2.1 Theoretical Methods in Chemistry

Chemistry has long ceased to be purely an experimental science. Theoretical methods are increasingly being employed now to solve more and more chemical problems. Theory holds such a prominent place in modern chemistry that many chemical problems are now first investigated computationally before an experimental study, if at all, is undertaken. The evolution of the subject to this level stems from the development of quantum mechanics in the first half of this century on the one hand and the revolutionary progress achieved in the fields of computer hardware and software in the past few decades on the other. Computational methods can provide reliable answers to even complicated chemical problems at a faster pace and at a lower cost compared to the alternative experimental approach.

Theoretical methods have been used in the present work to investigate the structures and stabilities of some small cyclic molecules. Computational methods have, in general, certain obvious advantages over the alternative experimental approaches to the solution of chemical problems. The foremost advantage is that theoretical studies can be carried out on a chemical species even before it is prepared in the laboratory. Therefore, it is possible to theoretically estimate the strain associated with a molecule which has hitherto not been prepared; the computed strain energy can give helpful information about the feasibility of its preparation. Transition states of reactions, unstable intermediates, excited states and hypothetical structures can all be studied with almost the same ease as the most stable molecules. In addition, the energies of the least stable up to the most stable of a given set of molecules can be obtained without bothering about the physical and chemical
properties and such hindrances which can make experimental studies difficult. Most of the computer programs implementing the theoretical methods can reliably provide a vast mass of information concerning the structure, energetics, etc. as the output of a single calculation, whereas to derive the same information by experimental means one may have to do several sets of experiments. In the present work since strain is quantified as the energy change associated with suitable homodesmic reactions, which conserve bonds of the same kind, the effects of electron correlation tend to cancel out and, therefore, Hartree Fock calculations are more reliable.

There are also drawbacks in the use of theoretical methods. The major drawback is the one concerning the reliability of the theoretical models. Although significant advances have been made in computing standards, in relation to sophistication in computer hardware, exact or near exact studies on the molecules considered in the present study are still not possible. All the same, most of the computational procedures available have been tested thoroughly for a variety of chemical problems. Some of these methods have been shown to make errors which are relatively systematic in nature. Such methods can also be valuable, provided they are used with appropriate calibration on known systems. Two general procedures have been employed in the present study. The first methodology is molecular mechanics which is empirical in nature. The second is the so-called ab initio procedure in which a well defined form of a trial wave function is variationally optimised, without recourse to empirical parameterisation. Both theories have their merits and demerits for application to chemical problems. These two methods have been employed in the present work and are discussed in the following sections.

2.2 Molecular Mechanics

The molecular mechanics method affords a quick way of computing the structures, energies and certain other properties of molecules. The method essentially treats a molecule as a collection of atoms held together by binding forces that vary with the relative arrangement of the atoms comprising the system. The steric energy is written as the sum of several potential energy terms for distortion from ideal geometrical parameters. The extent of strain due to the stretching of a bond is computed using expressions such as Hooke's law used in classical mechanics.
to obtain the change in potential energy of a macroscopic system such as a spring when it is stretched or compressed. Molecular mechanics, in its original form, can be considered to be completely a non-quantum mechanical method and it doesn't explicitly take into account electronic interactions.

The model nature of this computational method is particularly noteworthy. In molecular modeling one tries to predict the nature of large and more complex molecules using experimental data available on simple molecules. This kind of an approach to describe molecules was first proposed by Westheimer, and hence the method is also known as the Westheimer method. It is also referred to as a force field method since it considers chemical species as a collection of atoms held together by elastic or harmonic forces. The method is applicable to the ground states of most organic and some organometallic molecules.

2.2.1 The 'Force Field'

The steric energy, $E$, of a molecule can be expressed as a sum of energy contributions as follows:

$$E = E_s + E_b + E_\omega + E_nb + \cdots$$

(2.1)

The steric energy is the difference in energy between the real molecule and a hypothetical molecule where all the structural features like bond lengths, bond angles, etc., are exactly at their ideal or "natural" values. $E_s$ is the energy of a bond being stretched or compressed from its natural bond length, $E_b$ is the energy of bending bond angles from their natural values, $E_\omega$ is the torsional energy due to twisting about bonds and $E_nb$ is the energy of nonbonded interactions. If there are other intramolecular mechanisms affecting the energy, such as electrostatic (coulombic) repulsions or hydrogen bonding, these too may be added to the force field. Generally speaking, there are no strict rules governing how many or what types of potential energy functions should be used and, because of this, many different molecular mechanics force fields have been developed.

It is important to recognise that $E$ is only a measure of intramolecular strain relative to a hypothetical situation. By itself $E$ has no physical significance. In
addition, the component terms in equation 2.1 will change depending on their functional form and choice of parameters. The sum of components is what matters. Thus, difference in E for different geometries of the same molecule are appropriate for comparison to experimentally observable physical properties, such as rotational barriers or conformer populations.

Molecular Mechanics is an attempt to formulate a recipe as reliable as possible for reproducing the potential energy surface for the movement of atoms within a molecule. The basic philosophy of the method rests on the fact that the force field is a computational model for describing the potential surface for all internal degrees of freedom in a molecule. Strictly speaking, each molecule has its own unique force field. Fortunately, however, the interpolation, or sometimes extrapolation, of existing data is usually adequate. The parameterisation of the force field relies heavily on experimental data collected over the years, and judicious choice must be made in sorting out good and bad data because the reliability of the method can be no better than the data used for parameterisation. Force fields have been parameterised, to give excellent geometries, relative conformational energies, heats of formation, crystal packing arrangements, and even transition state structures and reactivities.

The mathematical form of the potential functions which model the contribution to the steric energy due to bond stretching, bending and so on, are described in the following section.

2.2.1a Bond Stretching and Bond Bending Potentials

We know that any compression or stretching of the “natural” alkane carbon-carbon bond length from 1.54Å will lead to an increase in the energy of the system. Similarly any deviations from the “natural” value of a typical alkane C-C-C bond angle, which is between 109° and 114°, will also lead to an increase in energy.

For many molecules, including alkanes, it is entirely reasonable to consider a molecule as a collection of masses held together by springs, and, by applying Hooke’s Law we can calculate how much energy is involved in stretching or bending bond from their natural values.
Where $N$ is the total number of bonds in the molecule, and $M$ is the total number of bond angles in the molecule. The $k^s$ and $k^b$ are stretching and bending force constants selected empirically, the $l_i$ and $\theta_{ij}$ are the actual bond lengths and bond angles. $\theta_{ij}$ represents the angle between bonds $i$ and $j$. Equation 2.2 says that the energy change due to deviations in bond lengths from their ideal (natural) values to their actual values can be taken as a sum over the individual bonds. Likewise, the bending energy is proportional to the square of the deviation of the bond angle from its natural value.

It is important to note some points concerning bending and stretching forces. First, for equal atomic displacements it takes more energy to stretch a bond than it does to bend typically, by a factor of ten. If the molecule is deformed, we would hence expect to find most of the distortion in the bond angles, rather than the bond lengths. This was recognised very early, and the workers who performed force field calculations before computers were available usually held the bond lengths constant and varied other structural features.

