization of the vibrational, rotational, and electronic motion of the molecules, and the phenomena arising from intermolecular forces. Quantum chemistry is the branch of science that deals with the application of quantum mechanics to chemical problems. So these two fields, molecular physics and quantum chemistry, exist as a twin with one heart, quantum mechanics.

In brief, quantum chemistry is the application of quantum mechanics and statistical methods to the interpretation and prediction of molecular properties. It strives to introduce a mathematical structure within molecular population. Quantum mechanics permits the calculation of the properties of each molecule. Statistical mechanics makes it possible to go from these microscopic molecular properties to the macroscopic properties of the population. In principle, all physical and chemical properties can be considered as spectroscopic, electrical, magnetic, and thermodynamic properties. However, the quantum theory of chemical reactions remains as the central part of quantum chemistry. Furthermore, the application of quantum mechanics to spectroscopic, electrical, and magnetic molecular properties is very often considered to be a part of quantum molecular physics. Thus these two fields, molecular physics and quantum chemistry are inseparable.
The hydrogen like atom is the single most important system in quantum chemistry. The exact solution of the Schrödinger equation, explaining all the properties of atoms and molecules, for atoms with more than one electron cannot be obtained accurately because of the interelectronic repulsions. If, as a first approximation, these repulsions have been ignored, then the electrons can be treated independently. The atomic wave function will be approximated by the product of one electron functions, which will be hydrogen like wave functions. A one electron wave function is called an orbital. An orbital for an electron in an atom is called an atomic orbital. The atomic orbitals can be used to construct approximate wave functions for many-electron atoms. It should be mentioned that the wave function specifying the state of an electron depends not only on the coordinates x, y, and z but also on the spin state of the electron.

Thus for many electron molecules, which (unlike $H_2^+$) cannot be solved exactly, the ideas of some approximate treatments have been used. For this, first, one is able to write an approximate molecular wave function as a Slater determinant of (one-electron) spin orbitals. The one-electron spatial part of a molecular spin orbital will be called a molecular orbital. Because of the Pauli principle, each molecular orbital can hold no more than two electrons, just as for atomic orbitals.

The molecular hamiltonian is formidable enough to strike terror in the heart of any quantum chemist. Fortunately, there exist a highly accurate, simplifying approximation. The first major step in simplifying the general molecular problem in quantum mechanics is the separation of the nuclear and electronic motions. This is possible because, the nuclear masses are much greater than those of the electrons, and, therefore, nuclei move very slowly. As a consequence, the electrons in a molecule adjust their distributions to change the nuclear positions rapidly. This makes it a reasonable approximation to suppose that the electron distribution depends only on the instantaneous positions of the nuclei and not on
their velocities. In other words, the quantum mechanical problem of electron motion in the field of fixed nuclei may first be solved, leading to an effective electronic energy $E_{\text{eff}}(R)$, which depends on the relative nuclear coordinates, denoted by $R$. This effective energy is then used as a potential energy for the subsequent study of the nuclear motion. For a diatomic molecule, only the internuclear distance, $R$, 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. This separation of the general problem into two parts is frequently called Born-Oppenheimer approximation [1]. Quantitatively, the Born-Oppenheimer approximation may be formulated by writing down the Schrödinger equation for electrons in the field of fixed nuclei as

$$H_{\text{elec}} \Psi_{\text{elec}} (r, R) = E_{\text{eff}} (R) \Psi_{\text{elec}} (r, R)$$  \hspace{1cm} (1.1)$$

Here, $\Psi_{\text{elec}}$ is the electronic wavefunction, which depends on the electronic coordinates, $r$, as well as on the nuclear coordinates, $R$. The electronic Hamiltonian, $H_{\text{elec}}$, corresponds to the motion of the electrons only in the field of fixed nuclei and is given as

$$H_{\text{elec}} = T_{\text{elec}} + V$$  \hspace{1cm} (1.2)$$

where $T_{\text{elec}}$ is the electronic kinetic energy

$$T_{\text{elec}} = - \left( \frac{\hbar^2}{8\pi^2 m} \right) \sum_i \nabla_i^2$$  \hspace{1cm} (1.3)$$

and $V$ is the Coulomb potential energy

$$V = - \sum_{\alpha} \sum_i Z_{\alpha} \frac{e^2}{r_{i\alpha}} + \sum_i \sum_{j > i} \frac{e^2}{r_{ij}} + \sum_{\alpha > \alpha} \sum Z_{\alpha} Z_{\beta} \frac{e^2}{r_{\alpha\beta}}$$  \hspace{1cm} (1.4)$$
The i and j represents electrons, while $\alpha$ and $\beta$ are nuclei. The first part of eqn.(1.4) corresponds to the electron-nuclear attraction, the second to the electron-electron repulsion, and the third to the nuclear-nuclear repulsion. The last one is independent of the electronic coordinates and is a constant contribution to the energy for any particular nuclear configuration. The main task of theoretical studies of electronic structure is to solve, at least approximately, the electronic Schrödinger eqn. (1.1), and hence to find the effective nuclear potential $E^{\text{eff}}(R)$. From this point, the superscript in eqn.(1.1) can be omitted; it is assumed that the Hamiltonian, $H$, wavefunction, $\Psi$, and the energy $E$, refer to electronic motion only, each quantity being implicitly a function of the relative nuclear coordinates.

The search of accurate electronic wave functions of polyatomic molecules uses mainly the molecular orbital method. The presence of several nuclei causes greater computational difficulties than for diatomic molecules. Moreover, the electronic wave function of a diatomic molecule is a function of only one parameter - the internuclear distance; in contrast, the electronic wave function of a polyatomic molecule depends simultaneously on several parameters - the bond distances, bond angles, and dihedral angles of rotation about single bonds. Molecular quantum mechanical methods are classified as either ab initio or semi-empirical methods. Semi-empirical methods use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit the experimental data or the results of ab initio calculations. In contrast, ab initio calculation uses the correct Hamiltonian and does not use the experimental data other than the values of the fundamental physical constants. A Hartree-Fock calculation seeks the antisymmetrized product $\phi$ of one electron functions that minimizes $\int \phi^* H^* \phi \, d\tau$, where $H$ is the true Hamiltonian, and is thus an ab initio calculation [2].
Two theories have been frequently used to solve the Schrödinger equation for molecules. They are,

(i) Molecular orbital (MO) theory
(ii) Valence bond (VB) theory

The VB theory treats the formation of the molecule as arising from the bringing together of complete atoms which, interact, to a large extent to retain their original character, while the MO theory allocates electron into molecular orbitals similar in many respects to atomic orbitals, but each electron contains two or more nuclei. Thus in the valence bond theory, all bonds are considered to be two-centered bonds, that is, to subsist between two atoms. It is only an afterthought, more or less, that account is taken of any interaction between such bonds. In addition, there is no priori way to decide which pairs of atoms should be considered as bonded and which non-bonded, whereas in the MO theory, with the idea that all orbitals in a molecule extend over the entire molecule, which therefore means that electrons occupying these orbitals may be delocalized over the entire molecule. The theory does, naturally, admit the possibility that one or more of these molecular orbitals (MO's) may have significantly large values of the wave functions only in certain parts of the molecule. That is, localized bonding is a special case which is adequately covered by MO theory, but localization is not 'built in' as a postulate at the outset as in the valence bond treatment. Because MO theory treats orbitals which in general spread over the entirety of a molecule, considerations of molecular symmetry properties are extremely useful in this theory. They make it possible to determine the symmetry properties of the MO wave functions. If elaborate calculations are to be carried out, the use of MO symmetry properties can immensely alleviate the labour involved by showing that many integrals must be identically zero.
1.1.2. The LCAO approximation

