CHAPTER 2

Methodology

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Methodology:
For polyatomic molecules, the presence of several nuclei makes quantum mechanical calculations harder than for diatomic molecules. Moreover the electronic wave function of a diatomic molecule is a function of only one parameter, the internuclear distance. In contrast, the electronic wave function of a polyatomic molecule depends on several parameters - bond distances, bond angles, and dihedral angles of rotation about single bonds (these angles define the molecular conformation). A full theoretical treatment of a polyatomic molecule involves calculation of the electronic wave function for a range of each of these parameters. The equilibrium bond distances and angles are then found as those values that minimize the electronic energy including nuclear repulsions.

The four main approaches to calculating molecular properties are ab initio methods, semi-empirical methods, the density-functional method, and the molecular-mechanics method.

Semi-empirical and Ab Initio Methods:
The molecular orbitals are formed by the linear combination of basis functions. Most molecular quantum-mechanical methods (such as SCF, CI etc.) begin the calculation with the choice of a basis functions $\chi_r$, which are used to express the MOs $\phi_i$ as $\phi_i = \sum c_{ri} \chi_r$ ($c$ = coefficient of $\chi$, $r$ = number of atomic orbital, $i$ = molecular orbital number). The use of an adequate basis set is an essential requirement for the calculation. The basis functions are usually taken as AOs. Each AO can be represented as a linear combination of one or more Slater-type orbitals (STOs).\(^{(1-3)}\) Each molecular orbital $\phi_i$ is expressed as

$$\phi_i = \sum c_{ri} \chi_r$$

(1)

where, the $\chi_r$ s are the STO basis functions. Here we use the STO-6G basis set (which is contracted Gaussian)\(^{(4-7)}\) for the SCF calculation.

The coefficients in linear combination for each molecular orbital being found by solution of the Roothaan equation.\(^{(8)}\) The most efficient way to solve the Roothaan equation is to use matrix-algebra methods. In matrix-algebra methods, the matrix elements are computed,\(^{(9)}\) and the secular equation is solved to give the set of orbital energies (i.e. eigenvalues). These orbital energies \(^{(10-12)}\) are used to solve Roothaan equations for the set of coefficients (i.e. eigenvectors) giving a set of molecular orbitals. The calculations are done using a computer.
By the above calculation, the values of orbital energies (eigenvalues) and eigenvectors (coefficients) have been calculated.

A widely used method to analyze SCF wave function is population analysis, introduced by Mulliken.\textsuperscript{(13, 14)} He proposed a method that apportions the electrons of an $n$-electron molecule into net populations $n_{i}$ in the basis functions $\chi_{i}$ and overlap populations $n_{i,j}$ for all possible pairs of basis functions.

For the set of basis functions $\chi_{1}, \chi_{2}, \ldots, \chi_{m}$, each molecular orbital $\phi_{i}$ has the form $\phi_{i} = \sum c_{ji} \chi_{j} = c_{i1} \chi_{1} + c_{i2} \chi_{2} + \ldots + c_{im} \chi_{m}$. For simplicity, we shall assume that the $c_{ji}$'s and $\chi_{j}$'s are real. The probability density associated with one electron in $\phi_{i}$ is (s and b are the number of the atomic orbital other than r)

$$| \phi_{i} |^{2} = c_{i1}^{2} \chi_{1}^{2} + c_{i2}^{2} \chi_{2}^{2} + \ldots + 2c_{i1}c_{i2} \chi_{1} \chi_{2} + 2c_{i1}c_{i3} \chi_{1} \chi_{3} + 2c_{i2}c_{i3} \chi_{2} \chi_{3} + \ldots$$

Integrating this equation over three-dimensional space and using the fact that $\phi_{i}$ and the $\chi_{j}$'s are normalized, we get

$$1 = c_{i1}^{2} + c_{i2}^{2} + \ldots + 2c_{i1}c_{i2} S_{12} + 2c_{i1}c_{i3} S_{13} + 2c_{i2}c_{i3} S_{23} + \ldots$$ \hspace{1cm} (2)

Where the $S$'s are overlap integrals: $S_{ij} = \int \chi_{i} \chi_{j} dv_{1} dv_{2}$, etc. Mulliken proposed that the terms in Eq.2 be apportioned as follows. One electron in the molecular orbital $\phi_{i}$ contributes $c_{i1}^{2}$ to the net population in $\chi_{1}$, $c_{i2}^{2}$ to the net population in $\chi_{2}$, etc., and contributes $2c_{i1}c_{i2} S_{12}$ to the overlap population between $\chi_{1}$ and $\chi_{2}$. $2c_{i1}c_{i3} S_{13}$ to the overlap population between $\chi_{1}$ and $\chi_{3}$, etc.