Next, Hooke's Law overestimates the energies required to achieve large distortions. For example, if an alkane C-C-C angle is deformed from its normal tetrahedral value towards $90^\circ$ or $180^\circ$, the usual $sp^3$ hybrid atomic orbitals do not overlap well, and the effective force constants are reduced. Equations 2.2 and 2.3 assume constant values for the force constants regardless of how severe the angle is deformed or a bond is stretched. In order to correct Hooke's Law potential, cubic terms are usually added to equations 2.2 and 2.3.

The potential energy term, $E_b$, related to valency angles, $\theta$, takes the form:

\[
E_s = \sum_{i=1}^{N} \frac{k^s_i}{2} (l_i - l_i^0)^2
\]

\[
E_b = \sum_{i<j}^{M} \frac{k^b_{ij}}{2} (\theta_{ij} - \theta_{ij}^0)^2
\] 

(2.2) 

(2.3)
Where \( k_\theta^b \) and \( k_\theta^b' \) are force constants and \( \Delta \Theta = \theta_{ij} - \theta_{ij}^o \), \( \theta_{ij}^o \) being the appropriate strain-free value.

### 2.2.1b Torsional Potential

The third term in equation 2.1 describes the potential energy function that describes the fact that rotation about bond changes the molecular energy. Rotation around a double bond involves bond breaking and bond making (a very high energy process). Hand-held models generally can indicate the difficulty in rotating about double bonds. On the other hand, such models can be quite misleading when it comes to rotation about single bonds. These models predict free rotation around ethane type linkages, whereas in reality it takes, albeit less than for alkenes, some energy to rotate around these bonds.

Internal rotation about bonds is most commonly expressed in terms of "torsional angle" \( \omega \). Synonymous names for \( \omega \) are "dihedral angle" or "twist angle". The barrier to rotation about bonds must be built into the force field. The most common mathematical expression used to describe how the energy of molecule changes with torsional angle \( \omega \) is the Fourier series,

\[
E_\omega = \sum [ \frac{1}{2} V_1 (1 + \cos \omega) + \frac{1}{2} V_2 (1 - \cos 2\omega) + \frac{1}{2} V_3 (1 + \cos 3\omega) + \ldots ]
\]

(2.5)

Here the sum is over all unique sequences of bonded atoms A-B-C-D in the molecule. For most problems in organic chemistry, the series equation 2.5 is truncated at the third term, and \( V_1 \), \( V_2 \) and \( V_3 \) are parameters chosen so that predicted conformations agree well with experiment for some test molecules.

Generally, it takes less energy to distort a dihedral angle from its preferred value (for single bonds) than it does to bend an angle from its normal value. Therefore, a molecular distortion will usually show up to a greater extent in
the torsional energy than in $E_b$ or $E_s$. In fact, in the treatment of very large molecules, such as polypeptides, it is common to hold bond lengths and bond angles fixed and to vary only the dihedral angles that define the backbone and side chain conformations.

### 2.2.1 Nonbonded Interactions

The fourth term in equation 2.1 is the potential energy term relating the pairwise nonbonded interactions of atoms as a function of distance between nuclei. As two atoms approach one another, there is the usual attraction due to London dispersion forces and finally a van der Waals repulsion as the atoms get too close. A couple of the more common potential energy functions that describes this behaviour are the Lennard-Jones potential and the Buckingham potential.

\[
V_{\text{LJ}} = \frac{A}{r^{12}} - \frac{B}{r^6} \quad (2.6)
\]

\[
V_{\text{Buck}} = A' \exp(B'/r) - C/r^6 \quad (2.7)
\]

In most circumstances the Buckingham potential function behaves similarly to the Lennard-Jones equation but at very short interatomic distances the function inverts and goes to $-\infty$, an obvious danger in poorly constructed model structures. Either of these equations or any other representative function can be used; the exact form of the potential function is not too critical. Allinger, for example, uses the Hill equation,

\[
E_{\text{vdw}} = \sum e^* \{ -c_1 (r^*/r)^6 + c_2 \exp[-c_3 (r/r^*)] \} \quad (2.8)
\]

where the $c$'s are universal constants, and $e^*$ and $r^*$ are parameters dependent on the type of atoms involved. By using a two-parameter equation, one maintains a certain amount of simplicity and convenience. The value of $e^*$ is calculated from $(e_Ke_l)^{1/2}$, where $e_k$ is an atomic parameter for atom $k$ and is sometimes referred to loosely as the "hardness" of an atom; $e^*$ characterises the depth of an atomic pair potential well. The $r^*$ parameter is the sum of the van der Waals radii of the interacting...
The "hardness" of an atom is actually related to the steepness of the repulsive segment of the potential well, and this is governed by an interplay of the constants in equation 2.8 and the parameters for a given pair of nonbonded atoms. The sum in equation 2.8 is over all the unique pairs of atoms that are not bonded to each other or to a common third atom. The latter exclusion stems from the interactions being taken care of by $E_b$. Note that a nonbonded potential or 1,4 interactions does not replace the torsional potential term; both are needed to describe a rotational potential adequately.

The second component of the nonbonded potential is the electrostatic term. This is usually calculated using partial charges ($q$) on the atom centres with the energy calculated using Coulomb's law

$$E_{el} = \sum q_i q_j / D r_{ij}$$

(2.9)

with the dielectric constant $D$ taking a value appropriate to a given solvent or made proportional to the distance $r_{ij}$ between the charges. The electrostatic contribution is one of the most controversial in molecular mechanics and will be discussed further as part of the parameterisation procedure.

### 2.2.1d Other Potentials

The potentials outlined above constitute the core of almost all molecular mechanics force fields, and in some cases, the entire energy function. In many situations, however, it is necessary for additional terms to be included.

For systems where hydrogen bonding is vital for stability, e.g., biological molecules, it has been common to include an additional, explicit hydrogen bond energy function to ensure correct geometries. In certain protein force fields this takes the form:

$$E_{hb} = \sum (C_{ij} / r_{ij}^{12}) - (E_{ij} / r_{ij}^{10})$$

(2.10)
Other force fields attempt to simulate hydrogen bonds using just the van der Waals and electrostatic terms without the inclusion of a special attractive potential. This latter method could well be the more valid as, in an attempt to retain optimum hydrogen bonding geometries, the explicit function might give correct configurations at the expense of creating strain elsewhere.

A second problem which can arise is restricting the planarity of isolated unsaturated centres. In such cases refinement can be achieved by distinguishing between the in-plane and out-of-plane bending force constants at $sp^2$-hybridised atoms. This is especially important in describing the structure of molecules like cyclobutanone and cyclobutene, where the ring bond angle is less than $120^\circ$. Without distinguishing the in-plane and out-of-plane deformations, the exocyclic atom (O or H in these examples) would bend sharply out of the plane of the ring in an attempt to achieve natural $120^\circ$ bond angles. The four atoms in this grouping should be kept in a plane; however, the branch atom - e.g., in the case carbonyl groups, the oxygen - can be distorted. If the distortion is measured as the height of the central atom, from the plane formed by the other three atoms, then a simple restraining force can be used to hold the group in its correct geometry.

$$E_{\text{opl}} = \sum k_\chi \chi^2 \quad (2.11)$$

where $k_\chi$ is the force constant and $\chi$ the height above the plane. A modified version of this type of function can also be used as a chirality constraint.

