

**STUDIES ON
SATURATED MOLECULES USING
BOND ORBITAL APPROACH**

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OF DOCTOR OF PHILOSOPHY (SCIENCE)*

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A C K N O W L E D G E M E N T

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PART I

APPROXIMATE MOLECULAR ORBITAL THEORIES :
A LOCALISED MO APPROACH.

1.1 Introduction

In order to interpret molecular properties by quantum mechanical methods, two different approaches are usually employed. One is to reproduce the experimental data as well as to predict molecular properties by means of exact calculations. While this approach is, in principle, the ideal one, it is of limited applicability in chemical sciences because of the computational difficulties associated with the rigorous application of quantum mechanics to many-particle systems. Fortunately, accurate wave functions are usually not necessary for the interpretation and correlation of a majority of molecular data. This has made it possible to develop a second approach, perhaps more useful than the first one, since it concerns the methodology for promoting progress in Chemistry by formulating non-empirical or semiempirical methods of interpretation through effective approximations to facilitate the application of theoretical principles to complex chemical problems. One of the earliest as well as a brilliant example of such an approach is provided by the Hückel method⁽¹⁻²⁾. With passage of time the Hückel method has given place to more rigorous and sophisticated approaches. In fact, the development and applications of quantum chemistry is closely parallel the development of better approximate methods^(3-7, 40-43).

The approximate methods of today are generally more complex than those of earlier days, primarily due to the development in computers which makes the numerical solution of more and more complex problems feasible with passage of time. Nevertheless, the search for simpler approaches which may not be applicable to all types of molecules, but only to a special type, continues in order to facilitate the acquirement of theoretical insights, without too much of complex computations, to chemical problems. The localized MO or Bond orbital approach (8-12, 52-55) is an example where the chemist's concept of describing molecules in terms of "electron groups" such as inner shells, lone pairs and bond pairs has found a theoretical formulation. Although several approaches, varying widely in complexities and nature of approximations involved, are available for the study of σ -system (12-15, 63) the need for an approach which meet the following criteria can hardly be overemphasized:

- (I) The concept of inner shells, lone pairs and bond pairs should not be obscured as in the fully delocalized MO approach where much additional computational labour is needed to construct suitable localized MO's.
- (II) The method should have a strong theoretical basis without being computationally too complex so that information on any

molecules may be quickly obtained.

(iii) The use of empirical parameters should be kept to the absolute minimum and when used, such parameters should be based on theoretical arguments.

(iv) The method should be reliable in predicting such information as orbital hybridization, charge distribution, dipole moment etc. without time consuming calculations.

Before considering a suitable methodology satisfying the above criteria as far as possible, a brief discussion on the Hartree-Fock approach⁽⁴⁻⁵⁾ to many-electron systems and its application to molecular systems, developed by Roothaan⁽⁶⁾ will be presented as the Hartree-Fock - Roothaan approach to molecular wavefunctions constitute the best available approximate approach to electronic structures of molecules. This will also help us to assess the nature and magnitude of the approximations involved in the simplified approach to G-bonded systems that we propose to develop in this work.

1.2 The Basic Framework of the Method.

The variational approach^(16,17) which forms the mathematical basis of approximate solution of the Schrodinger equation involves minimization of energy expectation value $\langle \Psi | H | \Psi \rangle$. For algebraic manipulation it is therefore necessary to have a convenient expression for this quantity

in terms of orbitals involved. The Hartree-Fock method is one such approach in this direction. The MO's are determined in this approach by minimizing the energy of an approximate many electron wavefunction corresponding to a given electronic configuration built from suitable one-electron wavefunctions of the molecule. For the molecule with $2n$ electrons, many electron wavefunction is generally written in terms of Slater determinants

$$\Psi = \left| \Psi_1(1), \Psi_2(2), \dots, \Psi_{2n}(2n) \right| \quad \dots (1.1)$$

where the equation is written in short-hand notation and $\{\Psi_i\}$ is a product of space orbital ϕ and spin function α or β and may be written as

$$\Psi = \left| \phi_1 \bar{\phi}_1, \phi_2 \bar{\phi}_2, \dots, \phi_n \bar{\phi}_n \right| \quad \dots (1.2)$$

where bar over ϕ_i indicates a β spin. The total electronic energy associated with this wavefunction is

$$\mathcal{E} = \left\langle \Psi \left| H^{\text{core}} + V_{ee} \right| \Psi \right\rangle \quad \dots (1.3)$$

$$= 2 \sum_i H_{ii} + \sum_i \sum_j (2J_{ij} - K_{ij}) \quad \dots (1.4)$$

The one electron Hamiltonian, H^{core} , is given by

$$H^{\text{core}} = -\frac{1}{2} \nabla^2 - \sum_A Z_A r_A^{-1} \quad \dots (1.5)$$

and V_{ee} is the operator corresponding to the mutual potential energy between electrons. H_{ii} , J_{ij} and K_{ij} have the following meaning

$$H_{ii} = \left\langle \phi_i(1) \left| H^{\text{core}}(1) \right| \phi_i(1) \right\rangle \quad \dots (1.6)$$

$$J_{ij} = \left\langle \phi_i(1) \phi_i(1) \left| \frac{1}{r_{12}} \right| \phi_j(2) \phi_j(2) \right\rangle \quad \dots (1.7)$$

$$K_{ij} = \left\langle \phi_i(1) \phi_j(1) \left| \frac{1}{r_{12}} \right| \phi_i(2) \phi_j(2) \right\rangle \quad \dots (1.8)$$

These are called respectively the core, coulomb and exchange integrals.

Minimization of the energy (1.4) with respect to all possible variations of the orbitals, subject to the condition that the spin-orbitals be orthonormal leads quite generally to one-electron eigen value equations of the form

$$\mathcal{H}\phi_i = \epsilon_i \phi_i \quad \dots (1.9)$$

where \mathcal{H} is the Hartree-Fock Hamiltonian operator and is equal to

$$\mathcal{H} = \left[H^{\text{core}} + \sum_j (2J_j - K_j) \right] \quad \dots (1.10)$$

J_j , the coulomb operator, and K_j , the exchange operator, are defined through the relations

$$J_j(1) \phi_i(1) = \left\langle \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_j(2) \right\rangle \phi_i(1) \dots (1.11)$$

$$K_j(1) \phi_i(1) = \left\langle \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_i(2) \right\rangle \phi_j(2) \dots (1.12)$$

The equations, (1.9), known as Hartree-Fock equations, can be more conveniently written in the matrix form

$$F\Phi = \epsilon\Phi \quad \dots (1.13)$$

Hartree-Fock equations are determined within a unitary transformation among the orbitals. These transformation keeps both F and ϵ invariant.

The form of the Fock operator shows that the Hartree-Fock equations are integro - differential equations and thus can be solved only by numerical integration techniques. This disturbing aspect of HF method can be averted, as Roothaan⁽⁶⁾ has shown, when the molecular orbitals are expressed in LCAO form. The resulting equations are known as Hartree-Fock-Roothaan (HFR) equations. These can be derived as follows:

Denoting a set of n basis orbitals by ϕ_μ , an MO ψ_i is expressed as

$$\psi_i = \sum_{\mu=1}^n c_{\mu i} \phi_\mu \quad \dots (1.14)$$

There will be n such MO's which can be written in the matrix form

$$\Psi = \Phi C \quad \dots (1.15)$$

substituting (1.15) in (1.13) one gets

$$\mathcal{H}\bar{\phi}c = \bar{\phi}c\varepsilon \quad \dots (1.16)$$

$$\bar{\phi}^*\mathcal{H}\bar{\phi}c = \bar{\phi}^*\bar{\phi}c\varepsilon \quad \dots$$

$$\text{or } Fc = Sc\varepsilon \quad \dots (1.17)$$

The equations contained in (1.17) are HFD equations. Here F is the matrix representation of \mathcal{H} in ϕ_μ basis, and its elements $F_{\mu\nu}$ are given by,

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left\{ (\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma) \right\} \dots (1.18)$$

where, $P_{\lambda\sigma} = 2 \sum_j^{occ.} C_{j\lambda} C_{j\sigma}$... (1.19)

define the matrix elements of the first order density matrix, S is the overlap matrix whose elements are given by

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle \quad \dots (1.20)$$

The orthonormality relation of the MO's becomes

$$\langle \phi_i | \phi_j \rangle = C_i^* S C_j = \delta_{ij}$$

The total electronic energy can be written in terms of integrals over atomic orbitals if we substitute the linear expansion of eqn. (1.14) in the molecular orbital integrals. Thus

$$H_{ii} = \sum_{\mu, \nu} C_{\mu i}^* C_{\nu i} H_{\mu \nu} \quad \dots (1.21)$$

where $H_{\mu \nu}$ is the matrix of the core Hamiltonian with respect to atomic orbitals.

$$H_{\mu \nu} = \int \phi_{\mu}(1) H^{\text{core}} \phi_{\nu}(1) d\tau, \quad \dots (1.22)$$

Similarly we may write

$$J_{ij} = \sum_{\mu \lambda \nu \sigma} C_{\mu i}^* C_{\lambda j}^* C_{\nu i} C_{\sigma j} (\mu \nu | \lambda \sigma) \quad \dots (1.23)$$

$$K_{ij} = \sum_{\mu\nu\lambda\sigma} c_{\mu i}^* c_{\lambda j}^* c_{\nu i} c_{\sigma j} (\mu\nu|\lambda\sigma) \quad \dots \quad (1.24)$$

Where $(\mu\nu|\lambda\sigma)$ is the general two-electron interaction integrals over atomic orbitals.

If these expressions are substituted in eqn. (1.4) for the total electronic energy, we obtain

$$\epsilon = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\nu\sigma) \right] \quad \dots \quad (1.25)$$

The non-trivial solution of eqn. (1.17) are obtained by solving for the n roots of the secular determinant.

$$\det(F_{\mu\nu} - \epsilon S_{\mu\nu}) = 0 \quad \dots \quad (1.26)$$

The matrix elements of the HF Hamiltonian operator are dependent on the orbital through the elements p and the $\mu\nu$ Boothian equations are solved by first assuming an initial set of linear expansion coefficient $c_{\mu i}$, generating the corresponding density matrix $P_{\mu\nu}$ and computing a first guess at $\epsilon_{\mu\nu}$. The diagonalization procedure is effected by standard matrix eigen value techniques and a new matrix of linear expansion coefficients are obtained. The whole process is then repeated until the coefficients no longer change within a given

tolerance on repeated iteration.

Several variants of the ab initio method for computing molecular wavefunctions and energies directly from HF equation has evolved, primarily due to the flexibility and practical considerations in the choice of basis set of atomic orbitals. Because all LCAO MO SCF calculations have to be carried with a finite basis set, its choice is often of paramount importance as far as the accuracy of the result is concerned. The computational limitation in implementing LCAO MO SCF method arises primarily due to the different electron repulsion integrals of the type $(\mu\nu|\lambda\sigma)$ whose number varies as the fourth power of the number of basis orbitals. This severely restricts the exact application of LCAO MO SCF method to molecules, the present limits of this technique being molecules of about the size of ethane and diborane using Slater type orbitals as the basis.

1.3 Choice of Basis set in 'ab initio' LCAO MO SCF method

Though the Slater type functions⁽¹⁰⁾ for basis atomic orbitals (STO) form a satisfactory basis for molecular orbitals, STO's have been only occasionally used in ab initio calculations because of the great difficulties associated with the evaluation of the electron repulsion integrals in the STO basis. The STO's are of the type

$$\phi_{nlm} = N_{nl} r^{n-1} \exp(-\zeta r) Y_{lm} \quad \dots (1.27)$$

where Y_{lm} is the spherical harmonics representing the angular part of the Slater function, N_{nl} is the normalization constant and ζ , the orbital exponent, is calculated according to Slater rule or other modifications or may even be used as a variational parameter.

This has led to the increasing use of Gaussian type orbitals (GTO), eqn. (1.28), introduced by Boys⁽¹⁹⁾ as an alternative to STO's. The evaluation of two centre electron repulsion integrals became much easier with these functions and as such GTO's are now almost exclusively used in ab initio LCAO MO SCF calculations.

$$\phi_{nlm} = N_{nl} r^{n-1} \exp(-\gamma r^2) Y_{lm} \quad \dots (1.28)$$

where the exponents γ are to be determined either by variational procedure or other suitable procedures.

In order to reduce the computational problem to manageable proportions, contracted Gaussian functions⁽²⁰⁻²²⁾ which are

linear combinations of Gaussian with fixed coefficients are used. For example, six sets of D -type Gaussian can be contracted into two sets of linear combinations⁽²²⁾.

A somewhat different approach to the contraction of molecular basis is to simulate the Slater functions by representing each Slater function of minimal basis as a fixed linear combination of a given small number of Gaussian functions. These Gaussian representations of Slater functions are determined most directly by a least-square fitting procedure which has been extensively used by Pople and co-workers^(26,23). A basis in which each Slater function is represented by combination of N Gaussians is generally denoted by STO - n . The results of several of this type of calculations are reported by Hehre⁽²⁹⁾. Pople and co-workers have investigated the variations in the calculated molecular properties with increasing size and flexibility of the basis used to represent the valence molecular orbitals, whilst keeping a minimal basis for the inner-shells. For example, in the basis set $N^* - 3^*2$ ($N = 4$ and 3) each inner-shell orbital is represented by a single basis function which is a combination of N Gaussians and each atomic valence - orbital is split into inner and outer parts described by three Gaussians and one Gaussian respectively. The main disadvantage in using a Gaussian basis is that about

two to five times as many Gaussian functions as Slater functions are required to produce a given accuracy. The main reason for this increase in the basis size on going from Slater to Gaussian functions is the incorrect behaviour of the latter at the end and near the nucleus⁽³³⁾. The problem of evaluating a relatively small number of difficult integrals over STO's has, therefore, been replaced by that of evaluating and manipulating a much larger number of simple integrals in the STO basis. This makes ab initio calculations of molecules of average size almost prohibitive, even when only a moderate accuracy is desired. Increasing attention has therefore been devoted by theoretical chemists to the possibilities and problems of devising reliable theoretical methods through use of simplifying approximations into the exact Hartree-Fock equations.

2.4 Approximate Semiempirical SCF MO Methods

As already mentioned, with present computing facilities reasonably accurate ab initio calculations are possible only for small molecules because of the very large number of multi-centre electron repulsion integrals needed for such calculations. For example, if no approximations are made, ab initio molecular orbital calculation of even a small chemical species like sulphate anion would require the evaluation of 94,380 unique electron repulsion integrals even without including

sulphur 3d orbitals in the basis set. It is, therefore, imperative to make rather drastic, yet reasonable approximations to make the problem manageable for larger molecules which constitute the bulk of Chemistry. This problem has been very lucidly reviewed and analysed by Brown and Toby in a series of papers (34-37).

The primary aim of the approximate methods are to provide simple and responsive computational methods for predicting the molecular properties and structural features with enough accuracy and reliability to be of chemical usefulness. To achieve this, two types of modifications are generally introduced into the full Hartree-Fock treatment:

(i) Approximations which drastically reduce the number of two electron repulsion integrals, e.g., reducing the size of the basis set as in all valence electron methods or by neglecting some of the electron repulsion integrals as in the popular CNDO method.

(ii) To counter balance the loss of accuracy due to approximations for drastically reducing the number of repulsion integrals, most approximate methods employ adjustable parameters which are empirically determined to enhance the accuracy of the predictions. When such adjustable parameters are used the method is generally called 'semiempirical SCF MO' method.

Most of the approximate methods are based on partial or full application of core differential overlap (38)

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approximation embodied in eqn. (1.29) and (1.30) ⁽³³⁾.

$$S_{\mu\nu} = \delta_{\mu\nu} \quad \dots (1.29)$$

$$\text{and } (\mu\nu|\lambda\sigma) = (\mu\mu|\lambda\lambda) \delta_{\mu\nu} \delta_{\lambda\sigma} \quad \dots (1.30)$$

where δ is the Kronecker delta.

The ZDO approximation follows from the approximate equality

$$F^{ZDO} \approx \lambda F \quad \dots (1.31)$$

where F^{ZDO} and λF are the elements of the F -matrix in the ZDO approximation and the Luedin basis ⁽³⁹⁾ respectively.

Although a large number of approximate semiempirical methods can be found in the literature, these may broadly be classified into two categories depending on the form of the secular equation used.

(1) Those methods in which eqn. (1.17) is used to obtain the molecular orbitals may be collectively termed "full overlap methods" since the full overlap matrix is used in the calculation.

(ii) The secular equations in basis of orthogonalised atomic orbitals can be transformed to the form

$$\lambda_F \lambda_C = \lambda_C \epsilon \quad \dots (1.32)$$

where, $\lambda_F = S^{-1/2} F S^{-1/2} \quad \dots (1.33)$

and $C = S^{-1/2} \lambda_C \quad \dots (1.34)$

The methods which employ the secular equation (1.32), whether or not orthogonalised basis set is used, may be collectively termed 'zero differential overlap (ZDO) method'. Three variants of the ZDO method are generally used in all semiempirical calculations:

(a) The complete neglect of the Differential Overlap Method

In this method, developed by Pople et al⁽⁴³⁻⁴⁸⁾, the ZDO approximation given by eqn. (1.29) and (1.30) are applied rigorously to all integrals.

Further, to satisfy the condition of invariance to local orthogonal transformation of basis orbitals, all repulsion integrals of the type $(\mu\mu/\lambda\lambda)$ and nuclear attraction integrals of the type $(\mu/\nu/\mu)$ are replaced by the spherically averaged values computed from the appropriate S^- type orbitals.

The core matrix elements, $H_{\mu\nu}$ are computed from the empirical relation

$$H_{\mu\nu} = (\mu | H^c | \nu) = \beta_{\mu\nu}^{\circ} S_{\mu\nu} \quad \dots (1.35)$$

where $\beta_{\mu\nu}^{\circ}$ is an empirically determined parameter characteristic of the bond $\mu-\nu$.

