N | Theoretical Aspects
2.1 INTRODUCTION

When nuclei are disturbed from their mean positions, then the restoring force between them acts and this force can be calculated from a potential function. This potential function depends on the inter-nuclear separations and inter-bond angles in the molecules. It is possible to determine the frequencies and relative amplitudes of vibrations from the knowledge of restoring force in the molecules. The reverse process of determining force fields from the observed vibrational frequencies of the molecule is more important for the evaluation of the valence force constants and elucidation of molecular dynamics. To describe vibrational frequencies of nuclei, this procedure requires a special set of coordinates called normal coordinates. This simplifies the mathematical analysis and the method is termed as Normal Coordinate Analysis. Force field can be calculated by molecular orbital and Wilson's G.F. matrix methods. Many versions of molecular orbital methods are currently available. These include semi-empirical, ab-initio and density functional methods. We have used MOPAC and HYPERCHEM software for calculations.

Development in performance of computers and of the theory has made computational simulations an important tool in understanding the molecular dynamics. Today increasingly accurate results can be obtained in a reasonable time for even large and complicated molecular systems. Still more reliable methods are, however, needed to obtain more realistic determinations of molecular properties to be utilized in different applications and to understand the physics of molecular systems. The basic question is how to describe real materials by simplified theoretical models. For example in a classical atomistic description, in which the detailed chemical structure of a molecular system is taken into account, still more reliable models have to be found to represent the interactions between atoms (Wales 1999). One-way to classify the most frequently used methods in molecular modeling is illustrated in Fig.2.1. The methods can be roughly divided into atomistic simulations, in which every atom is explicitly included and non-atomistic simulation, in which groups of atoms, or entire chains, are collectively modeled. According to the Born-Oppenheimer (BO) approximation (Born, 1927) the motions of electrons and nuclei can be separated due to their different masses. Thus, quantum mechanical (QM) methods (ab-initio, density functional theory (DFT) and semi-empirical) (Hehre et al., 1986; Szabo and Ostlund, 1982; Atkins, 1996; Parr and Yang, 1989; Sadlej, 1985) are based on solving the time-independent Schrödinger equation for
**QM methods**
- Ab initio
- DFT
- Semi-empirical

\[ \hat{H}_{el} \Psi_{el} = E_{el} \Psi_{el} \]

**Schrödinger equation**

**Parameterisation**

**Classical atomistic simulations**
- MM
- MD

Force field:
\[
V = \sum V_{\text{bonds}} + \sum V_{\text{valence angles}} + \sum V_{\text{torsion angles}} + \sum V_{\text{non-bonded non-bonded}} + \sum V_{\text{non-bonded bonded}}
\]

**Parameterisation**

**Coarse grained methods**
- Wormlike chains
- Mesoscale modelling

**Statistical mechanical methods**
- Lattice models
- RIS
- MC (e.g. RMMC)

**Fig. 2.1: The most frequently used methods in molecular modeling**
the electrons of a molecular system as a function of the positions of the nuclei. In classical atomistic simulations, atoms are treated as basic units and the interactions between the atoms are described by classical potential energy functions (force fields (FFs)). High-level ab-initio and DFT calculations are computationally demanding. The computing time depends on the number of electrons. Therefore QM methods are usually limited to molecules and molecular systems consisting of less than about 30 non-hydrogen atoms. Classical FF methods such as molecular mechanics (MM) (Burkert and Allinger, 1982; Allen, 1987) and molecular dynamics (MD) (Allen, 1987; Haile, 1992) methods can be applied to much larger molecular systems containing thousands of atoms. The FF contains parameters that are derived from QM and/or experimental data. These parameters and the functional forms of the energy terms determine the ability of the FF to describe the molecular system under investigation. The microscopic details of the molecular behavior are unnecessary to know, when the long time-scale motion of large molecular systems is considered. In these cases coarse grained methods, such as wormlike chain- or mesoscale models (Fraaije et al., 1997; Rouse, 1953; Bueche, 1954; Peticolas, 1963; Zimm, 1956; Gennes, 1971; Doi and Edwards, 1986; Doi and Edwards, 1978 and 1979; Yamakawa, 1997; Espagnol, 1995) or statistical mechanical methods, such as lattice models (Flory, 1942; Huggins, 1942) Rotational Isomeric State (RIS) model (Flory, 1989; Flory, 1974; Mattice, 1994) or Monte Carlo (MC) method (Binder, 1988), can be applied. In coarse-grained molecular theories the motion of a polymer chain is simplified by describing it with parameterized models such as a bead and spring model (Rouse, 1953; Bueche, 1954; Peticolas, 1963; Zimm, 1956) or as continuous wormlike chains (Gennes, 1971; Doi and Edwards, 1986; Doi and Edwards, 1978 and 1979; Yamakawa, 1997).

2.2 THE HARTREE-FOCK METHOD

In 1928 Hartree devised a method that made it possible to find, to a reasonable approximation, the most accurate wave function, and hence solution to the Schrödinger equation for a poly-electronic system (Hartree, 1928) The approximation employed by Hartree was to treat the electron-electron repulsions in an average way. In this approximation each electron moves in a field of nuclei and the average field of the other n-1 electrons. This approximation allows the many electron wave functions to be replaced by a product of one-electron wave functions. (eq. 2.1).
\[ \psi(r) = \psi_1(r_1) \psi_2(r_2) \ldots \ldots \psi_n(r_n) \]  \hspace{1cm} (2.1)

where \( \psi_i(r_i) \) is a spatial orbital that is a function of the position vector \( r \) such that the probability of finding an electron at a distance \( dr \) from \( r \) is \( |\psi_i(r_i)|^2 dr \) (Hehre et al., 1986). The overall wavefunction therefore depends on all the electron co-ordinates and parametrically on the nuclear locations. Thus different nuclear arrangements will produce different solutions.

### 2.2.1 The Pauli Exclusion Principle

The Pauli Exclusion Principle states that "the wavefunction must be antisymmetric with respect to interchange of any two electrons" (Atkins and Friedman, 1997). Equation 2.1 does not satisfy this requirement, as the spin of electrons is not considered. Electron spin can be introduced using the concept of spin orbitals. A spin orbital \( \phi(x) \) can be defined where \( x \) describes both the spin of the electron and the spatial coordinates (eq. 2.2).

\[ \phi(x) = \phi(r) \alpha(\omega) \text{ or } \phi(r) \beta(\omega) \]  \hspace{1cm} (2.2)

where \( \alpha(\omega) \) and \( \beta(\omega) \) are orthonormal spin functions describing the electron spin as either up or down (Szabo and Ostlund, 1989).

### 2.2.2 Slater Determinants

By writing the many-electron wavefunction as a Slater determinant (eq. 2.3) made up of spin orbitals it is possible to include electron spin in the product of one-electron wavefunctions.

\[ P(x) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(x_1)\phi_2(x_1) & \ldots \phi_n(x_1) \\ \phi_1(x_2)\phi_2(x_2) & \ldots \phi_n(x_2) \\ \vdots & \ddots & \vdots \\ \phi_1(x_n)\phi_2(x_n) & \ldots \phi_n(x_n) \end{vmatrix} \] \hspace{1cm} (2.3)

Here \( n \) represents the number of electrons and \( 1/\sqrt{n!} \) is a normalization constant. Equation 2.3 can be simplified and written as Eq.2.4.

\[ \psi(x) = (n!)^2 \det|\phi_1(1)\phi_2(2)\ldots\phi_n(n)| \] \hspace{1cm} (2.4)

The Slater determinant can then be used to evaluate the Hartree-Fock energy via the use of variation theory.
2.2.3 Variation Theory

The Slater determinant for an antisymmetric, ground-state, normalised electronic wavefunction can be written, using Dirac notation, as follows (eq. 2.5)

$$|\psi_0\rangle = |\phi_1 \phi_2 \ldots \phi_n\rangle$$  \hspace{1cm} (2.5)

where $\psi_0$ represents the ground-state wavefunction.