Thus far, all of the potential functions have been concerned with isolated features of molecules. If any structural changes are correlated then, in this type of force field, they must result from a combination of appropriate forces. If only structural and thermodynamic data are required to be reproduced, this form of the force field (the so-called second generation) is adequate. However, to fit, in addition, vibrational frequencies, the coupling between geometric features must be explicitly included in the representation of the molecule.

A third point is that further improvement in molecular mechanics modeling can be obtained by recognising the physical fact that as a bond angle is compressed the two associated bond lengths become longer. One way to account for
this phenomenon is to assign a natural distance between two atoms bonded to a common atom. Thus, geminal interactions contribute to the steric energy through the non-bonded term. A force field of this type is called Urey-Bradley force field.\textsuperscript{411} Another way to handle the phenomenon is to include a "cross term", such as stretch-bend energy in equation 2.12, as an additional term in equation 2.1.

\[ E_{sb} = \sum_{i<j} \frac{k_{ij}}{2} (l_i - l_i^0 + l_j - l_j^0) (\theta_{ij} - \theta_{ij}^0) \]  

(2.12)

Other commonly used cross terms include bend-bend and torsion-bend. The functional forms are as follows:

\textit{bend-bend}

\[ E_{\theta \theta'} = \sum \sum k_{\theta \theta'} (\theta - \theta^0) (\theta' - \theta'^0) \]  

(2.13)

\textit{torsion-bend}

\[ E_{\theta \theta' \omega} = \sum \sum k_{\theta \theta' \omega} (\theta - \theta^0) (\theta' - \theta'^0) \cos \omega \]  

(2.14)

where the k terms are the force constants; \( l, l^0, \theta, \theta^0 \) and \( \omega \) are as before.

A force field including all of the valence, nonbonded and cross terms can be parameterised to give very close agreement with experiment for a large number of properties. Problems may occur, however, when highly polarisable groups or ions are present. In this situation the static charge distribution assumed in the electrostatic term is no longer realistic or adequate and an additional polarisation potential will be required. Also, the van der Waals potential assumed strict pairwise interactions but more complex, many-body terms might also come into play. Attempts to include these effects are still at an experimental stage and no simple representation can be presented.

The final situation to be considered is the presence of delocalised \( \pi \) systems. This does not have any bearing on protein and other biological systems as the \( \pi \) systems are isolated from other unsaturated regions, e.g., aromatic amino-
acids and DNA bases. This allows the use of large twofold barrier constants which will resist deformation out of the plane without interfering with the conformational mobility of other regions of the molecule. For many small, unsaturated molecules, and systems based upon porphyrins, this is not possible, unless one creates a new set of atom types for every instance. Here, some account must be taken of the degree of partial double-bond character and this should be allowed to vary according to structural changes. An elegant way of getting around this problem has been implemented in the MMP2 program. The molecule in question is divided into conjugated segments and a simple SCF scheme is used to calculate bond orders about this fragment. These bond orders allow new bending, stretching and torsional parameters to be calculated which are sensitive to the degree of local $\pi$ character at any given atom. A cosine dependence can also be used for the torsion angles indicating the degree of $p$-orbital overlap. As the structure is optimised the parameters for the $\pi$ system can be recalculated if the geometry changes beyond a certain tolerance.

These refinements can be incorporated on the basis of empirically improving the agreement between calculations and experiment. The exact form of the refinements need not concern us here. However, they do point out an advantage of a molecular mechanics computational model over a hand-held molecular model: the former can be easily improved upon, and the improvements generally have some chemically understandable foundation.

2.2.2 Evaluation of Heats of Formation

From calculations based on equation 2.1, the geometry of a single minimum energy conformation of a molecule and the associated steric energy can be obtained. Such steric energies are raw numbers, but may be used directly to obtain energy differences between stereoisomers and isologous molecules (i.e., isomers differing in connectivity but possessing the same number of different kinds of groups (CH$_3$, CH$_2$, CH, C, etc.)). The energy difference between boat and chair conformations of cyclohexane, the cis and trans isomers of 1,4-dimethylcyclohexane, and ethylcyclopentane and methylcyclohexane provide examples where steric energies are applicable directly. Heats of formation are required for other types of energy comparisons.
The energies calculated by equation 2.1 in principle are appropriate to molecules in a hypothetical motionless state at 0 K. Corrections for the chemical binding energy, the vibrational zero point energy, and the thermal energy of translation, rotation and vibration (as well as errors inherent in the parameterisation) have to be made in order to convert steric energies to heats of formation in the gas phase at 25°C.

Molecular mechanics takes the zero level of energy as corresponding to all bond lengths and bond angles having their customary values 1° and 0°, there being no nonbonded van der Waals interactions or internal rotation interactions. In such a hypothetical state, the molecular binding energy can be approximated as the sum of empirical bond energies. Therefore, the equilibrium electronic energy, $U_{eq}$, of a molecule can be found by combining the molecular-mechanics-calculated equilibrium-geometry energy, called the steric energy, $E_{\text{steric}}$, with bond energies. For a saturated hydrocarbon with formula $C_xH_y$, we have

$$U_{eq} = E_{\text{steric}} - n_{CH}b_{CH} - n_{CC}b_{CC}$$ (2.15)

where $n_{CH}$ and $n_{CC}$ are the numbers of C-H and C-C single bonds in the molecule, $b_{CH}$ and $b_{CC}$ are C-H and C-C bond energies and the zero level of energy corresponds to separated (gas phase) atoms C(g) and H(g). Thus for the following formation reaction:

$$x \text{C(graphite)} + \frac{y}{2} \text{H}_2(g) \rightarrow C_xH_y(g)$$ (2.16)

the change in molar equilibrium electronic energy is

$$E_{\text{steric}} - n_{CH}b_{CH} - n_{CC}b_{CC} - x U_C - \frac{y}{2} U_{H_2}$$

where $U_C$ and $U_{H_2}$ are the molar equilibrium electronic energies of graphite and $H_2(g)$ with respect to the same zero level of energy as above. If we temporarily ignore zero-point vibrational energy, we can take this change in equilibrium electronic energy as equal to the change in standard-state thermodynamic internal energy for the formation reaction at absolute zero:
\[
\Delta U'_{f,0} = E_{\text{steric}} - n_{CH}b_{CH} - n_{CC}b_{CC} - xU_C - y/2U_{H2} \tag{2.17}
\]

For a saturated hydrocarbon (acyclic or cyclic), it is not hard to see that the numbers of C and H atoms are related to the numbers of C-C and C-H bonds by

\[
x = \frac{1}{2} n_{CC} + \frac{1}{4} n_{CH} \quad \text{and} \quad y = n_{CH} \tag{2.18}
\]