Let there be $n_{i}$ electrons in the molecular orbital $\phi_{i}$ ($n_{i} = 0, 1, 2$) and let $n_{i,j}$ and $n_{i,j,k}$ symbolize the contributions of electrons in the molecular orbital $\phi_{i}$ to the net population in $\chi_{i}$ and to the overlap population between $\chi_{i}$ and $\chi_{k}$, respectively. We have

$$n_{i,j} = n_{i} c_{i,j}^{2}$$ \hspace{1cm} (3)

$$n_{i,j,k} = n_{i} (2c_{i,j}c_{i,k} S_{jk})$$ \hspace{1cm} (4)

Based on the above principle, the contributions of electrons in each occupied molecular orbital has been calculated with the help of eigenvector values. The overlap population analysis has also been made with the help of the values of eigenvector and overlap matrix for distinguishing the bonding, nonbonding and antibonding nature of molecular orbital.

**Density-Functional Theory (DFT):**

In the last decade of the twentieth century, DFT attained great prominence in quantum chemistry research. The enthusiasts of DFT- and there are a host of them-
claim that this theory will be the theory of chemical bonding in the twenty-first century.\(^{15}\)

In DFT we do not calculate the molecular wave function. Instead, we work with electron probability density \(\rho (x, y, z)\). DFT is based on the Hohenberg-Kohn theorem, proposed in 1964 by P. Hohenberg and W. Kohn. This theorem\(^{16}\) states that the energy and all other properties of a ground state molecule are uniquely determined by the ground state electron probability density. This is expressed by saying that the ground state electronic energy \(E_{gs}\) is a functional of \(\rho\). This is written as \(E_{gs} = E_{gs} [\rho (x, y, z)]\) or simply as

\[
E_{gs} = E_{gs} [\rho]
\]  

(5)

Where the square brackets denote a functional relation. (In mathematics a function of a function is called a functional.)

The Kohn-Sham Method:

Unfortunately, the functional \(E_{gs} [\rho]\) in above equation is unknown, so the Hohenberg-Kohn theorem does not tell us how to calculate \(E_{gs}\) from \(\rho\) or how to find \(\rho\) without first finding the ground state molecular electronic function. In 1965, W. Kohn and L. J. Sham devised a practical method to calculate \(E_{gs}\) from \(\rho\).\(^{17}\) Of course, the Kohn-Sham equations do contain an unknown functional, but using a combination of physical insight and guesswork, theorists have developed approximations to this functional that allow accurate calculations of molecular properties thereby turning DFT into a landmark in quantum theory.\(^{18}\)

The Kohn-Sham method uses a fictitious reference system (usually denoted by the subscript \(s\)) that contains the same number of electrons \((n)\) as the molecule understudy, but differs from the molecule in that \((a)\) the electron in the reference system do not exert forces on one another, \((b)\) each electron \(i (i = 1, 2, ..., n)\) in the reference system experiences a potential energy \(V_s (x_i, y_i, z_i)\), where \(V_s\) is the same function for each electron and is such as to make the electron probability density \(\rho_s\) in the reference system exactly equal to the ground state electron probability density \(\rho\) in the real molecule: \(\rho = \rho_s\). The actual form of \(V_s\) is not known. (In the real molecule, the electrons experience attractions to the nuclei but these are not present in the reference system.)
Because the electrons in the reference system do not interact with one another, the Hamiltonian $\hat{H}_s$ of the reference system is the same of the Hamiltonians of the individual electrons:

$$\hat{H}_s^{KS} = -\frac{\hbar^2}{2m_e} \nabla^2 + V_s(x, y, z)$$  \hspace{1cm} (6)