The variational principle states that an approximate wave function has an energy which is above or equal to the exact energy (Jenson, 1999). The equality only holds true if the wave function is exact. Thus any approximations will result in an energy that is greater than the ground state energy but tends asymptotically towards the exact ground state energy as the degree of approximation is reduced. If we take the n-electron Slater determinant (eq. 2.4) then, using Dirac notation, the ground state electronic energy is given as (eq. 2.6)

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle$$  \hspace{1cm} (2.6)

Thus the variational principle can be used to find the determinant $\psi_0$ for which the energy $E$ is a minimum. This leads to the formation of the Hartree-Fock equations which allow the energy to be found using an iterative method known as the Self-Consistent Field (SCF) approach.

2.2.4 The Hartree-Fock Equations

The Hartree-Fock equations can be derived using functional variation. The determinant $\psi_0$ for which the energy $E$ is a minimum (eq. 2.6) is found by seeking a solution such that a small change $\psi \rightarrow \psi + \delta \psi$ yields no change in the value of $E$ to first order in $\delta \psi^2$.

For an infinitesimal change $\delta \psi$ the energy is given by (eq. 2.7)

$$E[\psi + \delta \psi] = \langle \psi | H | \psi \rangle + \delta \langle \psi | H | \psi \rangle$$  \hspace{1cm} (2.7)

Since the $E$ is expressed in terms of spin-orbitals there exists the constraint that they must be orthogonal and normalised. This constraint is of the form (eq. 2.8)

$$g = \sum_{i,j=1}^{n} \left[ \langle \phi_i | \phi_j \rangle - \delta_{ij} \right]$$  \hspace{1cm} (2.8)

Therefore when the spin-orbitals are changed by an amount $\delta \phi$, $g$ changes by (eq. 2.9)
\[ \delta g = \sum_{j=1}^{n} \delta \langle \phi_j | \phi_j \rangle \] (2.9)

since \( \delta \theta \) is constant. It is then possible to take the constraints into account by the use of Lagrange multipliers such that (eq. 2.10)
\[ \delta E = \sum_{j=1}^{n} \lambda_j \delta \langle \phi_j | \phi_j \rangle = 0 \] (2.10)

where \( \lambda_j \) is the Lagrange multiplier. By introducing the concept of a Coulomb and exchange operator, where \( J \) is the Coulomb operator representing electron repulsion and \( K \) is the exchange operator representing the exchange of electrons that leads to bonding (eq. 2.11)
\[ J_w(1)\phi_a(1) = \phi_a(1) \int \phi_a^*(2) \left( \frac{e^2}{4\pi \varepsilon_0 r_{12}} \right) \phi_a(2) dx_2 \] (2.11)
\[ K_w(1)\phi_a(1) = \phi_a(1) \int \phi_a^*(2) \left( \frac{e^2}{4\pi \varepsilon_0 r_{12}^2} \right) \phi_a(2) dx_2 \]

we can form an eigenvalue eigenfunction equation (eq. 2.12) that will yield the orbital energies of the spin orbitals.
\[ h_1\phi_a(1) + \sum_{j=1}^{n} [J_j(1)\phi_j(1) - K_j(1)\phi_j(1)] \sum_{j=1}^{n} \lambda_j \phi_j(1) \] (2.12)

An application of the Hartree-Fock procedure for individual spin-orbitals can then be found that yields the energy of each spin orbital (eq. 2.13)
\[ f_i \phi_a(1) = \epsilon_a \phi_a(1) \] (2.13)
where \( \epsilon_a \) is the spin-orbital energy and \( f_i \) is the Fock operator (eq. 2.14)
\[ f_i = h_i + \sum_{w} [J_w(1) - K_w(1)] \] (2.14)

Where \( h_i \) is the core Hamiltonian for electron 1, \( J_w \) is the Coulomb matrix and \( K_w \) is the exchange matrix (eq. 2.15).
\[ J_{ab} = \sum_{ad} D_{ad} \langle \phi_a \phi_b | \phi_c \phi_d \rangle \]
\[ K_{ab} = \sum_{ad} D_{ad} \langle \phi_a \phi_c | \phi_b \phi_d \rangle \] (2.15)

and \( D_{ad} \) is the density matrix (eq. 2.16)
\[ D_{ad} = 2 \sum_{\mu} C_{dp} C_{ep}^* \]  

(2.16)

Bach spin-orbital can then be obtained from equation (2.13) with the corresponding Fock operator \( f \). The fundamental problem, however, is that the Fock operator depends on the spin-orbitals of all the other (n-1) electrons. Thus it is necessary to solve the equations in an iterative fashion that stops when the solutions become self-consistent.

2.2.5 Closed Shell Systems

For a closed shell system, all electrons are paired so it is possible for the HF-SCF procedure to assume that the spatial components of the spin-orbitals are identical for each member of an electron pair. This leads to there being, for a system containing \( n \) electrons, \( \frac{n}{2} \) spatial orbitals of form \( \psi_a(r) \) yielding a Restricted Hartree-Fock wavefunction (eq. 2.17).

\[ \psi_\alpha = (nt)^{-\frac{1}{2}} \det | \psi_\alpha^a(1) \psi_\alpha^b(2) \psi_\beta^a(3) \ldots \psi_\beta^b(n) | \]  

(2.17)

2.2.6 Open Shell Systems

For an open shell system all the electrons are not necessarily paired in the orbitals such that equation (2.17) no longer holds. There are two common methods for dealing with open shell systems. The first is to use Restricted Open-Shell Hartree-Fock (ROHF). Here all electrons except those occupying open shell orbitals are forced to occupy doubly occupied spatial orbitals. Thus for, e.g. Lithium, the Hartree-Fock wave function is (eq. 2.18).

\[ \psi_\alpha = (6)^{-\frac{1}{2}} \det | \psi_\alpha^a(1) \psi_\beta^b(2) \psi_\beta^a(3) | \]  

(2.18)

There are, however, severe constraints imposed by this formalism. The major problem is that while the 1s\( \alpha \) electron has an exchange interaction with the 2s\( \alpha \) electron the 1s\( \beta \) electron does not. A big advantage of this method, however, is that it is an eigenfunction of \( \Sigma^2 \) hence fundamentally the wave-function, in terms of the Slater determinant, is correct. Thus anything calculated from this wave-function will be correct within the constraints imposed.

The second method is the use of unrestricted Hartree-Fock (UHF). Here the electrons are not implicitly paired and so aren't constrained to the same spatial wave
function. Thus the Hartree-Fock wavefunction for an unrestricted system is (eq. 2.19).

$$
\psi_o = (\mathbf{m})^{-\frac{1}{2}} \det \begin{vmatrix} \psi_\alpha^\alpha(1) & \psi_\beta^\beta(2) & \psi_\epsilon^\epsilon(3) & \ldots \ldots \end{vmatrix}
$$

(2.19)

UHF gives a lower energy than ROHF but has the disadvantage that it is not an exact eigenfunction $S^2$ hence it is possible to get spin contamination. This means that any properties calculated from the UHF result that depend on spin (NMR, ESR etc.) will not necessarily be correct.

2.2.7 The Roothaan-Hall Equations

In the early days of quantum chemistry interest was centered, due to the lack of computational power, on solutions of equation 2.13 for atoms. The spherical symmetry of atoms means that the Hartree-Fock equations can be solved numerically to find the spin-orbitals. In the case of molecules, however, this symmetry does not exist hence numerical solution of the HF equations is not possible.

