# CHAPTER I

## Introduction

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CHAPTER I

Introduction

1.1 Introduction

The ability to determine the structure, stability and other physical and chemical characteristics of a molecule is the prime task for many structural scientists. To understand the physical and chemical properties of matter, the basic information is always provided by the structure of the molecule and recent years have witnessed an explosive proliferation in the use of all kinds of quantum chemical methods to evaluate the structures of the molecules and as well as to explore the field of vibrational dynamics.

The electron diffraction, microwave spectroscopy and vibrational spectroscopy are the appropriate experimental techniques that are used to 'determine' the gas phase structure of the molecule and many scientists reserve the word, 'determination of structure' to refer only to experimental results. No matter how much theoretical interpretation may have gone into the analysis of experiment, they speak of only 'prediction' when referring to the theoretical results. But the experimental methods are also having their own constraints irrespective of the accuracy 'observed' from them; For example, in electron diffraction studies, it is quite difficult to obtain structural parameters for a molecule which has more than one conformers at ambient temperature. The large amplitude vibration and the delicate measurement of relative intensities of
scattered electrons have much influence on the determination of intermolecular distances and vibrational parameters. On the other hand, the validity of structural studying theoretical methods has now become quite an increasing factor and the computational determination of molecular structure are at present fully comparable to high quality experimental techniques.

The theoretical 'state of art' method 'ab initio' is now one of the latest powerful tool which provides a relatively simple and straightforward method in several areas of chemical problems and in the field of vibrational spectroscopy. Very high level quantum chemical calculations, with the help of recent computer developments can obtain geometrical and vibrational molecular parameters with as high accuracy as is available from very good experiments.

The following sections of this chapter gives a brief account of the various molecular orbital theories and their refinements with special emphasis on ab initio self consistent Field Molecular Orbital (SCF MO) theory. A concise discussion has also been given about the informations derived from ab initio studies such as conformational analysis, electron population, dipole moment and the features of density functional theory (DFT), etc.,

1.2 Ab initio Molecular Orbital Calculations

A 'rigorous variational calculation' on a chemical system involves the following steps.
(i) Evolving the detailed expression for the Hamiltonian operator $H$ for the system.

(ii) Selecting some mathematical functional form as the trial wave function.

(iii) Minimising the energy $E$ given by the expression

$$ E = \int \Psi^* H \Psi \, d\tau / \int \Psi^* \Psi \, d\tau $$

with respect to variations in parameters.

The simple and extended Hückel methods are not rigorous variational calculations since, eventhough, both of them make use of the secular determinant technique from linear variation theory, no hamiltonian operators are ever written out explicitly and the integrations in $H_{ij}$ are not performed. These are known as 'Semi empirical' methods since they combine the theoretical form with parameters fitted from experimental data.

The term 'ab initio' ("from the beginning") is used to describe calculations in which the three steps listed above are all explicitly performed. By far, the most commonly encountered type of ab initio calculation to arrive at better descriptions of molecules, their energies and their electronic distributions is known to be the method of self consistent field (SCF). The technique was then modified by Fock and Slater to include the effect of electron exchange and the orbitals obtained by the method are called "Hartree - Fock Orbitals".

The assumption behind the technique is that an electron moves in a potential which is a spherical average of the potential due to all other electrons. The schrödinger equation is integrated numerically for that electron and for that average potential.
theory supposes that the wave functions for all the other electrons are already known, so that their average potential can be evaluated. This is in general not the case, and so the calculation is started by guessing the form of their wave functions (e.g. by supposing that they are Slater type orbitals). The Schrödinger equation for the electron of interest is then solved, and the wave function so found is used in the calculation of the potential experienced by one of the other electrons. The latter’s Schrödinger equation is then solved, and in turn is used to refine the average potential experienced by another electron. This is repeated for all the electrons in the atom, and the potential experienced by the first electron can be recalculated. Usually this refined potential differs from the original guess, and so the whole cycle is repeated until the solutions for all the electrons are unchanged in a cycle of calculation then the orbitals are said to be ‘self-consistent’.

1.3 Hartree - Fock Equation

The molecular Hartree-Fock wave function is written as an antisymmetrized product of spin orbitals, each spin orbital being a product of a spatial orbital $\varphi_i$ and a spin function ($\alpha$ or $\beta$). The Hartree-Fock energy of a polyatomic molecule with only closed subshells is

$$E_{HF} = 2 \sum_{i=1}^{n/2} H_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} (2J_{ij} - K_{ij}) + V_{NN}$$  \hspace{1cm} (1.2)

The one electron Hamiltonian $H_i$ omits the interactions of electron $i$ with the other electrons. The sums over $i$ and $j$ are over the $n/2$ occupied spatial orbitals $\varphi_i$ of the $n$-electron molecule. The value of $H_{ii}$ is given by
\[ H_{ij} = \langle \varphi_i(1) | -\frac{1}{2} \nabla^2 - \sum_n Z_n / r_{i\alpha} | \varphi_i(1) \rangle \]  

(1.3)

\emph{I}_ij and \emph{K}_ij are known as 'Coulomb integral' and 'exchange integral' respectively and are given as

\[ J_{ij} = \langle \varphi_i(1) \varphi_j(2) | 1/r_{12} | \varphi_i(1) \varphi_j(2) \rangle \]  

(1.4)

and

\[ K_{ij} = \langle \varphi_i(1) \varphi_j(2) | 1/r_{12} | \varphi_j(1) \varphi_i(2) \rangle \]  

(1.5)

where the integration goes over the spatial coordinates of electrons 1 and 2. The Hartree-Fock equation is given as

\[ F(1) \varphi_i(1) = \varepsilon_i \varphi_i(1) \]  

(1.6)

Where \( \varepsilon_i \) is the orbital energy and the 'Fock Operator' is given as

\[ F(1) = H(1) + \sum_{j=1}^{n/2} \left[ 2J_{ij}(1) - K_{ij}(1) \right] \]  

(1.7)

\[ H(1) = -\frac{1}{2} \nabla^2 + \sum_{\alpha} Z_{\alpha} / r_{1\alpha} \]  

(1.8)

Where the coulomb operator \( J_j \) and the exchange operator \( K_j \) are defined by

\[ J_j(1) f(1) = f(1) \int | \varphi_j(2) |^2 1/r_{12} dv_2 \]  

(1.9)

\[ K_j(1) f(1) = \varphi_j(1) \int \varphi_j^*(2) f(2) 1/r_{12} dv_2 \]  

(1.10)
where \( f \) is an arbitrary function and the integrals over all space.