By far the commonest approximation employed to reduce the notion of MO to an explicit, practical form is the linear combination of atomic orbitals (LCAO) approximation. Each MO is written as a linear combination of atomic orbitals on the various atoms. Denoting the \( i \)th atomic orbital as \( \phi_i \) the \( k \)th molecular orbital \( \psi_k \), is written as

\[
\psi_k = \sum_i c_{ik} \phi_i \tag{1.5}
\]

The \( \phi_i \)'s are a basis set, and it is convenient to choose or adjust them so that they are normalized.

\[
\int \phi_i^* \phi_i \, d\tau = 1 \tag{1.6}
\]

By using LCAO - MOs, a particular form of the wave equation, called the secular equation, is developed in the following way. The wave equation is written in the form

\[
H\psi - E\psi = (H-E)\psi = 0 \tag{1.7}
\]

LCAO expression for \( \psi \) is now introduced, giving

\[
\sum_i c_i (H-E) \phi_i = 0 \tag{1.8}
\]

For clarity, it is easier to continue the development explicitly for the case of a two-term LCAO-MO; thus eqn. (1.8) takes the form

\[
C_1 (H-E) \phi_1 + C_2 (H-E) \phi_2 = 0 \tag{1.9}
\]
Eqn. (1.9) is now multiplied by \( \phi_1 \), and the left side is integrated over all spatial coordinates of the wave functions:

\[
C_1 \int \phi_1 (H-E) \phi_1 \, d\tau + C_2 \int \phi_1 (H-E) \phi_2 \, d\tau = 0 \quad (1.10)
\]

To simplify the above equation, the following definitions will now be introduced:

\[
H_{ii} = \int \phi_i H \phi_i \, d\tau \quad (1.11)
\]
\[
H_{ij} = \int \phi_i H \phi_j \, d\tau \quad (1.12)
\]
\[
S_{ij} = \int \phi_i \phi_j \, d\tau \quad (1.13)
\]

The integral \( H_{ii} \) gives the energy of the atomic orbital \( \phi_i \). The \( H_{ij} \) integrals give the energies of interaction between pairs of atomic orbitals. The \( S_{ij} \) are called overlap integrals. Because the energy, \( E \), is simply a number

\[
\int \phi_i E \phi_j \, d\tau = E \int \phi_i \phi_j \, d\tau = ES_{ij} \quad (1.14)
\]

Eqn. (1.10) may now be written as

\[
C_1 (H_{11} - E) + C_2 (H_{12} - ES_{12}) = 0 \quad (1.15)
\]

Eqn. (1.9) could also be multiplied by \( \phi_2 \) and integrated, leading to

\[
C_1 (H_{21} - ES_{21}) + C_2 (H_{22} - E) = 0 \quad (1.16)
\]
These two equations form a system of homogeneous linear equations in $C_1$ and $C_2$. They obviously have the trivial solutions $C_1 = C_2 = 0$. It is proved in the theory of homogeneous linear equations that other, nontrivial solutions can exist only if the matrix of the coefficients of the $C_i$'s form a determinant equal to zero. Thus, the so-called secular equation has been obtained:

\[
\begin{vmatrix}
H_{11} - E & H_{12} - ES_{12} \\
H_{21} - ES_{21} & H_{22} - E
\end{vmatrix} = 0
\]

(1.17)

The numerical values of $H_{ii}$'s and $H_{ij}$'s and $S_{ij}$'s can be guessed, estimated, or computed at some level of approximation, and the secular equation is then solved for the values of $E$. From the algebra of determinants, it follows that $n \times n$ determinant will give rise to $n^{th}$ order polynomial equation in the energy. Eqn.(1.17) for example, gives the quadratic equation.

\[
(1 - S_{12}^2) E^2 - (H_{11} + H_{22} - 2H_{12} S_{12}) E + H_{11} H_{22} - H_{12}^2 = 0
\]

(1.18)

where the relations $S_{ij} = S_{ji}$ and $H_{ij} = H_{ji}$ have been invoked. This equation can be solved to give two roots $E_1$ and $E_2$ which was shown to be the upper limits to the energies of the ground and first excited states.

If the value $E_1$ is inserted into equations 1.15 & 1.16, these equations may then be solved for the coefficients $C_{11}$ & $C_{12}$, which give the MO $\psi_1$ having the energy $E_1$. Similarly, $E_2$ may be substituted to obtain equations for the coefficients $C_{21}$ and $C_{22}$ giving the MO $\psi_2$, which has the energy $E_2$. 

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Thus, in summary, by using the values of the various integrals (often called matrix elements) $H_{ij}$, $H_{ij}$, $S_{ij}$, the energies of MO's may be calculated in the LCAO-MO approximation without knowing the explicit form of the LCAO-MO's. After the energy values are known, it is possible to determine the coefficients, $C_{ij}$, and thus obtain the explicit expressions for the LCAO-MO's.

Finally, a many electron wave function is constructed from the molecular orbitals in the form of single determinant. This MO theory is an approach to molecular quantum mechanics which uses one-electron functions or orbitals to approximate the full wave function i.e., the electron distribution and motion assigns individual electrons to one electron functions, termed as spin orbitals. These comprise a product of spatial functions, termed as molecular orbitals, $\psi_1(x,y,z)$, $\psi_2(x,y,z)$... and either $\alpha$ or $\beta$ spin components. This spin component takes one of the two possible values ($\pm \frac{1}{2}$), and measures the spin angular momentum component along the $2$ axis in units of $\hbar/2\pi$. These spin orbitals are allowed to enjoy complete freedom to spread throughout the molecule, their exact form being determined variationally to minimize the total energy. These orbitals are then brought together to form a suitable many electron wave function $\Psi$ which is the simplest MO treatment to the solution of the Schrödinger equation i.e., the complete wave function for a single electron is the product of a molecular orbital and as spin function $\psi(x,y,z) \alpha(\varepsilon)$ or $\psi(x,y,z) \beta(\varepsilon)$. It is termed a spin orbital $\Psi(x,y,z,\varepsilon)$. For $n$ electron system, the wave function would be in the form of product of spin orbitals,

$$\Psi_{\text{product}} = \Psi_1(1) \Psi_2(2) \ldots \Psi_n(n)$$

where $\Psi_i(i)$ is written for $\Psi_i(x_i,y_i,z_i,\varepsilon_i)$, the spin orbital of electron $i$. 

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However, it does not have the property of antisymmetry. If the coordinates of electrons $i$ and $j$ are interchanged in this wave function, the product $\Psi_i(i) \Psi_j(j)$ becomes $\Psi_j(j) \Psi_i(i)$ which is not equivalent to multiplication by -1. To ensure antisymmetry, the spin orbitals may be arranged in a determinantal form

$$\Psi_{\text{det}} = \begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \ldots & \Psi_n(1) \\ \Psi_1(2) & \Psi_2(2) & \ldots & \Psi_n(2) \\ \vdots \\ \Psi_1(n) & \Psi_2(n) & \ldots & \Psi_n(n) \end{vmatrix} \quad (1.20)$$

Here the elements of the first row of the determinant contain assignation of electron 1, to all the spin orbitals $\Psi_1, \Psi_2, \ldots, \Psi_n$ and second row all possible assignation of electron 2, and so on.