A solution to the problem was devised by C.C.J. Roothaan (Roothan, 1951) and G.G. Hall (Hall 1951) who in 1951 independently derived a method for solving the HF equations for a molecule by expanding the molecular orbitals $\phi_a$ as linear combinations of known basis functions $\chi_j$ (eq. 2.20).

$$
\phi_a = \sum_{j=1}^{N} c_\mu \chi_j
$$

(2.20)

The Hartree-Fock equations (eq. 2.21) can then be rewritten as:

$$
f_i \sum_{j=1}^{N} c_\mu \chi_j = \varepsilon_i \sum_{j=1}^{N} c_\mu \chi_j
$$

(2.21)

Thus the problem of calculating the wavefunctions has been reduced to computing the coefficients $c_\mu$. Multiplication of equation (2.21) by the basis function $\phi_a$ followed by integration over $dr_j$ yields the Roothaan-Hall equations for a closed shell system (eq. 2.22).

$$
\sum_{j=1}^{N} c_\mu \int \chi_i^*(1) f_i \chi_j(1) \, dr_j = \varepsilon_i \sum_{j=1}^{N} c_\mu \int \chi_i^*(1) f_i \chi_j(1) \, dr_j
$$

(2.22)

These are the Fock equations in the atomic orbital basis. It is possible to use a more compact notation by collecting all the N equations from Eq. 2.22 and expressing them in matrix form (eq. 2.23).

$$
F_C = S_C \varepsilon \quad \quad (2.23)
$$
where $\varepsilon$ represents the orbital energies, $c$ the coefficient matrix and $S$ and $F$ the overlap and Fock matrices respectively (eq. 2.24).

$$S = \langle \chi_i | \chi_j \rangle$$  \hspace{1cm} (2.24)

$$F = \langle \chi_i | f | \chi_j \rangle$$

By drawing on the properties of matrix equations it can be shown that the Roothaan-Hall equations only have a non-trivial solution if the secular equation (eq. 2.25) is satisfied.

$$\det | F - \varepsilon_i S | = 0$$  \hspace{1cm} (2.25)

Unfortunately equation (2.25) cannot be solved directly since the Fock matrix $F$ is composed of Coulomb and exchange matrices (eq. 2.15), the values of which depend on the spatial wavefunctions that we are trying to find. Thus, as before an iterative procedure is required to solve this. The HF equations are then solved to obtain a new set of spin-orbitals, which are fed back into the Fock matrix and so on. The cycle is repeated until pre-defined convergence criteria are fulfilled.

2.3 BASIS SETS

By introducing the Roothaan-Hall equations to solve the HF-SCF procedure it was necessary to express the molecular orbitals $\phi_a$ as linear combinations of known basis functions $\chi_j$ (eq. 2.26).

$$\phi_a = \sum_{j=1}^{N} c_{\mu} \chi_j$$  \hspace{1cm} (2.26)

In order to form the Overlap and Fock matrices it is necessary to choose a function that represents the form of $\chi_f$.

If an infinite number of basis functions were used to represent the molecular orbitals it is clear from the discussion above that the wave function solution would essentially be correct, allowing for the neglect of electron correlation. This is known as the Hartree-Fock limit. In practice it is not possible to solve for an infinite number of basis functions so basis sets are chosen to describe the atomic orbitals to varying degrees of accuracy. The choice of basis set is an important factor in electronic structure calculations and fundamentally controls the accuracy of the results that can be expected.
2.3.1 Basis Functions

In choosing the type of basis function used to describe the molecular orbitals there are two practical considerations that have to be taken into account. The first is the accuracy to which the function describes the orbital and the second is the speed with which the two-electron integrals can be evaluated.

2.3.1.1 Slater Functions

The most efficient and accurate functions to use, such that equation 2.26 requires the fewest possible terms for accurate representation of the molecular orbital, are Slater functions (Slater, 1930), which have the functional form, in spherical harmonics, given in equation 2.27.

\[ \chi_{\ell,n,l,m} (r, \theta, \phi) = \text{NY}_{l,m} (r, \theta, \phi) r^{n-1} e^{-\rho} \]  
(2.27)

Where: \( N \) is a normalization constant and \( Y_{l,m} \) is the spherical harmonic function.

Slater functions have a finite value at zero, which correctly describes the cusp at the nucleus. Slater type functions also decay slowly and so represent the wavefunction accurately far from the nucleus. The correct solution to the hydrogen atom is of Slater form, hence using Slater functions is akin to using hydrogen atomic orbitals. However, use of Slater functions leads to difficulties in the evaluation of the one- and two-electron integrals for polyatomic systems. Thus for systems containing four or more atoms the use of Slater functions is very inefficient.

2.3.1.2 Gaussian Functions

In 1950 S.F. Boys proposed the use of Gaussian type functions in place of Slater functions to make evaluation of the one- and two-electron integrals more computationally efficient (Boys, 1950).

Gaussian type functions have the functional form, in spherical harmonics, given in equation 2.28.

\[ \chi_{\ell,n,l,m} (r, \theta, \phi) = \text{NY}_{l,m} (r, \theta, \phi) r^{2n-1/2} e^{-\rho} \]  
(2.28)

Where: \( N \) is a normalization constant and \( Y_{l,m} \) is the spherical harmonic function.

Gaussian type orbitals, differ from Slater type orbitals in two respects. Firstly at a distance of zero from the nucleus a Gaussian type function has zero gradients while a Slater type function has a finite gradient. Thus Gaussian type functions fail to describe the cusp at the nucleus correctly. Secondly at large distances from the nucleus Gaussian type functions tail off with an exponential quadratic dependence while Slater type
functions show a linear dependence. Thus at first sight it would appear that Slater type functions are vastly superior to Gaussian type functions.

However, despite these disadvantages Gaussian type functions have one big advantage over Slater type functions; they allow the one- and two-electron integrals to be evaluated much faster by exploiting the Gaussian product theory. This theory states that the product of two Gaussians on different centres is a single Gaussian situated on a third center. This allows the three- and four-centre two-electron repulsion integrals to be reduced to two-centre integrals so giving Gaussian type functions a massive computational advantage over Slater type functions.

This leads to the dilemma that the ideal representation would be to use Slater type functions to represent the molecular orbitals, however, Gaussian type orbitals are significantly easier to evaluate. Fortunately there exists a solution that involves constructing a basis function from a linear combination of Gaussian type functions. Such linear combinations are called contractions and the resulting function is termed a contracted Gaussian function (eq. 2.29).

\[ \chi_{ij}^{CGF} = \sum_{p=1}^{L} d_{pj} \chi_{ij}^{GTF} \]  

(2.29)

Where: L is the length of tile contraction and \(d_{pj}\) is a contraction coefficient.

2.3.2 Standard Basis Sets

Standard basis sets use contracted Gaussian type functions to represent Slater type orbitals. The number of primitive Gaussian type orbitals that are used to form each contracted Gaussian type function reflects on the accuracy of the basis set. The more primitive Gaussians used the more accurate the orbital description is.

Typically combinations between one and 6 Gaussian primitives are used to form a single Slater type orbital, termed a basis function. The contraction coefficients used in each case are those that give the best fit to a Slater type orbital.

2.3.2.1 Minimal Basis Sets

A minimal basis set is the least expensive basis set that can be used to describe the molecular orbitals for the system. It is minimal in the sense that it has the least number of functions per atom required to describe the occupied atomic orbitals of that atom.
The general form of a minimal basis set is STO-LG where $L$ is the number of Gaussian primitives contracted to form a basis function. An example is the STO-3G basis set by (Pople et al., 1969), which uses 3 primitive Gaussians for each of the inner and valence shell orbitals of each atom. For first row elements and hydrogen, the basis set is denoted by $(6s3p/3s)$ primitives contracted to $[2s1p/1s]$. Thus for Hydrogen and Helium there is 1 basis function (1s orbital), for Li to Ne 5 functions ($1s, 2s, 2p_x, 2p_y, 2p_z$), for Na to Ar 9 functions etc.

The unique aspect of the STO-LG basis sets is that in the least squares fit to the Slater type orbitals the contraction exponents are constrained to be identical so that the 2s and 2p fits are performed simultaneously. Thus the 2s and 2p functions have the same radial behavior and hence can be treated as one function in the integral evaluation step, which leads to a very efficient evaluation procedure.

Minimal basis sets are relatively inexpensive and so can be used for calculation on quite large molecules (Szabo and Ostlund, 1989). However, they are so small that at best can only offer qualitative results, but they do include the essentials of chemical bonding.

### 2.3.2.2 Double Zeta Basis Sets

A significant improvement in results can be obtained by adopting a double-zeta (DZ) basis set instead of a minimal STO-LG basis set. In a DZ basis set each STO is replaced by two STOs that have different contraction coefficients. This gives more flexibility to the size of the orbitals being described and hence gives a more accurate solution. However, this representation doubles the number of basis functions that need to be evaluated and hence increases the number of integrals that needs to be solved (analogous to computational complexity), by $2^4$.

For the first row atoms the Dunning DZ basis set (Dunning et al. 1999) consists of $(6s5p)$ primitives contracted to $[4s2p]$. It is of course also possible to have higher orders such as triple zeta basis sets that have three functions per orbital etc.