In Eq. 6, $\hat{H}_s^{KS}$ is the one-electron Hamiltonian. Since the reference system $s$ consists of non-interacting particles, its ground state wave function, including both the spatial and spin wave functions, is a Slater determinant of spin-orbitals, one for each electron. Each spin-orbital is the product of a spatial orbital $\theta_i^{KS}$ and a spin function (either $\alpha$ or $\beta$). The Kohn-Sham orbitals $\theta_i^{KS}$ are eigenfunctions of $\hat{H}_i^{KS}$:

$$\hat{H}_i^{KS} \theta_i^{KS} = \varepsilon_i^{KS} \theta_i^{KS}$$  \hspace{1cm} (7)

where $\varepsilon_i^{KS}$ is the Kohn-Sham orbital energy of $\theta_i^{KS}$. Each Kohn-Sham orbital holds two electrons of opposite sign.

By definition,  

$$\rho = \rho_s = \sum_{i=1}^{n} |\theta_i^{KS}|^2$$  \hspace{1cm} (8)

**The Kohn-Sham Energy Expression:**

Next we need the energy expression for the molecule's ground state electronic energy $E_e$. (The reference system and the molecule have the same probability density function but they do not have the same ground-state energy.) Kohn and Sham derived the following exact equation for $E_e$:

$$E_e = \langle K_{e,3} \rangle + \langle V_{Ne} \rangle + J + V_{NN} + E_{\infty} [\rho]$$  \hspace{1cm} (9)

In Eq. 9, $\langle K_{e,3} \rangle$ is the average electronic kinetic energy in the reference system; $\langle V_{Ne} \rangle$ is the average potential energy of attractions between the electrons and nuclei in the molecule; $J$ is the classical energy of electrical repulsion that arises between the infinitesimal charge elements of a hypothetical smeared-out electron charge whose arability density is $\rho (x, y, z)$. $\langle K_{e,3} \rangle$ and $\langle V_{Ne} \rangle$ can be calculated from Kohn-Sham orbitals of the reference system. The internuclear repulsion potential energy, $V_{NN}$, is a constant that depends on the nuclear charges and the internuclear distances and is calculated from the molecular geometry at which the
calculation is being made. $E_{xc} [\rho]$, called the exchange-correlation energy functional, is a functional of $\rho$ that is defined as

$$E_{xc} [\rho] \equiv <K_e> - <K_{es}> + <V_{ee}> - J$$ (10)

$E_{xc} [\rho]$ is the sum of two differences: (a) the difference $<K_e> - <K_{es}>$ between the average electronic kinetic energy in the molecule and in the reference system; and (b) the difference $<V_{ee}> - J$ between the average potential energy of interelectronic repulsion $<V_{ee}>$ in the molecule and the classical charge-cloud self-repulsion energy $J$. The values of $<K_e>$ and $<K_{es}>$ are expected to be similar to each other; also the values of $<V_{ee}>$ and $J$ are similar. Hence, the two differences in Eq. 10 are relatively small quantities. These two differences are not zero because the Pauli exclusion principle requirement that the wave function be antisymmetric with respect to exchange, produces exchange effects on the energy, and because the instantaneous correlation between the motions of the electrons produces correlation effects on the energy.

Eq. 9 is an exact expression for the molecular electronic energy. However the true mathematical expression for the functional $E_{xc}$ is not known. The term $E_{xc} [\rho]$ can be found if we know $\rho$ and if we know that the functional $E_{xc}$ is. If Eq. 10 is substituted into Eq. 9, we obtain

$$E_e = <K_e> + <V_{Ne}> + <V_{ee}> + V_{NN}$$ (11)

an equation that follows from the Born-Oppenheimer approximation, viz., $\hat{H}_e = K_e + V_{Ne} + V_{ee} + V_{NN}$ by taking average values of each side of this approximation.