This determinantal wave function does have the property of antisymmetry. For instance, the interchange of the coordinates of electrons $i$ & $j$ is equivalent to the interchange of rows $i$ & $j$ in the determinant which does have the effect of changing the sign. So, many electron molecular wave function for the closed shell ground state of a molecule with $n$ (even) electrons, i.e., doubly occupied $n/2$ orbitals given as

$$\Psi = (n!)^{1/2} \begin{vmatrix} \Psi_1(1) \alpha(1) & \Psi_1(1) \beta(1) & \ldots & \Psi_{n/2}(1) \beta(1) \\ \Psi_1(2) \alpha(2) & \Psi_1(2) \beta(2) & \ldots & \Psi_{n/2}(2) \beta(2) \\ \vdots \\ \Psi_1(n) \alpha(n) & \Psi_1(n) \beta(n) & \ldots & \Psi_{n/2}(n) \beta(n) \end{vmatrix} \quad (1.21)$$
1.1.3. The Hartree-Fock Self Consistent Field MO theory

The self consistent field (SCF) treatment of Hartree suffers from a shortcoming that the orbital product wave function is not antisymmetric. Fock used antisymmetrized wave function and followed the same iterative procedure as described by Hartree [3,4]. This is the most popular Hartree-Fock (HF-SCF) method, used to obtain the approximate solutions to the Schrodinger equation as in the case of atoms. But there are some new difficulties encountered in the case of molecules; for example, the potential energy is no longer spherically symmetrical (i.e., dependent on r only) as in the case of atoms; and the existence of more than one nucleus makes the calculations complicated. Therefore, while the HF equations for atoms can be solved numerically, it is not easy to do so in the case of molecules. The use of LCAO approximations, however, simplifies the task and the equations can be solved analytically.

It has been already seen that in order to meet the antisymmetry requirement of the molecular wave function $\Psi$, Fock introduced a new operator $F$, called the "Fock-operator", replacing the hamiltonian. The operator $F$ for an electron $i$ is defined as,

$$
F(i) = -\frac{1}{2} \nabla_i^2 \sum_{i} Z_p/r_{pi} + \sum_{j=1}^{n/2} (2 J_j - K_j)
$$

Here $Z_p$ is the nuclear charge on the $p^{th}$ nucleus of the molecule and $r_{pi}$ is the distance of the electron $i$ from the $p^{th}$ nucleus. $J_j$ and $K_j$ are known as the coulomb operator and exchange operator, respectively, are defined by the equations,

$$
J_j\psi_i (1) = \left[ \int \psi_j (2) \frac{1}{r_{12}} \psi_j (2) \, d\tau_2 \right] \psi_i (1) \quad \text{and} \quad (1.23)
$$

$$
K_j\psi_i (1) = \left[ \int \psi_j (2) \frac{1}{r_{12}} \psi_i (2) \, d\tau_2 \right] \psi_j (1) \quad (1.24)
$$
The first two terms in eqn.(1.22) constitute the one-electron (or core) hamiltonian of the molecule.

The HF eigen value equations are,

\[ F(i) \psi_i = E_i \psi_i \]  

(1.25)

where \( \psi_i \) is an MO. The expectation value of \( F \) over the MO \( \psi_i \) gives the one-electron (orbital) energy of the MO (eqn. 1.26),

\[ E_i = \int \psi_i F \psi_i \, d\tau \]

\[ = \int \psi_i \left[ -\frac{1}{2} \nabla_i^2 - \sum_p Z_p/r_p \right] \psi_i \, d\tau + \int \psi_i \sum_{j=1}^{n/2} \psi_j (2J_{ij} - K_{ij}) \psi_i \, d\tau \]

(1.26)

\[ = E_i^0 + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) \]

(1.27)

The first term \( E_i^0 \) in (1.27) is the energy of one electron in \( \psi_i \) in the absence of all other electrons in the molecule. The second term represents the total interelectronic interaction energy, which consists of repulsion and exchange energies due to all pairs of electrons in all the MOs \( \psi_1 \) to \( \psi_{n/2} \). For a particular MO, say \( \psi_k \), the interelectronic interaction energy is,

\[ 2J_{ik} - K_{ik} = 2 \int \psi_i (1) \psi_k (2) 1/r_{12} \psi_i (1) \psi_k (2) \, d\tau_1 \, d\tau_2 \]

\[ - \int \psi_i (1) \psi_k (2) 1/r_{12} \psi_k (1) \psi_i (2) \, d\tau_1 \, d\tau_2 \]

(1.28)
The two terms in (1.28) represent the repulsion and exchange energies. An electron in an MO \( \psi_i \) experiences repulsion by two electrons in another MO \( \psi_k \), but it can undergo exchange with only one electron in that MO \( \psi_k \), with which it matches in spin. The first (i.e. repulsion) term in (1.28) is actually the repulsion between the electron clouds \( \psi_i^2 \) and \( \psi_k^2 \) due to electrons 1 and 2 respectively. When \( i=k \), the term \( 2J_{ij} - K_{ij} = J_{ii} \), as the equation 1.28 shows that \( J_{ii} = K_{jj} \). Then \( J_{ii} \) represents the repulsion energy between the two electrons in the same MO \( \psi_i \), and there is no point in exchanging the electrons of spins \( \alpha \) and \( \beta \) in the same MO.

The total energy \( E \) of all the electrons in all the MOs is obtained by subtracting from \( \sum_i 2E_i \) an amount equal to interelectronic interaction energy \((2J_{ij} - K_{ij})\) to eliminate double counting, i.e.,

\[
E = \sum_i 2E_i - \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})
\]

or

\[
E = \sum_i 2E_i + \sum_{j=1}^{n/2} (2J_{ij} - K_{ij})
\]

1.1.4. Roothaan's Equations

The HF equations in the LCAO approximation, when used to calculate the coefficients, take the form of Roothaan's equations [5]. The equations may be obtained as follows:

\[
F(i) \psi_i = E_i \psi_i \quad \text{or} \quad F(i) \sum_k a_{ik} \phi_k = E_i \sum_k a_{ik} \phi_k
\]

where \( \phi_k \)'s are atomic orbitals. Multiplying both sides of this equation by say \( \phi_i \) and integrating,
\[ \sum_{k} a_{ik} \int \phi_{i} F \phi_{k} \, d\tau = E_{i} \sum_{k} a_{ik} \int \phi_{i} \phi_{k} \, d\tau \quad \text{or} \]
\[ \sum_{k} a_{ik} (F_{ik} - E_{i} S_{ik}) = 0 \]  

(1.31)

where
\[ F_{ik} = \int \phi_{i} F \phi_{k} \, d\tau, \quad \text{and} \]
\[ S_{ik} = \int \phi_{i} \phi_{k} \, d\tau \]

The set of equations corresponding to various values of \( i \), the Roothaan's equations, can be solved only if the following secular determinant becomes zero,

\[ |F_{ik} - E_{i} S_{ik}| = 0 \]  

(1.32)

The matrix elements \( F_{ik} \), rather than \( H_{ik} \), and \( S_{ik} \) are to be evaluated. These on expansion are ultimately expressed in terms of atomic integrals. The greater is the number of atomic orbitals (basis functions) in the LCAO-MO, the better is the result. But, with a little increase in the basis functions, the number of atomic integrals grow very rapidly and may go up to many thousands even for very small molecules. This necessitates the use of large computers in such calculations.