At temperature T, the change in translational energy for the above formation reaction is \(\frac{3}{2}RT - y/2(\frac{3}{2}RT)\), and the change in rotational energy is \(\frac{1}{2}RT - y/2RT\). The relation \(\Delta H^0_f = \Delta U^0_f + \Delta(PV)^0 = \Delta U^0_f + \Delta n_g RT\), where \(\Delta n_g\) is the change in number of moles of gas in the formation reaction, gives \(\Delta H^0_f = \Delta U^0_f + (1 - \frac{1}{2})RT\). Combining all these relations and continuing to ignore the contribution from the change in vibrational energy, we have for the standard enthalpy of formation at temperature T.

\[
\Delta H^0_{f,T} = E_{\text{steric}} - n_{CH}b_{CH} - n_{CC}b_{CC} - \left(\frac{1}{2} n_{CC} + \frac{1}{4} n_{CH}\right)U_C - \frac{1}{2}n_{CH}U_{H2} + 4RT - \frac{7}{4}n_{CH}RT \tag{2.19}
\]

\[
\Delta H^0_{f,T} = E_{\text{stere}} - n_{CH}(b_{CH} + \frac{1}{4}U_C + \frac{1}{2}U_{H2} + \frac{7}{4}RT) - n_{CC}(b_{CC} + \frac{1}{2}U_C) + 4RT \tag{2.20}
\]

Defining \(a_{CH} = -(b_{CH} + \frac{1}{4}U_C + \frac{1}{2}U_{H2} + \frac{7}{4}RT)\) and \(a_{CC} = -(b_{CC} + \frac{1}{2}U_C)\), we have

\[
\Delta H^0_{f,T} = E_{\text{stere}} - n_{CH}a_{CH} - n_{CC}a_{CC} + 4RT \tag{2.21}
\]

One uses equation 2.21 to determine \(a_{CH}\) and \(a_{CC}\) by a least-squares fit to 25°C experimental \(\Delta H^0_f\) data for several gas-phase hydrocarbons. (Typically, \(a_{CH} \approx -4.5\) kcal/mol and \(a_{CC} \approx 2.5\) kcal/mol.) Then equation 2.21 can be used to find the gas-phase \(\Delta H^0_{f,298}\) for any saturated hydrocarbon from its steric energy calculated by molecular mechanics. A similar derivation gives an analogous equation for other kinds of compounds. In arriving at equation 2.21, the contributions of vibrational
energy were ignored. It is assumed that these contributions are allowed for when 
\( a_{CH} \) and \( a_{CO} \) are fit to 25°C \( \Delta H_f^0 \) data. If more than one conformation is significantly 
populated at 25°C, one uses \( \Delta H_f^0 = \sum_i x_i \Delta H_f^0 \), where \( x_i \) is the mole fraction of 
conformation \( i \) as calculated using the enthalpy and entropy differences between 
conformations, and where \( \Delta H_f^0 \) is calculated from equation 2.21 for each 
conformation.

2.2.3 Energy Minimisation

In order for consistent and credible calculated results to be obtained, a 
reliable minimisation procedure is necessary. If one has generated a model using 
molecular graphics, based upon standard molecular fragments, or from a Z-matrix 
of typical internal coordinates, the energy obtained from molecular mechanics 
calculation is likely to be high and not representative of the actual structure. To 
obtain more reliable geometries and energies one must attempt to minimise the 
energy of the system. This can be done in two ways: either one can vary the actual 
internal coordinates to find their optimum value, or, as is more common, work in 
Cartesian coordinate space and optimise the atomic positions subject to the 
restraining forces generated by the molecular force field. Since most minimisation 
methods require first, and sometimes second derivatives of the energy the latter 
method is more convenient and the potential functions are easily differentiated.

A second issue which must be addressed is local versus global 
minimisation. Given that there are three degrees of freedom per atom, for a 
molecule of \( N \) atoms there are \( 3N-6 \) variables to be minimised (subtracting those 
due to rotation and translation). A multi-dimensional problem of this nature is 
further complicated by the presence of many local energy troughs on the potential 
ergy surface which are minima in a mathematical sense, these local minima are 
higher in energy than the lowest energy state, or global minimum. This situation 
manifests itself even in the simple potential for a 1,2-di-substituted ethane. The 
gauche (\( \omega = 60^\circ \)) conformation is a stable one; but the molecule’s preference would 
be for the trans (\( \omega = 180^\circ \)) conformation. This almost trivial example highlights 
perhaps one of the most difficult problems in computational chemistry: how does 
one find the global minimum (and how can one be certain that it is, in fact, the 
lowest energy structure).
Many of the minimisation programs currently in use today are based upon the mathematical principles of the Newton-Raphson method. This requires first and second derivative information about the energy surface, but a family of algorithms exist which use different approximations to the second derivative matrix (the Hessian).

An important property of the functions used for force field calculations is that they are continuous and differentiable. From simple calculus we know that the condition for a minimum on a curve, the point \( x^* \), is that the first derivative equals zero, i.e.

\[
f'(x) = 0 \tag{2.22}
\]

Since our starting point is \( x \) and not the minimum \( x^* \), we can write

\[
x^* = x + \delta x \tag{2.23}
\]

where \( \delta x \) represents the changes which \( x \) must undergo to reach the minimum value. The condition for the minimum can therefore be written in terms of \( x \)

\[
f'(x + \delta x) = 0 \tag{2.24}
\]

and expanded as a Taylor series,

\[
f'(x + \delta x) = f'(x) + f''(x)\delta x + f'''(x)\delta x^2 + \cdots \tag{2.25}
\]

which is also set equal to zero. Truncating the Taylor series after the second order term gives,

\[
f'(x) + f''(x)\delta x = 0 \tag{2.26}
\]

Rearranging equation 2.26 gives the expression for the change which must be made to \( x \) to reach the minimum.
\[ \delta x = -f'(x) / f''(x) \]  

which can be substituted back into 2.23 to give

\[ x^* = x - [f'(x) / f''(x)] \]  

This is the simple one dimensional case. When considering molecules, each atom has three degrees of freedom - in \( x, y \) and \( z \) - and the term \( f'(x) \) must be replaced by a \( 3N \times 1 \) matrix \( F \) containing terms \( \delta V / \delta x_i \), the derivatives of the potential energy \( V \) with respect to a change in coordinate \( i \). The corresponding second derivative matrix is constructed using all the cross-derivative terms \( (\delta^2 V / \delta x_i \delta x_j) \) involving each coordinate. Since matrices have replaced the single values in equation 2.28, it is no longer possible to carry out the simple division. Fortunately standard computational procedures exist to derive the inverse of the Hessian matrix and the second term in equation 2.28 can be replaced by \( H^{-1}F \). Here \( H^{-1} \) represents the inverse of the Hessian.

It should be noted that by truncating the Taylor series the assumption is made that the minimum is exactly quadratic in behaviour. For a complex surface this will not hold true far from the minimum but will be a better approximation as it moves closer. This forces the calculation to be carried out in a stepwise, iterative fashion, rather than reaching the minimum first time.