**DFT Calculational Procedure:**

If we assume that a reasonable approximation for the exchange-correlation energy functional $E_{xc} [\rho]$ exists, then we proceed as follows. We start with an initial guess for the molecule’s electron density $\rho (x, y, z)$ found by superimposing calculated electron densities of the individual atoms at the nuclear geometry chosen for the calculation. From the initial $\rho$, we find $E_{xc} [\rho]$ and then find its functional derivative to obtain an initial estimate of the exchange correlation potential, $V_{xc}$ (i.e. $V_{xc} (x, y, z) = \delta E_{xc} [\rho] / \delta \rho$ where the notation $\delta E_{xc} / \delta \rho$ indicates the functional derivative of the functional $E_{xc}$ that occurs in the energy equation 9. This $V_{xc}$ is used in the Kohn-Sham
equations (Eq. 7) to solve for initial estimates of the orbitals $\theta_i^{KS}$. (As is done in solving the Hartree-Fock equations, we usually expand the unknown orbitals using a basis set. Many of the same basis sets used for the Hartree-Fock calculations are also used in the Kohn-Sham calculations.)\(^{(19,20)}\) The initial orbitals $\theta_i^{KS}$ are used to calculate an improved probability density $\rho$ from Eq. 8. This improved $\rho$ is used to find an improved $E_{xc}[\rho]$ from which an improved $V_{xc}$ is found. The improved $V_{xc}$ is used in the KS equations (Eq. 7) to find improved KS orbitals. The iterations are continued until no further significant change is found from one cycle to the next. The molecular energy is then found from Eq. 9 using the final orbitals and $\rho$.

**Molecular Mechanics Method:**

The *molecular mechanics method* is not a quantum-mechanical method and does not use a molecular Hamiltonian operator or wave function. Instead, it views the molecule as a collection of atoms held together by bonds and express the molecular energy in terms of force constants for bond bending and stretching and other parameters. This method has been well elaborated in each chapter under the caption Methodology.

**Computational Chemistry:**

Thanks to the pioneering contribution of J. A. Pople\(^{(21)}\) and his colleagues\(^{(21-24)}\) whose work in computational quantum chemistry has revolutionized research in theoretical chemistry since the 1960s. Much of the modern computational quantum chemistry uses Gaussian orbitals as a basis set. Pople has developed algorithms for the *ab initio calculation* of molecular properties based on Gaussian orbitals. The computer programs developed by Pople and his many collaborators have been packaged as a commonly available program called GAUSSIAN 94. This program, released in 1994, was developed at Carnegie-Mellon University in the U.S.A. In the *ab initio calculations* (which use the exact Hamiltonian), the task is greatly simplified by expressing the AOs used in the LCAO as linear combinations of Gaussian orbitals. A Gaussian type orbital (GTO) is a function of the form $e^{-\alpha r^2}$. However, in the *semi-empirical calculations*, the AO's have been used as Slater-type orbitals as basis sets. A Slater-type orbital (STO) is a function of the form $e^{-\alpha r}$. (Hydrogenic orbitals as basis sets are not all satisfactory.) We may recall that the set of AOs used to construct LCAO-MOs is called the basis set. In the case of diatomic molecules, the hydrogenic
orbitals from the basis set. For example, the 1s orbitals of the two atoms constitute the basis for the MO $\sigma_\parallel (1s)$. For polyatomic molecules, the first basis set used in large scale computational studies consisted of STOs:

$$S_{nml}(r, \theta, \phi) = N_n r^{l+1} e^{-\xi r} Y_{l,m}(\theta, \phi)$$

(31)

where $N_n$ is the normalization constant defined as

$$N_n = \frac{(2\xi)^{n+1/2}}{[(2n)!]^{1/2}}$$

where $\xi$ is the orbital exponent (zeta), $n$ and $l$ are the principal and orbital momentum (azimuthal) quantum numbers and $Y_{l,m}(\theta, \phi)$ are the angularly dependent spherical harmonics. The STOs differ from the hydrogenic orbitals in that the STOs have no nodes and the orbital exponent is not necessarily equal to $Z/n$. In principle, the orbital exponents should be chosen to minimize the energy but this selection is still a formidable task even with modern computer. Slater has given a set of empirical rules for determining $\xi$ for orbital in free atoms. $\xi$ increases with increasing atomic number, reflecting the contraction of the orbital as the nuclear charge increases.