Using these approximations, the elements of F-matrix take the form (17, 40-42)

$$F_{\mu\mu} = H_{\mu\mu} + \left(P_{AA} - \frac{1}{2} P_{\mu\mu} \right) \gamma_{AA} + \sum_{B(\neq A)} P_{BB} \gamma_{AB} \quad \dots (1.36)$$

(ϕ_{μ} on atom A)

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \quad \dots (1.37)$$

(ϕ_{μ} on atom A and ϕ_{ν} on atom B)

where P_{AA} = total electron population on A

$$= \sum_{\mu}^A P_{\mu\mu}$$

and $P_{\mu\nu}$'s are the elements of the bond order matrix.

Because of the drastic nature of the approximations CNDO method is capable of providing semi-quantitative information only. Some of the deficiencies of the CNDO method are corrected in the following modifications.

(15,43)
 (b) The Many-centre Core differential Overlap (MCOO) Method

In this method, in addition to the COO integrals all one centre integrals are retained and the average values for two centre integrals are used as in the COO method.

The INDO and MINDO methods which differ only in the method of computing the integrals belong to this class.

The inclusion of core integrals in the MCOO method makes it more reliable compared to the COO method.

(42)
 (c) The Neglect of Diatomic Differential Overlap (NDDO) Method

Most of the serious deficiencies of the COO method are removed in the NDDO method by retaining even two centre integrals of the type $(\mu\nu | \lambda\sigma)_{AB}$. The NDDO approximation is given by the condition

$$(\mu\nu | \lambda\sigma) = 0, \quad \text{unless}$$

ϕ_μ and ϕ_ν are on the same atom A and ϕ_λ and ϕ_σ on the same atom B which may equal A.

In the contrast to the COO method, the full overlap methods retain both the overlap integrals and integrals involving two centre charge distribution.

The orbital energies and molecular orbitals are obtained by solving the secular determinant.

$$|F - SE| = 0 \quad \dots (1.38)$$

Two approaches are generally used for computing the different many centre integrals.

(1) The Mulliken Method (44)

In this method, the two centre one electron and two electron integrals are obtained from the Mulliken approximations (44-46) given by the equations:

$$\left(\mu_A | \hat{M} | \lambda_B \right) = \frac{S_{\mu\lambda}}{2} \left[\left(\mu_A | \hat{M} | \mu_A \right) + \left(\lambda_B | \hat{M} | \lambda_B \right) \right] \dots (1.39)$$

$$\begin{aligned} \left(\mu_A \nu_B | \lambda_C \sigma_D \right) = \frac{S_{\mu\nu} S_{\lambda\sigma}}{4} & \left[\left(\mu_A \mu_A | \lambda_C \lambda_C \right) + \left(\mu_A \mu_A | \sigma_D \sigma_D \right) \right. \\ & \left. + \left(\nu_B \nu_B | \lambda_C \lambda_C \right) + \left(\nu_B \nu_B | \sigma_D \sigma_D \right) \right] \dots (1.40) \end{aligned}$$

It has been pointed out that invariance to local orthogonal transformation can be maintained only if average values are used for the integrals in R.H.S. of eqn. (1.39) and (1.40).

(ii) The Huzenberg method⁽⁴⁷⁾ which is the full overlap counter part of the HDO method, consists of replacing the two centre charge distribution of the type $|\mu_A \nu_B\rangle$ by

$$|\mu_A \nu_B\rangle = \frac{1}{2} \left\{ \sum_{\tau}^A S_{\tau\lambda} |\mu_A \tau_A\rangle + \sum_{\sigma}^B S_{\mu\sigma} |\sigma_B \nu_B\rangle \right\} \quad \dots (1.41)$$

The interrelationship between the various approximations involved have been discussed by Brown and Roly⁽³⁴⁻³⁷⁾.

1.5 Localised Molecular orbitals and the Bond orbital Approach:

The molecular orbitals in the Hartree-Fock model are symmetry orbitals which belong to the irreducible representations of the symmetry group of the molecule, and they are usually delocalised orbitals extending over several or all the nuclei of the molecule. In the classical language this amounts to saying that the electrons may be regarded as belonging to the different parts of the molecule and, therefore, seems to run counter to our chemical description of the molecule, whereby the electrons in the molecule are divided into groups such as inner shells, lone pairs and bond pairs. The deficiency of the Hartree-Fock MO's is only apparent rather

than real, because it is possible to manipulate the form of molecular orbitals so as to generate localized orbitals, orbitals that are localized almost wholly in the vicinity of different groups of the molecule corresponding to our chemical concepts of lone pairs, bond pairs, inner shells etc.

The closed-shell ground state of an N -electron system can be mathematically represented by a single determinant wavefunction Ψ , constructed from $N/2$ doubly occupied orthonormal orbitals.

$$\Psi = \left| \phi_1 \alpha, \phi_1 \beta, \dots, \phi_{N/2} \alpha, \phi_{N/2} \beta \right| \quad \dots (1.42)$$

A linear transformation of the orbitals

$$\lambda_k = \sum_{n=1}^{N/2} \phi_n C_{nk} \quad \dots (1.43)$$

($k = 1, 2 \dots N/2$)

gives a new wavefunction

$$\Psi' = \left| \lambda_1 \alpha, \lambda_1 \beta \dots \lambda_{N/2} \alpha, \lambda_{N/2} \beta \right| \quad \dots (1.44)$$

Equation (1.44) is related to the equation (1.42) by

$$\Psi = \Psi' (\det C)^2 \quad \dots (1.45)$$

If the transformation given by eqn. (1.43) is orthogonal, then

$$(C)(\tilde{C}) = 1, \quad (\det C)^2 = 1$$

$$\text{and } \Psi = \Psi'$$

Thus Ψ is invariant to orthogonal transformations of the real ϕ 's ϕ and such a transformation of eqn. (1.43) is unitary and this property of the basis functions allows the orbital to be chosen in most convenient way for the interpretation of the molecular properties of the system. Similarly, the localised molecular orbitals can also be generated by suitably choosing C_{nk} 's through transformation (1.43).

Several methods have been proposed for the localization of molecular orbitals. The most objective localization procedure that could be employed would involve the construction of orbitals which are separated from each other as much as possible without having to stipulate in advance the location of these orbitals in space. Such a localization would require that the

definition of separation be decided upon.

The "Degree of separation" can be measured in a number of ways such as steric-chemically and energetically. The two most commonly used methods adopt these two different measures. In the Boys method of localisation⁽⁴⁸⁾, the sum of the distance between the centroids of electron pairs is maximised, while in Rabinstein - Ruedenberg method⁽⁴⁹⁾, the separation of electron pairs is achieved through the maximisation of 'total self energy'. The 'total self energy' is defined by the relation

$$D = \sum_{i=1}^{N/2} J_{ii} = \sum_{i=1}^{N/2} K_{ii} \quad \dots (1.46)$$

where J_{ii} and K_{ii} are diagonal elements of Coulomb and exchange integrals and D is known as total self energy which provides criterion for the localisation of the electrons in pairs.

Since there is nothing unique about the localisation criteria, several other criteria⁽⁵⁰⁻⁵¹⁾ have also been used to generate localized orbitals from delocalized MO's. These procedures so far discussed are known as "intrinsic localisation".

Problem with the intrinsic localization procedure is that none of these localization criteria are unique and their application requires, in general, a significant amount of extra computational labour. It is hardly worthwhile to succumb to this huge computational work required to obtain orbitals which fit better to our traditional chemical language.

Obviously, the simplest approach to localized orbitals will be to use the chemical concept of bonds, lone pairs, inner shells etc. This can be achieved by using hybridised atomic orbitals (HAO) that are already localized in a specified region of space. The localized molecular orbital (LMO) representing a chemical bond can then be constructed by making linear combination of the appropriate HAO's. Such a localization procedure is often termed "the external localization".

The molecular orbitals can then be written as

$$\Psi_{M_0} = \sum_i c_{ij} \phi_i \quad \dots (1.47)$$

where ϕ_i 's are appropriately chosen bond orbital localized at each bond (HAO's).

Leppard - Jones et al (52-55) showed that in asymmetrical molecule the set of Ψ_i obtained by LMO scheme can be transformed by a unitary transformation into another set of

equivalent ψ_i is localized essentially at each bond or each lone pair orbital. The orbitals, thus obtained, are called 'equivalent orbitals' and are reasonably expected to resemble the basis function in the LCAO scheme. In other words the obscuration of the bond concept owing to the procedure of the LCAO scheme is recovered by the Lennard - Jones concept of equivalent orbitals.

The foregoing analysis forms the physical basis for adopting 'Bond orbital' concept in the discussion of saturated molecules yielding a variety of simplified methods (12,36-31,78).

Although the 'Bond orbitals' which are fully localized within the bond (i.e. strictly two centre molecular orbitals) cannot describe the electron distribution in a molecule as accurately as the delocalized LCAO MO, they provide a sufficiently accurate description of the situation in saturated molecules. Further, the computational ease coupled with their close correspondence to our chemical description of molecules have made the bond orbital approach a very useful method for the interpretation of ground state molecular properties in saturated systems. With proper parametrization such methods can give a very good account of many molecular properties with almost insignificant computational labour. This is, perhaps, best illustrated by the H₂ Ko⁽¹²⁾ method which has found

extensive applications in organometallic chemistry as a single tool for the interpretation and correlation of chemical and physical properties, such as, reactivity, IR and NMR data, dipole-moment, Heisenberg spectral data, hybridisation etc (56-60). Because of this, the localized MO approach has not lost its relevance to chemistry even today though the advent of fast and large computers has made more sophisticated SCF MO calculations on fairly large molecules now possible.

That a fully localized SCF MO calculation based on two centre MO's can provide a reasonably good account of ground state charge distributions and dipole moments in saturated systems has been demonstrated by Del Re et al (61). The practical advantage of such a procedure lies primarily in saving computer time required to diagonalise the Fock matrix in the full SCF MO counterpart, such as, CNDO or INDO methods, apparently without any significant difference in the calculated charge distributions. The Del Re method (61) can, however, at best be regarded as a simplified procedure for obtaining charge distribution in saturated molecules using CNDO or INDO parametrisation and satisfies only the first of the four criteria that we set for the proposed approach (sec 1.1).

We shall now consider the nature of approximations and a suitable procedure for obtaining the best possible description

of the electronic structure of a molecule in terms of one and two centre MO's representing respectively, the lone pairs and bond pairs in a molecule.

1.3 Criteria for 'best possible' bond orbital or fully localised MO description

Since our general aim is to develop a computationally simple approach for the description of a molecule in terms of chemical concepts such as inner shells, lone pairs and bond pairs, we shall first consider the construction of hybrid orbitals for a 'best possible' description in terms of localised orbitals constructed by combining suitable hybrids on adjacent atoms.

Although several methods have been devised for constructing a set of localised orbitals from a wavefunction based on non-localised SCF MO's or for constructing the hybrid MO's from which such orbitals may be constructed (62-66), they do not suit our requirements.

Consider a closed shell one determinant wavefunction in which the MO's have been obtained by Hartree-Fock SCF procedure using a basis set ϕ . The electronic energy E_{HF} of the system in one determinant approximation is then given by (40-41)

$$E_{HF} = \frac{1}{2} \sum_{\mu, \nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) \quad \dots (1.48)$$

$$= \frac{1}{2} \text{tr.} \{ P (H + F) \} \quad \dots (1.49)$$

Where tr denotes the trace and H , F and P are, respectively, the core, Fock and density matrices whose elements $H_{\mu\nu}$, $F_{\mu\nu}$ and $P_{\mu\nu}$ are given by eqns. (1.22), (1.18) and (1.19).

Provided a full LCAO MO SCF calculation is done it is irrelevant whether these are ordinary atomic orbitals (AO) or orthogonalised AO's or hybrids formed by mixing AO's since the total electron density at any point and energy remain invariant⁽³⁹⁾. However, if we introduce some restrictions on the form of MO's or improper approximations, the choice of basis orbital will have effect on the calculated energy and charge distribution. To elaborate this, let us consider another basis ϕ' , which we shall assume to be hybrids formed by mixing the atomic orbitals which constitute the basis ϕ . The two basis ϕ and ϕ' will be related to each other through an orthogonal transformation matrix O by

$$\phi' = O \phi \quad \dots (1.50)$$

Although the total energy and electron density at any point must remain invariant to such change of basis, the matrices P , H and F will assume different forms in the new basis ϕ' . If we represent these matrices by P' , H' and F' , respectively, in the basis ϕ' , then we have

$$P' = O P O^{-1} \quad \dots (1.51)$$

$$H' = O H O^{-1} \quad \dots (1.52)$$

$$F' = O F O^{-1} \quad \dots (1.53)$$

This relationship between the old and new set of matrices will hold only if both sets are obtained through full LCAO MO SCF calculations.

We now introduce the localized MO approximation whereby we assume that an MO, $\Psi_{\mu\nu}$, representing a bond is formed by the overlapping of strictly concentric hybrids (hybrids formed by mixing AO 's on the same centre only) ϕ'_{μ} and ϕ'_{ν} on two adjacent atoms and has the form

$$\Psi_{\mu\nu} = C_{\mu} \phi'_{\mu} + C_{\nu} \phi'_{\nu} \quad \dots (1.54)$$

Similarly, a lone pair is assumed to be representable by a strictly monocentric hybrid orbital. These assumptions impose a restriction on the form of the density matrix in the localised MO approach. Obviously, the density matrix in this approximation (which we shall denote by P_{Loc}) will be of block diagonal form consisting of $S \times S$ submatrices corresponding to MO's given by eqn. (1.54) and diagonal S 's representing lone pairs as shown below:

$$P_{Loc} = \begin{matrix} & \begin{matrix} \mu & \nu & \lambda & \sigma & \dots \end{matrix} \\ \begin{matrix} \mu \\ \nu \\ \lambda \\ \sigma \\ \vdots \end{matrix} & \begin{bmatrix} P_{\mu\mu} & P_{\mu\nu} & 0 & 0 & 0 & \dots \\ P_{\nu\mu} & P_{\nu\nu} & 0 & 0 & 0 & \dots \\ 0 & 0 & P_{\lambda\lambda} & P_{\lambda\sigma} & 0 & \dots \\ 0 & 0 & P_{\sigma\lambda} & P_{\sigma\sigma} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{bmatrix} \end{matrix} \quad \dots (1.55)$$

This form of the density matrix can result from a full LCAO MO SCF calculation only if all $F_{\mu\nu}$'s ($\mu \neq \nu$) in the hybrid basis ϕ' vanish except when $\mu-\nu$ represents a bond. Although hybrid orbitals have strong directional character and may be so chosen as to maximize the overlap with only one orbital on the adjacent atom, in general, other orbitals will also overlap to some extent so that the F -matrix is not really of block diagonal form in the hybrid basis ϕ' , although the elements which are neglected in the localized approximation are usually very small in a properly chosen hybrid basis. Because of this, P_{Loc} , the density matrix obtained by localized MO calculation and P' , the density matrix obtained in full LCAO MO calculation using the same hybrid basis, ϕ' , are not identical. We may, therefore, write

$$P' = P_{Loc} + \Delta P \quad \dots (1.59)$$

where ΔP is the difference matrix of P' and P_{Loc}

We now have,

$$\begin{aligned} E_{HF} &= \frac{1}{2} \text{tr} \{ P(H+F) \} \\ &= \frac{1}{2} \text{tr} \{ O P O^{-1} (O H O^{-1} + O F O^{-1}) \} \\ &= \frac{1}{2} \text{tr} \{ P' (H' + F') \} \\ &= \frac{1}{2} \text{tr} \{ P_{Loc} (H' + F') \} + \frac{1}{2} \text{tr} \{ \Delta P (H' + F') \} \\ &= E_{Loc} + \Delta E \end{aligned} \quad \dots (1.57)$$

where

$$\Delta E = \frac{1}{2} \text{tr} \{ \Delta P (H' + F') \} \quad \dots (1.58)$$

$$E_{Loc} = \frac{1}{2} \text{tr} \{ P_{Loc} (H' + F') \} \quad \dots (1.59)$$

is the energy which will obtain through localised MO calculation using ϕ' as our basis.

Though eqn. (1.57) is invariant to an orthogonal transformation, the individual elements on the R.H.S. i.e., E_{loc} and ΔE are not separately invariant because the matrix ΔP which reflects the error in charge distribution obtained by localised MO approach will depend on the choice of our hybrids ϕ' . Clearly, if it were possible to describe the SCF MO charge distribution exactly by strictly one and two centre MO's as envisaged in the bond orbital approach, both ΔE and ΔP would be zero for correctly chosen hybrid orbitals. This, however, is not generally possible. Therefore, the best possible localised description will result only when the hybrid basis ϕ' is so chosen that $|\Delta E|$ is as small as possible. Therefore, in a localised approach, it is imperative that the basis ϕ' be so chosen that

$$\delta |\Delta E| = \text{minimum}$$

$$\text{or } \delta (E_{loc} - E_{HF}) = 0$$

$$\text{or } \delta E_{loc} = 0$$

... (1.60)

Since E_{HF} is invariant to the choice of basis set as long as they are related by orthogonal transformation,

We shall use eqn. (1.60) as a fundamental one for the choice of fully localized MO's of a molecule. The computational problem for its implementation will be discussed later.

1.7 (1) Approximations for the evaluation of the core, Fock and density matrix elements

The diagonal and the off-diagonal elements of the Fock matrix, $F_{\mu\mu}$ and $F_{\mu\nu}$ are given by ⁽⁶⁾

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\mu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\mu\sigma) \right] \dots (1.61)$$

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\lambda|\nu\sigma) \right] \dots (1.62)$$

Where $P_{\lambda\sigma}$'s are the elements of the density matrix.