1.1.5. Electron correlation

A Hartree-Fock SCF wave function takes into account the interactions between the electrons only in an average way. Actually, one must consider the instantaneous interactions between the electrons. Since electrons repel each other, they tend to keep out of each others way. For example, in helium if one electron is close to the nucleus at a
given instant, it is energetically more favorable for the other electron to be far from the nucleus at that instant. One sometimes speaks of a Coulomb hole surrounding each electron in an atom, this is a region in which the probability of finding another electron is small. The motions of electrons are correlated with each other, and this one is termed as electron correlation.

Consider the probability that in the n-electron system, electron 1 occupies a volume element $d\tau_1$, electron 2 $d\tau_2$, and so on. If the wave function is $\psi$, the probability $P$ is given by:

$$P = \psi^2 d\tau_1 d\tau_2 \ldots d\tau_n$$

In the Hartree approximation, the corresponding probability $P'$ is given by:

$$P' = (\psi)^2 d\tau_1 d\tau_2 \ldots d\tau_n = (\psi_1 \psi_2 \ldots \psi_n)^2 d\tau_1 d\tau_2 \ldots d\tau_n$$

$$= (\psi_1^2 d\tau_1)(\psi_2^2 d\tau_2) \ldots (\psi_n^2 d\tau_n) = P_1 P_2 \ldots P_n$$

where $P_i$ is the probability of an electron, represented by the wave function $\psi_i$, to be found in the volume element $d\tau_i$. The last equation implies that $P'$ can be expressed as the product of these individual probabilities; this in turn implies that the probability of finding the electron $i$ in a volume element $d\tau_i$ has the same fixed value $\psi_i^2 d\tau_i$, no matter what the positions of the other n-1 electrons may be. This is obviously incorrect. Consider for example, a helium atom. The probability of finding the first electron in a small volume element $d\tau_1$ will obviously be less if the other electron is far away, for the electrons repel each other, and so will tend to keep apart. The probability of finding the electron 1 in $d\tau_1$ therefore depends on the positions of the other electron; in other words, the electrons in helium tend to synchronize their motions about the nucleus in such a way to keep apart as
much as possible, a good analogy being provided by two men circling a very attractive (+2e) girl. This phenomenon, the tendency of electrons to keep apart, is known as electron correlation, which is neglected by the Hartree method.

1.1.6. Moller-Plesset perturbation theory

The perturbation theory of Moller-Plesset [6], closely related to many-body perturbation theory, is an alternative approach to the correlation problem. Within a given basis set, its aim is still to find the lowest eigenvalue and the corresponding eigen vector of the full hamiltonian matrix. Moller-Plesset models are formulated by first introducing a generalized electronic hamiltonian, $H_\lambda$, according to

$$H_\lambda = H_0 + \lambda V$$  \hspace{1cm} (1.33)

Here, $H_0$ is an operator such that the matrix with elements

$$\int \ldots \int \psi_s H_0 \psi_t \, d\tau_1 \, d\tau_2 \ldots \, d\tau_n$$  \hspace{1cm} (1.34)

is diagonal. The perturbation, $\lambda V$, is defined by

$$\lambda V = \lambda (H - H_0)$$  \hspace{1cm} (1.35)

where $H$ is the correct hamiltonian and $\lambda$ is a dimensionless parameter. Clearly, $H_\lambda$ coincides with $H_0$ if $\lambda = 0$, and with $H$ if $\lambda = 1$. In Moller-Plesset theory, the zero-order hamiltonian, $H_0$, is taken to be the sum of the one-electron Fock operators. The eigen value, $E_s$, corresponding to a particular determinant, $\psi_s$, is the sum of the one-electron energies, $E_i$, for the spin orbitals which are occupied in $\psi_s$, $\psi_\lambda$, and $E_\lambda$, the exact (within a
given basis set) ground-state wave function and energy for a system described by the
hamiltonian $H$, may now be expanded in powers of $\lambda$ according to Rayleigh-Schro"{d}inger
perturbation theory [7],

$$\psi_\lambda = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots$$  \hspace{1cm} (1.36)

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

Practical correlation methods may now be formulated by setting the parameter $\lambda = 1,$
and by truncation of the series in eqn.(1.36) to various orders. It has been referred to the
methods by the highest-order energy term allowed, that is, truncation after second-order
as MP2, after third-order as MP3 and so on.

The leading terms in expansion (1.36) are

$$\psi^{(0)} = \psi_0$$ \hspace{1cm} (1.37)

$$E^{(0)} = \sum_{i} E_i$$ \hspace{1cm} (1.38)

$$E^{(0)} + E^{(1)} = \int \ldots \int \psi_0^* \psi_0 d\tau_1 d\tau_2 \ldots d\tau_n$$ \hspace{1cm} (1.39)

where $\psi_0$ is the Hartree-Fock wave function and $E_i$ are the one-electron energies. The
Moller-Plesset energy of first-order is thus the Hartree-Fock energy. Higher terms in the
expansion involve other matrix elements of the operator $V$. The first-order contribution to
the wave function is

$$\psi^{(1)} = \sum_{s \neq 0} \frac{E_0 - E_s}{V_{so}} \psi_s$$ \hspace{1cm} (1.40)
where $V_{so}$ are matrix elements involving the perturbation operator, $V$,

$$\int \cdots \int \psi_s \, V \, \psi_0 \, d\tau_1 \, d\tau_2 \, \ldots \, d\tau_n$$

(1.41)

After corrections, the second-order contribution to the Møller-Plesset energy is

$$\sum_s \left( E_0 - E_s \right)^{-1} \left| V_{so} \right|^2$$

(1.42)

where $\sum$ indicates that summation is to be carried out over all double substitutions. This probably represents the simplest approximate expression for the correlation energy. If $\psi_s$ is the double substitution $ij \rightarrow ab$, the explicit expression for $V_{so}$ is

$$V_{so} = (ij \parallel ab)$$

(1.43)

where $(ii \parallel ab)$ is a two-electron integral over spin orbitals, defined by

$$(ii \parallel ab) = \iiint \chi_i^*(1) \chi_j^*(2) \left( 1/r_{12} \right) \left[ \chi_a(1) \chi_b(2) - \chi_b(1) \chi_a(2) \right] \, d\tau_1 \, d\tau_2$$

(1.44)

Here the integration is over all coordinates (cartesian and spin) for both the electrons. The final formula for the second-order contribution to the energy then becomes

$$E^{(2)} = \sum_{occ} \sum_{virt} \left( E_a + E_b - E_i - E_j \right)^{-1} \left| (ij \parallel ab) \right|^2$$

(1.45)
1.1.7. Basis set expansions

The individual molecular orbitals can be expressed as linear combinations of a finite set of \( N \) prescribed one-electron functions known as basis functions. If the basis functions are \( \phi_1, \phi_2, \ldots, \phi_n \), then an individual orbital \( \psi_i \) can be written as

\[
\psi_i = \sum_{\mu=1}^{N} C_{\mu i} \phi_\mu
\]

where \( C_{\mu i} \) are the molecular orbital expansion coefficients. These coefficients provide the orbital description with some flexibility, but clearly do not allow complete freedom unless the \( \phi_\mu \) defines a complete set. However, the problem of finding the orbitals is reduced from finding complete description of the three-dimensional function \( \psi_i \) only a finite set of linear coefficients for each orbital.