The STOs are not used directly in modern theoretical research because the integral in the resulting secular determinants are difficult to evaluate. In particular, integrals involving more than one nuclear center, called multilcentre integrals, are awkward to evaluate using STOs. If we use GTOs instead to STOs, however, all the multilcentre integrals are very easy to evaluate. As a matter of fact, the four-center integrals can become two-center integrals which can be easily computed. The use of GTOs was suggested in 1950 by S. F. Boys. The advantage of GTOs is that the product of two Gaussian functions is itself a Gaussian function that lies between the centres of the two contributing functions. The GTOs may be represented by

$$G_{nml}(r, \theta, \phi) = N_n r^{l+1} e^{-\alpha r^2} Y_{l,m}(\theta, \phi)$$

(32)

for the basis set in MO calculations.

The GTO does a reasonably good job of describing the STO for values of $r$ greater than $a_0$ (the Bohr radius) but it underestimates its magnitude for values of $r$ less than $a_0$. These discrepancies turn out to be very significant in molecular calculations. To overcome this difficulty quantum theorists prefer the use of curve fit STOs to sums of Gaussian functions; the curve fit improving with $N$, the number of
Gaussian functions used. If, for instance, \( N = 3 \), i.e., we use a sum of three Gaussian functions to represent one STO; such a basis set is called the \textbf{STO-3G basis set}. In the STO-3G basis set, all AOs are described by a sum of three Gaussian functions. Although this procedure leads to a proliferation of integrals to evaluate, each one is relatively easy. Thus, the overall procedure is quite efficient. However, there are some disadvantages, too, in using GTOs since many GTOs are needed to obtain for atoms the same degree of accuracy as the STOs.

It will be pertinent to define here the so-called \textit{valence state ionization potentials}. Consider the electronic configuration of carbon atom, \( \text{viz., } 1s^2 \chi_1 \chi_2 \chi_3 \text{ 2p}_y^1 \) where \( \chi_i \) (i=1, 2, 3) are the three triply hybridized orbitals in the \( sp^2 \) hybridized state, the hybrids being formed from \( 2s \), \( 2p_x \) and \( 2p_y \) AOs. Here the carbon atom is said to be promoted to a \textit{valence state} obtained through electronic rearrangement prior to the bond formation. This electronic configuration may be considered to be equivalent to the configuration \( 1s^2 \text{ 2s}^1 \text{ 2p}_x^1 \text{ 2p}_y^1 \text{ 2p}_z^1 \). The valence state ionization potential of the \( 2p_z \) orbital in the carbon atom is given by the difference in energy between neutral carbon atoms in the configuration \( 1s^2 \text{ 2s}^1 \text{ 2p}_x^1 \text{ 2p}_y^1 \text{ 2p}_z^1 \). Similarly, the valence state ionization potential of the \( 2s \) orbital in carbon atom is given by the energy difference between the neutral atom configurations \( 1s^2 \text{ 2s}^1 \text{ 2p}_x^1 \text{ 2p}_y^1 \text{ 2p}_z^1 \) and the \( \text{C}^+ \) in the configuration \( 1s^2 \text{ 2p}_x^1 \text{ 2p}_y^1 \text{ 2p}_z^1 \). Typical values of the valence state ionization potentials are \(-13.60\text{ eV}\) (for hydrogen 1s), \(-21.4\text{ eV}\) (for carbon 2s), \(-11.4\text{ eV}\) (for carbon 2p) and \(-26.0\text{ eV}\) (for nitrogen 2s).

A few remarks are in order for three important terms, \textit{viz.,} correlation energy, electron correlation and configuration interaction, which are often involved in both the Hartree-Fock SCF theory of multielectron atoms and Hartree-Fock-Roothaan SCF theory of polyatomic molecules. It may be recalled that for helium atom, the use of a hydrogenic 1s orbital with variable orbital exponent gives a ground state energy of \(-77.5\text{ eV}\), compared with the true value of \(-79.0\text{ eV}\). The Hartree-Fock wave function for the helium ground state gives an energy of \(-77.9\text{ eV}\), which is still in error by 1.1 eV. The energy error of the Hartree-Fock wave function is called the \textbf{correlation energy} since it results from the fact that the Hartree-Fock wave functions neglects the instantaneous correlations in the motions of electrons. Electrons repel one another and correlate their motions to avoid being close together; this phenomenon is called \textbf{electron correlation}. 