Since our aim is to reduce computational labour as much as possible with reasonable approximations, we shall adopt Mulliken approximation ⁽⁶⁷⁾ for the evaluation of integrals. In this approximation we write

$$(\mu\mu|\lambda\sigma) = \frac{1}{2} \left[(\mu\mu|\lambda\lambda) + (\mu\mu|\sigma\sigma) \right] S_{\lambda\sigma} \dots (1.63)$$

Using this approximation (eqn. 1.63) we have

$$\begin{aligned} \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\mu|\lambda\sigma) &= \frac{1}{2} \left[\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\mu|\lambda\lambda) S_{\lambda\sigma} \right. \\ &\quad \left. + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\mu|\sigma\sigma) S_{\lambda\sigma} \right] \\ &= \sum_{\lambda} P'_{\lambda\lambda}(\mu\mu|\lambda\lambda) \quad \dots (1.64) \end{aligned}$$

where, $P'_{\lambda\lambda} = \sum_{\sigma} P_{\lambda\sigma} S_{\lambda\sigma} \quad \dots (1.65)$

is Mulliken's gross population⁽⁶³⁾.

Similarly,

$$\begin{aligned} \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\lambda|\mu\sigma) &= \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\mu|\mu\mu) + (\mu\mu|\sigma\sigma) \right. \\ &\quad \left. + (\lambda\lambda|\mu\mu) + (\lambda\lambda|\sigma\sigma) \right] \frac{S_{\mu\lambda} S_{\mu\sigma}}{4} \\ &= \frac{1}{2} \sum_{\sigma} P_{\mu\sigma}(\mu\mu|\mu\mu) S_{\sigma\mu} \\ &\quad + \frac{1}{2} \sum_{\lambda} P_{\mu\lambda}(\mu\mu|\mu\mu) S_{\lambda\mu} + O(S^2) \\ &= P'_{\mu\mu}(\mu\mu|\mu\mu) + O(S^2) \quad \dots (1.66) \end{aligned}$$

where,
$$P'_{\mu\mu} = \sum_{\sigma} P_{\mu\sigma} S_{\sigma\mu} \quad \dots (1.67)$$

In eqn. (1.66), the last term is effectively second order in overlap and is dropped to make the approximation consistent since Mulliken approximation itself is correct to first order in overlap.

Eqn (1.61) can now be written as

$$F'_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P'_{\mu\mu} (\mu\mu|\mu\mu) + \sum_{\lambda} P'_{\lambda\lambda} (\mu\mu|\lambda\lambda) \quad \dots (1.68)$$

which is identical in form to the expression used in the CNDO approximation. However, this derivation clearly shows that the CNDO expression for the repulsion interaction is expected to give a reasonable value only if gross population is used instead of density matrix elements obtained in the full LCAO MO SCF method.

This condition is automatically fulfilled within the approximations inherent in the derivation of eqn. (1.67) in the CNDO method due to the form of the Fock equation used:

$$F' C' = C' \epsilon \quad \dots (1.69)$$

Comparison with the Fock equation in any arbitrary non orthogonal basis set

$$FC = SC \epsilon \quad \dots (1.70)$$

then shows

$$C' = S^{1/2} C$$

Again, the density matrix P obtained from the solution of eqn. (1.69) is related to the density matrix obtained through full calculation (eqn. 1.70) by

$$P' = C' \bar{C}' = S^{1/2} C \bar{C} S^{1/2} = S^{1/2} P S^{1/2} \quad \dots (1.71)$$

Using S -expansion technique ⁽⁶⁹⁻⁷⁰⁾ it is easy to show

$$P'_{\lambda\lambda} = \sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda} + O(S^2) \quad \dots (1.72)$$

Therefore, use of eqn. (1.69) results in a density matrix whose diagonal elements represent the Mulliken's gross population correct to the first order in overlaps.

This analysis, thus, provides a better insight into the CNDO approximations than the analysis reported so far^(61,34-37).

In order to ensure rotational invariance of the electron repulsion energy, the following simplification is necessary⁽¹⁷⁾.

$$\left. \begin{aligned} (\mu\mu|\lambda\lambda) &= \gamma_{AB} \\ (\mu\mu|\mu\mu) &= \gamma_{AA} \end{aligned} \right\} \dots (1.73)$$

where all μ on atom A and all λ on atom B.

This approximation implies that all interactions are replaced by the spherical average.

Using eqn. (1.73), we therefore, have

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P'_{\mu\mu} \gamma_{AA} + \sum_B \sum_A P'_{\mu\lambda} \gamma_{AB} \dots (1.74)$$

(ii) Approximations used for the evaluation of the diagonal elements, $H_{\mu\mu}$ and $F_{\mu\mu}$

In order to correct for the deficiencies of Slater type orbitals (STO's) in representing the core binding energies in

atoms, we shall adopt the CNDO procedure for evaluating the diagonal elements from the atomic spectroscopic data.

The core matrix element,

$$H_{\mu\mu} = \langle \mu | H | \mu \rangle \quad \dots (1.75)$$

where the core Hamiltonian operator H is defined by

$$H = \hat{T} + V_A + \sum_{B(\neq A)} V_B \quad \dots (1.76)$$

where \hat{T} and V are the kinetic and potential energy operators respectively, can be written in the form

$$H_{\mu\mu} = U_{\mu\mu} + \sum_{B(\neq A)} \langle \mu | V_B | \mu \rangle \quad \dots (1.77)$$

where the core binding energy $U_{\mu\mu}$ is defined as

$$U_{\mu\mu} = \langle \mu | \hat{T} + V_A | \mu \rangle \quad \dots (1.78)$$

and represents the energy of an electron in the orbital ϕ_{μ} (one electron orbital energy).

Using the procedure adopted for the estimation of $U_{\mu\mu}$ from atomic data in the CNDO/2 method⁽⁴⁰⁻⁴²⁾ we may write

$$U_{\mu\mu} = -\frac{1}{2} (I_{\mu} + A_{\mu}) - (Z_A - \frac{1}{2}) \gamma_{AA} \quad \dots (1.79)$$

where I_{μ} and A_{μ} are the ionisation potential and electron affinity appropriate to the orbital ϕ_{μ} .

The core potential terms, $\langle \mu | V_B | \mu \rangle$ are also evaluated by the CNDO/2 procedure, i.e.,

$$\langle \mu | V_B | \mu \rangle = -Z_B \gamma_{AB} \quad \dots (1.80)$$

where Z_B is the core charge on atom B.

This gives

$$H_{\mu\mu} = -\frac{1}{2} (I_{\mu} + A_{\mu}) - (Z_A - \frac{1}{2}) \gamma_{AA} - \sum_{\substack{B \\ B \neq A}} Z_B \gamma_{AB} \dots (1.81)$$

Substituting this in the expression for $F_{\mu\mu}$ (eqn. 1.74) we have

$$F_{\mu\mu} = -\frac{1}{2} (I_{\mu} + A_{\mu}) + \frac{1}{2} (1 - P_{\mu\mu}') \gamma_{AA} + \sum_B \sum_{\lambda}^B (P_{\lambda\lambda}' - n_{\lambda}) \gamma_{AB} \dots (1.82)$$

since, $Z_B = \sum_{\lambda}^B n_{\lambda}$

where n_{λ} is the number of electron in the orbital ϕ_{λ} .

Using the partial charges q_{λ} defined by

$$q_{\lambda} = (n_{\lambda} - P_{\lambda\lambda}') \dots (1.83)$$

we arrive at the final expression for $F_{\mu\mu}$:

$$\begin{aligned}
 F_{\mu\mu} &= \alpha_{\mu} + \frac{1}{2} q_{\mu} \gamma_{AA} - \sum_B \sum_A^B q_A \gamma_{AB} \\
 &= \alpha_{\mu} + \frac{1}{2} q_{\mu} \gamma_{AA} - \sum_K q_K \gamma_{AK} \quad \dots (1.34)
 \end{aligned}$$

where, $\alpha_{\mu} = -\frac{1}{2} (I_{\mu} + A_{\mu}) \quad \dots (1.35)$

In equation (1.34), we have replaced summation over λ (on B) and B by a single summation over K covering the entire set of basis orbitals with the implicit assumption that γ_{AR} is to be replaced by the spherically average value.

(iii) An approximate expression for the off diagonal elements, $F_{\mu\nu}$.

While the deficiencies of the approximate procedure for the evaluation of $F_{\mu\mu}$ can be atleast partly compensated by proper choice of empirical values for the off-diagonal elements which strongly influence the calculated charge distribution and energy, such a procedure is hardly desirable

since our aim is to develop a method with a strong theoretical justification.

In order to be able to correctly assess the order of approximations involved, vis-a-vis, a nonempirical SCF calculations, it is desirable to develop a suitable expression for the off diagonal elements, $F_{\mu\nu}$'s. It will now be shown that a computationally simple expression can be deduced for $F_{\mu\nu}$ using Mulliken approximation (87).

We shall first express the electron repulsion terms in eqn. (1.62) in terms of the Mulliken gross population, defined by eqn. (1.67). Using Mulliken approximation for two centre overlap charge distribution we have

$$\sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) = \frac{1}{2} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda} \left[(\mu\nu|\lambda\lambda) + (\mu\nu|\sigma\sigma) \right]$$

$$= \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu|\lambda\lambda) \quad \text{eq. (1.86)}$$

because

$$\begin{aligned} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda} &= \sum_{\lambda} (u\lambda|\lambda\lambda) \sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda} \\ &= \sum_{\lambda} P'_{\lambda\lambda}(u\lambda|\lambda\lambda) \quad \dots (1.07) \end{aligned}$$

similarly:

$$\begin{aligned} \sum_{\lambda} P_{\mu\lambda}(u\lambda|uv) &= \frac{1}{2} \sum_{\lambda} P_{\mu\lambda} S_{\lambda\mu} [(u\mu|uv) + (\lambda\lambda|uv)] \\ &= \frac{1}{2} P'_{\mu\mu}(u\mu|uv) + \frac{1}{2} \sum_{\lambda} P_{\mu\lambda} S_{\lambda\mu} (\lambda\lambda|uv) \\ &= P'_{\mu\mu}(u\mu|uv) + \frac{1}{2} \sum_{\lambda} P_{\mu\lambda} S_{\lambda\mu} [(\lambda\lambda|uv) \\ &\quad - (u\mu|uv)] \\ &= P'_{\mu\mu}(u\mu|uv) + O(S^3) \quad \dots (1.08) \end{aligned}$$

$$\approx P_{\mu\mu}'(\mu\mu|\mu\nu) \quad \dots (1.88)$$

In eqn. (1.88), the last term is effectively third order in overlap because the terms of the type $(\mu\mu|\mu\nu)$ and $(\lambda\lambda|\mu\nu)$ are first order in S (Mulliken approximation) and also the bond order $P_{\mu\lambda}$ is proportional to $S_{\mu\lambda}$. In fact, $P_{\mu\lambda} S_{\lambda\mu}$ is appreciable only if the orbitals ϕ_μ and ϕ_λ are spatially close to each other in which case $(\mu\nu|\lambda\lambda) \approx (\mu\nu|\mu\mu)$ making the difference $[(\mu\nu|\lambda\lambda) - (\mu\nu|\mu\mu)]$ very small. Therefore, the last term can be neglected without introducing much error.

Using eqn. (1.86) and (1.88) we, therefore, have

$$\begin{aligned} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma}(\mu\lambda|\nu\sigma) &= \sum_{\lambda} P_{\mu\lambda}(\mu\lambda|\mu\nu) + \sum_{\sigma} P_{\nu\sigma}(\mu\lambda|\nu\sigma) \\ &+ P_{\mu\nu}(\mu\mu|\nu\nu) + \left[\sum_{\lambda} \sum_{\sigma(\neq\mu,\nu)} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) \right. \\ &\quad \left. - P_{\mu\nu}(\mu\nu|\mu\nu) \right] \\ &\approx P_{\mu\mu}'(\mu\mu|\mu\nu) + P_{\nu\nu}'(\mu\nu|\nu\nu) \\ &+ P_{\mu\nu}'(\mu\mu|\nu\nu) \quad \dots (1.89) \end{aligned}$$

Again, only the second order terms in β are neglected and $P_{\mu\nu}$ is replaced by $P'_{\mu\nu}$ since the difference is always small and is partly compensated by the neglect of the second order terms.

Combining eqn. (1.98), (1.99) and (1.90) we have

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu} + \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu/\lambda\lambda) - \frac{1}{2} P'_{\mu\mu}(\mu\mu/\mu\nu) \\ &\quad - \frac{1}{2} P'_{\nu\nu}(\nu\nu/\mu\nu) - \frac{1}{2} P'_{\mu\nu}(\mu\mu/\nu\nu) \\ &= \beta_{\mu\nu} - \frac{1}{2} P'_{\mu\nu}(\mu\mu/\nu\nu) \quad \dots (1.91) \end{aligned}$$

where

$$\begin{aligned} \beta_{\mu\nu} &= H_{\mu\nu} + \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu/\lambda\lambda) - \frac{1}{2} P'_{\mu\mu}(\mu\mu/\mu\nu) \\ &\quad - \frac{1}{2} P'_{\nu\nu}(\nu\nu/\mu\nu) \quad \dots (1.92) \end{aligned}$$

Now

$$\begin{aligned}
 H_{\mu\nu} &= \left(\mu | \hat{T} + V_A + V_B | \nu \right) + \sum_{C(\neq A, B)} (\mu | V_C | \nu) \\
 &= \frac{1}{2} \left[(\nu | \hat{T} + V_A | \mu) + (\mu | \hat{T} + V_B | \nu) \right. \\
 &\quad \left. + (\mu | V_A | \nu) + (\nu | V_B | \mu) \right] \\
 &\quad + \sum_{C(\neq A, B)} (\mu | V_C | \nu) \dots (1.93)
 \end{aligned}$$

In eqn. (1.93), the orbitals ϕ_μ and ϕ_ν are assumed to be associated, respectively, with atoms A and B.

Using core binding energies defined by eqn. (1.76) along with Mulliken approximation for the charge distribution $\phi_\mu \phi_\nu$ in eqn. (1.93), we have

$$\begin{aligned}
 H_{\mu\nu} &= \frac{1}{2} \left[(U_{\mu\mu} + U_{\nu\nu}) S_{\mu\nu} - (\mu | V_A | \nu) \right. \\
 &\quad \left. - (\nu | V_B | \mu) \right] - \sum_{C(\neq A, B)} (\mu | V_C | \nu) \dots (1.94)
 \end{aligned}$$

Use of Goepfert-Hoyer, Sklar procedure⁽⁷¹⁾ for the evaluation of the nuclear attraction integrals $(\mu|V_c|\nu)$ then gives

$$(\mu|V_c|\nu) = - \left[(\mu|V_c^0|\nu) + \sum_{\lambda}^c (\mu\nu|\lambda\lambda) \right] \dots (1.95)$$

where $(\mu|V_c^0|\nu)$ denotes the interaction energy of the charge distribution $\phi_{\mu}\phi_{\nu}$ with neutral atom C.

Combining eqns. (1.92), (1.94) and (1.95) we have

$$\begin{aligned} \beta_{\mu\nu} = & \frac{1}{2} \left[(U_{\mu\mu} + U_{\nu\nu}) S_{\mu\nu} - \sum_{A,B} (\mu\nu|\lambda\lambda) \right. \\ & \left. + (\mu|V_A^0|\nu) + (\mu|V_B^0|\nu) \right] \\ & - \sum_{\lambda(\neq A,B)} (\mu\nu|\lambda\lambda) + \sum_{c(\neq A,B)} (\mu|V_c^0|\nu) \\ & + \sum_{\lambda} P'_{\lambda\lambda} (\mu\nu|\lambda\lambda) - \frac{1}{2} P'_{\mu\mu} (\mu\mu|\mu\nu) \\ & - \frac{1}{2} P'_{\nu\nu} (\nu\nu|\mu\nu) \dots (1.96) \end{aligned}$$

Using the partial charge defined by

$$q_{\lambda} = (1 - P_{\lambda\lambda}) \quad \dots (1.97)$$

eqn. (1.96) may be rearranged to give

$$\begin{aligned} \beta_{\mu\nu} &= \frac{1}{2} \left[(U_{\mu\mu} + U_{\nu\nu}) S_{\mu\nu} + \sum_{\lambda \neq \mu, \nu}^{A, B} (u\nu | \lambda\lambda) \right. \\ &\quad \left. + (u | v_A^{\circ} | v) + (u | v_B^{\circ} | v) - q_{\mu} (u\mu | \nu\nu) \right. \\ &\quad \left. - q_{\nu} (\nu\nu | \mu\mu) \right] - \sum_{\lambda} q_{\lambda} (u\nu | \lambda\lambda) \\ &\quad + \sum_{C \neq A, B} (u | v_C^{\circ} | v) \\ &\cong \frac{1}{2} \left[(U_{\mu\mu} + U_{\nu\nu}) S_{\mu\nu} + \sum_{\lambda \neq \mu, \nu}^{A, B} (u\nu | \lambda\lambda) \right. \\ &\quad \left. + (u | v_A^{\circ} | v) + (u | v_B^{\circ} | v) \right] \quad \dots (1.98) \end{aligned}$$

The three centre penetration integrals $(\mu|V_C^\circ|v)$ are always small (of the order of ξ^2 or less) and have been neglected in deriving eqn. (1.95). Further, the term $\sum_{\lambda} q_{\lambda}(\mu|\lambda)$ is also small, not only because $q_{\lambda} \ll 1$, but because of the electrical neutrality condition

$$\sum_{\lambda} q_{\lambda} = 0$$

gives

$$\sum_{\lambda} q_{\lambda}(\mu\nu|\lambda\lambda) \approx (\mu\nu|\lambda\lambda)_{av.} \sum_{\lambda} q_{\lambda} = 0$$

where $(\mu\nu|\lambda\lambda)_{av.}$ is the average value. The two small terms $q_{\mu}(\mu\mu|\mu\nu)$ and $q_{\nu}(\nu\nu|\mu\nu)$ are also effectively second order in ξ and are dropped.