In simple qualitative version of molecular orbital theory, atomic orbitals of constituent atoms are used as basis functions. Such treatments are often described as linear combination of atomic orbitals (LCAO). However, the mathematical treatment is more general, and any set of appropriately defined functions may be used for a basis expansion.

To provide a basis set that is well defined for any nuclear configuration and therefore useful for a theoretical model, it is convenient to describe a particular set of basis functions associated with each nucleus, depending only on the charge of that nucleus. Such functions may have symmetry properties of atomic orbitals, and may be classified as \( s, p, d, f \ldots \) types according to their angular properties.
Two types of atomic functions have received widespread use. Slater-type atomic orbitals (STOs) have exponential radial parts. They are labeled like hydrogen atomic orbitals, 1s, 2s, 2p_x,... and have the normalized form,

\[ \phi_{1s} = \left( \frac{\xi_1^3/\pi}{r^3/2} \right)^{1/2} \exp \left( -\frac{\xi_1 r}{2} \right) \]
\[ \phi_{2s} = \left( \frac{\xi_2^5/96\pi}{r^5/2} \right)^{1/2} r \exp \left( -\frac{\xi_2 r}{2} \right) \]
\[ \phi_{2p_x} = \left( \frac{\xi_2^5/32\pi}{r^5/2} \right)^{1/2} x \exp \left( -\frac{\xi_2 r}{2} \right) \]

where \( \xi_1 \) and \( \xi_2 \) are the constants determining the size of the orbitals. STOs provide reasonable representations of atomic orbitals with standard \( \xi \) values recommended by Slater [9]. They are, however, not well suited to numerical work, and their use in practical molecular orbital calculations have been limited.

The second type of basis consists of gaussian-type atomic functions. These are powers of \( x, y, z \) multiplied by \( \exp \left( -\alpha r^2 \right) \), \( \alpha \) being a constant determining the size, that is, radial extent, of the function. In normalized form, some of the functions are

\[ g_s(\alpha, r) = \left( \frac{2\alpha/\pi}{r^3/2} \right)^{3/4} \exp \left( -\alpha r^2 \right) \]
\[ g_x(\alpha, r) = \left( 128\alpha^5/\pi^3 \right)^{1/4} x \exp \left( -\alpha r^2 \right) \]
\[ g_{xx}(\alpha, r) = \left( 2048 \alpha^7/9\pi^3 \right)^{1/4} x^2 \exp \left( -\alpha r^2 \right) \]
\[ g_{xy}(\alpha, r) = \left( 2048 \alpha^7/\pi^3 \right)^{1/4} xy \exp \left( -\alpha r^2 \right) \]

The gaussian functions \( g_s, g_x, g_y \) and \( g_z \) have the angular symmetries of the s-and the three p-type atomic orbitals. The second order functions \( g_{xx}, g_{yy}, g_{zz}, g_{xy}, g_{xz} \) and \( g_{yz} \) do not all have the angular symmetry of atomic orbitals. However, they may be combined to give a set of five d-type atomic functions, that is, \( g_{xy}, g_{xz}, g_{yz} \) and the two further functions...
\[ g_{3zz-rr} = \frac{1}{2} \left( 2g_{zz} - g_{xx} - g_{yy} \right) \]
\[ g_{xx-yy} = (3/4)^{1/2} \left( g_{xx} - g_{yy} \right) \]

A sixth linear combination yields an s-type function,

\[ g_{rr} = 5^{1/2} \left( g_{xx} + g_{yy} + g_{zz} \right) \]

In a similar manner, the ten third-order gaussian functions may be recombined into a set of seven f-type functions and an additional set of three p functions.

Gaussian-type functions were introduced into molecular orbital computations by Boys [10]. They are less satisfactory than STOs as representations of atomic orbitals, particularly because they do not have a cusp at the origin. Nevertheless, they have the important advantage that all integrals in the computations can be evaluated explicitly without recourse to numerical integration.

The third possibility is to use linear combinations of gaussian functions as basis functions. For example, an s-type basis function \( \phi_{\mu} \) may be expanded in terms of s-type gaussians,

\[ \phi_{\mu} = \sum_{s} d_{\mu s} g_{s} \]

Here the coefficients \( d_{\mu s} \) are fixed. Basis functions of this type are called contracted gaussians, the individual \( g_{s} \) being termed as primitive gaussians.
1.1.7.1. Minimal basis sets

The simplest level of ab initio molecular orbital theory involves the use of a minimal basis set of nuclear-centered functions. In this strictest sense, such a representation comprises exactly of the number of functions required to accommodate all of the electrons of the atom, while maintaining overall spherical symmetry. Thus, within the framework of a minimal basis set, hydrogen and helium are represented by a single s-type function, lithium and beryllium by a pair of such functions, and the remaining first-row elements (boron to neon) by two s functions and a complete set of three p-type functions. Second-row atoms are treated similarly by adding the 1s, 2s, 2p inner-shell description to a single s-type basis functions for sodium and magnesium, and a s-and three p-type functions for the elements aluminium to argon. For the third-row elements, 1s,2s,2p,3s, and 3p basis functions comprise the inner shell. For potassium and calcium, these are supplemented by a single 4s function. The set of (five) 3d functions is required for the remaining elements in the row (scandium through krypton), the proper atomic description of the main group elements (gallium through krypton) also necessitating addition of valence 4p type basis functions. Fourth-row elements are treated similarly.

1.1.7.2. STO-KG minimal basis sets: The STO-3G basis set

The series of minimal basis sets termed STO-KG consists of expansion of Slater type atomic orbitals (STOs) in terms of K gaussian functions.

\[ \phi_{nl} (\xi = 1,r) = \sum_{k=1}^{K} d_{nl,k} \, g_{l}(\alpha_{n,k}, r) \]

where the subscripts \( n \) and \( l \) define the specific principal and angular quantum numbers, for example, \( \phi_{1s} \), and \( g_{l} \) are normalized gaussian functions. The values of the gaussian exponents, \( \alpha \), and the linear expansion coefficients, \( d \), have been determined by
minimizing, in a least square sense, the error in the fit of gaussian expansion to the exact Slater orbital.

\[ \varepsilon_{nl} = \int (\phi_{nl}^{\text{Slater}} - \phi_{nl}^{\text{gaussian}})^2 \, d\tau \]

Minimization is performed simultaneously for all expansions of the given quantum number.

In practical, among STO-KG basis set, the STO-3G is the only basis set to have found wide use, although the bases STO-2G to STO-6G were originally tested [11]. In early tests on the STO-KG bases it was found that basis sets with \( n \geq 3 \) gave very similar results, so the smallest of these, STO-3G, was chosen for an extensive series of calculations in the early 1970s. Thus STO-3G is a minimal basis set. This means that it has only as many orbitals as necessary to accommodate the electrons of the neutral atom.

Minimal basis sets, such as STO-3G, have several inherent inadequacies. Because the number of atomic basis functions is not apportioned according to electron count— for example, the lithium atom, which has only three electrons, is provided with the same number of functions (five) as fluorine with its nine electrons—it follows that minimal basis set description of compounds containing elements such as oxygen and fluorine are likely to be poorer than that of molecules comprising elements with fewer electrons. A second problem arises because a minimal basis set using fixed gaussian exponents is unable to expand and contract in response to differing molecular environments. Finally, minimal representations lack the ability to describe adequately the non-spherical anisotropic aspirants of molecular charge distribution.