The first and second terms on the right of (1.8) represents kinetic energy and potential energy operators respectively. The coulomb operator \( J(1) \) is the potential energy interaction between electron 1 and a smeared-out electron; The exchange operator \( K(1) \) represents that the wave function is antisymmetric with respect to electron exchange. The Hartree-Fock MOs in (1.6) are eigen functions of the same operator \( F \), with orbital energies \( \epsilon_i \) as eigen values.

Orbital energies can be obtained from

\[
\epsilon_i = H_{ii} + \sum_{j=1}^{n/2} [ 2J_{ij} - K_{ij} ]
\]

(1.11)

Where \( H_{ii}, J_{ij} \) and \( K_{ij} \) are defined by (1.3), (1.4) and (1.5) respectively. Summation of (1.11) over the \( n/2 \) occupied orbitals gives

\[
\sum_{i=1}^{n/2} \epsilon_i = \sum_{i=1}^{n/2} H_{ii} + \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} [ 2J_{ij} - K_{ij} ]
\]

(1.12)

Solving this equation for \( \sum H_{ii} \) and substituting the result in (1.2), the Hartree-Fock energy is obtained as

\[
E_{HF} = 2\sum_{i=1}^{n/2} \epsilon_i - \sum_{i=1}^{n/2} \sum_{j=1}^{n/2} [ 2J_{ij} - K_{ij} ] + V_{NN}
\]

(1.13)

To calculate accurate SCF wave functions, Roothan has proposed to expand the spatial orbitals \( \varphi_i \) as linear combination of a set of one electron basis functions \( \chi_s \),
\[ \phi_i = \sum_{s=1}^{b} C_{si} \chi_s \]  \hspace{1cm} (1.14)

For an exact representation of the MOs, an infinite number of basis functions are required. But in practice, if \( b \) is large enough and the functions \( \chi_s \) well chosen, MOs can be represented with negligible error.

Substituting the expansion into the Hartree - Fock equation, multiplying by \( \chi_r^* \) and integrating

\[ \sum_{s=1}^{b} C_{si} (F_{rs} - \varepsilon_i S_{rs}) = 0, \quad r = 1,2,3,..., b. \]  \hspace{1cm} (1.15)

where

\[ F_{rs} = \langle \chi_r | F | \chi_s \rangle \]  \hspace{1cm} (1.16)

and

\[ S_{rs} = \langle \chi_r | \chi_s \rangle \]  \hspace{1cm} (1.17)

The equation (1.15) form a set of \( b \) simultaneous linear homogeneous equations and for a nontrivial solution

\[ \det (F_{rs} - \varepsilon_i S_{rs} ) = 0 \]  \hspace{1cm} (1.18)

This is a secular equation whose roots give the orbital energies \( \varepsilon_i \). The Hartree-Fock Roothan equation (1.18) must be solved by an iterative process since the \( F_{rs} \) integrals depend on the orbitals \( \phi_i \), which in turn depend on the unknown co-efficients \( C_{si} \).

In the iterative process, one starts with guesses for the occupied - MO expressions as linear combination of the basis functions as in (1.14). The initial set of
MOs is used to compute the Fock operator $F$ from (1.7) to (1.10). The matrix elements (1.16) and (1.17) are computed and the secular equation (1.18) is solved to give an initial set of $E_i$'s; these $E_i$'s are used to solve (1.15) for an improved set of coefficients, giving an improved set of MOs, which are then used to compute an improved $F$, and so on. This process is repeated until no further improvement in MO coefficients and energies occurs from one cycle to the next.

1.4 The Molecular Hamiltonian

The complete molecular Hamiltonian includes nuclear and electronic kinetic energy operators, electrostatic interactions between all charged particles, and interactions between all magnetic moments due to spin and orbital motions of nuclei and electrons. An accounting for the fact that a moving particle experiences a change in mass due to relativistic effects is also included in the complete Hamiltonian. The resulting Hamiltonian is too much complicated to work with and in practice, one usually does not use the complete Hamiltonian. Usually, the relativistic mass effects are ignored, the Born-Oppenheimer approximation is made to remove nuclear kinetic energy operators and all magnetic interactions are ignored except in special cases where the spin coupling is involved. The resulting Hamiltonian for the electronic energy, in atomic units is given by

$$H = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{\mu=1}^{N} \sum_{i=1}^{n} \left( \frac{Z_{\mu}}{r_{\mu i}} \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \left( \frac{1}{r_{ij}} \right)$$  \hspace{1cm} (1.19)

where $i$ and $j$ are indices for the $n$ electrons and $\mu$ is an index for the $N$ nuclei. $Z_{\mu}$ is the nuclear charge on the $\mu$th nucleus of the molecule and $r_{\mu i}$ is the distance of the electron $i$ from $\mu$th nucleus.
The nuclear repulsion energy \( V_{NN} \) is given by

\[
V_{NN} = \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^{N} \left[ Z_{\mu} Z_{\nu} / r_{\mu\nu} \right]
\]  

(1.20)

In choosing the Hamiltonian it has been restricted to seek an upper bound for the energy of an idealized nonexistent system - a nonrelativistic system with clamped nuclei. To make a very accurate comparison between the computed results and experimental measured energies, it is necessary to modify either the experimental or theoretical results to compensate for the omissions in \( H \).