A further simplification is achieved by using Mulliken approximation for overlap charge and neglecting all the centre penetration integrals. Thus

$$\beta_{\mu\nu} = \frac{1}{2} \left[(U_{\mu\mu} + U_{\nu\nu}) + \frac{1}{2} \left\{ \sum_{\lambda(A,B)}^{\neq \mu, \nu} (\mu\mu|\lambda\lambda) + \sum_{\lambda(A,B)}^{\neq \mu, \nu} (\nu\nu|\lambda\lambda) + (\mu|V_A^\circ|\mu) + (\nu|V_B^\circ|\nu) \right\} \right] S_{\mu\nu}$$

... (1.99)

In order to satisfy the condition of invariance to local orthogonal transformation, the repulsion integrals are to be replaced by their spherical averages, γ_{AA} , γ_{AB} etc, so that

$$\beta_{\mu\nu} = \frac{1}{2} [U_{\mu\mu} + U_{\nu\nu} + \frac{1}{2} \{ (Z_A - 1) \gamma_{AA} + (Z_B - 1) \gamma_{BB} + (Z_A + Z_B - 2) \gamma_{AB} + (\mu | v_A^\circ | \mu) + (\nu | v_B^\circ | \nu) \}] S_{\mu\nu} \quad \dots (1.100)$$

The one centre penetration integral $(\mu | v_A^\circ | \mu)$ represents the energy of interaction of the charge distribution ϕ_μ^2 with neutral atom A, and may, therefore, be interpreted as the energy of interaction of adding an electron to the orbital ϕ_μ of the neutral atom A. These terms can, therefore, be replaced by the orbital electron affinity, with appropriate sign.

Further, using the relations

$$I_{\mu\mu} = -U_{\mu\mu} - (Z_A - 1) \gamma_{AA} \quad \dots (1.101)$$

and

$$A_{\mu} = I_{\mu} - \gamma_{AA} \quad \dots (1.102)$$

so can express $\beta_{\mu\nu}$ as

$$\beta_{\mu\nu} = -\frac{1}{4} \left[3(I_{\mu} + I_{\nu}) + (Z_A^{-2})\gamma_{AA} + (Z_B^{-2})\gamma_{BB} - (Z_A + Z_B^{-2})\gamma_{AB} \right] S_{\mu\nu} \quad \dots (1.103)$$

$$= \beta_{\mu\nu}^{\circ} S_{\mu\nu} \quad \dots (1.104)$$

where

$$\beta_{\mu\nu}^{\circ} = -\frac{1}{4} \left[3(I_{\mu} + I_{\nu}) + (Z_A^{-2})\gamma_{AA} + (Z_B^{-2})\gamma_{BB} - (Z_A + Z_B^{-2})\gamma_{AB} \right] \quad \dots (1.105)$$

Since most of the semiempirical SCF MO methods, such as CNDO, INDO, MNDO methods use $\beta_{\mu\nu}^{\circ}$ as a parameter invariant to hybridization thereby making $\beta_{\mu\nu}^{\circ}$ dependent only on the nature of the atoms A and B, I_{μ} and I_{ν} should be replaced by the average values I_A and I_B as defined in eqn. (1.105) into eqn. (1.105)

$$I_{\text{average}} = (I_s + 3I_p) / 4 \quad \dots (1.106)$$

where I_s and I_p are the ionization potentials of the s and p electron respectively.

This gives

$$\beta_{\mu\nu}^{\circ} = \beta_{AB}^{\circ} = -\frac{1}{4} \left[3(I_A + I_B) + (Z_A - 2)r_{AA} + (Z_B - 2)r_{BB} - (Z_A + Z_B - 2)r_{AB} \right]$$

$$= \frac{1}{2} (\beta_A^{\circ} + \beta_B^{\circ}) \quad \dots (1.107)$$

where,

$$\beta_A^\circ = -\frac{1}{2} \left[3I_A + (Z_A - 2)\gamma_{AA} - (Z_A - 1)\gamma_{AB} \right] \dots (1.108)$$

with similar expression for β_B° .

Although β_A° given by eqn. (1.108) is not a truly mono-atomic parameter because of the presence of γ_{AB} which depends both on A and B, it may be made effectively so by choosing standard bonds, e.g. A-A bond as the reference for computing β_A° which may be subsequently used for A-B bonds.

Incidentally, eqn. (1.107) provides a strong theoretical back ground for the form of $\beta_{\mu\nu}^\circ$ used in CNDO, INDO or ABDO methods.

1.8 Charge Distribution in the two centre MO approximation.

The Fock matrix as well as the density matrix in the two centre MO approximation assume block diagonal form consisting of 2×2 blocks corresponding to the bonds. The secular equation, therefore, reduces to a number of equations of order 2. A general 2×2 block can be represented as

$$\begin{vmatrix} F_{\mu\mu} - E & F_{\mu\nu} \\ F_{\mu\nu} & F_{\nu\nu} - E \end{vmatrix} = 0 \quad \dots (1.109)$$

Where the MO, $\Psi_{\mu\nu}$, is constructed from the orbitals ϕ_{μ} and ϕ_{ν} and expressed as

$$\Psi_{\mu\nu} = C_{\mu}\phi_{\mu} + C_{\nu}\phi_{\nu} \quad \dots (1.110)$$

The normalisation condition,

$$C_{\mu}^2 + C_{\nu}^2 = 1 \quad \dots (1.111)$$

assures that the computed electron densities represent the gross population which are required for use of eqn. (1.84) to evaluate $F_{\mu\mu}$.

It can be easily shown from eqn. (1.109) - (1.111) that the partial charges are given by

$$q_{\mu} = (1 - P'_{\mu\mu}) = 1 - 2C_{\mu}^2$$

$$= \frac{F_{\mu\mu} - F_{\nu\nu}}{\left\{ (F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2 \right\}^{1/2}}$$

$$= \frac{F_{\mu\mu} - F_{\nu\nu}}{D_{\mu\nu}} \quad \dots (1.112)$$

where, $D_{\mu\nu} = \left[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2 \right]^{1/2} \quad \dots (1.113)$

Since, $F_{\mu\mu}$ and $F_{\nu\nu}$ (eqn. 1.114) and (1.115) are also functions of the partial charges, the following procedure may be adopted for the computation of charges.

$$F_{\mu\mu} = \alpha_{\mu} + \frac{1}{2} q_{\mu}^{\gamma} r_{\mu A A} - \sum_k q_k^{\gamma} r_{A k} \quad \dots (1.114)$$

(ϕ_{μ} on atom A)

Similarly,

$$F_{\nu\nu} = \alpha_{\nu} + \frac{1}{2} q_{\nu} r_{BB} - \sum_K q_K r_{BK} \quad \dots (1.115)$$

(ϕ_{ν} on atom B)

The normalization condition eqn. (1.111) requires

$$q_{\mu} = (1 - 2C_{\mu}^2) = 2C_{\nu}^2 - 1 = -q_{\nu} \quad \dots (1.116)$$

Therefore, eqn. (1.114) may also be written as

$$F_{\mu\mu} = \alpha_{\mu} + \frac{1}{2} q_{\mu} r_{AA} - \sum_{K-L(\text{bond})} q_K (r_{AK} - r_{AL}) \quad \dots (1.117)$$

where $K-L$ represents a bond.

This leads to

$$F_{\mu\mu} - F_{\nu\nu} = (\alpha_{\mu} - \alpha_{\nu}) + \frac{1}{2} q_{\mu} (r_{AA} + r_{BB}) - \sum_{K-L} q_K [(r_{AK} - r_{AL}) - (r_{BK} - r_{BL})] \quad \dots (1.118)$$

Using eqn. (1.115) this becomes

$$\left(D_{\mu\nu} - \frac{\gamma_{AA} + \gamma_{BB}}{2} \right) q_{\mu} + \sum_{k=1} q_k \left[(\gamma_{AR} - \gamma_{AL}) - (\gamma_{BR} - \gamma_{BL}) \right] = d_{\mu} - d_{\nu} \quad \dots (1.116)$$

Each band $\mu-\nu$ will lead to one such equation in q 's. Therefore provided $D_{\mu\nu}$ is computed, the solution of the set of simultaneous equations will lead to charges directly.

Although eqn. (1.116) is quite simple and involves only two centre repulsion integrals of the type $(11|j)$, their number can also be further reduced by neglecting all the terms in the summation except those arising out of bands connecting A and B only because, not only $q_k \ll 1$, but the quantity within brackets involve the difference between two differences of the same order. As may be judged from the results to be presented later, this approximation does not introduce any significant error in the calculated charge distribution while drastically reducing the computational labour. The simultaneous equation corresponding to a band $\mu-\nu$ then, takes the simple form

$$\epsilon_{\mu\nu} q_{\mu} + \sum_{R-L(\neq\mu,\nu)} q_{R} (\gamma_{AA} - \gamma_{AL}) - \sum_{R-L(\neq\mu,\nu)} q_{R} (\gamma_{BB} - \gamma_{BL})$$

$$= \alpha_{\mu} - \alpha_{\nu} \quad \dots (1.120)$$

where,
$$\epsilon_{\mu\nu} = D_{\mu\nu} + \frac{\gamma_{AA} + \gamma_{BB}}{2} - 2\gamma_{AB} \quad \dots (1.121)$$

One advantage of this simplification is that each bond R-L is associated with a constant parameters $(\gamma_{AA} - \gamma_{AL})$ and $\epsilon_{\mu\nu}$, irrespective of the molecular environment. Once these quantities are calculated for different bonds, they may be used simply as parameter in all calculations, thus, leading a simple form which is one of our primary aims.

Now,

$$D_{\mu\nu} = \left| \left[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2 \right]^{1/2} \right|$$

$$\approx \left| 2F_{\mu\nu} \right|,$$

Now,

$$D_{\mu\nu} = \left| \left[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2 \right]^{1/2} \right|$$
$$\approx \left| 2F_{\mu\nu} \right|, \text{ because } (F_{\mu\mu} - F_{\nu\nu})^2 \ll 4F_{\mu\nu}^2$$

$$\approx \left| 2\beta_{\mu\nu} - \gamma_{AB} \right| = 2 \left| \beta_{\mu\nu} \right| + \gamma_{AB} \quad \dots (1.128)$$

Since,

$$P_{\mu\nu} = 2c_{\mu}c_{\nu} = (1 - v_{\mu}^2)^{1/2} \approx 1$$

($v_{\mu}^2 \ll 1$)

With this approximation we have

$$\epsilon_{\mu\nu} = 2 \left| \beta_{\mu\nu} \right| + \gamma_{AB} + \frac{\gamma_{AA} + \gamma_{BB}}{2} - 2\gamma_{AB}$$

$$= 2 \left| \beta_{\mu\nu} \right| + \frac{\gamma_{AA} + \gamma_{BB}}{2} - \gamma_{AB} \quad \dots (1.129)$$

Since all terms appearing in eqn. (1.120) are easily computable, the partial charges in a σ -bonded system can be directly obtained by the solution of the set of simultaneous equations resulting from eqn. (1.120).

When necessary, the initial q 's determined by using the above prescription may be used to compute D and new values of q 's may be calculated. The process may be iterated till the successive values differ by less than a prescribed limit.

1.9 Optimization of hybridization

It has been shown in Sec. 1.6 that best hybrid orbitals for a localized approximation to GCF MO's should satisfy energy minimization condition, i.e.,

$$\delta \xi = 0 \quad \dots (1.124)$$

where ξ is the electronic energy calculated in the localized model.

We shall now describe a numerical technique for implementing this condition. The μ th hybrid orbital ϕ_μ on atom A may be represented as

$$\phi_\mu = \sum_i^A c_{\mu i} \chi_i \quad \dots (1.125)$$

Where $C_{\mu i}$'s are the mixing coefficients and χ_i 's are the atomic orbitals (s, p, d etc) constituting the basis set for hybridisation.

Since it is more convenient to directly calculate the fraction of each of the basis atomic orbitals in the hybrid (e.g. s-character, p-character, etc. of the hybrid orbital), we shall express hybrid in the form:

$$\phi_{\mu} = \sum_i^A C_{\mu i} \chi_i \quad \dots (1.126)$$

Where $C_{\mu i}^2 (= C_{\mu i}^2)$ denotes χ_i character of the hybrid.

For optimization of the hybrid orbitals we must minimize the calculated electronic energy with respect to variation in the $C_{\mu i}$'s subject to the constraints imposed on the choice of hybrid orbitals due to orthogonality of the hybrid on a given centre. The orthogonality of the hybrids on any centre requires

$$\sum_i^A C_{\mu i} C_{\nu i} = \delta_{\mu\nu} \quad \dots (1.127)$$

and

$$\sum_{\mu}^A c_{\mu i} c_{\mu j} = \delta_{ij} \quad \dots (1.128)$$

Consequently, $\rho_{\mu i}$'s must satisfy the condition:

$$\sum_i \rho_{\mu i} = 1 \quad \dots (1.129)$$

and

$$\sum_{\mu} \rho_{\mu i} = 1 \quad \dots (1.130)$$

The first of these two conditions may be satisfied by normalizing the hybrid orbitals. For example, for a basis set consisting of s and p AO's only, we may write ϕ_{μ} as

$$\phi_{\mu} = \rho_{\mu s}^{1/2} s_A + (1 - \rho_{\mu s})^{1/2} p_A \quad \dots (1.131)$$

where s_A and p_A are the s and p AO's of A.

Energy minimisation with respect to variations in $\rho_{\mu i}$'s subject to the constraint given by eqn. (1.130) can then be achieved by minimising the function

$$G = \epsilon + \sum_{A, i, \mu} a_i^A \rho_{\mu i} \quad \dots (1.132)$$

a_i^A 's are the yet undetermined Lagrangian multipliers with one multiplier for each constraint (one each for every subset χ_i on atom A).

The minimisation then requires

$$\frac{\delta G}{\delta \rho_{\mu i}} = \frac{\delta \epsilon}{\delta \rho_{\mu i}} + a_i^A = 0 ; \lambda = 1, 2, \dots, n_i^A$$

$$A = 1, 2, \dots, n \quad \dots (1.133)$$

where n_i^A is the number of hybrid orbitals on A; the number of atoms A in the molecule being n.

Since the derivatives, $\frac{\delta E}{\delta \lambda_i}$'s are themselves function of $\rho_{\mu i}$'s, the set of equations obtained from eqn. (1.133) cannot be used to calculate the optimized ρ 's directly. For solution of these equations we shall therefore use an iterative procedure through linearisation using Taylor's expansion. Using Taylor's expansion we have

$$\frac{\delta E}{\delta \rho_{\mu i}} = \left(\frac{\delta E}{\delta \rho_{\mu i}} \right)_0 + \sum_{l,j} \frac{\delta^2 E}{\delta \rho_{\sigma j} \delta \rho_{\mu i}} \Delta \rho_{\sigma j} + \text{higher order terms} \dots \quad (1.134)$$

where $\left(\frac{\delta E}{\delta \rho_{\mu i}} \right)_0$ refers to the value of the derivative at some initially chosen approximation to ρ 's and $\Delta \rho$'s are the differences between the optimum value and initial approximation to ρ 's.

Neglecting the higher order terms in eqn. (1.134) eqn. (1.133) takes the form

$$\sum_{l,j} \frac{\delta^2 E}{\delta \rho_{\sigma j} \delta \rho_{\mu i}} \Delta \rho_{\sigma j} + a_i^A = - \left(\frac{\delta E}{\delta \rho_{\mu i}} \right)_0 \dots \quad (1.135)$$

The set of simultaneous equations generated by eqn. (1.133) may be written in more convenient matrix form

$$|\epsilon''| |\Delta p, a| = |\epsilon'| \quad \dots (1.136)$$

Where $|\epsilon''|$ represents the matrix whose elements are $\frac{\delta^2 \mathcal{E}}{\delta p_i \delta p_{hi}}$'s and 1's corresponding to the Lagrangian multipliers a_i 's ; $|\Delta p, a|$ is the matrix of Δp 's and a_i 's which are to be determined and $|\epsilon'|$ is a column matrix consisting of $\left(\frac{\delta \mathcal{E}}{\delta p_{hi}}\right) \Delta p$ and a 's can then be easily obtained from eqn. (1.136) by standard procedure and a new set of p 's given by

$$p = p_{\text{initial}} + \Delta p \quad \dots (1.137)$$

will be obtained. The new set may then be used to generate the next approximations to p 's and the process may iterated till Δp 's are smaller than a prescribed limit.

In order to implement this procedure it is now necessary to evaluate the elements of the matrices $|\epsilon''|$ and $|\epsilon'|$.

The total energy, ξ of the system in the localized approximation is given by

$$\xi = \sum_{\mu-\nu(\text{bonds})} P_{\mu\nu} \left[H_{\mu\nu} + \frac{1}{2} \sum_{\lambda\sigma(\text{bond})} P_{\lambda\sigma} \{ (u\nu|\lambda\sigma) - (u\lambda|\nu\sigma) \} \right] \dots (1.138)$$

In the integral approximations used by us (Sec. 1.7) this reduces to the form

$$\xi = \sum_{\mu-\nu(\text{bonds})} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu,\lambda} P_{\mu\mu} P_{\lambda\lambda} \gamma_{\mu\lambda} - \frac{1}{4} \sum_{\mu-\nu(\text{bonds})} P_{\mu\nu}^2 \gamma_{\mu\nu} \dots (1.139)$$

where the P 's are now gross populations obtained by solving SCF eqn. (1.70), and γ 's are appropriately averaged electron repulsion integrals.