In principle, the first two deficiencies may be alleviated simply by allowing more than a single valence function of each symmetry type in the basis set description. In this way, the
number of basis functions for all elements, not just those on the left-hand side of the periodic table, would be substantially in excess of the number actually required. Furthermore, the allocation of two or more valence basis functions of each given symmetry type would provide the needed flexibility for overall radical size to be determined, simply by the adjustment of the relative weights of the individual components in the variational procedure. The third deficiency, the inability of a minimal basis set to describe properly anisotropic molecular environments, may be alleviated in one of the two ways. The conceptually simpler way would be to allow each of the x, y, and z p components describing the valence region of a main-group element to have a different radial distribution, that is, to employ an anisotropic rather than an isotropic minimal basis set [12].

One solution to the problem is to use split-valence or double zeta basis sets. In these basis sets, the atomic orbitals are split into two parts, an inner, compact orbital and an outer, more diffuse one. The coefficients of these two types of orbitals can be varied independently during construction of the molecular orbitals in the SCF procedure. Thus the size of the atomic orbital that contributes to the molecular orbitals can be varied within the limits set by the inner and outer basis functions. Split-valence basis sets split only the valence orbitals in this way, whereas double-zeta basis set has spilt core orbitals.

1.1.7.3. The 6-21G & 3-21G split-valence basis sets

The 6-21G and 3-21G basis sets, the former presently defined through the second row of the periodic table and the latter through the fourth row, typify representation in which two basis functions, instead of one, have been allocated to describe each valence atomic orbital. In the 6-21G basis set, each inner shell atomic orbital is represented by a single function, which in turn is written in terms of six gaussian primitivies, that is with K=6
The contracted and diffuse functions representing valence-shell orbitals are written with expansion lengths $K'$ and $K''$ chosen as 2 and 1, respectively. The subscripts $n$ and $l$, define the specific atomic functions.

1.1.7.4. Larger split-valence representations: The 4-31G and 6-31G basis sets

An early split-valence basis set which, while now largely replaced by 3-21G, has received widespread use, is the 4-31G representation. This means that the core orbitals consist of 4 and the inner and outer valence orbitals of 3 and 1 gaussian functions respectively. Closely related is the 6-31G basis set, which has now been defined through the second row of the periodic table. It comprises inner-shell functions each written in terms of a linear combination of six gaussians, and two valence shells represented by three and one gaussian primitives, respectively.

1.1.7.5. The 6-31G* and 6-31G** polarization basis sets

Among the simplest of polarization basis sets are two representations originally proposed by Hariharan and Pople [13] for first-row atoms and later extended to second-row elements [14]. The simpler of the two, termed 6-31G* is constructed by the addition of a set of six second-order (d-type) gaussian primitives to the split-valence 6-31G basis set description of each heavy (non-hydrogen) atom.

The 6-31G* basis set contains no provision for polarization of the s orbitals on hydrogen and helium atoms. As this feature is desirable for the description of the bonding in many systems, particularly those in which hydrogen is a bridging atom, a second more complete basis set, termed 6-31G**, has been constructed. It is identical to 6-31G* except
for the addition of a single set of gaussian p-type functions to each hydrogen & helium atoms.

1.1.7.6. Larger polarization basis sets: The 6-311G** basis set

A number of larger gaussian basis sets have been proposed in the literature and applied to studies of chemically interesting systems. Although these are generally more flexible than the simple 6-31G* and 6-31G** polarization basis sets, their size has generally limited their application to only quite small molecular systems. One basis set which has been formulated through the first row, and deserves special mention, is the 6-311G** representation [15]. It comprises an inner shell of six s-type gaussians, and an outer (valence) region, which has been split into three parts, represented by three, one, and one primitives, respectively. The basis is supplemented by a single set of five d-type gaussian functions for first row atoms, and a single set of uncontracted p-type gaussians for hydrogen. The 311 triple split has been chosen in place of the 31 separate and in the 6-31G* & 6-31G** polarization basis sets so as to increase the overall flexibility of the representation, and to improve the description of the outer valence region. One special feature of the 6-311G** basis set is that, the gaussian exponents and expansion coefficients have been chosen so as to minimize the energy of the atomic ground state at the second-order Moller-Plesset (MP2) perturbation level, rather than at the corresponding Hartree-Fock level. This allows for the possibility of specific basis functions contributing to the electron correlation within the atomic valence region [15,16].

1.1.7.7. Basis set incorporating diffuse functions

The basis sets that have been discussed so far, although developed with no intended bias, are more suitable for molecules in which the electron are tightly held to the nuclear centers than they are for species with significant electron density far removed from those centers. Calculation involving anions pose special problems [17]. Since the electron
affinities of the corresponding neutral molecules are typically quite low [18], the extra
electron in the anion is only weakly bound. Even the larger basis sets considered so far do
not incorporate functions with significant amplitude far distant from their center, and
therefore do not provide a completely adequate description of molecules in which a large
portion of the valence-electron density is allowed to diffuse lone-pair or to antibonding
orbitals. For most stable anions, application of these basis sets yields positive energies for
the highest-occupied molecular orbitals, indicating erroneously that the outermost valence
electrons are unbound.

One way to overcome this problem associated with anion calculation is to include in the
basis representation one or more sets of highly diffuse functions. The commonly used
diffuse basis sets are 3-21+G, 6-31+G and 6-31+G*. These basis sets are obtained by
adding a single set of very diffuse s- and p-orbitals to the heavy atoms in a standard basis
set such as 6-31G*. This basis set is then designated as 6-31+G*, or 6-31++G* if diffuse
s-functions are added also to hydrogen.

1.1.8. Molecular geometry

The equilibrium geometry of a molecule corresponds to the nuclear configuration that
minimizes the molecular electronic energy including nuclear repulsion. The geometry of a
nonlinear molecule with N nuclei defined by 3N-6 independent nuclear coordinates, and its
electronic energy is a function of these 3N-6 coordinates. The number 6 is subtracted from
the total number of nuclear coordinates because there are 3 translational and 3 rotational
degrees of freedom, and these leave electronic energy unchanged. To find the equilibrium
geometry of a molecule using the SCF MO method, one starts with an initially assumed
plausible structure and calculates the SCF wave function, energy and energy gradient for
this structure. Using the calculated gradient, the computer program changes the 3N-6
nuclear coordinates to a new set that is likely to be closer to the equilibrium geometry than the initial set, and the SCF wave function, energy, energy gradient are calculated at this new structure. Using the results of the new calculation, a further improved set of nuclear coordinates is calculated, and the SCF calculation is repeated at this new geometry. The process is repeated until the first derivatives of electronic energy are all less than a tiny preset value, indicating that the minimum-energy geometry (at which the gradient of electronic energy is zero) has been found.