1.5 Slater Orbitals

The combined space and spin functions of an electron is called a spin orbital and the overall wave function of a many electron system is given by

\[
\varphi_1(1) \varphi_2(2) \varphi_3(3) \varphi_4(4) \ldots \ldots \ldots \varphi_n(n)
\]

(1.21)

in which \( \varphi_1 \) is a spin-orbital which accommodates the electron 1, \( \varphi_2 \) the electron 2 etc. But since electrons are indistinguishable particles, an equally good overall wave function would be

\[
\varphi_1(2) \varphi_2(1) \varphi_3(4) \varphi_4(3) \ldots \ldots \varphi_n(n-1)
\]

(1.22)

In fact one can write the \( n! \) number of such product functions and the most general overall wave function will be a linear combination of these \( n! \) functions.
Pauli put forth a fundamental principle which states that the overall wave function of a system must be antisymmetric with respect to interchange of every pair of electrons. For a system of two electrons, a wave function of the form

$$\Psi(1,2) = \varphi_1(1) \varphi_2(2) - \varphi_1(2) \varphi_2(1)$$  \hspace{1cm} (1.23)

changes sign on interchanging the positions of the electron pair in the orbitals \(\varphi_1\) and \(\varphi_2\). Thus

$$\Psi'(1,2) = \varphi_1(2) \varphi_2(1) - \varphi_1(1) \varphi_2(2) = -\Psi(1,2)$$  \hspace{1cm} (1.24)

But to have a set of \(n\) spin orbitals, an anti symmetric \(n\) - electron wave function is to be constructed. In the early 1930s, Slater introduced the use of determinants to construct anti symmetric wave functions. Slater’s \(n\)-electron determinantal wave function is given by

$$\Psi(1,2,3 \ldots n) = \begin{vmatrix}
\varphi_1(1) & \varphi_2(1) & \cdots & \varphi_n(1) \\
\varphi_1(2) & \varphi_2(2) & \cdots & \varphi_n(2) \\
\varphi_1(3) & \varphi_2(3) & \cdots & \varphi_n(3) \\
\cdots & \cdots & \cdots & \cdots \\
\varphi_1(n) & \varphi_2(n) & \cdots & \varphi_n(n)
\end{vmatrix} \frac{1}{(n!)^{1/2}}$$  \hspace{1cm} (1.25)

Determinantal wave functions are always antisymmetric and vanish when two electrons occupy the same spin orbital. The standard method of determining the best form of the spacial part of the spin orbitals in a determinental wave function is the Hartree - Fock self consistent field method, that has been outlined in the previous section.
1.6 Basis Sets

The set of atomic orbitals in an LCAO - MO is called as a basis set and a great deal of research effort has gone into devising and comparing basis sets for ab initio calculations. The two important and essential criteria of the basis sets are

(i) it should be capable of describing the actual wave function well enough to give chemically good results and

(ii) it should lead to integrals which could be able to be evaluated with reasonable accuracy and cheaply on a computer.

The two types of the basis sets that have come to dominate the area of ab initio calculations are the Gaussian and the Slater-type-orbital (STO) basis sets and are actually very similar in many aspects.

The least sophisticated end of the spectrum of choices is the ‘minimal basis set’ of STOs that includes only those STOs that correspond to occupied Atomic Orbitals (AO) in the separated atomic limit. One may improve this basis by adding additional STOs to various nuclei. For example each carbon 2p AO were represented as a linear combination of two p type STOs, each having a different orbital exponent. If the ‘linear’ coefficient for the “inner” STO is much larger it means that the p type charge cloud around this atoms in the molecule is calculated to be fairly “contracted” around the nucleus. To describe a more diffuse charge cloud, the wave function would contain
quite a lot of the “outer” STO and not so much of the “inner” STO. A basis set in which every minimal basis AO is represented by an “inner-outer” pair of STOs is often referred to as a double zeta basis set.

A further kind of extension is also frequently made in which one includes STOs with symmetries different from those present in the minimal basis. This has the effect of allowing charge to be shifted in or out of bond regions; For example, one could add p-type STOs on hydrogen nuclei, by mixing with s-type STOs and a skewed charge distribution in the regions of the protons can be described. Similarly, d-type STOs may be added to atoms which, in the minimal basis set, carried only s and p type STOs. Functions of this nature are often called ‘polarization functions’ because they allow charge polarization to occur within the molecule as a result of the internally generated electric field.

It is evident that one could go on indefinitely, adding more and more STOs to the basis even placing some of them in bonds, rather than on nuclei. But this will enhance the computing task to go up enormously. In fact, the number of integrals to be evaluated eventually increases as \( N^4 \), where \( N \) is the number of basis functions. The evaluation of integrals is the logistic bottleneck in ab initio calculations and for this reason, non linear variations or orbital exponents become impractical for larger molecules. Each new orbital exponent value requires reevaluation of all the integrals involving the orbital. In essence, a change of orbital exponent is a change of basis set. In linear variations, the basis functions are mixed together but they do not change.
The STO basis set can be considered as a standard choice but for the fact that the many integrals encountered in calculating $F_{ij}$ elements are extremely time consuming to evaluate, even on a computer. This has led to the development of an alternative basis sets class, which is based on 'gaussian-type functions'.

Gaussian functions include an exponential term of the form $\exp(-\alpha r^2)$. The radial dependence of such a function is compared with the hydrogenlike function in Fig 1.1. The two obvious problems connected with using gaussian functions are

(i). they do not have cusps at $r=0$ as s-type hydrogen like AOs do.

(ii). they decay faster at larger $r$ than do hydrogen like AOs.

The advantage that is balanced against these difficulties is that the gaussian functions have mathematical properties that make it extremely easy to compute the integrals that lead to $F_{ij}$. Now each STO can be replaced by a 'number' of gaussian functions and by choosing several values of $\alpha$ in $\exp(-\alpha r^2)$ a set of “primitive” gaussian functions can be created ranging from very compact to very diffuse. Then a linear combination of these functions is taken to build up an approximation to the radial part of an STO function. Multiplication by the standard $\theta$ and $\varphi$ dependences (spherical harmonics) generates p,d, etc., functions. Once this approximation is optimized, the linear combination of gaussian functions is “frozen”, being treated thereafter as a single function insofar as the subsequent molecular variational calculation is concerned. This linear combination of primitive gaussian functions is called a “contracted gaussian function”. Typically, ab initio calculations involve anywhere from 1 to 7 primitive gaussian
Fig. 1.1 Radial dependence of hydrogen-like and gaussian functions
functions for each contracted gaussian function. Some of the basis set descriptions that one could encounter in the literature are as follows:

(i) **Minimal basis set** (It consists of one STO for each inner shell and valence-shell AO of each atom. For example, for C₂H₂, a minimal basis set consists of 1s, 2s, 2pₓ, 2pᵧ and 2p₂ AOs on each carbon and a 1s STO on each hydrogen).