From eqn. (1.139) we get

$$\frac{\delta \xi}{\delta P_{\lambda i}} = \sum_{\mu,\nu} \left[\frac{\delta \xi}{\delta P_{\mu\nu}} \frac{\delta P_{\mu\nu}}{\delta P_{\lambda i}} + \frac{\delta \xi}{\delta H_{\mu\nu}} \frac{\delta H_{\mu\nu}}{\delta P_{\lambda i}} + \frac{\delta \xi}{\delta \gamma_{\mu\nu}} \frac{\delta \gamma_{\mu\nu}}{\delta P_{\lambda i}} \right] \dots (1.140)$$

Since the ψ 's obtained through the secular eqn. (1.109) satisfy the condition

$$\frac{\delta \epsilon}{\delta \rho_{\mu\nu}} = 0 \quad \dots (1.141)$$

and, for spherically averaged repulsion integrals which are invariant to hybridisation i.e.

$$\frac{\delta \gamma_{\mu\nu}}{\delta \rho_{\lambda i}} = 0 \quad \dots (1.142)$$

eqn. (1.140) then reduces to

$$\frac{\delta \epsilon}{\delta \rho_{\lambda i}} = \sum_{\mu, \nu} \frac{\delta \epsilon}{\delta H_{\mu\nu}} \frac{\delta H_{\mu\nu}}{\delta \rho_{\lambda i}} = \sum_{\mu, \nu} \rho_{\mu\nu} \frac{\partial H_{\mu\nu}}{\partial \rho_{\lambda i}} \quad \dots (1.143)$$

We shall now consider the case where the basis set of atomic orbitals consists of only s and p type orbitals, as we are primarily interested in molecules where the bonding can be adequately represented in terms of valence s and p orbitals. In such a case the hybrids may be written as in eqn. (1.131). So, therefore, have

$$H_{\mu\mu} = \langle \phi_{\mu} | H | \phi_{\mu} \rangle$$

$$\begin{aligned}
 &= \rho_{\mu s} \langle s_A | H | s_A \rangle + (1 - \rho_{\mu s}) \langle p_A | H | p_A \rangle \\
 &= \rho_{\mu s} \cdot H_{ss}^A + (1 - \rho_{\mu s}) H_{pp}^A \\
 &= H_{pp}^A - \rho_A \cdot \rho_{\mu s} \quad \dots (1.144)
 \end{aligned}$$

where, $\rho_A = (H_{pp}^A - H_{ss}^A)$,

the subscript or superscript A is used to specify that the orbital μ is centered on atom A and the minus sign in eqn. (1.144) is used to make ρ_A positive. With spherically averaged core-electron attraction integrals we have (eqn. 1.77)

$$H_{ss}^A = U_{ss}^A - \sum_{B(\neq A)} V_{AB} \quad \dots (1.145)$$

$$H_{PP}^A = U_{PP}^A - \sum_{B(\neq A)} V_{AB} \quad \dots (1.146)$$

where U_{SS} and U_{PP} are given by (see eqn. 1.79)

$$U_{SS} = -\frac{1}{2} (I_{SA} + A_{SA}) - \left(Z_A - \frac{1}{2} \right) \gamma_{AA} \quad \dots (1.147)$$

$$\text{and, } U_{PP} = -\frac{1}{2} (I_{PA} + A_{PA}) - \left(Z_A - \frac{1}{2} \right) \gamma_{AA} \quad \dots (1.148)$$

Therefore,

$$\begin{aligned} P_A &= H_{PP}^A - H_{SS}^A \\ &= \frac{1}{2} (I_{SA} + A_{SA}) - \frac{1}{2} (I_{PA} + A_{PA}) \end{aligned} \quad \dots (1.149)$$

Differentiating eqn. (1.149) w.r.t $\rho_{\mu s}$ we get

$$\frac{\partial H_{\mu\mu}}{\partial \rho_{\mu s}} = -P_A \quad \dots (1.150)$$

$$\text{and, } \frac{\partial H_{\mu\mu}}{\partial \rho_{\lambda i}} = 0 \quad ; \quad \lambda \neq \mu \quad \dots (1.151)$$

Again,

$$H_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} ; \phi_{\mu} \text{ on } A, \phi_{\nu} \text{ on } B \quad \dots (1.152)$$

Using the expressions for hybrids in terms of the component AO's (eqn. 1.126), we have

$$\begin{aligned} S_{\mu\nu} &= (\phi_{\mu} | \phi_{\nu}) \\ &= \rho_{\mu s}^{1/2} \left[\rho_{\nu s}^{1/2} (s_A | s_B) + (1 - \rho_{\nu s})^{1/2} (s_A | p_B) \right] \\ &\quad + (1 - \rho_{\mu s})^{1/2} \left[\rho_{\nu s}^{1/2} (p_A | s_B) + (1 - \rho_{\nu s})^{1/2} (p_A | p_B) \right] \dots (1.153) \end{aligned}$$

$$\begin{aligned} \frac{\delta S_{\mu\nu}}{\delta \rho_{\mu s}} &= \frac{1}{2} \left[\rho_{\mu s}^{-1/2} \left\{ \rho_{\nu s}^{1/2} (s_A | s_B) + (1 - \rho_{\nu s})^{1/2} (s_A | p_B) \right\} \right. \\ &\quad \left. - (1 - \rho_{\mu s})^{1/2} \left\{ \rho_{\nu s}^{1/2} (p_A | s_B) + (1 - \rho_{\nu s})^{1/2} (p_A | p_B) \right\} \right] \\ &= C_{\mu} \text{ (say)} \quad \dots (1.154) \end{aligned}$$

Similarly,

$$\begin{aligned} \frac{\delta S_{\mu\nu}}{\delta P_{\nu s}} &= \frac{1}{2} \left[P_{\mu s}^{1/2} \left\{ P_{\nu s}^{-1/2} (s_A | s_B) - (1 - P_{\nu s})^{-1/2} (s_A | P_B) \right\} \right. \\ &\quad \left. + (1 - P_{\mu s})^{1/2} \left\{ P_{\nu s}^{-1/2} (P_A | s_B) \right. \right. \\ &\quad \left. \left. - (1 - P_{\nu s})^{-1/2} (P_A | P_B) \right\} \right] \\ &= C_\nu \quad (\text{say}) \quad \dots (1.151) \end{aligned}$$

and,

$$\frac{\delta S_{\mu\nu}}{\delta P_{\lambda i}} = 0 \quad ; \quad \lambda \neq \mu, \nu \text{ and } i \neq s \quad \dots (1.152)$$

Combining eqn. (1.143) and eqns. (1.150) - (1.152) we get

$$\frac{\delta \mathcal{E}}{\delta P_{\mu s}} = -P_A \cdot P_{\mu\mu} + 2P_{\mu\nu} \cdot \beta_{AB}^{\circ} C_{\mu} \quad \dots (1.157)$$

Further differentiation w.r.t to $P_{\lambda s}$ gives

$$\begin{aligned} \frac{\delta^2 \mathcal{E}}{\delta P_{\lambda s} \delta P_{\mu s}} &= -P_A \cdot \frac{\delta P_{\mu\mu}}{\delta P_{\lambda s}} + 2 \frac{\delta P_{\mu\nu}}{\delta P_{\lambda s}} \cdot \beta_{AB}^{\circ} C_{\mu} \\ &\quad + 2P_{\mu\nu} \beta_{AB}^{\circ} \frac{\delta C_{\mu}}{\delta P_{\lambda s}} \quad \dots (1.158) \end{aligned}$$

Unless $\lambda = \mu$ or ν , all derivatives in the R. H. S of eqn. (1.158) will be zero, so that only non zero elements will be of the type $\frac{\partial^2 \epsilon}{\partial \rho_{\mu s}^2}$ and $\frac{\partial^2 \epsilon}{\partial \rho_{\nu s} \partial \rho_{\mu s}}$.

Further, as shown in appendix, both $\frac{\partial P_{\mu\mu}}{\partial \rho_{\lambda s}}$ and $\frac{\partial P_{\nu\nu}}{\partial \rho_{\lambda s}}$ ($\lambda = \mu$ or ν) are small compared to the last term, so that eqn. (1.158) effectively reduces to

$$\frac{\partial^2 \epsilon}{\partial \rho_{\lambda s} \partial \rho_{\mu s}} = 2 \rho_{\mu\nu} \beta_{AB}^0 \frac{\partial C_{\mu}}{\partial \rho_{\lambda s}} \quad \dots (1.159)$$

The derivatives $\frac{\partial C_{\mu}}{\partial \rho_{\lambda s}}$ are obtained by straight forward differentiation of eqn. (1.154). Thus, we have

$$\begin{aligned} \frac{\partial C_{\mu}}{\partial \rho_{\mu s}} &= -\frac{1}{4} \left[\rho_{\mu s}^{3/2} \left\{ \rho_{\nu s}^{1/2} (S_A | S_B) + (1 - \rho_{\nu s})^{1/2} (S_A | P_A) \right\} \right. \\ &\quad + (1 - \rho_{\mu s})^{-3/2} \left\{ \rho_{\nu s}^{1/2} (P_A | S_B) \right. \\ &\quad \left. \left. + (1 - \rho_{\nu s})^{1/2} (P_A | P_B) \right\} \right] \\ &= C'_{\mu\mu} \text{ (say)} \quad \dots (1.160) \end{aligned}$$

$$\begin{aligned} \frac{\partial C_{\mu}}{\partial \rho_{vs}} &= \frac{1}{4} \left[\rho_{us}^{-1/2} \left\{ \rho_{vs}^{-1/2} (s_A | s_B) - (1 - \rho_{vs})^{-1/2} (s_A | p_B) \right\} \right. \\ &\quad \left. - (1 - \rho_{us})^{-1/2} \left\{ \rho_{vs}^{-1/2} (p_A | s_B) \right. \right. \\ &\quad \left. \left. - (1 - \rho_{vs})^{-1/2} (p_A | p_B) \right\} \right] \\ &= C'_{\mu\nu} (s_{\nu}) \end{aligned} \quad \dots (1.161)$$

Having thus deduced the various terms occurring in eqn. (1.155), the simultaneous equations for atoms with basis set consisting of s and p AO's only can be written in the form

$$\begin{aligned} 2 \rho_{\mu\nu} \beta_{AB}^{\circ} C'_{\mu\mu} \Delta \rho_{us} + 2 \rho_{\mu\nu} \beta_{AB}^{\circ} C'_{\mu\nu} \Delta \rho_{vs} \\ + \alpha_A = P_A \cdot P_{\mu\mu} + 2 \rho_{\mu\nu} \beta_{AB}^{\circ} C_{\mu} \end{aligned} \quad (1.162)$$

With one such equation for each hybrid ϕ_μ on atom. The remaining equation comes from constraints on the $P_{\mu s}$'s as expressed by eqn. (1.155) which give

$$\sum_{\mu}^A \Delta P_{\mu s} = 0 \quad \dots (1.155)$$

When ϕ_μ is a lone pair orbital, eqn. (1.157) takes the form

$$\frac{\partial \epsilon}{\partial P_{\mu s}} = -2 P_A \quad \dots (1.156)$$

Since $P_{\mu\mu} = 2$ for a lone pair and the second term does not exist in this case because the lone pair orbital is not involved in bonding.

Hence, for lone pair, we have

$$\frac{\partial^2 \epsilon}{\partial P_{\mu s}^2} = 0 \quad \dots (1.157)$$

The equation for loss pair corresponding to the general eqn. (1.162) then becomes

$$a_A = \sum_A \dots (1.168)$$

The set of equations given by (1.162), (1.163) and (1.168) may then be solved for ΔP 's to give a better approximation to ρ_{us} 's in the different bands. This may then be used to generate the new set of equations for a second iteration. The process may be repeated till $|\Delta P|$ is less than the prescribed limit. Usually 3 iterations are sufficient to obtain ρ_{us} values correct to 4 digits.

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PART - II

PARAMETERIZATION AND COMPUTATIONAL PROCEDURES.

2.1 Parametrization

The localized MO calculation according to the prescription developed in Part I requires values for overlap integrals, ionization potentials, electron affinities of the atomic orbitals and the electron repulsion integrals γ_{AB} . Unlike the MO method the bonding parameter β_{AB}^0 is not required as an empirical parameter in our method, but can be calculated by eqn. (1.107) using the appropriate ionization potential, core charge and electron repulsion integrals.

Because of the complexities involved in the optimization of hybrid orbitals for localized MO description, the method has been used in cases where the bonding can be adequately represented in terms of hybrids consisting of atomic s and p type orbitals only. Slater functions (eqn. 1.37) are used to describe the AO's and orbital exponents are chosen according to Slater's rules.

(1) Overlap integrals, $S_{\mu\nu}$

Overlap integrals in terms of hybrid AO's is very simple because they can be obtained as a linear combinations of Slater-type overlaps.

For example, the hybrid AO's which can be formed from s and p AO's may be written as

$$\phi_{\mu} = \rho_{\mu}^{1/2} S_A + (1 - \rho_{\mu})^{1/2} P_A \quad \dots (2.1)$$

$$\phi_v = \rho_v^{1/2} s_B + (1 - \rho_v)^{1/2} p_B \quad \dots (2.2)$$

where ρ_v 's are the s-character of the hybrid orbitals. The hybrid overlap integrals $S_{\mu\nu}$ is then given by

$$\begin{aligned} S_{\mu\nu} &= (\phi_\mu | \phi_\nu) \\ &= \rho_\mu^{1/2} \left[\rho_\nu^{1/2} (s_A | s_B) + (1 - \rho_\nu)^{1/2} (s_A | p_B) \right] \\ &\quad + (1 - \rho_\mu)^{1/2} \left[\rho_\nu^{1/2} (p_A | s_B) \right. \\ &\quad \left. + (1 - \rho_\nu)^{1/2} (p_A | p_B) \right] \quad \dots (2.3) \end{aligned}$$

The evaluation of hybrid overlap integral requires ultimately the knowledge of the appropriate Slater AO's overlap which are determined using standard technique⁽¹⁻³⁾.

(ii) Repulsion integrals

The electron repulsion integral γ_{AB} which represents a spherical average interaction between electrons in valence

atomic orbitals on atom A and B, is calculated as the two centre coulomb integrals involving valence s functions⁽⁵⁾.

$$V_{AB} = \iint \psi_A(1) (\gamma_{12})^{-1} \psi_B(2) d\tau_1 d\tau_2 \quad \dots (2.4)$$

where γ_{12}^{-1} is the interelectronic repulsion operator and the Slater valence s function in terms of spherical polar coordinates system (r, θ, ϕ) centered on atom A, is defined by

$$\psi_A(r, \theta, \phi) = N_A r^{n_a-1} \exp(-\rho_a r) Y_{l_a m}(\theta, \phi) \quad \dots (2.5)$$

where N_a is the radial normalization constant and n_a, l_a and m are the principal, azimuthal and magnetic quantum numbers respectively and ρ_a is the orbital exponent. $Y_{l_a m}(\theta, \phi)$ are the angular parts of the function, defined as

$$Y_{l_a m}(\theta, \phi) = \Theta_{l_a m}(\cos \theta) \Phi_m(\phi) \quad \dots (2.6)$$

where

$$\Theta_{l_a m}(\cos\theta) = \left[\frac{(2l_a+1)(l_a-m)!}{2(l_a+m)!} \right]^{1/2} P_{l_a}^m(\cos\theta) \dots (2.7)$$

and

$$\Phi_m(\phi) = \begin{cases} \pi^{-1/2} \cos m\phi, & m \neq 0 \\ (2\pi)^{-1/2}, & m = 0 \end{cases} \dots (2.8)$$

$P_{l_a}^m(\cos\theta)$ are the normalized associated Legendre polynomials.

Using the eqns. (2.5 - 2.8) in eqn. (2.4), two centre integrals Y_{AB} are determined using standard technique (4,6-7).

The centre integral Y_{AA} is determined similarly using the valence s functions.

(iii) Evaluation of α_u

\mathcal{L}_u defined by eqn. (2.9) are computed from the values α_s and α_p {eqn. (2.10) and (2.11)} which are taken from the GDO method.

$$\alpha_u = -\frac{1}{2} (\bar{I}_u + A_u) \dots (2.9)$$

$$\alpha_s = -\frac{1}{2}(I_s + A_s) \quad \dots (2.10)$$

$$\alpha_p = -\frac{1}{2}(I_p + A_p) \quad \dots (2.11)$$

α_μ which refers to hybrid AO of the type given by eqn. (2.1) is then easily computed by the relation.

$$\alpha_\mu = \alpha_p + p_s \alpha_s \quad \dots (2.12)$$

where p_s is the s-character of the hybrid orbitals.

The values of α_s and α_p are given in table 2.1.

Table 2.1

Values of α_s and α_p in electron volts^a.

	H	Li	Be	B	C	N	O	F
$-\alpha_s$	7.176	3.106	3.246	9.594	14.691	19.316	25.390	32.278
$-\alpha_p$		1.258	2.583	4.001	5.573	7.275	9.111	11.030

a) Ref. 4 and 9

(iv) Bond resonance parameters.

Evaluation of Bond resonance parameters from eqn. (1.107) requires the knowledge of average ionization potential, core charge and repulsion integrals. The ionization potentials, I_s and I_p , used to calculate the "orbital average" (eqn. 2.13) are taken from the CNDO/1 method⁽¹⁰⁾ except for hydrogen where the experimental value is used. The average values, I_{av} , used for the evaluation of the resonance parameters calculated from I_s and I_p using eqn. (2.13) are given in table 2.2.

$$I_{av} = (I_s + 3.I_p) / 4 \quad \dots (2.13)$$

Table 2.2

Average ionization potentials (in electron volts)
used to calculate β_A^o

	H	Li	Ba	D	C	N	O	F
I_{av}	13.60	4.00	6.50	9.74	12.06	16.29	19.99	24.05

As already mentioned (see Part I), β_A° may be effectively made a monotonic parameter by choosing A_2 molecules as standards. Under this specification β_A° takes the form

$$\beta_A^\circ = -\frac{1}{2} \left[3I_A + (Z_A - 2) \gamma_{AA} - (Z_A - 1) \gamma'_{AA} \right] \dots (2.14)$$

where γ'_{AA} is the two centre repulsion integrals between the electrons of the two A atoms in A_2 molecule.