### 2.3.2.3 Split Valence Basis Sets

Split valence basis sets offer a compromise between the inadequacy of STO-LO minimal basis sets and the high computational demand of double or triple zeta basis sets.

In a split valence basis set such as 3-21G (Pople et al., 1980) or 6-31G (Pople et al., 1972) the valence shell atomic orbitals are described by two basis functions, as in
the double zeta example above, while each core atomic orbital is represented by a single basis function. This is a reasonable approximation to make, as it is generally only the valence shells that are responsible for the chemical properties of an atom or molecule.

In the 3-21G basis set, 3 primitive Gaussians, contracted to a single basis function, are used to describe the core orbitals while 2 primitives, contracted to a single basis function and an additional, more diffuse, function collectively describe the valence orbitals. For first row atoms this basis set consists of (6s2p) primitives contracted to [3s2p] (9 basis functions).

Similarly the 6-31 G basis set uses 6 primitives for the core orbitals and 2 functions composed of 3 primitives and a single primitive to describe the valence orbitals. The contraction here, for first row atoms, is (10s4p) to [3s2p].

Along the same lines as discussed in (2.3.2.2) it is possible to have triple split valence basis sets such as 6-311G (Pople et al., 1980) where the valence orbitals are described by three functions, formed from a contraction of 3, 1 and 1 Gaussian primitives respectively, and the core orbitals by one function formed from a contraction of 6 Gaussian primitives. For the first row atoms the contraction is (11s5p) to [4s3p]:

2.3.2.4 Extended Basis sets

Up to this point the basis sets that have been described have not allowed for the possibility of contributions from orbitals representing higher angular momentum values such as d or f functions. In order to account for the distortion of electron density due to other adjacent atoms such higher angular momentum functions are essential.

Extended basis sets offer an improvement over split valence basis sets by including additional functions to describe the valence electrons. The extra functions that are added can be in the form of polarization or diffuse functions. Polarization function basis sets such as 3-21G* (Binkley et al., 1980) and 6-31G* (Pople et al., 1973) work in the same way as split valence basis sets but also add additional polarisation functions. 3-21G* adds d-type functions to all first row atoms while 6-31G* adds these functions to 1d heavy atoms. The 6.31G** basis set also adds p-type functions to hydrogen. As discussed above basis sets of this type are required to describe the atom correctly in a non-uniform electric field that arises from the non-spherical environment of a molecule.

It is also possible to have diffuse functions included, large s-and p-type functions, that allow the valence orbitals to occupy a greater region of space. An example of this
type of basis set is the 6-31++G (Hehre et al., 1972) basis set. Inclusion of diffuse functions in the basis set has the effect of reducing basis set superposition error (BSSE) in binding energy calculations. This is a phenomenon that results in the stabilisation of one monomer in a donor-acceptor-complex being over estimated due to the presence of basis functions on the other (Stone, 1996). While this is one way of reducing the error in binding energy calculations it has the disadvantage that the inclusion of diffuse functions increases the calculation complexity considerably. Thus for relatively large systems such as the heme unit of myoglobin in their use is not really practical.

2.4 ELECTRON CORRELATION

2.4.1 Electron Correlation Energy

As mentioned in section (2.3) Hartree-Fock theory does not account for the instantaneous electron-electron repulsions and thus it is possible for electrons to effectively come too close together. This is especially acute in large systems that have a large number of electrons. Calculations carried out with complete or infinite basis sets, while at the Hartree-Fock limit, will therefore be subject to error known as the correlation energy. This energy is defined as the difference between the exact non-relativistic energy of a system $E_0$ and the energy at the Hartree-Fock limit $E_{\text{HF}}$ (eq. 2.30).

$$E_{\text{corr}} = E_0 - E_{\text{HF}}$$  \hspace{1cm} (2.30)

It can be shown, using variational theory (2.2.3), that $E_{\text{corr}}$ is negative since $EM$ is an upper bound to the exact wavefunction energy. Neglecting electron correlation typically leads to an error of about 1% of the total Hartree-Fock energy. This is roughly equivalent to the energy of a single covalent bond (Foresman and Frisch, 1996).

There exist two types of electron correlation. Dynamical correlation is the instantaneous electron-electron repulsion experienced between two electrons of opposite spin. Non-dynamical correlation is due to degeneracy present in the configuration of electrons in partly filled orbitals (Shavit, 1977).

2.4.2 Electron Correlation Energy

There are corrections for the non-dynamical correlation in Hartree-Fock theory but this does not have a significant effect on the energy of the resulting wave function. Improvement of the wave function solution is thus only possible by taking into account the dynamical correlation. There exist a number of different methods for including this in
a calculation, Moller-Plesset (MP) Perturbation theory accounts for the correlation energy by including higher excitations in the ground state wave function as linear corrections (Pople et al., 1986). Configuration Interaction (CI) includes electron correlation by noting that a single Slater determinant is insufficient to describe the wavefunction and instead considers the alternative electron configurations that are possible, within a given basis set. Correct weighting of the importance of each of these different configurations then leads to the construction of an accurate, within the basis set approximation, wavefunction.

2.5 DENSITY FUNCTIONAL THEORY

Density Functional Theory (DFT) forms the basis and framework of all the work that is presented in this thesis. DFT has recently gained increasing recognition and acceptance as a powerful and flexible tool within chemistry. This is evident by the growing number of papers devoted to the subject (recent reviews are contained in articles by Ziegler (Ziegler, 1991 and 1995) books dedicated to the subject include a textbook (Parr and Yang 1989) and several volumes of conference proceedings (Ziegler et al., 1996; Labanowski and Andzelm, 1991; Politzer and Seminario, 1995). The increasing popularity of DFT is due to the combination of accuracy and efficiency, which are particularly important for large systems (e.g., transition metal complexes or heavy element compounds). Examples of its applications are the accurate calculation of molecular structures and bonding energies, the determination of transition state structures, activation energies, reaction pathways, the assignment of various kinds of spectra, as well as the computation of harmonic force fields (Ziegler, 1991 and 1995). This list is by no means complete; other examples will be discussed throughout this thesis. Furthermore, the results obtained by DFT are usually in good agreement with experiment.

2.5.1 Total Energy; Kohn-Sham Equations

Non-relativistic DFT is based on an exact expression for the total electronic energy of the $n$-electron system (Parr and Yang 1989; Hohenberg and Kohn 1964)

$$E^\text{NR}[\rho] = \sum_{i} \int d \mathbf{\tilde{r}}_i \psi_i^* \psi_i^\text{NR} \psi_i$$  \hspace{1cm} (2.31)
The energy is a functional of the electron density, $\rho$. Further, the $\{\psi_i\}$ form a set of $n$ orthonormal one-electron functions. The density follows from these Kohn-Sham (KS) orbitals (Parr and Yang 1989; Kohn and Sham 1965) as they are often called, by

$$\rho(\vec{r}) = \rho(\vec{r}, \vec{r})$$  \hspace{1cm} (2.32)

with

$$\rho(\vec{r}, \vec{r}) = \sum_{i} \psi_i^* (\vec{r}) \psi(\vec{r})$$  \hspace{1cm} (2.33)

In Eqs. 2.32 and 2.33, we have introduced the one-electron density matrix of the system; the electronic density proper is given by the diagonal elements of the density matrix, Eq. 2.32.

The first term in Eq. 2.34 contains the operator $h^{NR}$,

$$h^{NR} = \frac{P^2}{2} + V_N (\vec{r}),$$  \hspace{1cm} (2.34)

where $P$ is the electronic momentum operator (NR stands for non-relativistic). Thus, $h^{NR}$ describes the interaction of the electronic density with the external nuclear potential, $V_N(\vec{r})$, as well as the kinetic energy of a model system with exactly the same electron density, but without electron-electron interactions (Ziegler 1991; Parr and Yang 1989; Hohenberg and Kohn 1964). The next term in Eq. 2.31 describes the interaction of the electron density with itself. Finally, $E_{XC}[\rho]$ is the exchange-correlation (XC) energy functional. It contains the difficulties of the many-electron problem, and its exact form is unknown (Ziegler et al., 1996; Ziegler, 1991 and 1996; Parr and Yang, 1989; Labanowski and Andzelm, 1991; Politzer and Seminario, 1995). The XC energy functional can be expressed in terms of the XC energy density $E_{XC}$ according to (Kohn and Sham 1965; Slater 1951).

$$E_{XC}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho(\vec{r})] d\vec{r}$$  \hspace{1cm} (2.35)

For practical purposes, some meaningful approximation has to be chosen for $E_{XC}[\rho]$ (Nusair et al., 1980; Preuss et al., 1980; Becke, 1986 and 1988; Perdew, 1986).