(ii) **Double-Zeta (DZ) basis set** (This is obtained by replacing each STO of a minimal basis set by two STOs that differ in their orbital exponents Zeta. For C₂H₂ a double-zeta set consists of two 1s STOs on each H, two 1s STOs, two 2s STOs, two 2pₓ, two 2pᵧ and two 2p₂ STOs on each carbon).

(iii) **Double-Zeta plus polarization set (DZ+P or DZP)** (It consists of an addition of a set of five 3d functions on each ‘first row’ and each ‘second row’ atom and a set of three 2p functions (2pₓ, 2pᵧ, 2p₂) on each hydrogen atom, with the double-zeta set).

(iv) **Split valence basis set** (It uses two STOs for each valence AO but only one STO for each inner shell AO).

(v) **3-21G basis set** (In this set, each inner shell AO (1s for Li-Ne; 1s, 2s, 2Px, 2Py, 2Pz for Na-Ar; and so on) is represented by a single contracted gaussian type function (CGTF) that is a linear combination of three primitive Gaussians; for each valence shell AO, there are two basis functions, one of which is a CGTF and the other is a single diffuse Gaussian).
(vi) **3-21G** (It is constructed by adding a set of six d-type Gaussian functions on each second row atom, with the 3-21G basis set.)

(vii) **4-31G basis set** (This set uses four primitives in each inner shell CGTF and represents each valence shell AO by one CGTF with three primitives and one Gaussian with one primitive).

(viii) **6-31G** (In this basis set, each inner shell is represented by the sum of six gaussians and each valence shell splits into inner and outer parts (double zeta) described by three and one gaussian primitives respectively).

(ix) **6-31G** (Here the 6-31G basis set is augmented with six d-type gaussian primitives on each heavy (Z > 2) atom to permit polarization).

(x) **6-31G** (This basis set is same as 6-31G but with a set of gaussian p-type functions on H and He atoms. Good for systems where hydrogen is a bridging atom, as in diborane or in hydrogen bonds).

### 1.7 The Hartree-Fock Limit

It is evident that different choices of basis set produce different SCF wave functions and energies. The total energy of a molecule obtained by a double - zeta basis set is less than the minimal basis set energy and if the calculation is repeated by adding polarization functions, energy can be lowered further. If this is continued by
increasing the capabilities of the basis set, the energy decreases with each basis set improvement and it approaches a limiting value, as the basis set approaches mathematical completeness. This limiting energy value is the lowest that can be achieved for a single determinantal wave function. It is called the 'Hartree-Fock energy'. The MOs that correspond to this limit are called Hartree-Fock orbitals (HF orbitals) and the determinant is called the HF wave function.

If the wave function is restricted to be a single determinantal function for a configuration wherein electrons of α spin occupy the same space orbitals as do the electrons of β spin, the term “restricted Hartree-Fock” (RHF) is used. When this restriction is relaxed, and different orbitals are allowed for electrons with different spins, an “unrestricted Hartree-Fock” (UHF) is obtained. This refinement is most likely to be important when the numbers of α- and β- spin electron differ.

1.8 Correlation Energy

The Hartree-Fock energy can be lowered further by introducing additional mathematical flexibility by allowing to contain many determinants instead of a single determinant. A corresponding physical reason for the HF energy being too high is connected with the independence of the electrons in a single determinantal wave function. To understand this, consider the four-electron wave function

\[ \Psi = |\phi_1(1) \phi_1(2) \phi_2(3) \phi_2(4)| \] (1.26)
where the numbers in parentheses stand for the spatial coordinates of an electron; that is \( \phi_1(l) \) really means \( \phi_1(x_1, y_1, z_1) \alpha(1) \) or \( \phi_1(r_1, \theta_1, \phi_1) \alpha(1) \). By choosing \( r, \theta \) and \( \phi \) for each of the four electrons a numerical value for \( \psi \) and \( \psi^2 \) can be obtained. Here \( \psi^2 \) represents the probability for finding one electron in the volume element \( dv_1 \) around \( r_1, \theta_1, \phi_1 \), another electron simultaneously in \( dv_2 \) at \( r_2, \theta_2, \phi_2 \) etc. The important point to notice is that the effect on \( \psi^2 \) of a particular choice of \( r_1, \theta_1, \phi_1 \), is not dependent on choices of \( r, \theta \) and \( \phi \) for other electrons. This can be stated physically that the probability for finding an electron in \( dv_1 \) at some instant is not influenced by the presence or absence of other electron in some nearby element \( dv_2 \) at the same instant. This is consistent with the fact that the Fock operator treats each electron as though it is moving in the time-averaged potential field due to other electrons. There is a tendency among the electrons to keep out of each others way as they repel each other, and hence, in reality, their motions are 'correlated'. Since the HF wave function is formally incapable of describing correlated motion the HF energy is always higher than the true energy. For a simplified non relativistic Hamiltonian, the energy difference between the HF and the 'exact' energy for a system is referred to as the 'correlation energy'.

### 1.8.1 Möller - Plesset Treatment of Correlation

A correlation method that is size consistent (A size - consistent quantum mechanical method is one for which the energy and hence the energy error in the calculation increase in proportion to the size of the molecule. Size consistent is important whenever calculations on molecules of substantially different sizes are to be
compared, as for example, in calculation of the energy change in the dissociation reaction \( A \rightarrow B + C \) has been developed by Pople and coworkers [1], which is based on perturbation theory that was introduced many years ago by Moller and Plesset [2]. In this perturbation theory of atoms and molecules the unperturbed wave function is taken to be the Hartree-Fock wave function.