When working with small molecules (<100 atoms) this approach is efficient and will converge after relatively few steps. As the number of atoms is increased, the number of matrix elements in the Hessian goes up rapidly making the calculation much slower. Additional problems with computer memory requirements for the storage of the Hessian may also be a severe limitation. This has necessitated the application of less efficient, but more practical algorithms, usually through an approximation of the Hessian. These include neglecting off-diagonal interactions between atoms (block diagonal Newton-Raphson), and the diagonal Newton-Raphson method which only calculates \( \delta^2 V / \delta x^2 \) values, neglecting correlation between the three degrees of freedom for a given atom.
A much more severe approximation to the Hessian is to consider it as a constant. This produces the steepest descent method which is driven purely by force gradients along the potential surface. If one imagines the energy surface as being rather like a hilly landscape then the most reliable way to find a valley, or energy well, is to follow the gradient downhill. As the gradient method has no information about the local curvature of the energy surface, minimisation by this method slows considerably as the gradient decreases. Close to the bottom of the potential well the energy differences can be rather small, however, the forces acting on the molecule can still be relatively large compared to those obtained by a less approximate method. The principal advantage of the steepest descent method is that it is very efficient when very large forces are present, since poor geometries can be tidied up using this approach prior to further refinement by other methods.

It is possible to exert more control in first derivative methods by including some kind of history of the minimisation path. In pattern search methods the previous step is used to accelerate movement if the gradient is in the same direction as before. If the gradient changes, the pattern is abandoned and a new one set up.

A more elegant improvement to this method is that of conjugate gradient which, like pattern search, uses information from previous steps to modify the move in the next step. Unlike pattern search, it does not abandon the history if the direction changes. In the first step, where the gradient vector is $g_1$, the move is given by:

$$s_1 = -g_1$$  \hspace{1cm} (2.29)

The new direction from this step takes into account the previous gradient and follows the search direction

$$s_k = -g_k + b_k s_{k-1}$$  \hspace{1cm} (2.30)

where $s_{k-1}$ is the search direction from the previous step and $b_k$ is a scaling factor given by
\[ b_k = g_{i+1} \cdot g_{i+1} / g \cdot g_i \] (2.31)

The effect of the second term in equation 2.30 is to release the constraint that the \( i+1 \)th gradient should be orthogonal to the \( i \)th gradient. Hence, better search directions are usually obtained by this method than by steepest descents and it has much better convergence properties.

In addition to its speed and memory requirements, the conjugate gradients method has the additional advantage that it is unlikely to maximise rather than minimise. This is one of the shortcomings of the Newton-Raphson family of methods, which use only derivative information to search for stationary points: this could be either a maximum or a minimum. If a maximum on the energy surface is close to the starting point it is likely that it will be found, and a transition state structure will be obtained rather than a stable ground state.

The choice of the minimiser should be tempered by the state of the starting structure: if it is a model, far from a minimum, then a method such as steepest descents should be applied. Once a low energy has been obtained it is advisable to switch to a method with better convergence properties - some variant of the Newton-Raphson method or conjugate gradients - which will have greater success in actually finding the minimum. Applying Newton-Raphson methods to poor structures could lead to catastrophic results, including maximised structures.

2.2.4 Force Field Parameterisation

It is obvious that the quality of a given force field depends crucially on the parameters which are derived as constants in the potential function. Just as a given application can dictate which functional form is the most appropriate, the parameterisation procedure must include this data when developing force constants and equilibrium values, in order to be valid. This can be both a strength and weakness of the force field method; the predictive ability of the method cannot easily extend beyond certain predetermined bounds, while within these limits the results can be very good indeed.
When discussing the different terms incorporated into the energy function, force fields were referred to as second or third generation. This reflects both the functional form of the potential equation and the scope of the data used in the fitting procedure. Available computer power must be considered as a vital factor in this historical division; obviously some kind of balance must be met between accuracy of calculation and time taken. Another consideration is the types of application of the force field. In the 1970s the principal interest was structure, which can be quite well described by the simple potential forms. More recently, interest restricted to the minima on the energy surface and this requires better defined descriptions between the extrema. Only by using complex energy functions which incorporate correlation between internal coordinates has this improvement been achieved.

A parameterisation can be approached from two directions. One can attempt to automate the procedure and use least-squares optimisation methods to obtain a simultaneous best fit of calculated results to experimental data. Like all multi-dimensional problems, local minimisation is a hazard leading to mathematical solutions which have little physical significance. Optimisation in this way must be closely watched to avoid excessive bias towards some parameters at the expense of others.

Alternatively, a trial and error procedure can be used. Here the user makes small changes to the parameters in an attempt to achieve the best possible fit. One advantage of this constant intervention is that a greater feel is obtained for the inter-relationships between parameters. In combination with a limited least-squares optimisation better results should be possible than by the completely automated method.

As stated earlier, the data to be fitted should reflect the kind of applications for which the program will be used. For small molecules the most reliable source of data on geometries is gas phase structural studies, usually microwave or electron diffraction. The use of solution phase or crystal geometries is to be avoided as the influence of the environment is an unknown factor. Spectroscopic data can also provide information on rotational barriers and vibrational frequencies. Thermodynamic data such as heats of formation can also be
included, but group contributions to $\Delta H_f$ must also be derived. Data from ab initio (discussed in the next section) molecular orbital calculations can also provide target values if few experimental data are available. More recently, the latter method has been extended. Ab initio molecular energy surfaces are calculated for typical molecules using basis sets of reliable quality. Rather than using equilibrium geometries, these surfaces and their first and second derivatives have been evaluated for a collection of geometries distorted along the normal modes of vibration. These surfaces now describe not just minimum energy positions but give a more accurate representation of the complete potential energy surface. By fitting a potential function and its derivatives to this kind of data one can be sure that energies of non-minimum energy structures are considered as 'real' behaviour. The obvious limitation of this approach is that the surface is only as good as the ab initio calculations used in its derivation, but with enough computer time this ceases to be a problem. The main problem remaining is that the attractive part of a van der Waals function is not amenable to calculations at the Hartree-Fock level.

The next issue is the origin of the starting values for each of the parameters. The important thing which must be remembered is that the resultant geometries come from the total interactions of the force field and not simply the force constant and equilibrium values for a given internal coordinate. This has the serious disadvantage that it is not strictly correct to place physical significance on the components of a force field generated data as the equilibrium values ($l^\circ$, $\theta^\circ$ etc.) become additional variable parameters.

A reasonable starting point for the bond-stretch and angle-bend force constants would be a consensus value from all those that are available in the spectroscopic literature; standard equilibrium values for bond lengths and angles must also be taken. For dihedral angles it should be remembered that there is an additional contribution from the nonbonded energy terms to the rotational potential. This must be subtracted before fitting $V_n$ values.

Finding suitable values for van der Waals parameters presents one of the greatest problems in force field development. Although the close-packed geometry of crystal would appear to provide details about interatomic distances, a simple deconvolution into atomic contributions is not easy; the close approach of hydrogen
in an alkane crystal is mediated not just by H·H interactions but by C·C and C·H pairs. The resultant intermolecular arrangement is a balance over all the interactions at short range. Using heat of sublimation data, however, the crystal energetics can be calculated as a test of the parameters. Typically, however, the van der Waals radii are used as 'soft' parameters, that is to say, the exact values have less influence upon the final geometry than the high force constant bond-stretch and angle-bend terms. Therefore, these parameters can be used to fine-tune the potential.