The energy expression in Eq. 2.31 allows the derivation of effective one-electron equations for the KS orbitals. This is achieved by requiring the total energy expression of Eq. 2.31 to be stable with respect to any variation of the total density (Ziegler, 1991; Parr and Yang, 1989; Kohn and Sham, 1965). The resulting KS equations are
\[ f^{NR} \Psi_i = e_i \Psi_i, \tag{2.36} \]

where

\[ f^{NR} (\vec{r}) = h^{NR} (\vec{r}) + V_H (\rho, \vec{r}) + V_{XC} (\rho, \vec{r}) \tag{2.37a} \]

and

\[ V_{XC} (\rho, \vec{r}) \equiv \frac{\delta E_{XC}[\rho]}{\delta \rho}. \tag{2.37b} \]

The XC potential \( V_{XC} \) of Eq. 2.37b is the functional derivative of the XC energy with respect to the electron density. The second term in Eq. 2.37a is the Hartree (or Coulomb) potential, i.e., the electrostatic potential of the electron density

\[ V_H (\rho, \vec{r}_1) = \int d\vec{r}_2 \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \tag{2.37c} \]

Finally, the first term in Eq. 2.37a, \( h^{NR} \), has been defined earlier in Eq. 2.34. The Kohn-Sham equations, Eqs. 2.36 and 2.37, have to be solved self-consistently for the Kohn-Sham orbitals.

**2.5.2 Basis Set Expansion, Frozen Core Approximation**

The Kohn-Sham equations, Eq. 2.36, are often solved by expanding the Kohn-Sham orbitals into a (finite) basis set according to

\[ \Psi_i = \sum_{\mu} d_{i\mu} \chi_\mu. \tag{2.38} \]

The \( \{\chi_\mu\} \) form a set of \( 2M \) basis functions. These basis functions are in most cases "atomic orbitals" (AO). Each AO is centered on one particular nucleus. The expansion Eq. 2.38 is then called the "linear combination of atomic orbitals" (LCAO) expansion. The task of solving the KS equations, Eq. 2.36, is now transformed into finding the LCAO expansion coefficients \( \{d_{i\mu}\} \).

One major problem for the theoretical description of many-particle systems is the large number of electrons involved. It is on the other hand well established that only valence electrons participate in chemical bonds. Thus, it would be desirable to reduce the
computational effort by treating only the valence electrons explicitly. Probably the most common approach to achieve this is by the use of pseudopotentials (Christiansen et al., 1988; Pyykko, 1988 and 1991; Snijders, 1979; Pitzer, 1984). Another way to make use of this fact is the so-called frozen core approximation (Baerends, 1973; Baerends and Ros, 1973) that is also used in some of the following chapters. In this approximation, it is assumed that molecular orbitals (MO) describing inner-shell electrons remain unperturbed in going from a free atom to a molecule. Consequently, these "core electrons" can be excluded from the variational procedure. Instead, they are pre-calculated in an atomic calculation, and kept "frozen" thereafter (Baerends, 1973; Baerends and Ros, 1973).

However, when employing this approximation, we have to ensure orthonormality of all MOs. In particular, the valence MOs have to be orthogonal to all core orbitals within the molecule. An elegant way to achieve this is the following: We shall make already the valence basis orthogonal to the cores. Thus, we modify the AO expansion of Eq. 2.38 according to

$$\psi_i = \sum_{\mu} c_{\mu} \lambda_{\mu},$$

(2.39)

where \{\lambda_{\mu}\} is the set of the \(2M_{\text{val}}\) modified valence basis functions and \(\psi_i\) is one of the \(n_{\text{val}}\) valence MOs. These basis functions are given by (Berces et al., 1996; Baerends, 1973; Baerends and Ros, 1973; Berces, 1995).

$$\lambda_{\mu} = \chi_{\mu}^{\text{val}} + \sum_{\tau} b_{\mu \tau} \chi_{\tau}^{\text{core}}$$

(2.40)

Here, \(\chi_{\mu}^{\text{val}}\) is one of the valence AOs that have been introduced before in Eq. 2.38. The \(\{\chi_{\tau}^{\text{core}}\}\) form an auxiliary set of \(2M_{\text{core}}\) core AOs. We employ exactly one such core AO (one core type basis function) per frozen core MO. It is thus possible to split the total density matrix \(\rho(\vec{r}, \vec{r}^\prime)\) of Eq. 2.33 into a core and a valence part

$$\rho(\vec{r}, \vec{r}^\prime) = \rho_C(\vec{r}, \vec{r}^\prime) + \rho_V(\vec{r}, \vec{r}^\prime).$$

(2.41)

The core-orthogonalization coefficients \(b_{\mu \nu}\), Eq. 2.40, are found from the aforementioned orthogonality requirement

$$\left\langle \lambda_{\alpha} | \omega_{\beta}^{\text{core}} \right\rangle = 0.$$  

(2.42)
The condition in Eq. 2.42 must be satisfied for all $2M_{\text{val}}$ valence basis functions $\lambda_\mu$ and for all $2M_{\text{core}}$ frozen core orbitals $\omega_\beta^\text{core}$ (core MOs). This leads to the following equations for the $b_{\mu\tau}$ (Berces et al., 1996; Schreckenbach and Ziegler, 1996; Baerends, 1973; Baerends and Ros, 1973; Berces, 1995).

$$B^* = -R\left(S_{\text{core}}^\text{core}\right)^{-1}$$  \hspace{1cm} (2.43)

where

$$\left(R^*\right)_{\mu\tau} \equiv b_{\mu\tau}^*,$$  \hspace{1cm} (2.44a)

$$\left(R\right)_{\alpha\beta} \equiv \left\langle \chi_\alpha^\text{val} | \omega_\beta^\text{core} \right\rangle,$$  \hspace{1cm} (2.44b)

$$\left(S_{\text{core}}^\text{core}\right)_{\gamma\delta} \equiv \left\langle \chi_\gamma^\text{core} | \omega_\delta^\text{core} \right\rangle.$$  \hspace{1cm} (2.44c)

Thus, $R$ and $S_{\text{core}}^\text{core}$ represent the overlaps between the true core MO, $\omega_\beta^\text{core}$, and the primitive AOs, $\chi_\mu^\text{val}$ and $\chi_\tau^\text{core}$, respectively. Note the star in Eqs. 2.43 and 2.44a, denoting the complex conjugate of the core-orthogonalization coefficients (Schreckenbach and Ziegler, 1996).

We wish to emphasize again that the set $\{\chi_\gamma^\text{core}\}$ of Eq. 2.40 is chosen to be truly auxiliary in the frozen core approximation; it does not constitute any degrees of freedom within the variational space of the valence MOs (Berces et al., 1996; Schreckenbach and Ziegler, 1996; Baerends, 1973; Baerends and Ros, 1973; Berces, 1995). The variational space is spanned by the valence MOs of Eq. 2.40.

It is useful to rewrite the MO expansion of Eq. 2.39 to give it the same form as in the all-electron case, cf. Eq. 2.38. Thus, we write

$$\psi_i = \sum_\mu^{2M} c_{im} \chi_\mu$$  \hspace{1cm} (2.45)

where

$$2M = 2M_{\text{val}} + 2M_{\text{core}}$$  \hspace{1cm} (2.46)

The MO expansion of Eq. 2.83 goes now over all $2M$ primitive AOs, rather then over the $2M_{\text{val}}$ modified basis functions $\lambda_\mu$ of Eq. 2.40. The new set of coefficients $\{c_{im}\}$ is readily obtained from the definition of the $\lambda_\mu$ in Eq. 2.40 as
\[ c_{\mu i} = c_{\mu i} \quad \text{if } \mu \text{ counts a valence AO,} \]
\[ c'_{\mu i} = \sum_{\alpha} b_{\alpha \mu} c_{\alpha i} \quad \text{if } \mu \text{ represents a core AO.} \quad (2.47) \]

We shall in this thesis use either form of the expansion for the valence MO \( \psi_i \), Eq. 2.39 or Eq. 2.45.