In the Moller-Plesset perturbation theory (MP theory) the starting point energy (MP0) is the sum of the HF one-electron energies. The first-order correlation to the energy (MP1) brings in the appropriate electronic, Coulomb and exchange integrals, giving the correct HF energy. MP2 brings in contributions wherein doubly excited configurations "interact with" the ground configuration. MP3 adds contributions due to doubly excited configurations interacting with each other. MP4 brings in interactions involving single, double and quadruple excitations.

MP2 calculations are usually the method of choice for dealing with the effects of electron correlation on molecular ground state equilibrium properties due to their computational efficiency and the good results they provide for molecular properties. The limitations of this method are (i) producing serious errors for open shell ground state problems (ii) not giving good results at geometries far from equilibrium and (iii) generally not applicable to excited electronic states.
1.9 Koopmans’ Theorem

Despite the fact that the total electronic energy is not given by the sum of SCF one electron energies, it is still possible to equate orbital energies with molecular ionization potentials or electron affinities, if certain assumptions are made. This identification is related to a theorem due to Koopmans.

Koopmans proved that the wave function obtained by removing one electron from \( \varphi_k \) or adding one electron to the virtual MO \( \varphi_j \) in a HF wave function is stable with respect to any subsequent variation in \( \varphi_k \) or \( \varphi_j \). The theorem suggests that the wave function for a positive ion is approximated by removing an electron from one of the occupied HF MOs for a neutral molecule without reoptimizing any of the MOs. In a closed shell system, if \( E \) and \( E_k^+ \) are the energies of a neutral molecule and the cation,

\[
E_k^+ = E - \varepsilon_k \tag{1.27}
\]

Where \( \varepsilon_k \) can be obtained from Eq. (1.13). The ionization potential \( I_{k^0} \) for ionization from the MO \( \varphi_k \) is

\[
I_{k^0} = E_k^+ - E = -\varepsilon_k \tag{1.28}
\]

Hence this illustrates that, within the context of this simplified model, the negative of the orbital energies for occupied HF MOs are to be interpreted as ionization potentials. A similar result holds for orbital energies of unoccupied HF MOs and electron affinities; however, this is less successful in practice. The ionisation potential obtained from the relation (1.28) is always higher than the value predicted by taking the difference between
separate SCF calculations on the molecule and cation (ΔSCF). This is because, Eq. (128) views ionization as removal of an electron without any reorganization of the remaining electronic charge. This neglects a process which stabilizes the cation and lowers the ionization potential.

Another error results from the neglect of change in correlation energy. The neutral molecule is having greater correlation energy since it has more electrons and the proper inclusion of this feature would lower the energy of the neutral molecule more than the cation, making the true $I_k^o$ bigger than that obtained by neglect of correlation. Hence, this leads to expect ΔSCF to underestimate $I_k^o$ since $-\varepsilon$ overestimates ΔSCF, and ΔSCF underestimates the ionization potential, some cancellation of error can also be expected.

1.10 Determination of Molecular Structure

Determination of molecular structure involves finding one or more of the several nuclear configurations, which are local minima on the potential energy surface. At such a configuration, the forces on all the nuclei are zero and the matrix of second derivates is positive definite. By definition this is the equilibrium geometry. Computational determination of the minimum-energy nuclear configuration proceeds in the following manner:

1. A nuclear geometry is assumed as an initial guess. The accuracy of this guess does not affect the accuracy of the final result, but it does affect the number of iterations which will be needed in the subsequent steps and it also determines which of several equilibrium geometries will be found in case, the system has multiple possible conformations.
2. With the assumed nuclear geometry, the electronic Schrödinger equation is solved. The accuracy with which this is done is the sole factor affecting the accuracy of the final result.

3. The approximate wave function obtained in the second step is used to calculate the expectation value of the first derivative of energy with respect to nuclear coordinates. This is the heart of the gradient technique, first developed by Pulay [3] and described in detail in the reviews by Pulay [4,5]. The computation of energy derivatives is one of the major developments in quantum chemistry in recent years since it has made application of quantitative MO techniques to larger molecules.

4. A molecular force field is now assumed. Usually only the harmonic force constants are used and all coupling constants and anharmonic terms are taken as zero. The computed forces on the nuclei and the assumed force constants are now used to predict a new nuclear geometry.

5. Steps 2-4 are iterated until the forces become as close to zero as desired. The result is the fully relaxed equilibrium geometry of the molecule. Computer programs are designed to carry out this iterative procedure automatically.

In practice, several important factors are to be considered; Firstly it is useful to optimize the geometry using a set of internal coordinates in which the vibrational force field is as nearly as diagonal as possible so that the neglect of interaction terms in the assumed force field is reasonable. Secondly, it is necessary to be sure that the
zero-force geometry obtained is truly a minimum-energy geometry and not a saddle point of the energy surface. This is only a hazard if there are periodic motions such as ring inversion or internal rotation or if some molecular symmetry element can lead to a zero-force maximum in some coordinate. A test can be made in such a situation by making a small displacement along the suspicious coordinate. This will lead either to a restoring force or a force leading away from a saddle point. Alternatively, the second derivatives of the energy can be calculated at the final geometry as a test for a true minimum, with greater computational effort.

1.11 Accuracy of the Ab initio Computations

Instead of simply asking about the highest accuracy that can be obtained, it is probably more useful to set a target of accuracy and inquire to what extent it can be achieved. For the molecules of a size sufficiently large to present complex structural and conformational questions, say up to about 20 atoms, the more sophisticated experimental techniques can give accuracies of a few thousandths of an angstrom and a few tenths of a degree, in favourable cases. This might then be considered as a reasonable goal to strive for by computational methods.

The stated accuracy goal can be achieved directly for small molecules using a large basis set (triple-zeta in the valence shell plus two sets of polarization functions) and a good treatment of electron correlation. Calculations of this level are not possible for molecules of larger size, the unfortunate difficulty being the electron correlation. Standard methods involving configuration interaction or MP4 perturbation theory have
a time requirement varying with the number of electrons in the molecule as \( n^6 \). This means that a 1000-fold increase in the speed of computer would increase the size of the molecule that could be handled by a factor of only 3.2. Currently, the major thrust of theoretical work is the effort to solve the correlation problem in a way, that is both computationally practical and sufficiently accurate.