1.1.9. Mulliken Population Analysis

The electron density function or electron probability distribution function, \( \rho(r) \), is a three-dimensional function defined such that \( \rho(r)dr \) is the probability of finding an electron in a small volume element, \( dr \), at some point in space, \( r \). Normalization requires that

\[
\int \rho(r) \, dr = n \quad (1.46)
\]

where \( n \) is the total number of electrons. For a single determinant wavefunction in which the orbitals are expanded in terms of a set of \( N \) basis functions, \( \phi_\mu \), \( \rho(r) \) is given by

\[
\rho(r) = \sum_\mu \sum_\gamma P_\mu\gamma \phi_\mu \phi_\gamma \quad (1.47)
\]

where \( P_\mu\gamma \) are the elements of the density matrix. Integration of the eqn. (1.47) leads to

\[
\int \rho(r) \, dr = \sum_\mu \sum_\gamma P_\mu\gamma S_\mu\gamma = n \quad (1.48)
\]

where \( S_\mu\gamma \) is the overlap matrix over basis functions. The total electron count \( n \) is thus composed of individual terms \( P_\mu\gamma S_\mu\gamma \). Given that the basis functions \( \phi_\mu \) are normalized,
that is, \( S_{\mu\mu} = 1 \), the diagonal terms in (1.48) are just \( P_{\mu\mu} \), each of which represents the number of electrons directly associated with a particular basis function \( \phi_\mu \). This is termed as the net population of \( \phi_\mu \). The off-diagonal components of (1.48) occur in pairs. \( P_{\mu\gamma} \), \( S_{\mu\gamma} \) and \( P_{\gamma\mu} S_{\gamma\mu} \), of equal magnitude. This sum

\[
Q_{\mu\gamma} = 2 P_{\mu\gamma} S_{\mu\gamma} \quad (\mu \neq \gamma), \quad (1.49)
\]

is referred to as an overlap population. Note that it is associated with two basis functions \( \phi_\mu \) and \( \phi_\gamma \) which may be the same atom or two different atoms.

The total electronic charge is now apportioned into two parts, the first associated with individual basis functions, the second with pairs of basis functions:

\[
\sum_\mu N P_{\mu\mu} + \sum_\mu \sum_\gamma Q_{\mu\gamma} = n \quad (1.50)
\]

Such a representation of the electron distribution is not always convenient, and it is sometimes desirable to partition the total charge among only the individual basis functions. One way to accomplish this is to divide the overlap population, \( Q_{\mu\gamma} \), equally between the basis functions \( \phi_\mu \) and \( \phi_\gamma \), and adding half to each of the net population \( P_{\mu\mu} \) and \( P_{\gamma\gamma} \). This gives a gross population for \( \phi_\mu \), defined according to

\[
q_\mu = P_{\mu\mu} + \sum_{\gamma \neq \mu} P_{\mu\gamma} S_{\mu\gamma} \quad (1.51)
\]

This sum of gross population for all \( N \) basis functions \( \phi_\mu \) is, of course equal to the total electron count.

\[
\sum_\mu N q_\mu = n
\]
This particular partitioning scheme is not unique. Nor is any other! This choice of division of the overlap population $Q_{\mu\nu}$ into equal contributions from $\phi_\mu$ and $\phi_\nu$ is arbitrary. The gross basis function population may be used to define gross atomic population

$$q_A = \sum_{\mu} q_{\mu}$$

Here the summation is carried out for all functions $\phi_\mu$ on a particular atom $A$. Assuming all basis functions to be atom centered, it follows that the sum of gross atomic population is equal to the total electron count. Finally, a total atomic charge on $A$ may be defined as $Z_A - q_A$, where $Z_A$ is the atomic number of $A$. The sum of charges must be zero for a neutral molecule, +1 for a singly charged cation and so forth.

### 1.1.10. Harmonic vibrational frequencies

The total energy of a molecule comprising $N$ atoms near its equilibrium structure may be written as

$$E = T + V = \frac{1}{2} \sum_{i=1}^{3N} q_i^2 + V_{\text{eq}} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{\text{eq}} q_i q_j$$

Here, the mass-weighted cartesian displacements $q_i$, are defined in terms of locations $x_i$ of the nuclei relative to their equilibrium positions $x_{i,\text{eq}}$ and their masses $M_i$.

$$q_i = M_i^{1/2} (x_i - x_{i,\text{eq}})$$
where \( V_{eq} \) is the potential energy at the equilibrium nuclear configuration, and the expansion (1.52) of the vibrational energy in terms of a power series is truncated at second order [8]. For such a system, the classical mechanics equation of motion takes the form

\[
\ddot{q}_j = -\sum_{i=1}^{3N} f_{ij} q_i \quad j = 1,2...,3N \tag{1.54}
\]

The quadratic force constants, \( f_{ij} \), are the second derivatives of the potential energy with respect to mass-weighted cartesian displacements, evaluated at the equilibrium nuclear configuration, that is,

\[
f_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{eq} \tag{1.55}
\]

The \( f_{ij} \) may be evaluated by numerical second differentiation,

\[
\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta (\Delta V)}{\Delta q_i \Delta q_j} \tag{1.56}
\]

By numerical first differentiation at analytical first derivatives

\[
\frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\Delta (\partial V/\partial q_j)}{\Delta q_i} \tag{1.57}
\]

or by direct analytical second differentiation, eqn (1.55). The choice of procedure depends on the quantum mechanical model employed, that is single-determinant or post-Hartree-Fock, and practical matters such as the size of the system. Eqn. (1.54) may be solved by standard methods [8] to yield a set of \( 3N \) normal-mode vibrational frequencies. Six of these (five for linear molecules) will be zero as they correspond to translational and rotational (rather than vibrational) degrees of freedom.
Generally, the HF-SCF frequencies were overestimated by 20-30% than the experimental frequencies, due to the omission of anharmonicities and the electron correlation effect. So the suitable scaling of force constants can give a reliable prediction of the fundamental vibrational frequencies. The ab initio force constants were transformed from cartesian coordinates to a set of suitable internal coordinates and then scaled according to the type of internal coordinates. \( F_{ij} \) (scaled) = \( F_{ij} \) (ab initio) \((x_i \times x_j)\), where \( x_i \) and \( x_j \) are scale factors for the diagonal force constants \( F_{ii} \) and \( F_{jj} \) respectively.

But in the present investigations, we are not very much interested to study the force constants of the molecules. In most of the molecules, we are interested only in the conformations of the molecules. So the frequencies of all molecules studied in the present investigation were arbitrarily scaled using the arbitrary scaling factor 0.9. In most of the conformational analyses, the arbitrary scaling factors have been used.

1.1.11. Dipole moment

The molecular dipole moment can be calculated from the charge distribution derived from MO calculations and the coordinates of the atoms. In the point charge approximation, each atom in a molecule is treated as a point charge and the components of the dipole moment in the directions of the cartesian coordinates are given by

\[
\begin{align*}
\mu_X &= \sum q_i x_i \\
\mu_Y &= \sum q_i y_i \\
\mu_Z &= \sum q_i z_i
\end{align*}
\]

The total dipole moment is therefore
Density functional theory (DFT) is a branch of quantum mechanics in which the emphasis is on the one-electron density function, \( \rho \), rather than on the more usual wave function, \( \psi \) [19]. It goes back to the work of Hohenberg and Kohn, who proved that the ground state energy of a chemical system is a function of \( \rho \) only. There are many important applications of DFT to chemistry. One is the calculation of properties of atoms and molecules. These are much easier than and of similar accuracy to calculating using very good wave functions. For a system containing \( N \) electrons, the wave function depends on \( 4N \) space and spin coordinates. The electron density depends on only three space coordinates, and \( N \) enters as a simple multiplicative factor. Hence computations are very much simpler in DFT, especially for large systems.