If the frozen core approximation was completely correct, i.e., if the core polarization was indeed negligible, then the two sets of coefficients \( \{c'_{\mu i}\} \) of the frozen core approximation, Eq. 2.45, and \( \{d_{\mu i}\} \) of the all-electron case, Eq. 2.38, must be identical.

2.6 AB INITIO METHOD

The term "Ab Initio" is Latin for "from the beginning." This name is given to computations which are derived directly from theoretical principles, with no inclusion of experimental data. Most of the time this is referring to an approximate quantum mechanical calculation. The approximations made are usually mathematical approximations, such as using a simpler functional form for a function or getting an approximate solution to a differential equation. The most common type of ab initio calculation is called a Hartree Fock calculation (abbreviated HF), in which the primary approximation is called the central field approximation. This means that the Coulombic electron-electron repulsion is not specifically taken into account. However, it's net effect is included in the calculation. This is a variational calculation, meaning that the approximate energies calculated are all equal to or greater than the exact energy. The energies calculated are usually in units called Hartrees (1 H = 27.2114 eV). Because of the central field approximation, the energies from HF calculations are always greater than the exact energy and tend to a limiting value called the Hartree Fock limit. The second approximation in HF calculations is that the wave function must be described by some functional form, which is only known exactly for a few one electron systems. The functions used most often are linear combinations of Slater type orbitals \( \text{exp}(-ax) \) or Gaussian type orbitals \( \text{exp}(-ax^2) \), abbreviated as STO and GTO respectively. The wave function is formed from linear combinations of atomic orbitals or more often from linear combinations of basis functions. Because of this approximation, most HF calculations
give a computed energy greater than the Hartree Fock limit. The exact set of basis functions used is often specified by an abbreviation, such as STO-3G or 6-311++g**. A number of types of calculations begin with a HF calculation then correct for the explicit electron-electron repulsion, referred to as correlation. Some of these methods are Mohler-Plesset perturbation theory (MPn, where n is the order of correction), the Generalized Valence Bond (GVB) method, Multi-Configurations Self Consistent Field (MCSCF), Configuration Interaction (CI) and Coupled Cluster theory (CC). As a group, these methods are referred to as correlated calculations. A method, which avoids making the HF mistakes in the first place is called Quantum Monte Carlo (QMC). There are several flavors of QMC variational, diffusion and Green's functions. These methods work with an explicitly correlated wave function and evaluate integrals numerically using a Monte Carlo integration. These calculations can be very time consuming, but they are probably the most accurate methods known today. An alternative ab initio method is Density Functional Theory (DFT), in which the total energy is expressed in terms of the total electron density, rather than the wavefunction. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. The good side of ab initio methods is that they eventually converge to the exact solution, once all of the approximations are made sufficiently small in magnitude. However, this convergence is not monotonic. Sometimes, the smallest calculation gives the best result for a given property. The bad side of ab initio methods is that they are expensive. These methods often take enormous amounts of computer CPU time, memory and disk space. The HF method scales as N^4, where N is the number of basis functions, so a calculation twice as big takes 16 times as long to complete. Correlated calculations often scale much worse than this. In practice, extremely accurate solutions are only obtainable when the molecule contains half a dozen electrons or less. In general, ab initio calculations give very good qualitative results and can give increasingly accurate quantitative results as the molecules in question become smaller.

2.7 SEMIEMPIRICAL MOLECULAR ORBITAL METHODS

Semiemperical molecular orbital methods are based on approximations to integrals and use of some adjustable parameters with the help of which experimental or ab-initio theoretical results are usually reproduced satisfactorily. In ab initio calculations, all integrals are evaluated properly. However, due to a large number of integrals, ab initio
calculations require a huge computer time, particularly for large molecules. Therefore, for calculations on large molecules, semiempirical methods are frequently used. Certain semiempirical methods and the related approximations are discussed below.

2.7.1 Zero Differential Overlap (ZDO) Approximation

The ZDO approximation (Parr, 1952) is expressed by the equation

$$\phi_\mu(1)\phi_\nu(1) = 0, \quad \text{if } \mu \neq \nu \quad (2.48)$$

Consequent to this approximation, evaluation of the various integrals, especially the two-electron integrals, which occur in molecular orbital calculations, becomes much easier. The Pariser-Parr-Pople (PPP) method was developed initially using the ZDO approximation. In this method (Pariser and Parr, 1953; Pople, 1953) only $\pi$-electrons are considered explicitly while the $\sigma$-electrons are considered to form a frozen core. This method yielded satisfactory results for $\pi-\pi^*$ transitions of molecules but it could not be satisfactorily used for geometry optimization. This objective could be achieved satisfactorily using all valence electron methods.

2.7.2 Modified Neglect of Diatomic Overlap (MNDO) Method

Dewar and his collaborators developed this semiempirical method that deals with all the valence electrons of atoms in atoms in molecules (Dewar and Thiel, 1977; Dewar and Zeobisch, 1988). This method has been used extensively by different workers to study molecular geometries, properties and reactions. Dewar and his coworkers developed methods, based on the Modified Intermediate Neglect of Differential Overlap (MINDO) approximation, known as MINDO/1 (Baird and Dewar, 1969), MINDO/2 (Dewar and Haselbach, 1970) and, MINDO/3 (Bingham et al., 1975). These methods were based on the concept of Intermediate Neglect of Differential Overlap (INDO) (Pople et al., 1967). Another method called Neglect of Diatomic Differential Overlap (NDDO) (Pople et al., 1965) was developed by removing discrepancies in the complete Neglect of Differential Overlap (CNDO) (Pople et al., 1970) and INDO approximations. Further modification and reparameterization of the NDDO method resulted in the Modified Neglect of Diatomic Overlap (MNDO) method (Dewar and Thiel, 1977; Dewar and Zeobisch, 1988). The Fock matrix elements in the MNDO methods are given by
\[ F_{\mu\nu} = U_{\mu\nu} + \sum_{B} V_{\mu\nu, B} + \sum_{P} \left( \left( \mu\mu | \nu\nu \right) - \frac{1}{2} \left( \mu\nu | \mu\nu \right) \right) + \sum_{B} \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\mu | \lambda\sigma) \]  
\hspace{2cm} (2.49)

\[ F_{\mu\nu} = \sum_{B} V_{\mu\nu, B} + \frac{1}{2} P_{\nu\nu} \left( \beta (\mu\nu | \mu\nu) - (\mu\nu | \nu\nu) \right) + \sum_{B} \sum_{\lambda\sigma} P_{\lambda\sigma} (\mu\nu | \lambda\sigma) \left( \mu \neq \nu \right) \]  
\hspace{2cm} (2.50)

\[ F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} \sum_{V} \sum_{\sigma} P_{\nu\sigma} (\mu\nu | \lambda\sigma) \]  
\hspace{2cm} (2.51)

Here the atomic orbitals \( \phi_\mu \) and \( \phi_\nu \) are taken to be centered on atom A while \( \phi_\lambda \) and \( \phi_\sigma \) are taken to be centered on atom B \((B \neq A)\). The various integrals appearing in the Fock Matrix elements are evaluated using the following approximations.