No calculation is possible that can directly give the desired level of accuracy in bond lengths without use of both a large basis set and a good treatment of electron correlation and this is currently impossible for molecules of the size under consideration.

The situation is saved by the observation that errors in computed bondlengths are highly systematic provided the basis set is of adequate size. Hence it is possible to add a predetermined correction, or 'offset' value to the computed bond length. There may be esthetic objections to such a 'contamination' of results from 'ab initio' MO theory by the use of empirical data, but if the objective is to obtain meaningful information at this level of accuracy, there is no other way.

Only extensive comparison with high-quality experimental results can show how meaningful and how accurate the results are, and a large body of evidence has been accumulated with extremely encouraging results. The relationships can be visualised by sketching as in the Fig. 1.2 the error in computation of a given bondlength against the size of the basis set used.

As shown, the infinite basis set limit deviates from the true value if electron
Fig. 1.2 Schematic representation of the error in calculating a single structural parameter as a function of basis set size in a variety of molecular environments [3].
correlation is neglected. The shaded area represents the results obtained for calculations with the bond imbedded in a wide variety of molecular environments. A known, fixed error is to be preferred for getting an exactly current answer, and the calculations should be made at the point marked X, using the smallest basis set that produces an adequately small variability in the error. Corrections with offset values is necessary to obtain the best possible estimates for the absolute values of bond lengths. Most often, however, the length of a chemical bond is seldom of interest and the 'difference' in length of similar bonds in related systems is of more useful; for example, how the relative C-C bond lengths in cyclopropane are affected by various substitutions on the ring. When the ab initio MO calculation is done at a level such that the error for a given type of bond is constant, these relative values are obtained directly, without any empirical corrections.

1.12 Density Functional Theory

The density functional theory (DFT) of many electron systems [6,7] has been found to be useful in providing rigorous quantitative definitions for several qualitative chemical concepts. Accordingly there has been an upsurge of interest in understanding structure, reactivity and dynamics of atoms and molecules using DFT. The theory provides a very interesting framework for the quantitative description of global and local indices that allow one to study the inherent reactivity of chemical species [7], and hence all the reactions considered in the present work have also been viewed through DFT, apart from the ab initio MO theory. The two important quantities provided by the DFT that help to characterize any chemical system are; the electronic chemical potential \( \mu \) [8] and the chemical hardness \( \eta \) [9].
The atomic parameter that has long been known to be of great use in chemistry is the electronegativity of Pauling and Mulliken which is the average of the ionization potential and electron affinity; In general, for a species $S$, the escaping tendency of electrons is measured by the quantity

$$\chi_s = \frac{1}{2} (I_s + A_s) = -\mu_s \quad (1.29)$$

Where $I_s$ and $A_s$ represents the ionisation potential and electron affinity respectively. Here $\chi$ is the absolute electronegativity [10] and its negative $\mu$, is the chemical potential of the electrons, which has the same significance as the chemical potential in the classical thermodynamics of macroscopic systems [8]. According to the original rationalization of Mulliken [10], the condition for the two systems $X$ and $Y$ to have equal electronegativities is that the energy changes for the two disproportionation reactions,

$$X + Y \rightarrow X^+ + Y^- \quad (1.30)$$

and

$$X + Y \rightarrow X^- + Y^+ \quad (1.31)$$

be equal. The first is given by $I_x - A_y$ and the second is $I_y - A_x$; they are equal, if

$$I_x + A_x = I_y + A_y \quad (1.32)$$

To establish the relation between $-\chi$ and $\mu$, another interpretation for the $\chi$ can also be obtained from the literature [11]. If the total electronic energy $E$ is plotted as a function of $N$, the total number of electrons, a result similar to that of Fig.1.3 will be obtained.
The first electron affinity of the neutral atom or molecule will be small and positive or zero. A zero value means that the electron will not add but will be more stable at infinity. The second electron affinity will be zero, except for very rare cases. The curve then flattens out at a constant value of the energy independent of further increase in \( N \). The first ionization potential for the species will be much larger than the electron affinity and much smaller than the second ionization potential. For third and fourth ionization potentials, the curve rises very sharply as \( N \) decreases. Experimentally, the points on the curve in the Figure 1.3, is only for integral values of \( N \) but for a molecule it is natural to think of the individual atoms, electron populations are not necessarily integral. Assuming a differential curve, the electronegativity may be defined as

\[
\chi_s = -\left( \frac{\partial E}{\partial N} \right)_z
\] (1.33)

since the slope, \( \left( \frac{\partial E}{\partial N} \right)_E \), is equal rigorously to the chemical potential \( \mu \) of the density functional theory [8].

1.12.1 Chemical Hardness

The importance of the first derivative of the \( E(N) \) curve has been demonstrated as chemical potential and the next property of importance of the curve is now defined as the second derivative, which is defined as chemical hardness. It is defined as

\[
\eta_s = 1/2 \left( \frac{\partial^2 E}{\partial N^2} \right)_z
\] (1.34)

and the corresponding operational definition is the corresponding finite difference
Fig. 1.3 Variation of total electronic energy with the total number of electrons.
From equation (1.33) and (1.34), hardness is related to electronegativity or chemical potential through the identity

\[ 2 \eta_s = \left( \frac{\partial \mu_s}{\partial N} \right)_z \]

\[ = - \left( \frac{\partial \chi_s}{\partial N} \right)_z \]

(1.36)

The nonchemical meaning of the work "hardness" is resistance to deformation or change. Eq. (1.36) shows that the chemical hardness is resistance of the chemical potential to change in the number of electrons. The hardness measures the rate of change of \( \mu \) with \( \rho \), \( \rho \) being the electron density function. The hardness acts as the resistance to change in the electron density for a given change in \( \mu \). The DFT does not require that \( \eta \) be constant everywhere in the system. Instead it has local values and the average of these local values over the molecule then gives the global value \( \eta \) [12]. Since always [13],

\[ I_s \geq A_s \]

(1.37)

the minimum value of hardness is zero. The softness is the reciprocal of the hardness and zero hardness constitutes maximum softness. A bulk metal has \( I = A \) and \( \eta = 0 \) and hence softness is maximum.
1.12.2 Molecular Orbital Relations

Fortunately it turns out that $\chi$ and $\eta$ are completely compatible and by correlating them with the molecular orbital (MO) theory other approximations to $\eta$ can be obtained and in fact it adds a new dimension to MO theory which seems to be very useful [14]. For example, from Koopman’s theorem,

$$ I = - \varepsilon_{\text{HOMO}} $$

and

$$ A = - \varepsilon_{\text{LUMO}} $$

(1.38)

where HOMO indicates the highest occupied MO and LUMO, the lowest unoccupied MO.