Values of β_A° computed from eqn. (2.14) using the average ionisation potential given in table 2.2 along with the values of γ_{AA} and γ'_{AA} obtained from Slater AO's using standard procedure are given in table 2.3. These data were obtained using the molecules H_2 (for β_H°), Li_2 (for β_{Li}°), B_2 (for β_B°), C_2 (for β_C°), N_2 (for β_N°) and O_2 (for β_O°) (11).

In case of Be, where the neutral diatomic molecule Be_2 does not exist, β_{BeH}° in BeH_2 was computed from eqn. (1.10.7) and β_{Be}° was then calculated from the relation

$$\beta_{BeH}^\circ = \frac{1}{2} (\beta_{Be}^\circ + \beta_H^\circ)$$

Similarly for β_F° we used β_{HF}° in HF molecule, rather than β_H molecule because of the large lone pair interactions in fluorine molecule.

Table - 3.5

Values of β_A° (in electron volt) computed from eqn. (2.14) using theoretical values of electron repulsion integrals obtained from Slater orbitals.

	H	Li	Be	B	C	N	O	F
β_A°	11.89	3.79	8.64	12.71	19.15	29.00	45.67	55.64

These values are somewhat large than would be expected from CNDO parameters and always yield heat of atomization values which are large compared to the experimental values. The reason for the failure of the theoretically computed β_A° to satisfactorily account for the heat of atomization is not difficult to find. It is well known that the one and two centre electron repulsion integrals computed from Slater orbitals are always too large. This makes the computed β_A° values too large. It is, therefore, necessary to properly scale

down the computed values. The scaled values, β_A° (corrected), are calculated from the empirical relation,

$$\beta_A^\circ(\text{corrected}) = K \cdot \beta_A^\circ \quad \dots (2.15)$$

where the scaling factor K is taken as the ratio of the average value of U_{μ} for the atom computed from eqn. (1.79) using the value of γ_{AA} determined from the atomic spectral data ($\gamma_{AA}^{\text{exp.}}$) and the calculated value using Slater AO (γ_{AA}^{t}). $\gamma_{AA}^{\text{exp.}}$ is obtained from the spectral data from the relation

$$\gamma_{AA}^{\text{exp.}} = I - A \quad \dots (2.16)$$

where I and A are the appropriate values of the ionization potential and electron affinity. Since we are interested in the average values, averaged I and A are used.

Using these values the scaling factor K becomes

$$K = \frac{U_{av.}^{\text{exp.}}}{U_{av.}^{\text{t}}} \quad \dots (2.17)$$

where

$$U_{av}^{exp} = \alpha_{av} - (Z_A - 1/2) \gamma_{AA}^{exp}$$

$$U_{av}^k = \alpha_{av} - (Z_A - 1/2) \gamma_{AA}^k$$

The values of the scaling factor K and β_A° (corrected) which are used in all calculations are given in table 2.4.

Table 2.4

Values of K and β_A° (corrected) in electron volts.

	H	Li	Be	B	C	N	O	F
K	.5671	.8115	.8103 (Self)	.7219	.6363	.663	.643	.6511(HF)
$-\beta_A^\circ$ (corrected)	10.3	2.3	4.0	9.2	13.1	19.2	22.5	36.1

Incidentally, the corrected β_A° values are very close to those used in the CNDO method and the present approach, thus, provides a theoretical justification for the bonding parameters used in the CNDO method. Since the corrected β_A° 's only used in calculations, we shall hence forth assume β_A°

always refer to the corrected values.

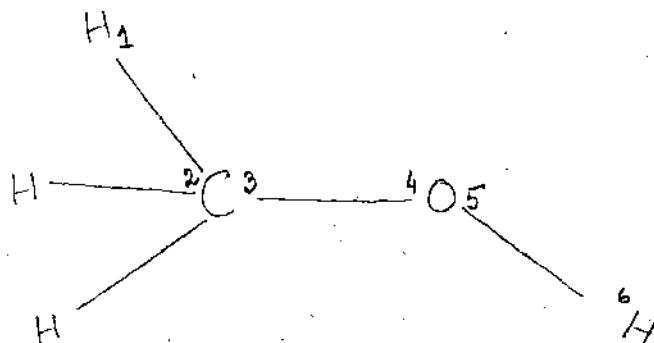
3.2 Computational Procedure

Having fully specified the parametrization we shall now consider the details of the computational procedure for obtaining the optimized two centre MO's for any molecule. The actual computation consists of the following steps.

Step 1: The first step requires an initial approximation to the orbital hybridisation as defined by the parameter ρ . This can be easily done in most cases from a consideration of geometry. As we are interested in saturated molecules involving basis set consisting of one E_s and three E_p orbitals only, all hybrid orbitals are initially assumed to be of sp^3 type and ρ is taken as 0.25. However, in case of fluorine atom which forms single covalent bond, the calculation with initial ρ as 0.25 led to a large correction in the s-character ($\sim .19$) and therefore in all calculations $\rho=0.18$ was used as initial s-character for fluorine hybrid orbitals in order to reduce the number of iterations.

Step 2: With the initial set of s-character of hybrid orbitals, the net charge associated with the orbitals are calculated according to the prescription given in section 1.3. We shall illustrate the procedure with an example.

Let us consider the case of methyl alcohol, CH_3OH (1)



(1)

Since the C - H bonds are equivalent, the system consists of only three non-equivalent bonds, viz., C-H, O-O and C-O and six non-equivalent valence AO's :

- (1) ϕ_1 , s-orbital of the H-atom in C-H bond.
- (2) ϕ_2 , hybrid orbital of C-atom used for forming the C-H bond.
- (3) ϕ_3 , hybrid orbital of C-atom used for forming the C-O bond.
- (4) ϕ_4 , hybrid orbital of O-atom used to form C-O bond.
- (5) ϕ_5 , hybrid orbital of O-atom used to form O-H bond.
- (6) ϕ_6 , s-orbital of H-atom of C-H bond.

We also note

$$q_2 = -q_1 \quad ; \quad q_4 = -q_3$$

and

$$q_6 = -q_5 \quad (\text{see eqn. 1.116})$$

The simultaneous equations for charges become
(eqn. 1.120)

$$\epsilon_{12} q_1 + 2q_1 (\gamma_{cc} - \gamma_{ch}) - q_3 (\gamma_{cc} - \gamma_{co}) = \alpha_H - \alpha_c \quad \dots (2.13a)$$

$$\epsilon_{34} q_3 - 3q_1 (\gamma_{cc} - \gamma_{ch}) - q_5 (\gamma_{oo} - \gamma_{oh}) = \alpha_c - \alpha_o \quad \dots (2.13b)$$

$$\epsilon_{56} q_5 - q_3 (\gamma_{oo} - \gamma_{co}) = \alpha_o - \alpha_H \quad \dots (2.13c)$$

The charges can be easily obtained provided ϵ_{uv} are computed.

Now, ϵ_{uv} is given by (eqn. 1.121)

$$\epsilon_{uv} = |D_{uv}| + \frac{\gamma_{AA} + \gamma_{BB} - 2\gamma_{AB}}{2}$$

$$\text{where, } D_{uv} = \left[(F_{uu} - F_{vv})^2 + 4F_{uv}^2 \right]^{1/2}$$

Since $F_{\mu\mu}$ and $F_{\mu\nu}$ depend on q_{μ} 's, the exact evaluation of $D_{\mu\nu}$ requires an iterative procedure. However, to a good approximation (see eqn. 1.123) $\epsilon_{\mu\nu}$ is given by

$$\epsilon_{\mu\nu} = 2 \left| \beta_{\mu\nu} \right| + \frac{\gamma_{AA} + \gamma_{BB}}{2} - \gamma_{AB} \quad \dots (2.19)$$

which can be easily evaluated and the charges calculated. These charges can be then used to compute a better approximation to $D_{\mu\nu}$ and new values of charges may obtained using the modified values of $\epsilon_{\mu\nu}$'s. This process may be repeated till two successive iteration yields same output within prescribed limit. However, in practice this is not necessary since use of expression (2.19) results in charges which differ from that calculated by iterative process only in the fourth place after decimal. This is shown in table 2.5.

Table 2.5

Molecules	Bond	Calculated charges	
		Using eqn (2.19)	by iterative procedure
(1) CH_4	H-C	0.0147	0.0147
(2) C_2H_2	H-C	0.0174	0.0174
	C-C	0.0022	0.0022

Contd..

Table 2.8 (Contd..)

Molecules	Bond	Calculated charge	
		Using eqn (2.19)	by iterative procedure
(3) NH ₃	H-N	0.0816	0.0816
(4) H ₂ O	H-O	0.1872	0.1861
(5) OF ₂	F-O	-0.0653	-0.0652
(6) CH ₃ NH ₂	H-C	0.0322	0.0322
	C-N	0.0711	0.0710
	N-H	-0.0777	-0.0776

The difference between these two set of charges, as anticipated, is found to be only of the order of 10^{-3} or less. Therefore, in all our calculations we have calculated the charges directly using expression (2.19) for $\epsilon_{\mu\nu}$.

Step 3: This step consists in optimizing the hybrids on the different centre and is done according to the procedure developed in section 1.8. To implement this we construct the set of simultaneous equations in $\Delta\rho$'s, the corrections to our initial approximation to s-characters needed to optimize the hybrid orbitals. In the example we are considering viz, CH₃NH₂, we have only two centres where hybrids involving s and p orbitals are involved in bonding. These are

Centre 1 . Carbon atom.

(I) Hybrid orbitals directed to the hydrogen atom of the respective C-H bond. Since all the three C-H bonds are equivalent, only one orbital ϕ_2 is to be considered.

(II) Hybrid orbitals of carbon atom connecting O- atom of C-O bond, ϕ_3

Centre 2, Oxygen atom

(A) Hybrid orbitals connecting O- atom, ϕ_4

(B) Hybrid orbitals connecting H- atom of C-H bond, ϕ_5

The s-character of the oxygen lone pair can be obtained by difference and needs no explicit inclusion in forming the set of simultaneous equations. Using eqn. (1.162), the required equation can be written as

$$2\beta_{CH}^{\circ} P_{12} C'_{22} \Delta P_2 + a_c = P_c \cdot P_{22} - 2\beta_{CH}^{\circ} P_{12} C_{22} \dots (2.20a)$$

$$2\beta_{CO}^{\circ} P_{34} C'_{33} \Delta P_3 + 2\beta_{CO}^{\circ} P_{34} C'_{34} \Delta P_4 + a_c = P_c \cdot P_{33} - 2\beta_{CO}^{\circ} P_{34} C_{33} \dots (2.20b)$$

$$2\beta_{CO}^{\circ} P_{43} C'_{44} \Delta P_4 + 2\beta_{CO}^{\circ} P_{43} C'_{43} \Delta P_3 + a_o = P_o \cdot P_{44} - 2\beta_{CO}^{\circ} P_{43} C_{43} \dots (2.20c)$$

$$2\beta_{OH}^{\circ} P_{56} C_{55}' \Delta P_5 + a_0 = P_0 \cdot P_{55} - 2\beta_{OH}^{\circ} P_{56} C_5 \quad \dots (2.200)$$

$$a_0 = 2P_0 \quad \dots (2.20e)$$

$$3\Delta P_2 + \Delta P_3 = 0 \quad \dots (2.20f)$$

The first four equations results from the four bonding hybrid orbitals, the fifth equation is due to the lone pair orbital on oxygen atom (eqn. 1.160), (note, the lone pair hybridization does not explicitly enter the equations), while the last equation is a result of the condition that the total s-character remains constant.

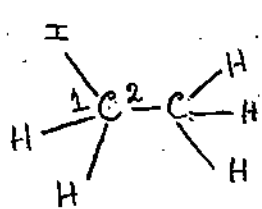
The elements of the matrix representing the simultaneous equation in 4 P 's are determined using the formulae given in section 1.9 and the parametrization procedure outlined in section 2.1.

If the changes in the s-character of all the orbitals is less than a prescribed limit then the changes are calculated using the newly determined hybrids following the procedure given in step 2 and the calculation is terminated.

otherwise, step 3 is followed until condition for termination is achieved. In most cases 3-4 iteration are sufficient to yield s-character with accuracy of 4 digits. This is illustrated in a few representative cases in table 2.6.

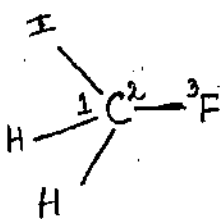
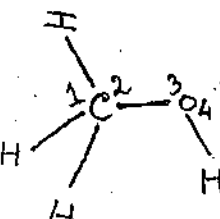
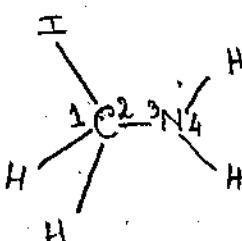
Table 2.6

Calculated s-character of different hybrid orbitals in some molecules

Compound	Orbital	Initial s-character	Calculated s-character			
			1st Iteration	2nd Iteration	3rd Iteration	Last Iteration
$\begin{array}{c} 1 \\ \text{H}-\text{O}-\text{H} \end{array}$	p_1	0.25	0.2172	0.2161	0.2159	0.2159
$\begin{array}{c} 1 \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	$p_2(\text{LP})$	0.25	0.2326	0.2330	0.2341	0.2341
	p_1	0.25	0.1936	0.1933	0.1936	0.1936
	$p_2(\text{LP})$	0.25	0.4132	0.4051	0.4042	0.4042
	p_1	0.25	0.2623	0.2624	0.2623	0.2623
	p_2	0.25	0.2116	0.2123	0.2129	0.2129

Contd..

Table 2.6 (Contd..)

Compound	Orbital	Initial s-character	Calculated s-character			
			1st Itera- tion	2nd Itera- tion	3rd Itera- tion	4th Itera- tion
	P ₁	0.25	0.2969	0.2882	0.2870	0.2870
	P ₂	0.25	0.1119	0.1359	0.1389	0.1391
	P ₃	0.25	0.1525	0.1683	0.1691	0.1689
	P ₄ (LP)	0.25	0.2825	0.2772	0.2769	0.2170
	P ₁	0.25	0.2814	0.2773	0.2773	0.2773
	P ₂	0.25	0.1550	0.1630	0.1630	0.1630
	P ₃	0.25	0.1529	0.1632	0.1701	0.1701
	P ₄	0.25	0.2091	0.2086	0.2079	0.2079
	P ₅ (LP)	0.25	0.3190	0.3110	0.3110	0.3110
	P ₁	0.25	0.2743	0.2719	0.2722	0.2723
	P ₂	0.25	0.1770	0.1844	0.1835	0.1831
	P ₃	0.25	0.1445	0.1628	0.1655	0.1657
	P ₄	0.25	0.1972	0.1997	0.1994	0.1992
	P ₅ (LP)	0.25	0.4613	0.4380	0.4339	0.4339

(*LP = lone pair)

The net charges on the atoms at each iteration is also given in table 2.7 .

Table 2.7

Calculated atomic charges of some molecules

Molecule	Atom	Net atomic charge			
		1st iteration	2nd iteration	3rd iteration	Last iteration
H ₂ O	O	-0.3144	-0.2336	-0.2336	-0.2336
	H	0.1572	0.1448	0.1444	0.1444
NH ₃	N	-0.2454	-0.1935	-0.1939	-0.1932
	H	0.0818	0.0685	0.0683	0.0664
C ₂ H ₆	C	-0.0307	-0.0613	-0.0609	-0.0609
	H	0.0169	0.0204	0.0203	0.0203
CH ₃ F	C	0.0649	0.0275	0.0334	0.0337
	H	0.0708	0.0323	0.0320	0.0795
	F	-0.2773	-0.2744	-0.2734	-0.2722
CH ₃ NH ₂	C	-0.0255	-0.0430	-0.0446	-0.0440
	H	0.0322	0.0367	0.0373	0.0360
	N	-0.2263	-0.1841	-0.1831	-0.1833
	H	0.0777	0.0615	0.0604	0.0594

Contd..

Table 2.7 (Contd..)

Molecule	Atom	Net atomic charges			
		1st iteration	2nd iteration	3rd iteration	last iteration
CH ₃ OH	C	-0.0055	0.0329	0.0101	0.0175
	H	0.0471	0.0536	0.0548	0.0536
	O	-0.2908	-0.2551	-0.2670	-0.2673
	H	0.1440	0.1271	0.1252	0.1240

Once the final values of charges and s-characters of optimum hybrid orbitals are determined, other molecular properties, e.g. dipole moment, heat of atomization etc. can be calculated using standard procedures. These are discussed in part III along with results obtained on different molecules.

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PART - III

RESULTS AND DISCUSSION

3.1 Charge distribution in different molecules.

The charge distribution in several molecules obtained by the procedure developed in Part I and II are given in table 3.1. For comparison, net atomic charges obtained by other methods, viz., the fully localized SCF MO method of Del Re et al ⁽¹⁾, the CNDO/2 method ⁽²⁾ and STO-3G method ^(3-5,30) are also included for several molecules. In general, there is a close agreement between the results of the present method and the CNDO/2 method.

This clearly illustrates that for 6-bonded system localized MO description is almost as good as CNDO/2 approach although the computational labour in the former is only a small fraction of that required for a CNDO type calculation.