(a) The one-center core integral \( U_{\mu\mu} \) (sum of the kinetic energy of an electron in atomic orbital \( \phi_\mu \) at an atom A and the potential energy of its attraction with the nucleus of the same atom). One-center two electron repulsion integrals \((\mu\mu/\nu\nu)\) and one-center two-electron exchange integrals \((\mu\nu/\mu\nu)\) are evaluated using the Oleari’s method \((\text{Oleari et al., 1966})\). The one-center integrals were evaluated using a least squares fitting to the total valence state energies \( (E_A) \) of an atom A as a function of the orbital occupancy number \( n_\mu \) as follows

\[ E_A = \sum_\mu n_\mu U_{\mu\mu} + \frac{1}{2} \sum_\mu \sum_{\mu\nu} n_\mu n_\nu g_{\mu\nu} + \frac{1}{2} \sum_\mu n_\mu (n_\mu - 1) g_{\mu\mu} \]  
\hspace{2cm} (2.52)

where \( g_{\mu\nu} = g_{\mu\nu} \frac{1}{2} h_{\mu\nu} \),

\[ g_{\mu\nu} = (\mu\nu/\nu\nu) \]
and
\[ h_{\mu\nu} = (\mu\nu/\mu\nu) \]

The valence state energies have been estimated by Skinner and Pritchard. The two-center two-electron repulsion integrals \((\mu\nu/\lambda\sigma)\) were evaluated using the classical concept of multipole-multipole interaction.

\[ (\mu\nu/\lambda\sigma) = \sum_{i_1} \sum_{i_2} \sum_{m} [M_{i_1}^{R} m, M_{i_2}^{R} m] \]  
\hspace{2cm} (2.53)

where \( M_{i_1}^{R} m \) and \( M_{i_2}^{R} m \) are multipole moments generated due to the charge distributions \((e\phi_\mu\phi_\nu)\) and \((e\phi_\lambda\phi_\sigma)\) belonging to the atoms A and B respectively, \( e \) being the electronic
charge. The indices \( l_1, l_2 \) and \( m \) define multipole moments. The multipole interaction energy is given by

\[
[M^A \cdot m, M^A \cdot m] = \frac{e^2}{2l_1 + l_2} \sum_{i=1}^{2l_1} \sum_{j=1}^{2l_2} f_1(R_{ij})
\]

(2.54)

Here, each multipole is represented by an appropriate configuration \([M/m]\) of 2\( l \) point charges of magnitude \( e/2^l \) each. The distance between two point charges \( i \) and \( j \) in the interacting configuration at atoms A and B respectively is denoted by \( R_{ij} \). The function \( f_1(R_{ij}) \) stands for an expression which behaves correctly when \( R_{AB} \rightarrow 0 \) and \( R_{AB} \rightarrow \infty \).

This function can be expressed using the Dewar-Sabelli-Klopman (DSK) approximation as follows:

\[
f_1(R_{ij}) = [R_{ij}^2 + (\rho_{l_1}^A + \rho_{l_2}^B)^2]^{1/2}
\]

(2.55)

or, by using Mataga-Nishimoto approximation (Mataga and Nishimoto 1962)

\[
f_1(R_{ij}) = \left( R_{ij}^2 + \frac{1}{\rho_{l_1}^A + \rho_{l_2}^B} \right)^{-1}
\]

(2.56)

Here the monopole, dipole and quadrupole configurations are characterized by \( l = 0, 1 \) and 2 respectively.

(c) The core- electron attraction \( V_{\mu \nu B} \) and the core-core repulsion \( E \) - are evaluated as follows.

\[
V_{\mu \nu B} = -Z_B (\mu^B \cdot v^A | s^B s^B) + f_2(R_{AB})
\]

(2.57)

and

\[
E_{AB}^{\text{Core}} = Z_A Z_B (s^A \cdot s^A | s^B s^B) + f_3(R_{AB})
\]

(2.58)

In these equations \( s^A \) and \( s^B \) stand for the valence s orbital of atoms A and B respectively. One of the functions \( f_2(R_{AB}) \) and \( f_3(R_{AB}) \) was assumed to be zero while the other was expressed in the form \( \exp(-\alpha R_{AB}) \) where \( \alpha \) is an adjustable parameter. Therefore, the repulsion energy vanishes in the limit \( R_{AB} \rightarrow \infty \).

(d) One-electron core core resonance integrals \( H_{\mu \nu}^{\text{core}} \), which are largely responsible for bonding are taken to be proportional to the corresponding overlap integrals \( S_{\mu \nu} \). Thus
\[ H_{\mu \nu}^{\text{core}} = f_4 (R_{AB}) S_{\mu \nu} \]  
(2.59)

where the orbital \( \phi_\mu \) is on atom A and the orbital \( \phi_\nu \) is on atom B (B \( \neq \) A). The integral \( S_{\mu \nu} \) is evaluated over STO's. The function \( f_4 (R_{AB}) \) is expressed as

\[ f_4 (R_{AB}) = 0.5 \left( \frac{\beta_A}{\mu} + \frac{\beta_B}{\nu} \right) \]  
(2.60)

Where \( \frac{\beta_A}{\mu} \) and \( \frac{\beta_B}{\nu} \) are adjustable parameters and characteristics of atomic orbitals \( \phi_\mu \) and \( \phi_\nu \) located at atoms A and B respectively.

### 2.7.3 Austin Model 1 (AM1) Method

The MNDO method fails to describe intermolecular hydrogen bonding satisfactorily (Dewar et al., 1985). The AM1 method was also developed by the Dewar group (Dewar et al., 1985) and it usually describes intermolecular hydrogen bonding satisfactorily. The AM1 method was obtained by modifying the core-core repulsion in the MNDO methods. Thus in the AM1 method

\[ E_{\text{core}}^{AB} = Z_A Z_B \gamma s \left[ 1 + f_A + f_B \right] \]  
(2.61)

Here

\[ f_A = \exp (-\alpha_B R_{AB}) + \sum_i K_{Ai} \exp \left[ L_{Ai}(R_{AB} - M_{Ai})^2 \right] \]  
(2.62)

\[ f_B = \exp (-\alpha_B R_{AB}) + \sum_i K_{Bi} \exp \left[ L_{Bi}(R_{AB} - M_{Bi})^2 \right] \]  
(2.63)

Here the \( K_s \) and \( M_s \) are adjustable parameters, and \( L_s \)'s are also adjustable parameters for which mostly a common value is used. In some cases, the AM1 method was found to underestimate hydrogen bond interaction energies (Dewar et al., 1985). It has been reported by Ventura et al. (1989) that the AM1 method fails to reproduce the experimental geometry of the water dimer (Galera et al., 1988), by studying clusters of hydrogen bonded molecules, it was found that the AM1 method is adequate for studying hydrogen bonding.
2.8 CALCULATION OF MOLECULAR PROPERTIES

Some of the important aspects and properties of molecules that can be studied using the different molecular orbital methods are as follows:

2.8.1 Molecular Geometry

The equilibrium molecular geometry is defined as the geometry corresponding to the global energy minimum of a system. Theoretically, equilibrium geometry of a system can be calculated by a systematic minimization of the total energy with respect to all the internal coordinates i.e. bond lengths, bond angles and dihedral angles, and this process is termed as geometry optimization. For a reliable and fast geometry optimization, different algorithms are used e.g. those due to Berny, and Fletcher and Powell etc. (Flanagan et al., 1977; Schlegel, 1982; Schlegel, 1994; Flether and Powell, 1963; Davidan, 1968; Pulay, 1970 and 1977).

2.8.2 Ionization Potential (IP)

The energy, required to remove an electron from a system A is called ionization potential. The process of ionization of a molecule A can be shown by

\[ A \rightarrow A^+ + e^- \]  \hspace{1cm} (2.64)

The ionization potential of a molecule can be obtained using the Koopmans’ theorem (Koopmass, 1933). According to this theorem, the ionization potential of a molecule corresponding to the \(i^{th}\) orbital (\(\varepsilon_i\)) is equal to the energy of the orbital taken with the negative sign (-\(\varepsilon_i\)). Thus

\[ \varepsilon_i = -\varepsilon_i \]  \hspace{1cm} (2.65)

This theorem does not take into account relaxation of the system consequent to ionization. Usually, the calculated ionization potentials using this theorem are larger than the experimental values by 10-20%.

2.8.3 Heat of Formation

The heat of formation (\(\Delta H_f\)) of a molecule (Sadlej 1985) can be defined as

\[ \Delta H_f = \sum_{\Lambda} \Delta H_f \Lambda \rightarrow \Delta \]  \hspace{1cm} (2.66a)
\[ D = \sum_A EA - E \]  \hspace{1cm} (2.66b)

Where the first term on the right side in equation 2.66a represents the sum of the heats of formation of all the constituent atoms of the molecule and \( D \) is the dissociation energy of the molecule. The first term on the right hand side in equation 2.66b represents the sum of total energies of the constituent atoms of the molecule while \( E \) represents the total energy of the molecule.