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Let us now consider configuration interaction. A method used to improve the Hartree-Fock wave function is configuration interaction. When a Hartree-Fock ground state wave function of an atom or a molecule is calculated, one also obtains expressions for unoccupied excited state orbitals. It is possible to show that the set of functions obtained by making all possible assignments of electrons to the available orbitals is a complete set. Hence, the true wave function of the ground state can be expressed as

$$\psi = \sum_j c_j \psi_{\text{orb},j}$$  \hspace{1cm} (33)

where the $\psi_{\text{orb},j}$s are approximate orbital functions that differ in the assignments of electrons to orbitals. Each $\psi_{\text{orb},j}$ is a Slater determinant of spin orbitals. The functions $\psi_{\text{orb},j}$ are called configuration functions (or configurations). One uses a variation procedure to find the values of the coefficients $c_j$ that minimize the variational integral. This type of calculation is called configuration interaction.\(^{(25)}\)

Description of Software Used for Evaluation of Above Parameters:

1. CAChe:
   CAChe is a computer-aided molecular design (CAMD) modeling tool for the Microsoft\textsuperscript{®} Windows ME, Microsoft\textsuperscript{®} Windows 98 or Microsoft\textsuperscript{®} Windows NT 4.0 operating systems. CAChe enables us to draw and model molecules and perform calculations on a molecule to discover molecular properties and energy values. CAChe uses computational chemistry as an essential part of computer-aided chemistry. By applying computational molecular models derived from mathematical equations to a chemical sample we create, we can calculate molecular properties such as the position and behavior of electrons, and nuclei in certain conditions.

   The computational chemistry tools that CAChe uses are derived from classical mechanics and quantum mechanics, and are applied to the chemical sample by a number of computational applications that perform calculations based on specified parameters.

2. MOPAC:
   MOPAC is a general-purpose semi-empirical molecular orbital package for the study of solid state and molecular structures and reactions.

   The semi-empirical Hamiltonians MNDO\(^{(26)}\), MNDO/3\(^{(27)}\), AM1\(^{(28)}\), PM3\(^{(29)}\), and MNDO-d\(^{(30,31)}\) are used in the electronic part of the calculation to obtain
molecular orbitals, the heat of formation and its derivative with respect to molecular geometry. Using these results MOPAC calculates the vibrational spectra, thermodynamic quantities, isotopic substitution effects and force constants for molecules, radicals, ions, and polymers. For studying chemical reactions, a transition state location routine\(^{32}\) and two transition state optimizing routines\(^{33-35}\) are available. For users to get the most out of the program, they must understand how the program works, how to enter data, how to interpret the results, and what to do when things go wrong.

3. PCMODEL Software:
PCMODEL Software has been obtained from Indian Institute of Science, Bangalore, by the courtesy of Prof. Chandrasekharan and has been installed in a P.C. in our Computer Laboratory. This software is used for molecular modeling and for geometry optimization to create data file for MOPAC input.

Geometry Optimization:
Many systematic mathematical procedures (algorithms) exist to find a local minimum of a function of several variables. These procedures will find a local minimum in \(E\) in the neighborhood of initially assumed geometry. The process of finding such a minimum is called Geometry Optimization or energy minimization. For a molecule with several conformations, one must repeat the local minimum search procedure for each possible confirmation, so as to locate the Global Minimum. For a large molecule, there may be too many confirmations for all of them to be examined. Moreover, the true-global minimum equilibrium geometry might correspond to a highly unconventional structure that might not think to be considered.

The most frequently employed geometry optimization schemes are those of Mc Iver and Komornicki\(^{36-37}\) and force method due to Pulay.\(^{38-39}\) The Mc Iver and Komornicki method utilizes the minimization algorithm of Murgath and Sargent, a quadratically convergent method which preserves the molecular symmetry during calculations.
References:
2. Clementi, E.; Roetti, C. At. Data Nucl. Data Tables, 1974, 14, 177.