Table 3.1

net atomic charges in different molecules

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Del Re ^(a)	CNDO/2 ^(b)	STO-3G ^(c)
1.	CH ₄	C	-0.0538	-0.006	-0.0500	-0.0730
		H	0.0147	0.0015	0.0125	0.0150
2.	C ₂ H ₂	C	-0.0609		-0.0580	-0.0260
		H	0.0203		0.0030	0.0030

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Del Re (a)	OH20/2 (b)	OH20-30 (c)
3	¹ H ² CH ₃ CH ₂ CH ₃	1 C	-0.0506			
		H	0.0217			
		2 C	-0.0516			
		H	0.0233			
4	¹ CH ₃ ² OH(CH ₃) CH ₃	1 C	-0.0581			
		H	0.0229			
		2 C	-0.0610			
		H	0.0331			
5	¹ (CH ₃) ₄ ² C	1 C	-0.0563			
		H	0.0239			
		2 C	-0.0592			
6	HF	F	-0.2571		-0.2300	-0.2230
		H	0.2371		0.2330	0.2230
7	CH ₃ F	C	0.0377		0.1570	0.1630
		H	0.0795		0.0919	-0.0040
		F	-0.2722		-0.1830	-0.1270

Contd..

Table 5.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Del Rio ^(a)	CMDC/2 ^(b)	STO-3G ^(c)
8	CH ₂ F ₂	C	0.1634			0.3830
		H	0.1499			0.0230
		F	-0.2316			-0.1630
9	CHF ₃	C	0.3829		0.5930	0.5320
		H	0.2362		-0.0070	-0.0130
		F	-0.1897		-0.1050	-0.1710
10	CF ₄	C	0.6536			0.8740
		F	-0.1634			-0.1630
11	¹ CH ₃ ² CHF ₂	¹ C	-0.0183			
		H	0.0518			
		² C	0.1840			
		H	0.1524			
		F	-0.2422			

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Del Re ^(a)	CSQC/2 ^(b)	STO-3G ^(c)
12	¹ CH ₃ ² CF ₃	C	0.0143		-0.1059	-0.0990
		H	0.0916		0.0529	0.0260
		C	0.3430		0.6000	0.5460
		F	-0.2109		-0.2160	-0.1750
13	C ₂ F ₆	C	0.4751			
		F	-0.1577			
14	¹ (CH ₃) ² CH ₂ F	C	-0.0422			
		H	0.0536			
		C	0.0562			
		H	0.0719			
		F	-0.2733			
15	BH ₃	B	-0.1392	-0.1170	-0.2200	-0.4060
		H	0.0664	0.0300	0.0700	0.1620
16	NH ₂ SH ₂	N	-0.1669			
		H	0.0830			

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Pol Re ^(a)	CMO/2 ^(b)	320-36 ^(c)
17	CH ₃ NH ₂	C	-0.0440	0.0690	0.0790	0.1130
		N	0.0330	0	-0.0210	-0.0130
		H	-0.1838	-0.2400	-0.2640	-0.4020
		H	0.0594	0.0860	0.0730	0.1510
18	(CH ₃) ₂ NH	C	-0.0466			
		N	0.0363			
		H	-0.1636			
		H	0.0539			
19	¹ CH ₃ ² OH _B	¹ C	-0.0532			
		H	0.0276			
		² O	-0.0424			
		H	0.0414			
		H	-0.1836			
		H	0.0535			

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	DoI Re ^(a)	CMC0/2 ^(b)	STO-3G ^(c)
20	CH ₃ ¹ NH ₂	C	-0.0374			
		H	0.0430			
		¹ N	-0.1835			
		H	0.0743			
		² N	-0.1722			
		H	0.0709			
21	H ₂ O	O	-0.2828	-0.2600	-0.2830	-0.4060
		H	0.1444	0.1300	0.1440	0.2030
22	H ₂ O ₂	O	-0.2000			
		H	0.2000			
23	CH ₂ OH	C	0.0176	0.1220	0.1260	0.1360
		H	0.0536	0.0030	0.003	0.0140
		O	-0.2375	-0.3050	-0.2470	-0.3500
		H	0.1240	0.1730	0.1430	0.2110

Contd..

Table 3.1 (Contd.)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Ref. 10 ^(a)	OSDC/2 ^(b)	STO-3G ^(c)
24	P ₂ O	O	0.1012		0.1200	
		P	-0.0606		-0.0600	
25	PF ₃	P	0.2706		0.3300	0.1470
		F	-0.0932		-0.1120	-0.0400

a) Ref. 1 b) Ref. 2 c) Ref. 30

3.2 s-characters in optimised hybrid orbitals

An important feature of our method which distinguishes it from the other available two centre MO approaches^(1,6,35) is the optimisation of the hybrids used to form the two centre molecular orbitals representing the bonds and one centre orbitals corresponding to the lone pairs. Because a quantitative idea of the hybridisation as measured by the s or p-characters of the hybrids can be used to interpret diverse type of molecular properties e.g. geometry, bond moment,

ionization potential, spin-spin coupling constants etc (6-14), the determination of localized canonical molecular orbitals from fully delocalized SCF MO has received considerable attention in recent years (15-17). Obviously, the determination of the s-character of the optimum hybrids for an atom in a given molecular environment directly without having to do much more difficult and time consuming Hartree-Fock type SCF MO calculations is of considerable advantage.

The calculated s-character in a number of molecules are given in table 3.2

Table 3.2

Calculated s-character of hybrid orbitals in different molecules

Sl. No.	Molecule	Bond A-B	s-character of orbital	
			A	B
1	CH ₄	C-H	0.25	1
2	C ₂ H ₆	C-H	0.2623	1
		C-C	0.2129	0.2129
3	1 2 CH ₃ CH ₂ CH ₃	1 C-H	0.2627	1
		1 2 C-C	0.2120	0.2241
		2 C-H	0.2769	1

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	s-Character of orbital on atoms	
			A	B
4	CH ₃ F	C-H	0.2889	1
		C-F	0.1391	0.1699
		F(1p)	0.2770	
5	CH ₂ F ₂	C-H	0.3407	1
		C-F	0.1594	0.1704
		F(1p)	0.2765	
6	C ₂ F ₆	F-C	0.1708	0.2226
		C-C	0.3323	0.3323
7	CH ₃ OH	C-H	0.2723	1
		C-O	0.1831	0.1658
		H-H	0.1992	1
		O(1p)	0.4588	
8	(CH ₃) ₂ NH	C-H	0.2718	1
		C-N	0.1845	0.1844
		N-H	0.1979	1

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	s-Character of orbital on atoms	
			A	B
9	$\overset{1}{\text{C}}-\overset{2}{\text{C}}-\overset{3}{\text{N}}$ $\text{CH}_3\text{CH}_2\text{NH}_2$	$\overset{1}{\text{C}}-\text{H}$	0.2645	1
		$\overset{1}{\text{C}}-\overset{2}{\text{C}}$	0.2070	0.2347
		$\overset{3}{\text{N}}-\text{H}$	0.2360	1
		$\text{C}-\text{H}$	0.1914	0.1661
		$\text{N}-\text{H}$	0.1992	1
10	CH_3OH	$\text{C}-\text{H}$	0.2774	1
		$\text{C}-\text{O}$	0.1679	0.1703
		$\text{O}-\text{H}$	0.2076	1
		$\text{O} (\text{LP})$	0.3110	
11	CH_3OCH_3	$\text{C}-\text{H}$	0.2765	1
		$\text{C}-\text{O}$	0.1706	0.1698
		$\text{O} (\text{LP})$	0.3532	
12	$\overset{2}{\text{C}}-\overset{1}{\text{C}}-\overset{3}{\text{C}}$ $\text{CH}_2(\text{OCH}_3)_2$	$\overset{1}{\text{C}}-\text{H}$	0.2773	1
		$\overset{1}{\text{C}}-\text{O}$	0.1680	0.1701
		$\overset{1}{\text{C}}-\overset{2}{\text{C}}$	0.1906	0.1909
		$\overset{3}{\text{C}}-\text{H}$	0.3151	1

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	S-character of orbital on atoms	
			A	B
13	$\overset{2}{\text{C}}(\overset{1}{\text{OCH}_2})_3$	$\overset{1}{\text{C-H}}$	0.2781	1
		$\overset{1}{\text{C-O}}$	0.1658	0.1732
		$\overset{2}{\text{O-C}}$	0.1549	0.2108
		$\overset{2}{\text{O-H}}$	0.3577	1
14	$(\text{CH}_2)_3\text{N}$	C-H	0.2710	1
		C-N	0.1697	0.1632
15	NH_2NH_2	N-H	0.2087	1
		N-N	0.1247	0.1267
16	$\overset{1}{\text{C}}(\overset{2}{\text{NH}_2})_3$	C-H	0.2736	1
		$\overset{1}{\text{C-N}}$	0.1792	0.1697
		$\overset{1}{\text{N-H}}$	0.2086	1
		$\overset{1}{\text{N-N}}$	0.1232	0.1267
		$\overset{2}{\text{N-H}}$	0.2047	1

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	s-character of orbital on atoms	
			A	B
22	H_2O_2	O-H	0.2534	1
		O-O	0.0733	0.0733
23	NH_3	N-H	0.1986	1
		N (1s)	0.4942	
24	P_2O	O-P	0.0639	0.0645
25	NF_3	N-F	0.1008	0.1043
26	CHF_3	C-H	0.4300	1
		C-F	0.1697	0.1740

The s-character of hybrid orbitals provide an excellent test for the reliability of the calculations as the nuclear spin-spin coupling constant between directly bonded nuclei is known to depend on the s-character^(6,18-23). The spin-spin coupling constant between directly bonded C-H atoms is given by the relation⁽¹⁹⁻²⁵⁾

$$J_{13C-H} = a \rho_c + b \quad \dots (3.1)$$

where ρ_c is the s-character of the carbon hybrid orbital, a and b are constants. The constant b is usually a small negative quantity⁽¹⁹⁻²⁵⁾.

For a number of compounds listed in table 3.3 we got the relation (3.2)

$$J_{13C-H} = 636 \rho_c - 39.4 \quad \dots (3.2)$$

by least square analysis having a correlation coefficient of 0.989 which is quite good.

A much improved agreement may be obtained when one considers the possible variation of the s-electron density at the nucleus, $s^2(0)$ ^(25,26,27). This variation may be taken into account by modifying eqn (3.1) into the form

$$J_{13C-H} = \frac{K^3}{K_0^3} a \rho_c + b \quad \dots (3.3)$$

where K and K_0 stand for the s -orbital exponents of the carbon orbital in the molecular environment and the reference state which may be taken as the neutral carbon atom in sp^3 configuration.

Using Slater's rule for calculating the orbital exponent we get

$$\frac{K}{K_0} = \frac{3.25 - 0.35 \cdot n_p}{3.25 - 0.35 \cdot n_p^0} \quad \dots (3.4)$$

where n_p and n_p^0 are the number of p electrons in the carbon atom in the molecular environment and the reference state.

For sp^3 configuration we have

$$n_p = 0.75 (n_p^0 - Q_c) \quad \dots (3.5)$$

where Q_c is the net charge on the carbon atom.

Using eqn (3.4), (3.5) along with binomial expansion and retaining only the first order term in Q_c we have

$$\frac{K^3}{K_0^3} \approx 1 + 0.24 Q_c \quad \dots (3.6)$$

which gives

$$J_{13C-H} = a(1 + 0.24 Q_c) P_c + b \quad \dots (3.7)$$

Thus, the relation

$$J_{13C-H} = 536(1 + 0.24 Q_c) P_c - 10.9 \quad \dots (3.8)$$

gives a much better agreement (correlation coefficient = 0.993). This excellent correlation illustrates the reliability of the present calculations.

Table 3.3

Molecule	P_c	Calculated J_{13C-H} (Hz)		Experimental (a)
		Using eqn(3.2)	Using eqn (3.8)	
CH_4	0.25	119.788	121.244	125
C_2H_6	0.262	127.428	127.463	126

Contd..

Table 3.3 (Contd..)

Molecule	ρ_0	Calculated $\delta_{150-H} (\text{Hz})$		Experimental (a)
		Using eqn(3.2)	Using eqn(3.3)	
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.265	128.665	128.001	128
CH_3F	0.237	143.347	144.237	143
CH_2F_2	0.341	177.730	179.108	176
CHF_3	0.431	233.036	233.636	233
CH_3OH	0.277	136.979	133.244	141
CH_3OCH_3	0.277	136.979	136.742	133
$\text{CH}_2(\text{OCH}_3)_2$	0.330	164.359	161.463	162
$\text{OH}(\text{OCH}_3)_3$	0.367	194.293	189.189	186
CH_2NH_2	0.272	133.796	133.364	133
$(\text{CH}_3)_2\text{NH}$	0.271	133.159	132.720	132
$(\text{CH}_3)_3\text{N}$	0.271	133.159	132.720	131
CH_3CF_3	0.280	139.339	139.746	139

a) Ref. 6, 36-41.

3.3 Dipole moments

The reliability of the calculated bond charges given in section 3.1 can also be tested by correlating charge distribution with some suitable molecular properties. Among many molecular properties, the dipole moment is most explicitly related to the orbital charges.

Quantum mechanically the value of the dipole moment in a state described by the normalised wave function Ψ is the expectation value

$$\langle \mu \rangle = \int \Psi^* \mu \Psi d\tau \quad \dots (3.9)$$

For a molecule we have a discrete set of charges $Z_\alpha e$ from the nucleus and a continuous charge density from the electrons, so that the dipole moment can be written as

$$\langle \mu \rangle = e \sum_{\alpha=1}^{\nu} Z_\alpha R_\alpha - e \int \Psi^* \left(\sum_{i=1}^N r_i \right) \Psi d\tau \quad \dots (3.10)$$

where $Z_\alpha e$ is the set of charges from the nuclei ν and the position of nucleus α is given by the vector R_α whose

components are the coordinates of the nucleus in a fixed coordinate system and \mathbf{r}_i is the position vector of electron i ($i = 1, 2, \dots, N$).

From eqn (3.10) it is obvious that the first part is due to nuclear contribution and the second part is due to electronic contribution to the total dipole moment.

For a single determinant wave function

$$\langle \mu \rangle = e \sum_{\alpha=1}^N Z_{\alpha} R_{\alpha} - e \sum_{n=1}^N \mu_n \quad \dots (3.11)$$

where $-e\mu_n$ is the contribution of an electron in the orbital Ψ_n

and

$$\mu_n = \int r \Psi_n^* \Psi_n d\tau \quad \dots (3.12)$$

If the molecular orbitals contain hybrid AO's, dipole moment contribution can arise from the asymmetric distribution of charge density because hybrid AO's are not centrally

asymmetric and the barycenter of an electron in such an orbital is not coincident with the nucleus to which A0 refers.

Let us consider a s-p hybrid to an atom A

$$\phi_u = \rho_s^{1/2} 2s + (1-\rho_s)^{1/2} 2p \quad \dots (3.13)$$

where ρ_s is the s-character of hybrid A0.

Let this hybrid be one of the constituent parts of filled MO

$$\Psi_{MO} = C_A \phi_u + C_B \phi_v \quad \dots (3.14)$$

(μ on atom A and ν on atom B)

Therefore, molecular orbital due to one electron of atom A can be written in terms of hybrid A0's and correspondingly eqn. (3.12) can be solved by using standard technique⁽³³⁻³⁹⁾ and the dipole moment due to hybridization per electron in Ψ of eqn. (3.14) is given by

$$\mu_{hyb} = -14.674 \rho_s^{1/2} (1-\rho_s)^{1/2} C_A^2 / \rho_s D \quad \dots (3.15)$$

where f is the Slater exponent, C_A is the orbital coefficient and D represents debye unit.

Therefore, for a bond represented by $\mu-\nu$ (where μ on atom A and ν on atom B), hybrid dipole moment for the bond is given by

$$\mu_{\text{hyb. bond}} = 7.337 \left\{ \frac{P_{\mu}^{1/2}(1-P_{\mu})^{1/2} P_{\mu\mu}}{L_{\mu}} - \frac{P_{\nu}^{1/2}(1-P_{\nu})^{1/2} P_{\nu\nu}}{L_{\nu}} \right\} \dots (3.16)$$

where $P_{\mu\mu} = 2C_A^2$ } ... (3.17)
 and $P_{\nu\nu} = 2C_B^2$ }

Dipole moment due to net charges located at the nuclear position for $\mu-\nu$ bond is represented by

$$\mu_{\text{charge}} = Z_{\mu} e R_A + Z_{\nu} e R_B \dots (3.13)$$

Simplifying eqn. (3.13) and using standard technique⁽²³⁾, dipole moment due to net charges can be written in terms of debye unit as

$$\mu_{\text{charge}} = 4.802 q_{\mu} R_{AB} \quad \dots (3.19)$$

where R_{AB} represents bond distance in terms of angstrom unit and q_{μ} the orbital charge.

Therefore, the total dipole moment for a bond μ - ν can be written as

$$\mu_{\text{bond}} = 4.802 q_{\mu} R_{AB} + 7.337 \left\{ \frac{\rho_{\mu}^{1/2} (1-\rho_{\mu})^{1/2} \rho_{\mu\mu}}{\rho_{\mu}} - \frac{\rho_{\nu}^{1/2} (1-\rho_{\nu})^{1/2} \rho_{\nu\nu}}{\rho_{\nu}} \right\} \quad \dots (3.20)$$

and for lone pair $C_{\lambda}^2 = 1$, therefore eqn. (3.15) becomes

$$\mu_{\text{lp}}(\lambda) = 14.674 \rho_{\lambda}^{1/2} (1-\rho_{\lambda})^{1/2} / \rho_{\lambda} \quad \dots (3.21)$$

where subscript λ indicates lone pair orbital.

Using the charges obtained by our approach (Table 3.1) we have calculated the dipole moments of a number of

molecules. These are listed in table 3.4. For comparison we have also included in table 3.4 the dipole moments obtained by more sophisticated methods (1-5,30). As would be expected from the charge distributions given in table 3.1, our results agree fairly satisfactorily with those obtained by the CNDO/2 method, and, in some cases, the agreement is even better.