Briefly, the system of interest has \( N \) electrons and a fixed set of nuclear positions. The nuclei give rise to an external potential, \( v(r) \) in which the electrons move and repel each other. The time-independent ground-state electronic wave function may be obtained by solving the Schrödinger equation. The wave function is determined by \( N \) and \( v(r) \), as in the electronic energy : \( E[N,v(r)] \). The electron density \( \rho(r) \) is \( N \) times the integral at the square of the wave function over all electronic space and spin coordinates except the space coordinates of one. The density determines \( v(r) \) and \( N \) uniquely ; hence \( E[N,v(r)] = E[\rho] \). Provided \( \rho \) is normalized to \( N \), \( E[\rho] \) is minimum when \( \rho \) is the correct ground state density. The total electronic energy is given by

\[
E[\rho] = F[\rho] + \int v(r) \rho(r) \, dr
\]

(1.58)
where the function $F[\rho]$, a universal function of $\rho$, is the sum of the kinetic energy functional $T[\rho]$ and the electron-electron repulsion function $v_{\text{ee}}[\rho]$. The variational principle determining the density is

$$\delta\left\{E[\rho] - \mu N[\rho]\right\} = 0$$  \hspace{1cm} (1.59)$$

where $\mu$ is a Lagrange multiplier for normalization of $\rho : \int \rho(r)dr = N[\rho] = N$

$$\mu = \nu(r) + \frac{\delta F[\rho]}{\delta \rho(r)} = \text{constant}$$  \hspace{1cm} (1.60)$$

The quantity $\mu$ is the chemical potential of the system of interest. Differentials of any change from one ground state to another are given by

$$dE = \mu dN + \int \rho(r) d\nu(r) dr$$  \hspace{1cm} (1.61)$$
and

$$d\mu = \eta dN + \int f(r) d\nu(r) dr$$  \hspace{1cm} (1.62)$$

$\mu$, $\eta$, and $f(r)$ are each of considerable chemical importance: $\mu$ is the negative of the absolute electronegativity [20], $\eta$ is the absolute chemical hardness [21], and $f(r)$ is the Fukui function or reactivity index [22].

The above two parameters of DFT, $\mu$ and $\eta$, are in elucidating familiar chemical concepts. The definitions of these quantities are

$$\mu = (\partial E/\partial N)_{\nu(r)}; \quad 2\eta = (\partial \mu/\partial N)_{\nu(r)} = 2/\sigma$$  \hspace{1cm} (1.63)$$
where $\sigma$ represents the softness of a molecule. In spite of these similarities, there is no real relationship between the two sets of quantities. The electronic chemical potential is not the electronic part of the thermodynamic chemical potential. It measures the escaping tendency of an electronic cloud. It is a constant, through all space, for ground state of an atom, molecule, or solid, and equals the slopes of the $E$ vs $N$ curve at constant $v(r)$. The absolute hardness is not resistant to mechanical deformation, but resistant to the change in the number of electrons in the system, or to changes in the one electron density function, $\rho$.

Operational, and approximate, definitions of $\mu$ and $\eta$ are

$$\mu = (I + A)/2 = \chi; \quad \eta = (I-A)/2$$ (1.64)\

where $I$ is the ionization potential and $A$ is the electron affinity and $\chi$ is the absolute electronegativity of the system. It is similar, but not equal, to the Mulliken's electronegativity.

According to Koopmans' theorem, the ionization potential is simply the orbital energy of the HOMO, with change in sign. For spin-paired molecules, the electron affinity is the negative of the orbital energy of the LUMO; therefore, on an orbital basis,

$$\mu = \left( E_{\text{HOMO}} + E_{\text{LUMO}} \right)/2; \quad \eta = \left( E_{\text{LUMO}} - E_{\text{HOMO}} \right)/2$$ (1.65)\

where $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are the energies of the highest occupied and lowest unoccupied molecular orbitals. The softness ($\sigma$), reciprocal of hardness, is also an interesting parameter in the field of reaction chemistry, since most of the reacting species is having the higher softness value. Thus the global hardness is termed as the chemical
hardness and acts as a good stability scale to find the stability among the molecules. High aromaticity being understood to signify high stability and low reactivity, thus the absolute hardness also measures the aromaticity [23]. Now-a-days, chemical hardness is getting more importance through local hardness, group hardness, bond hardness and activation hardness [19,24-26]. Among these, the former three are giving the hardness value of the particular point or group or bond sites, while the latter one is used for describing the orientation of electrophilic aromatic substitution [25]. Another interesting feature of \( \eta \) in recent times is, hardness profiles [27], and it has been defined as the change in the hardness of a species with reaction coordinate. This concept bags importance since it involves the reactivity of species along the reaction path and also, the change in hardness on moving towards the transition state is an index for predicting the orientation in aromatic substitution.

Density functional theory gains momentum after the introduction of the principle of maximum hardness (PMH), "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible " [28], and Hard and Soft Acids and Bases (HSAB) principle, "hard acids prefer to coordinate with hard bases and soft acid prefers soft bases for coordination" [29]. A recent review article by Parr and Yang [30] indicates that more number of papers have already been published to prove these theorems by analytical as well as numerical methods. A combination of the PMH and the local version of HSAB principle has already been tested as a tool to describe the stability and reactivity of polyatomic systems [31].

Parr and Chattaraj [32] have given a proof for the PMH using the fluctuation-dissipation theorem of statistical mechanics. They have considered the electronic system of interest as a member of a grand canonical ensemble with bath parameters \( \mu, v(r) \) and \( T \). It has been shown that any nearby non-equilibrium state of the system will evolve towards the
equilibrium state with maximum hardness provided the bath parameters do not change, where \( \mu, v(r) \) and \( T \), the bath parameters, are nothing but of chemical potential, potential due to the nuclei plus any external potential and temperature, respectively [32]. However, some queries have also been raised [33,34]. Sebastian [33] argued that, the result of Parr and Chattaraj [32] \( S - <S> \geq 0 \), can be true, while considering a particular non-equilibrium ensemble, but that does not prove it to be so for any other ensemble, where \( S \) and \(<S>\) are the softness and equilibrium ensemble, respectively. Subsequently, Chattaraj et al. [35] have used the Gyftopoulos-Hatsopoulos principle and explained the PMH in a better way.

1.3 Present work

In the present investigation, the theories, so far discussed in this chapter, at various levels have been used to calculate the molecular structure, conformational stability, vibrational frequencies, zero point vibration correction, IR intensities, atomic charges, dipole moments and some other important chemical properties of some polyatomic molecules. Various basis sets have been used for this purpose. Using density functional theory, chemical hardness and chemical potential have been obtained and used to analyze the conformational stability invoking the principle of maximum hardness. Energies from HF level of theory and chemical hardness from DFT have been used to study some reactions and hydrogen bonding interactions.
References

5. C.C.J.Roothaan, Rev.Mod.Phys. 23 (1951) 69.
6. C.Moller and M.S.Plesset, Phys.Rev. 46 (1934) 618.
7. For a discussion, I.N.Levine, Quantum Chemistry. 3rd ed., Allyn and Bacon, Boston, 1983.
16. For example, D.J.DeFrees, B.A.Levi, S.K.Pollack, W.J.Hehre, J.S.Binkley
17. For example, L.Radom in Modern theoretical Chemistry, H.F.Schaefer III,

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