2.8.4 Charge Distribution

The molecular properties like dipole and multipole moments, electrostatic interactions between molecules, reactivity etc. depend upon charge distributions in molecules (Mishra and Kumar, 1995; Tasi and Palinko, 1995; Naray-Szabo, 1993; Seri-Levy West and Richards, 1994; Burgess Ruell and Zalkoww, 1995; Naray-Szabo and Ferenczy, 1995; Lin Cheng and Wang, 1994). Several methods have been developed to compute molecular charge distribution (Kumar et al., 1995; Naray-Szabo and Ferenczy, 1995; Lin Cheng and Wang, 1994; Mulliken, 1995; Cisowski Hay and Ritchie, 1990; Meister and Schwarz, 1994). Here we will discuss only Mulliken charge distribution.

2.8.4.1 Mulliken Charges

The Mulliken atomic population \( Q^M(A) \) on an atom \( A \) in a molecule having \( 2n \) electrons is given by (Mulliken, 1995).

\[
Q^M(A) = \sum_{i=1}^{n_A} \left( P_{\mu_A} + \sum_{B=A}^{B=\infty} \sum_{\nu_B} P_{\mu_A\nu_B} s_{\mu_{A}\nu_B} \right) \hspace{1cm} (2.67)
\]

Where \( P_{\mu_A\nu_A} \) is the density matrix element as mentioned earlier and \( n_A \) is the number of atomic orbitals of the atom \( A \). The first term of the right hand side is the contribution arising due to the orbitals on atoms \( A \) while the second term arises due to the overlap of the orbitals \( \Phi_{\mu_A} \) of atom \( A \) with the orbitals \( \Phi_{\nu_B} \) of the other atoms \( B \). The quantity \( Q^M(A) \) is called total Mulliken population or charge. The sum of all the Mulliken atomic populations is equal to the total number of electrons in the molecule.

\[
\sum_A Q^M(A) = 2\mu \hspace{1cm} (2.68)
\]
2.8.5 Dipole Moment

The total dipole moment \( \vec{\mu}_i \) of a molecule is the vectorial sum of two components, one due to the net charges located at the nuclear positions (\( \vec{\mu}_{ch} \)) and the other due to the charges displaced away from the atomic centers due to atomic orbital hybridization (\( \vec{\mu}_{hyb} \)). Thus

\[
\vec{\mu}_i = \vec{\mu}_{ch} + \vec{\mu}_{hyb}
\]  

(2.74)

where

\[
\vec{\mu}_{hyb} = 2.5416 \sum_A \Delta qA
\]  

(2.75)

Here \( R_A \) is the position vector of a nucleus \( A \) and \( \Delta q_A \) is the net atomic charge at that point. We may write

\[
\Delta q_A = Z_A - P_A
\]

where \( Z_A \) is the core charge of atom \( A \) and \( P_A \) is the total calculated electron density on atom \( A \). The \( x \)-component of the hybridization dipole moment of a molecule, for example, is given by

\[
(\mu_{hyb})_x = - 14674 \sum_A \zeta_A^1 P_{2x} 2P_{x,A}
\]  

(2.76)

where \( \zeta_A \) is the exponent of an orbital centered on atom \( A \). In the above equations, charge and position vector are given in atomic units.

2.9 DESCRIPTION OF MOPAC

MOPAC is a general-purpose semi-empirical molecular orbital package for the study of chemical structures and reactions. The semi-empirical Hamiltonians MNDO, MINDO/3, AM1 and PM3 are used in the electronic of the calculation to obtain molecular orbitals, the heat of forms and its derivative with respect to molecular geometry. Using the results MOPAC calculates the vibrational spectra, thermodynamics molecules, radicals, ions, and polymers. For studying chemical reactions, a transition-state location routine and two transition-optimizing routines are available. For users to get the most out of program, they must understand how the program works, how to enter, how to interpret the results, and what to do when things go wrong.
While MOPAC calls upon many concepts in quantum theory thermodynamics and uses some fairly advanced mathematics, the user need not be familiar with these specialized topics. MOPAC is written with non-theoretician in mind. The input data are kept as simple as possible so users can give their attention to the chemistry involved and concern themselves with quantum and thermodynamic exotica.

The simplest description of how MOPAC works is that the user create a data-file which describes a molecular system and specifies what kind of calculations and output are desired. The user then commands MOPAC to carry out the calculation using the data-file. Finally the extracts of the desired output on the system from the output file is created by MOPAC.

2.10 INTERNAL COORDINATE DEFINITION

For any one atom (i) this consists of an interatomic distance in (Angstroms) from an already-defined atom (j), an interatomic angle in (degrees) between atoms i and j and an already defined k, (k and j must be different atoms), and finally a torsional angle (in degrees) between a i, j, k and an already defined atom 1 (l cannot be the same as k or see also dihedral angle coherency.

Exceptions:
1. Atom 1 has no coordinates at all: this is the origin.
2. Atom 2 must be connected to atom 1 by an interatomic distance only.
3. Atom 3 can be connected to atom 1 or 2, and must make an angle with atom 2 or 1 (thus – 3-2-1 or 3-1-2); no dihedral possible for atom 3. By default, atom 3 is connected to atom.

2.11 VIBRATIONAL ANALYSIS

Analyzing normal coordinates is very tedious. Users are normally familiar with the internal coordinates of the system they are studying the normal coordinates, a very simple analysis is done automatically and users are strongly encouraged to use this analysis first and to look at the normal coordinate eigenvectors.

In the analysis, each pair of bonded atoms is examined to see whether there is a large relative motion between them. By bonded is measured within the Van de Waals' distance. If there is such a motion, indices of the atoms, the relative distance in Angstroms, and percentage radial motion are printed. Radial plus tangential motion adds to 100%, but as there are two orthogonal tangential motions. The theoretical prediction of
vibrational spectra is of practical importance for the known and unknown compounds. The motivation behind this exercise is to make vibrational spectroscopy a more practical tool. However the main disadvantage of vibrational spectroscopy is the lack of direct spectral structure relations. If a method that could predict the vibrational spectra reliability is found, it comparison with the observed spectra would then confirm the identity of a particular product, even that of a new molecule.

However, in general the computation of the vibrational spectrum of the polyatomic molecule is cumbersome and one expects a large overestimation of the calculated wave number.

It is an usual practice to interpret the vibrational spectra of a more complex molecule by transposition of the results of the simpler molecules. It has become an accepted practice to use the tables of "vibrational assignment" for spectra of larger molecule. However to make such assignment for all the bonds in the spectra is risky, owing to the fact that while some of the assignments may be credible, other be higher speculative. Further, the modes assigned to these vibrations are grossly oversimplified in an attempt to describe them as group wave number in localized bond system. the use of the adequate quantum chemical methods and scaling procedure, remarkably reduce the risk in the assignment.

The scale factor is designed to correct the calculated wave number to be compared with the vibrational frequencies found by experiment. The scale factor is a consequence of the deficiency of the theoretical approach and potentially allows vibrational wave number of the useful accuracy to be obtained. Widespread application to molecule of moderate size is then possible. In the present thesis scale factor suggested by Mittal et al. (2003, 2005) is adopted for comparison an then scaled wavelengths are compared with experimental frequencies.

2.12 MECHANISM OF THE FRAME IN THE FORCE CALCULATION

The force calculation uses Cartesian coordinates, and all 3N modes are calculated, where N is the number of atoms in the system. Clearly there will be 5 or 6 "trivial" vibrations, which represent the translations and two or three rotations. If the molecule is exactly a stationary point, then these "vibrations" will have a force constant and frequency of precisely zero. If the force calculation was done correctly, and the molecule was not exactly at a stationary point, the three translations should be exactly zero, but the
rotations would be non-zero. The extent to which the rotations are non-zero is measure of the error in the geometry.

If the distortions are non-zero, the trivial vibrations interact with the low-lying genuine vibrations or rotations.

To prevent this the analytic form of the rotations and vibration is calculated, and arbitrary eigenvalues assigned; these are 500, 600, 700, 800, 900 and 1000 millidynes/angstrom for Tx, Ty, Tz, Rx, Ry and Rz (if present), respectively. The rotations are about the principal axes of inertia for the system, taking into account isotopic mass. The "Force matrix" for these trivial vibrations is determined, and adjusted on to the calculated force matrix. After diagonalization the arbitrate eigenvalues are subtracted off the trivial vibrations, and the result numbers are the 'true' values. Interference with genuine vibrations this avoided.
REFERENCES

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