By increasing $\chi$ and $\eta$ on the usual MO energy level diagram, it can be found that $-\chi = \mu$ is half-way between the HOMO and the LUMO on the energy scale [14]. The gap between the HOMO and LUMO is simply equal to $2\eta$ (both $\chi$ and $\eta$ are measured in electron volts). Thus hard molecules, like water have a large HOMO-LUMO gap and soft molecules like $\text{H}_2\text{Se}$ have a small gap.

Since the HOMO-LUMO energy gap also represents the energy difference between the ground state and the first excited state of the same multiplicity, a small energy gap is favourable for easy mixing of wavefunctions and hence soft molecules are more polarizable than the hard molecules. This is in agreement with earlier definitions of hardness and softness [15]. It can also be concluded that the soft molecules are more reactive and in fact, as pioneered by Fukui [16], DFT may be used to generate the whole frontier orbital theory of chemical reactivity.
Electron transfer between the reacting systems occurs between the HOMOs and LUMOs. The electron densities $\rho_{\text{HOMO}}$ and $\rho_{\text{LUMO}}$ play a critical role in reactions. The local softness $\sigma$ is controlled by the frontier orbital densities with the simple relationships,

$$\sigma_1 = \sigma \rho_{\text{HOMO}}$$

and

$$\sigma_2 = \sigma \rho_{\text{LUMO}}$$  (1.39)

where $\sigma_1$ is the local softness when electron density is given up and $\sigma_2$ that when accepted. However this is applicable only when the electron transfer is a dominant feature of the chemical reaction. In other cases, the reaction sites depend on the net charges at the several atoms due to the domination of electrostatic interaction [17].

If two systems B and C are brought together, as in a reaction, electrons will flow from that of less electronegative to the more electronegative system, until the chemical potentials become equal. The fractional number of electrons transferred, $\Delta N$ is given by

$$\Delta N = (\chi_c - \chi_B) / 2 (\eta_C + \eta_B)$$  (1.40)

There is an energy lowering due to electrons being transferred to a lower chemical potential and after this initial equalization of electronegativities, there are further changes in electron density corresponding to covalent and ionic bonding [18,19]. Eventhough (1.40) is incomplete, it is still useful since it measures the initial interaction between B and C using only the properties of the isolated systems. Furthermore it can
be assumed that the covalent bonding will show some proportionality of $\Delta N$ since coordinate covalent bonding is involved [20]. For neutral reactants, the ionic bonding will also depend on $\Delta N$. It is also reasonable to assume that a large value of $\Delta N$ means a strong, favourable interaction between B and C, indicating a strong bond between B and C, or a lowering of an activation barrier in other cases.

### 1.13 Hydrogen Bond

Hydrogen transfer reactions are a fundamental step in several chemical and biochemical processes [21,22] and the elucidation of the actual nature of the transferring hydrogen is essential for the understanding of the mechanism of these reactions. A broad range of experimental techniques has been applied and a moderately large number of ab initio quantum chemical methods have been carried out to explore the nature of the bond. Among the several significant insights that have been gained from the quantum chemical calculations, there are three simple qualitative bonding descriptions that have dominated long to organize the experimental data; they are (i) the two term Mulliken charge transfer expression [23] used by analogy with the more general class of donor-acceptor complexes [24] (ii) the set of four valence bond structures using hybridized atomic orbitals for the A-H bond and the B atom lone pair introduced by Coulson [25] and (iii) the three center, bonding, non bonding, molecular orbital picture proposed by Pimentel [26].

Recent experimental and computational additions to the literature has now brought together the above three descriptions and now it is possible to devise a more quantitative
Instead of going beyond the three-atom, three-center descriptions, now the quantum chemical interpretations show that the features of the both of the bonding non-hydrogen molecules are necessary to have a complete understanding of the hydrogen bonded complexes.

Ab initio MO calculations have proved to be a very good method in the study of hydrogen bonded complexes since the central features of the hydrogen bond are contained within the Hartree-Fock approximation and they have obtained a quantitative agreement with high resolution spectoscopic measurements on internuclear separation, bond angles, and dipolemoments. This is because the instantaneous electron-electron correlation is a less severe problem in hydrogen bonds than in covalent bonds.

In a hydrogen bond, a single hydrogen atom appears to be bonded to distinct atoms of which at least one is usually, oxygen which is also the case in all of the systems considered in the present work. The importance of the hydrogen bond lies in its smallest energy of the order of 6 kcal/mol, comparing to most of the other bonds that are having an energy range 50-100 kcal/mol. The hydrogen bond can be distinguished into at least four distinct types, as follows. (i) intermolecular, extending over many molecules (ii) intermolecular which form a dimer (iii) intramolecular, in which the hydrogen is bonded to two atoms of the same molecule, (iv) (FHF)⁻ in which the anion of the polar crystal KHF₂, exists as a distinct charged unit in the solid.

During recent years much progress has been made in determining, the position of the H atoms and its relation to the length of the bond A-H, the change in frequency of the valence vibration and the distance A...B in the bond A-H...B. Neutron diffraction
methods and nuclear magnetic resonance technique [27] have revealed a general pattern in all such bonds. Fig. 1.4 shows a particular case of O-H...O, in which the O-H distance increases as O...O distance decreases. When the O...O distance is as low as about 2.4 Å, the proton is appeared to be in centre. When this happens, the bond has become quite different from a normal O-H bond, and X-ray and neutron diffraction [28] suggests that even with a bond length as large as 2.54 Å, the H atom may some times be central.