The electrostatic interaction is unusual in that the charge density will be different for a given atom type across a range of compounds. One must either assign generic values to an atom type and make the assumption that an atom's contribution to the overall electrostatic energy is modulated by the other charges, or one can be consistent as to which method is used to calculate starting charges in the parameterisation. Only charges calculated by this method will be compatible with the given force-field.

Unless dealing with near ionic systems, the charges on a molecule will have less influence on the final geometry (since the electrostatic force falls off as \( r^{-2} \)) than on the energy of a system. This allows one to think in terms of molecular charge distributions rather than absolute values. In some applications (free energy calculations, molecular similarity) vast improvements have been found when using better quality charge distributions.

The charges themselves can be calculated by a number of methods. Empirical charge schemes, which have usually been parameterised to give close agreement with experimental dipole moment values, provide a fast way of generating charges. These are certainly suitable for structural calculations of large systems. Some force fields have been parameterised using charges obtained from molecular electrostatic potentials and this procedure should be followed when applying the program to unknown molecules. Although there can be a tendency to use 'the best possible charges' one must always bear in mind how crucial the absolute value will be to the application. There is little point in wasting computer time on expensive ab initio calculations when all one wishes to do is tidy up the stereochemistry of a model structure!
Strain energies are obtained by calculating the difference in energy between the molecule and that of a strain free molecule of the same constitution. The heat of formation for the strain free molecule can be calculated from strain-free group increments. There are a few factors to be considered when one chooses strain-free group increments. The \(-\text{CH}_2\) group increments obtained as discussed above, though at first sight seems to be strain free, are not perfectly strain free since they are derived from acyclic alkanes which are not entirely strain free. This is because the acyclic alkanes are conformationally flexible and hence the experimental heat of formation refers to an equilibrium mixture of a Boltzmann distribution of the various rotamers. The proportion of the higher energy conformations can be easily obtained and the experimental heats of formation corrected to the strain-free values. If such heats of formation are used to derive group increments, a more realistic strain free model is obtained.

Molecular mechanics methods are different from quantum mechanical approaches since the electrons in the system are not considered explicitly. But there are some notable exceptions. It was found useful to associate a steric volume to the lone pairs of oxygen in ethers and the lone pair of nitrogen in amines. In effect, a spherical pseudo atom is created at a position in space occupied by the lone pair and a van der Waals radius is associated with it. For other heteroatoms and for nitrogen and oxygen in other bonding situations it has proved unnecessary to do this.

Another case where electronic effects might be important is in molecules with highly polar groups. There are various ways of treating the interaction of these groups. One approach would be to associate bond dipoles with all polar groups such as between carbon and a heteroatom. Then the energy of interaction between the two carbonyls, for instance, can be evaluated as a dipole-dipole term.

2.2.5 Drawbacks of the method

A major drawback regarding molecular mechanics is that many molecules of interest to chemist are outside the range of molecules for which the molecular mechanics programs are currently parameterised. On the other hand, there are still a wealth of molecules which can be readily treated.
Another pitfall which should be obvious is that molecular mechanics is not appropriate for studying properties where electronic effects (e.g., orbital interactions, bond breaking, etc.) are predominant. In these situations, a quantum mechanical approach is better.

Yet another drawback is that the user of molecular mechanics must guard against overinterpreting his results. One single component of the steric energy $E$ in an molecule cannot be calculated in the absence of the other potentials. Thus, the values of the individual terms, such as stretching, torsion etc., have no absolute meaning. The components must be added together to produce $E$. It is important that the force field be reasonably balanced, i.e., no one component is so unrealistic that the other components must compensate for it in order to yield the net result in agreement with experiment.

Since empirical methods such as molecular mechanics suffer from drawbacks such as the ones mentioned above an obvious alternative is to employ methods based on quantum mechanics. The present work makes use of ab initio molecular orbital theory and is discussed in the ensuing section.

2.3 Ab Initio Molecular Orbital theory

The term ab initio molecular orbital theory implies a rigorous, nonparameterised molecular orbital treatment derived from first principles. However, the method is by no means exact; it is ab initio in the sense that it avoids any appeal to experiment, except for the values of certain fundamental physical constants. There are a number of simplifying assumptions in ab initio theory; but the calculations are more complete, and naturally, more expensive.

The Schrödinger equation lies at the heart of much of modern science. In its barest form it states:

$$\hat{H} \Psi = E \Psi$$

(2.32)
Here $\mathcal{H}$ is the Hamiltonian of the system, $\Psi$ is the wave function, which depends on the spatial coordinates and also on the spin coordinates, and $E$ is the energy of the system.

The energy of a stationary state of a molecule can be obtained by solution of this partial differential equation, which is widely referred to as the time-independent Schrödinger equation. In the case of the simplest systems like the hydrogen atom with a single electron outside a positively charged nucleus, the equation may be solved exactly provided the wave function, $\Psi$, obeys a set of reasonable restrictions on its behaviour.

Since the exact solution of the Schrödinger equation is not possible except for the simplest systems, various approximations are made. The first major step in simplifying the general molecular problem 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 much more slowly. As a consequence, the electrons in a molecule adjust their distribution to changing 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. Hence the molecular wavefunction is expressed as a product of a nuclear wavefunction and an electronic wavefunction which depends on the nuclear coordinates parametrically. This separation of the general problem into two parts is frequently called the adiabatic or Born-Oppenheimer approximation.

\[
\Psi_{\text{total}}(R,r) = \Psi_{\text{nuclear}}(R) \cdot \Psi_{\text{elec}}(R,r)
\]

Here, $R$ and $r$ denote the nuclear and electronic coordinates respectively.

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 a subsequent study of the nuclear motion. $E_{\text{eff}}(R)$ will depend on all of the relative nuclear coordinates. For a diatomic molecule, only the internuclear distance is required and $E_{\text{eff}}(R)$ is the potential curve for the
molecule. For a polyatomic system, more relative coordinates are needed, and $C_{\text{eff}}(R)$ is termed the potential surface for the molecule.

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

$$\mathcal{H}_{\text{elec}} \Psi_{\text{elec}}(R,r) = E_{\text{eff}}(R) \Psi_{\text{elec}}(R,r) \quad (2.34)$$

The electronic Hamiltonian, $\mathcal{H}_{\text{elec}}$, corresponds to motion of electrons only in the field of fixed nuclei and is the sum of the electronic kinetic energy operator, $T_{\text{elec}}$, and the coulomb potential energy operator, $V$.

A molecular orbital, $\psi(x, y, z)$, is a function of the Cartesian coordinates $x, y, z$ of a single electron. Its square, $\psi^2$ (or absolute square, $|\psi|^2$, if $\psi$ is complex), is interpreted as the probability distribution of the electron in space. To describe the distribution of an electron completely, the dependence on the spin coordinates, $x$, also has to included. The complete wavefunction for a single electron is therefore the product of a molecular orbital and a spin function, $\psi(x, y, z)\alpha(\xi)$ or $\psi(x, y, z)\beta(\xi)$. It is termed a spin orbital, $\chi(x, y, z, \xi)$.

It might appear that the simplest type of wavefunction appropriate for the description of an n-electron system would be in the form of a product of spin orbitals,

$$\Psi_{\text{product}} = \chi_1(1) \chi_2(2) \cdots \chi_n(n) \quad (2.35)$$

where $\chi_i(i)$, is written for $\chi_i(x_i, y_i, z_i, \xi_i)$, the spin orbital of electron $i$. However, such a wavefunction is not acceptable, as it does not have the property of antisymmetry. To ensure antisymmetry, the spin orbitals may be arranged in a determinantal wavefunction.

$$\Psi_{\text{determinant}} = \sum_{\pi} (-1)^\pi \mathcal{D} \left[ \chi_1(1) \chi_2(2) \cdots \chi_n(n) \right] \quad (2.36)$$
where $\mathcal{P}$ is the permutation operator, changing the coordinates $1, 2, \cdots, n$ according to any of the $n!$ possible permutations among the $n$ electrons and $P$ is the signature of the permutation. $(-1)^P$ is $+1$ or $-1$ for even and odd permutations, respectively. The wavefunction (2.36) is sometimes called an antisymmetrised product function.

Some further properties of molecular orbital wavefunctions are worth noting. It is possible to force the orbitals to be orthogonal to each other, that is,

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

(2.37)

Molecular orbitals may be normalised, that is,

$$S_{ii} = \int \psi_i^* \psi_i \, dx \, dy \, dz = 1,$$

(2.38)

by multiplication of the individual $\psi_i$ by a constant. Normalisation corresponds to the requirement that the probability of finding the electron anywhere in space is unity. Given equation (2.38), the determinantal wavefunction (2.36) may be normalised by multiplication by a factor of $(n!)^{-\frac{1}{2}}$.

With these features we can write down a full many-electron molecular orbital wavefunction for the closed-shell ground state of a molecule with $n$ (even) electrons, doubly occupying $n/2$ orbitals.

$$\Psi_{\text{determinant}} = (n!)^{-\frac{1}{2}} \sum_{\mathcal{P}} (-1)^P \mathcal{P} [ \chi_1(1) \chi_2(2) \cdots \chi_n(n)]$$

(2.39)

The determinant (2.39) is often referred to as Slater determinant.\(^{47}\)

In practical applications of the theory, a further restriction is imposed, requiring that the individual molecular orbitals 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:
where $c_{\mu i}$ are the molecular orbital expansion coefficients.

The application of the variational condition with the LCAO-MO approximation leads to a set of algebraic equations for the MO coefficients, which in matrix form may be written as:

$$ F C = S C C $$  \hspace{1cm} (2.41)$$

where $F$ is the Fock matrix and $S$ is the overlap matrix. The elements of the Fock matrix and the overlap matrix are given by:

$$ F_{\mu \nu} = \mathcal{H}_{\mu \nu}^{\text{core}} + \sum_{\lambda=1}^{N} \sum_{\sigma=1}^{N} \rho_{\lambda \sigma} \left[ (\mu \nu | \lambda \sigma) - \frac{1}{2} (\mu \lambda | \nu \sigma) \right] $$  \hspace{1cm} (2.42)$$

$$ S_{\mu \nu} = \int \phi_\mu^*(1) \phi_\nu(1) \, dx_1 \, dy_1 \, dz_1 $$  \hspace{1cm} (2.43)$$

In the above equations, the elements of the core Hamiltonian and the density matrices, as well as the typical electron repulsion integral are as shown below:

$$ \mathcal{H}_{\mu \nu}^{\text{core}} = \int \phi_\mu^*(1) \mathcal{H}_\nu^{\text{core}}(1) \phi_\nu(1) \, dx_1 \, dy_1 \, dz_1 $$  \hspace{1cm} (2.44)$$

$$ \mathcal{H}_\nu^{\text{core}}(1) = -\frac{1}{2} \nabla^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} $$  \hspace{1cm} (2.45)$$
Equation 2.44 gives a matrix representing the energy of a single electron in a field of “bare” nuclei. Here $Z_A$ is the atomic number of atom A, and summation is carried out over all atoms. The quantities $\langle \mu \nu | \lambda \sigma \rangle$ appearing in 2.42 are two-electron repulsion integrals:

$$(\mu \nu | \lambda \sigma) = \int \int \phi^*_\mu(1) \phi^*(1) \left( \frac{1}{r_{12}} \right) \phi^*_\lambda(2) \phi^*(2) \, dx_1 \, dy_1 \, dz_1 \, dx_2 \, dy_2 \, dz_2$$  \hspace{1cm} (2.46)$$

They are multiplied by the elements of the one-electron density matrix given by:

$$P_{\lambda \sigma} = 2 \sum_{i=1}^{\text{occ}} c_{\lambda i}^* c_{\sigma i}$$  \hspace{1cm} (2.47)$$

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

The above equations were derived independently for closed-shell systems by Roothaan and Hall and are called Roothaan-Hall equations.

The electronic energy, $E_{ee}$, is now given by:

$$E_{ee} = \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} P_{\mu \nu} \left( F_{\mu \nu} + \mathcal{E}_{\mu \nu}^{\text{core}} \right)$$  \hspace{1cm} (2.48)$$

which when added to equation 2.49, accounting for the internuclear repulsion, yields an expression for the total energy.

$$E_{nr} = \sum_{A < B}^{M} \frac{Z_A \, Z_B}{R_{AB}}$$  \hspace{1cm} (2.49)$$
(where $Z_A$ and $Z_B$ are the atomic numbers of atoms A and B, and $R_{AB}$ is their separation)

The Roothaan-Hall Equations 2.41 are not linear since the Fock matrix $F_{\mu\nu}$ itself depends on the molecular orbital coefficients, $c_{\mu i}$ through the density matrix expression 2.47. Solution necessarily involves an iterative process. Since the resulting molecular orbitals are derived from their own effective potential, the technique is frequently called self-consistent-field (SCF) theory.

A typical energy calculation begins with the specification of molecular geometry and the basis set employed. The necessary one- and two-electron integrals (equations 2.44 and 2.46) are evaluated in a well defined order and stored. An initial guess of the MO coefficients or the density matrix elements is made (either by diagonalising the core Hamiltonian or from an extended Hückel calculation on the molecule). The iterative solution of the molecular orbital coefficients, associated orbital energies and the total energy is begun. The process is carried out till a self consistent solution is obtained.

The theoretical model described so far is generally referred to as the ab initio molecular orbital theory. Since the method is based on optimising a relatively inflexible trial wavefunction, viz., a single determinant, it necessarily involves an error, known as the correlation energy. It is, in principle, possible to systematically obtain the correlation energy, e.g., by including additional determinants via a Configuration Interaction (CI) procedure or by appealing to Perturbation Theory.