Most of the hydrogen bond energies are in the range 2-8 kcal/mol, about one -tenth of an average conventional bond energy. The two possible ways in which these energies can be accounted are by means of (a) resonance or (b) electrostatic forces, whereas the divalent nature of H is disregarded due to its occasional occurrence. In earlier times the interpretation (a) was favoured, but this is not now regarded as adequate itself except perhaps in the (FHF)⁺ ion. For example Gillette and Sherman [30] in their discussion of formic acid dimer have stated that the resonance can only provide 50 percent of the total energy required, even when the H atoms are placed in the most favourable symmetrical positions. Hence it can be confirmed that the hypothesis (b) in which the binding is regarded as essentially electrostatic should be the nature of the hydrogen bond.

The electrostatic nature of the hydrogen bond can be confirmed by noticing that effective hydrogen bonds are formed only between electronegative atoms such as O,N,F, and S, so that there are strong dipoles already present.
Fig. 1.4 Variation of O-H distance with O$_1$ - H$...$O$_2$ distance.
Bond dipolemoment and charge transfer plays an important role in studying the qualitative nature of hydrogen bonds. When a monomer acts as a proton donor the bond dipolemoment along the A-H bonds, \( \mu_{A-H} \), becomes the principal characterizing feature and it can also be related to the total monomer dipolemoment. The sum of the projections of \( \mu_{A-H} \) for each legand along the molecular symmetry axis plus the effective dipolemoment of the lone pairs along this line is equal to the observed monomer dipolemoment. In the molecular orbital representation, lone-pair contributions to the dipolemoment come from those lone pairs with charge lobes lying along the symmetry axis. For a given electron donor, the equilibrium internuclear separation is also governed by \( \mu_{A-H} \). A large \( \mu_{A-H} \) means that the H orbital is less occupied and it pulls the A-H bond charge strongly to A, allowing the lone pair to penetrate further along A-H thereby resulting in a short \( r(\text{H...B}) \) [30].

Charge transfer from the proton acceptor to the proton donor is a central feature of the charge rearrangement that occurs upon formation of a hydrogen bond. It is defined as the sum of the difference in Mulliken atomic populations between the complex and proton acceptor monomer and is equal in magnitude but opposite in sign to the sum for the proton donor. The observation of charge transfer helps to determine the directionality, complex dipolemoments and IR intensity enhancement.

### 1.14 The Method of Normal Coordinate Analysis

The utilization of the molecular symmetry has proved to be the most powerful technique in the mathematical analysis of molecular vibrations. The usual procedure consists in first finding the number of genuine vibrations of each species by the group theoretical considerations. Knowing the number of vibrations under each symmetry type,
new coordinates are introduced. These new coordinates called the symmetry coordinates are linear combinations of the equivalent internal coordinates which are the changes in the bond distances and the interbond angles. The potential function is then a quadratic function of the symmetry coordinates.

The method of Wilson [30] using symmetry coordinates is the most convenient one for the treatment of complex molecules. In this method the number of active vibrations under each symmetry type is first determined. Corresponding to each vibration, the symmetry coordinates of the form \( R_j = \sum U_{jk} r_k \) are constructed out of the equivalent internal coordinates \( r_k \).

Using the above symmetry coordinates, the elements of a matrix \( F \) related to the potential energy are obtained. The general expression for the potential energy \( V \) is

\[
2V = \sum f_{ik} r_i r_k
\]

where \( f_{ik} = f_{ki} \) is the force constant and \( r_i \) and \( r_k \) are the internal coordinates. As the symmetry coordinates are of the form \( R_j = \sum U_{jk} r_k \) the potential energy in terms of the symmetry coordinates will take the form \( 2V = \sum F_{jl} R_j R_l \) Where \( j \) and \( l \) extend over all symmetry coordinates. Reducing both the above expressions for the potential energy to matrix notation, we have

\[
2V = r' F r = R' F R,
\]

where \( r' \) and \( R' \) are the transposes of the \( r \) and \( R \) matrices and
\[ F = U f U' \]  \hspace{1cm} (1.43)

where \( R = U r \). Thus the elements of the potential energy matrix may be calculated using the coefficients of the internal coordinates in the various symmetry coordinates and a force constant matrix whose columns and rows are labelled by the internal coordinates. The matrix \( U \) will be that formed by the coefficients \( U_{jk} \)'s in the corresponding symmetry coordinates. This form has the advantage of requiring only a single coordinate of each degenerate set.

As the kinetic energy is of the form \( 2 T = r'^{-1} G'^{-1}, P = P'GP, \)
where \( P \) is a column matrix whose elements are the momenta conjugate to the \( r_k \)'s and the prime denotes the transposed matrix,

\[ G_{kk'} = \sum_{i=1}^{n} \mu_i B_{ki} B_{k'i} \]  \hspace{1cm} (1.44)

where \( \mu_i \) is the reciprocal mass of the atom to which \( i \) refers. Substituting for \( B_{ki} \)'s,

\[ G_{kk'} = \sum_{t=1}^{n} \mu_t s_{kt} s_{k't} \]  \hspace{1cm} (1.45)

The above form has the advantage that it requires no coordinate system. Further, it is possible to express the \( s_{kt} \) vectors in terms of unit vectors directed along the chemical bond so that the problem of finding \( G \) reduces to one of finding the interbond angles.

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The secular equation is then made up of factors of the form

\[ |FG - E\lambda| = 0. \quad (1.46) \]

The \( \lambda \)'s are related to the normal frequencies \( \nu \) in \( \text{cm}^{-1} \) as \( \lambda = 4 \pi^2 C^2 \nu^2 \). Thus from the observed or theoretical frequencies, it is possible to evaluate the force constants appropriate to any molecule by solving the above secular equation which is in the form of an expanded algebraic equation [31].

The above FG matrix method [31] has been used in the present work in chapters II and III for the evaluation of force constants of different molecules by utilizing experimental and theoretical frequencies.
References

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