In addition to the electron correlation energy, there is another source of error in the single determinant theory. The Hartree-Fock limit can be reached only when the molecular orbitals are expanded over a complete set of basis functions. Typically, a small number of atom centered functions are chosen. As a result, the quality of ab initio calculations is heavily dependent on the choice of the basis set. This point is discussed in the next section.
2.3.1 Basis Set

A many-electron wavefunction is constructed from molecular orbitals in the form of a single determinant. In practical applications of theory, a further restriction is imposed, requiring that a further restriction is imposed, requiring that the individual molecular orbitals 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

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

(2.50)

where \( c_{\mu i} \) are the molecular orbital expansion coefficients. These coefficients provide the orbital description with some flexibility.

In selecting a suitable set of basis functions, several factors have to be considered. It is preferable to choose functions that resemble atomic orbitals as much as possible. The final wavefunction and the associated bonding should be easily interpretable. The integrals involved in the \textit{ab initio} calculations should be readily computable. The resultant computational problem should be easily solvable and the expansions should converge relatively rapidly.

To provide a basis set that is well defined for any nuclear configuration and therefore useful for a theoretical model, it is convenient to define a particular set of basis functions associated with each nucleus, depending only on that nucleus. Such functions may have the 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 basis functions have received wide-spread use. \textit{Slater-type atomic orbitals} (STOs) have exponential radial parts. The second type of basis consists of \textit{gaussian-type atomic functions}. These are powers of \( x, y, z \) multiplied by \( \exp(-\alpha r^2) \), \( \alpha \) being a constant determining the size, that is, radial extent, of the function.
In selecting a set of basis functions $\phi_\mu$, the size of the expansion and the nature of the functions $\phi_\mu$ need to be considered. A limiting Hartree-Fock treatment would involve an infinite set of basis functions $f_m$. This is clearly impractical since the computational expense of Hartree-Fock molecular orbital calculations is formally proportional to the fourth power of the total number of basis functions.

For computational facility, it is desirable to use gaussian basis functions. These may be chosen as single (uncontracted or primitive) gaussian functions or as fixed, predefined linear combinations of such functions, termed contracted.

The simplest level of ab initio molecular orbital theory involves the use of a minimal basis set of nuclear-centered functions. Such representations comprises exactly that number of functions required to accommodate all of the electrons of the atom, while maintaining overall spherical symmetry. The series of minimal basis sets termed STO-KG consists of expansion of STOs in terms of K gaussian functions.

While absolute energies of atoms and molecules calculated using STO-KG minimal basis set exhibit strong dependence on the value of K, other properties such as energy differences, optimum geometries, charge distributions and electric dipole moments, are far less sensitive to the size of the expansion.

Minimal basis sets, such as STO-3G, have several inadequacies. The number of atomic basis functions is not apportioned according to electron count. 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. This is because a minimal basis set contains only a single valence function of each particular symmetry type. Thus in the absence of radial exponent optimisation for each atom in a molecule, there is no mechanism for the individual sets of functions to adjust their sizes. Finally, minimal representations lack the ability to describe adequately the nonspherical anisotropic aspects of molecular charge distributions.

In principle, the first two deficiencies may be alleviated simply by allowing for more than a single valence function of each symmetry type in the basis set description. The allocation of two or more valence basis functions of each given
symmetry type would provide the needed flexibility for overall radial 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 two ways.
The conceptually simpler way would be to allow each of \( x \), \( y \), 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.\(^{52}\)

A more reasonable way to surmount the difficulties inherent in an
isotropic minimal basis set is to include more than a single set of valence \( p \)- and/or
\( d \)-type function. The allocation of two sets of isotropic valence functions in the basis,
one more tightly held to the nucleus than the other, permits independent adjustment
through the SCF procedure of the individual radial components between contracted
and diffuse extremes.

A basis set formed by doubling all functions of a minimal representation
is usually termed a \textit{double-zeta basis}. An even simpler extension of a minimal basis
set is to double only the number of basis functions representing the valence region.
While the inner-shell electrons are important with regard to the total energy, their
effect on molecular bonding is of little consequence.

\textit{Split-valence basis sets}\(^{53}\) like the 6-21G and 3-21G typify representations 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
primitives. The contracted and diffuse basis functions representing valence-shell
orbitals are written with expansion lengths chosen as 2 and 1.

\textit{Larger split-valence representations} like the 4-31G\(^{54}\) and 6-31G\(^{55}\) basis set
comprises inner-shell functions, each written in terms of a linear combination of four
and six gaussians, respectively, and two valence shells represented by three and one
gaussian primitives, respectively.
Polarisation basis sets\(^5^6\) like 6-31G* and 6-31G** are 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 polarisation 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 and helium atom.

The 6-31G* polarisation basis set does perform satisfactorily in the description of the equilibrium structures, relative energies and normal vibrational frequencies of molecules incorporating second-row elements, both normal and hypervalent species alike\(^{20c}\). Therefore 6-31G* basis set were used throughout the \textit{ab initio} calculations for the present investigation.

2.3.2 Electron Correlation Methods

Because Hartree-Fock procedures do not adequately account for the correlation of electron motion, the next step is the replacement of Hartree-Fock methods by a more elaborate model using a multiple determinant wavefunction. This is quite distinct from improvements in the basis set. However, it is important to recognise that the use of a small basis set may limit the fraction of the total correlation energy obtainable even with elaborate multiple-determinant techniques\(^{5^7}\).

As with basis set selection, choice of the electron correlation method may ultimately be governed primarily by practical considerations. The technique should, however, satisfy the general requirements. In particular, the model should be well defined and size consistent, so that application to an assembly of isolated molecules will give additive results. The latter requirement is particularly important if comparisons are to be made among molecules of different size. The two techniques that have been widely used are limited configuration interaction and Møller-Plesset perturbation theory. The first is variational but not size consistent, while the second is size consistent but not variational. In the following section some remarks are
made on the practical aspects of the Møller-Plesset method that are of concern to the overall choice of theoretical model.

2.3.2a Møller-Plesset Perturbation Treatments

The most economical general correlation methods are based on the perturbation theory of Møller and Plesset.\textsuperscript{58} These methods treat the complete Hamiltonian as the sum of two parts, the non-Hartree-Fock part being treated as perturbation on the Hartree-Fock part using Rayleigh-Schrödinger theory. The energy expression may be terminated at any desired order, although practical programs are presently limited to the fourth order. These energies have the property of size consistency, but do not represent rigorous upper bounds to the true energy. The complexity and cost of computing the energy terms in this expansion increase rapidly with the order.

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

2.4 Computational Details

All molecular mechanics calculations were carried out with the MMX force field developed by N. L. Allinger from his MM2 force field.\textsuperscript{43} Full geometry optimisation was carried out in each case without imposing any symmetry constraint. These calculations were done using the package PCMODEL\textsuperscript{59} developed by Serena software.

The ab initio calculations were done using the MICROMOL,\textsuperscript{60} GAMESS\textsuperscript{61} and GAUSSIAN 94\textsuperscript{62} programs. Full geometry optimisation was carried out at HF/6-31G* level in each case under the indicated symmetry constraints. Single point calculations on the HF/6-31G* optimised structures were carried out to get MP2/6-31G* energies. The calculations were done on an IBM PC/486 and IBM RS/6000 workstations.