Table 3.4

Calculated dipole moments for different molecules
(in Debye unit)

Sl. No.	Molecule	Our calculation	Exp.	CNDO/2 (a)	AMDO (b)	STO-3G (c)
1	$\text{CH}_3\text{OH}_2\text{CH}_3$	0.096	0.083	0.00	0.00	0.03
2	$(\text{CH}_3)_3\text{OH}$	0.017	0.132	0.00		
3	NH^+	2.10	1.32	1.05	1.09	1.41
4	OH_2^+	0.34	0.30	-0.21		
5	NH_3	0.23	0.24	0.43	0.20	0.62
6	CH_3F	2.31	1.36	1.66	1.78	0.96
7	CHF_3	2.60	1.66		2.25	0.96
8	CH_3CF_3	2.69	2.32	2.16		1.05

Contd..

Table 3.4 (Contd..)

Sl. No.	Molecule	Our calculation	Exp.	CMO/2 ^(a)	CMO ^(b)	CMO-3G ^(c)
9	H ₂ O	2.17	1.65	2.10	1.73	1.73
10	CH ₃ OH	2.25	1.63	1.94	1.48	1.51
11	NH ₃	2.12	1.47	1.97	1.16	1.66
12	CH ₃ NH ₂	2.21	1.35	1.66	1.43	1.41

a) Ref. 2 (b) Ref. 31 (c) Ref. 30

3.4 Heat of atomisation

Heats of atomisation provide a very good test of the reliability and accuracy of any molecular orbital calculations. In this section we shall therefore develop an expression for the heat of atomisation of molecules in a localized MO approximation and compare the results with the experimental values.

The total energy of a molecule is given by ⁽³³⁾

$$E_{\text{Total}} = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (H_{\mu\nu} + F_{\mu\nu}) + \sum_{A < B} Z_A Z_B R_{AB}^{-1} \quad \dots (3.22)$$

Using the appropriate expression for $H_{\mu\nu}$ and $F_{\mu\nu}$ along with integral approximations given in sections 1.7, this reduces to

$$E_{\text{Total}} = \sum_A \epsilon_A + \sum_{\mu-\nu(\text{bond})} \epsilon_{\mu\nu} \quad \dots (3.23)$$

where

$$\begin{aligned} \epsilon_A = & \sum_{\mu}^A P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu}^A \sum_{\nu}^A P_{\mu\mu} P_{\nu\nu} \gamma_{AA} \\ & - \frac{1}{4} \sum_{\mu}^A P_{\mu\mu}^2 \gamma_{AA} \end{aligned} \quad (3.24)$$

and

$$\epsilon_{\mu\nu} = 2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2 r_{AB} + Z_A Z_B R_{AB}^{-1} - (P_{AA} \cdot Z_B + P_{BB} \cdot Z_A - P_{AA} \cdot P_{BB}) r_{AB} \dots (3.25)$$

The orbitals ϕ_μ and ϕ_ν forming the bond $\mu-\nu$ are on the atoms labelled A and B respectively.

Using the net atomic charges Q_A and Q_B , given by

$$Q_A = n_A - P_{AA} \quad ; \quad Q_B = n_B - P_{BB} \quad \dots (3.26)$$

where n_A and n_B are the number of electrons on the two atoms, eqn. (3.26) takes the form.

$$\epsilon_{\mu\nu} = 2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2 r_{AB} + Z_A Z_B R_{AB}^{-1} - Z_A Z_B r_{AB} + Q_A Q_B r_{AB} \quad \dots (3.27)$$

The last term i.e. $Q_A Q_B \gamma_{AB}$ is always a very small fraction of $\epsilon_{\mu\nu}$ and may therefore be neglected. Hence to a good accuracy, we have

$$\epsilon_{\mu\nu} = 2P_{\mu\nu}\beta_{\mu\nu} - \frac{1}{2}P_{\mu\nu}^2\gamma_{AB} + Z_A Z_B (R_{AB}^{-1} - \gamma_{AB}) \dots (3.23)$$

Further,

$$\sum_{\mu}^A P_{\mu\mu} = \sum_{\mu}^A (n_{\mu} - q_{\mu}) = n_A - Q_A \dots (3.24)$$

where n_{μ} is orbital occupancy in the valence state of the atom A.

Eqn (3.24) then reduces to

$$\begin{aligned} \epsilon_A = & \sum_{\mu}^A n_{\mu} U_{\mu\mu} - \sum_{\mu}^A q_{\mu} U_{\mu\mu} + \frac{1}{2} n_A^2 \gamma_{AA} \\ & - n_A Q_A \gamma_{AA} + \frac{1}{2} Q_A^2 \gamma_{AA} - \frac{1}{4} \sum_{\mu}^A P_{\mu\mu}^2 \gamma_{AA} \dots (3.25) \end{aligned}$$

The electronic energy ϵ_A^0 of the atom A in its valence state is given by

$$\epsilon_A^0 = \sum_{\mu}^A n_{\mu} U_{\mu\mu} + \frac{n_A(n_A-1)}{2} \gamma_{AA} \quad \dots (3.31)$$

Therefore, the stabilization due to molecule formation is

$$\begin{aligned} \Delta \epsilon_A = \epsilon_A - \epsilon_A^0 = & - \sum_{\mu}^A q_{\mu} U_{\mu\mu} + \frac{1}{2} n_A \gamma_{AA} \\ & - n_A \theta_A \gamma_{AA} + \frac{1}{2} \theta_A^2 \gamma_{AA} \\ & - \frac{1}{4} \sum_{\mu}^A p_{\mu\mu}^2 \gamma_{AA} \quad \dots (3.32) \end{aligned}$$

since $U_{\mu\mu}$ is given by (eqn. 1.73)

$$U_{\mu\mu} = \alpha_{\mu} - (n_A - \frac{1}{2}) \gamma_{AA}$$

where, $\alpha_{\mu} = - (I_{\mu} + A_{\mu}) / 2$

We get

$$\begin{aligned} \Delta \epsilon_A = & - \sum_{\mu}^A q_{\mu} \alpha_{\mu} + \frac{1}{2} (n_A - \theta_A) \gamma_{AA} \\ & - \frac{1}{4} \sum_{\mu}^A p_{\mu\mu}^2 \gamma_{AA} + \frac{1}{2} \theta_A^2 \gamma_{AA} \\ \approx & \sum_{\mu}^A q_{\mu} \alpha_{\mu} + \frac{1}{2} (n_A - \theta_A) \gamma_{AA} - \frac{1}{4} \sum_{\mu}^A p_{\mu\mu}^2 \gamma_{AA} \quad \dots (3.33) \end{aligned}$$

Because the last term is only a very small fraction of $\Delta \epsilon_A$.

Noting that $P_{\mu\mu}$ in eqn (3.33) always refer to an orbital involved in a bond since the lone pairs do not contribute to the net stabilization so that n_{μ} (eqn. 3.29) may be taken as one. Eqn (3.33) then simplifies to

$$\Delta \epsilon_A = - \sum_{\mu}^A q_{\mu} \alpha_{\mu} + \frac{1}{4} \sum_{\mu}^A (1 - q_{\mu}^2) \gamma_{AA} \quad \dots (3.34)$$

The net stabilization energy, ϵ_s , due to molecule formation is therefore given by

$$\begin{aligned} \epsilon_s &= \sum_A \Delta \epsilon_A + \sum_{\text{bonds}} \epsilon_{\mu\nu} \\ &= \sum_A \left\{ - \sum_{\mu}^A q_{\mu} \alpha_{\mu} + \frac{1}{4} \sum_{\mu}^A (1 - q_{\mu}^2) \gamma_{AA} \right\} \\ &\quad + \sum_{\text{bonds}} \left\{ 2 P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}^2 \gamma_{AB} \right. \\ &\quad \left. + Z_A Z_B (R_{AB}^{-1} - \gamma_{AB}) \right\} \quad \dots (3.35) \end{aligned}$$

It may be noted that this expression is valid only in the localized approximation since, in conformity with our approximation, the interaction between non-bonded electrons is not included in eqn (3.35).

Since the heat of atomisation is the difference in the energy of the molecule and its constituent elements in their standard states, the promotion energy of the constituent atoms required to achieve the valence state electronic configuration must be added to the stabilisation energy. Therefore, the heat of atomisation, ϵ_{Hat} , is given by

$$\epsilon_{\text{Hat}} = \epsilon_s + \sum_A P_A \quad \dots (3.36)$$

where P_A is the energy required to promote the atom A from its standard state to the appropriate valence state. The quantity in eqn (3.36) is actually negative (showing net stabilisation), the absolute value is taken as the heat of atomisation since it is defined as the energy required to break the molecule into its constituent elements in their standard states and is, therefore, a positive quantity.

The calculated heats of atomisation of several molecules are given in table 3.5. Experimental values are also included for comparison. The agreement is very

satisfactory, the difference being somewhat larger in case of fluorinated compounds. This is probably due to the lone pair - lone pair interactions in such compounds which are not included in the localized molecular orbital model used in our calculation. The agreement is particularly noteworthy as the CNDO/3 method where the parametrization is nearly identical with those used in our calculations yields energy values which are always too high.

Table 3.5

Calculated observed heats of atomization of different compounds.

Sl. No.	Compound	Heat of atomization in (e.v)	
		Calculated	Experimental (a)
1	CH_4	17.121	17.229
2	C_2H_6	29.414	29.260
3	C_3H_8	41.630	41.397
4	C_4H_{10}	53.933	53.648
5	$\text{CH}_3\text{CH}(\text{CH}_3)\cdot\text{CH}_3$	53.947	53.6195
6	$\text{CH}_3\text{CH}(\text{CH}_3)\cdot\text{CH}_2\text{CH}_2$ $\text{CH}(\text{CH}_3)\text{CH}_3$	102.932	102.829

Contd..

Table 3.8 (Contd..)

Sl. No.	Compound	Heat of atomisation in (e.v)	
		Calculated	Experimental (a)
7	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot$ $\text{CH}(\text{CH}_3) \cdot \text{CH}_3$	30.633	30.152
8	$(\text{CH}_3)_4^{\ominus}$	66.133	65.011
9	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3)_2 \cdot$ CH_3	102.942	102.313
10	Cyclo- C_4H_8	48.121	47.650
11	Cyclo- C_6H_{10}	61.120	60.473
12	Cyclo- C_8H_{12}	73.253	72.670
13	NH_3	10.215	12.132
14	$\text{H}_2^{\ominus} \cdot \text{NH}_2$	19.949	17.312
15	CH_3NH_2	24.027	23.633
16	$\text{C}_2\text{H}_5\text{NH}_2$	36.230	36.016
17	H_2O	7.415	9.694
18	CH_3OH	23.334	21.107
19	HF	1.376	6.906
20	CH_3F	19.261	17.921
21	CH_2F_2	20.537	13.225

Contd..

Table 3.5 (Contd..)

Sl. No.	Compound	Heat of atomisation in (e.v.)	
		Calculated	Experimental (a)
22	CHF_3	20.404	19.292
23	CF_4	16.922	20.533
24	$\text{CHF}_2 \cdot \text{CH}_3$	32.143	30.788
25	CH_3CF_3	32.775	31.720
26	$(\text{CF}_3)_2\text{CHF}$	43.242	41.695
27	C_2F_6	34.408	33.632

(a) Experimental Heats of atomisation have been calculated from Ref. 34.

3.8 Molecular geometry : Bond angle and s-characters

Because of the directional properties of hybrid orbitals, s-characters are frequently used to calculate the bond angles. The angle, θ , between the axes of the two hybrid orbitals ϕ_{μ} and ϕ_{ν} is easily shown to be given by the relation

$$\theta = \cos^{-1} \left[-\rho_{\mu}^{1/2} \rho_{\nu}^{1/2} / \{ (1-\rho_{\mu})^{1/2} (1-\rho_{\nu})^{1/2} \} \right] \dots (3.37)$$

where ρ_{μ} and ρ_{ν} are the s-characters of the orbitals ϕ_{μ} and ϕ_{ν} respectively.

If the direction of the bonds coincide with the axes of hybrid orbitals used by it then eqn. (3.37) can be used to calculate the bond angles in different molecules from the s-characters of the hybrid orbitals. Obviously, such an assumption is expected to be valid only in molecules where the electron repulsion interactions and steric factors do not have significant role. The presence of lone pair in any atom is expected to lead to deviations from the calculated bond angles because of larger lone pairs - bond pair and

lone pair - lone pair interactions.

The bond angles in different molecules obtained from eqn. (3.37) using the calculated s-characters are given in table 3.6 along with the experimental data. The large difference between the calculated and observed results in NH_3 , H_2O , CH_2F_2 are probably due to large lone pair - lone pair interactions in these molecules.

Table 3.6

Molecule	Angle	Bond angles	
		Calculated	Experimental (a)
NH_3	HNH	104.4	107.3 ± 2
H_2O	HOH	105.9	$104.5 \pm .1$
NF_3	FNF	96.4	102.2
H_2O_2	HOH	93.9	96.9
F_2O	OFF	93.4	103.2 ± 1
CH_3F	HCH	113.7	110.0
	HCF	104.8	103.3
CH_2F_2	HCH	121.1	111.0 ± 4
	HCF	103.2	
	FCF	108.9	109.3 ± 1

Contd..

Table 3.6 (Contd..)

Molecule	Angle	Bond Angles	
		Calculated	Experimental (a)
CH_2F_2	FCF	102.2	108.8 ± 0.8
CH_2OH_2	HCH	110.9	109.3 ± 0.8
	HOC	106.1	
CH_3NH_2	HCH	111.9	109.5 ± 1
	HON	106.6	
	NNH	104.4	
	ONH	102.6	
CH_3OH	HCH	112.5	109.3 ± 0.8
	HCO	104.6	$107 - 109$
	COH	100.3	
$(\text{CH}_3)_4\text{O}$	HCH	110.9	
	HCO	107.9	
	OCO	109.6	
$(\text{CH}_3)_3\text{N}$	HCH	111.6	
	HCH	106.9	
	CNC	101.2	103 ± 4

Contd..

Table 3.6 (Contd..)

Molecule	Angle	Bond angles	
		Calculated	Experimental (a)
CH ₃ COH ₃	HCH	112.4	111° ± 3°
	HCO	106.3	
	COO	101.6	

(a) Reference -52

3.6 Conclusion

The results presented in this part provide ample justification for our approach. It is clear that a reasonably good account of ground state molecular properties may be obtained from a localized calculation utilizing only theoretically justified parameters. Even the bond resonance parameters which are used as purely empirical parameters in SMO and related calculation are obtained in our approach through a theoretically derived expression. The agreement between the calculated heats of atomization and the experimental values is particularly noteworthy.

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APPENDIX

The bond charge in a two centre MO derived from the hybrid ΔO 's, ϕ_μ and ϕ_ν is given by (eqn. 1.112)

$$q_\mu = \frac{F_{\mu\mu} - F_{\nu\nu}}{[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2]^{1/2}}$$

From eqn. (1.118) we get

$$q_\mu = \frac{\alpha_\mu - \alpha_\nu}{[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2]^{1/2}}$$

$$+ \frac{q_\mu}{2[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2]^{1/2}} (\gamma_{AA} + \gamma_{BB})$$

$$- \sum_{R \neq \mu, \nu} \frac{q_R}{[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2]^{1/2}} [(\gamma_{AR} - \gamma_{AL}) - (\gamma_{BR} - \gamma_{BL})]$$

$$\approx \frac{\alpha_\mu - \alpha_\nu}{[(F_{\mu\mu} - F_{\nu\nu})^2 + 4F_{\mu\nu}^2]^{1/2}}$$

... (A1)

Since $q_\mu \ll \left| F_{\mu\nu} \right|$ so that the last two terms are very small compared to the first term and may be neglected in the present discussion.

Further $(F_{\mu\mu} - F_{\nu\nu}) \ll \left| 2F_{\mu\nu} \right|$, so that, to a good approximation, q_μ is given by

$$q_\mu = \frac{\alpha_\mu - \alpha_\nu}{\left| 2F_{\mu\nu} \right|} \quad \dots (A2)$$

Differentiating eqn. (A2) we get

$$\frac{\partial q_\mu}{\partial p_{\mu s}} = \frac{1}{\left| 2F_{\mu\nu} \right|} \frac{\partial \alpha_\mu}{\partial p_{\mu s}} - \frac{(\alpha_\mu - \alpha_\nu)}{2F_{\mu\nu}^2} \frac{\partial \left| F_{\mu\nu} \right|}{\partial p_{\mu s}}$$

$$\approx \frac{1}{\left| 2F_{\mu\nu} \right|} \frac{\partial \alpha_\mu}{\partial p_{\mu s}} \quad \dots (A3)$$

as $2F_{\mu\nu}^2 \gg (\alpha_\mu - \alpha_\nu)$

Since α_μ can be written as

$$\alpha_\mu = -\frac{1}{2} (I_p + A_p) + \Delta \cdot p_{\mu s} \quad \dots (A4)$$

where,

$$\Delta = \frac{1}{2} [(I_p + A_p) - (I_s + A_s)]$$

we have

$$\frac{\partial \alpha_\mu}{\partial \rho_{\mu s}} = \Delta \quad \dots (A5)$$

which gives

$$\frac{\partial \eta_\mu}{\partial \rho_{\mu s}} = \frac{\Delta}{|2F_{\mu v}|} \quad \dots (A6)$$

Therefore,

$$\frac{\partial P_{\mu\mu}}{\partial \rho_{\mu s}} = \frac{\partial}{\partial \rho_{\mu s}} (1 - \eta_\mu) = - \frac{\Delta}{|2F_{\mu v}|} \quad \dots (A7)$$

$$\text{Now, } P_{\mu v} = 2c_\mu c_v = (2c_\mu^2 \cdot 2c_v^2)^{1/2} = (1 - \eta_\mu^2)^{1/2} \quad \dots (A8)$$

Differentiation of eqn. (A8) gives

$$\frac{\partial P_{uv}}{\partial \rho_{us}} = - (1 - \gamma_{\mu}^2)^{-1/2} \gamma_{\mu} \frac{\partial \gamma_{\mu}}{\partial \rho_{us}}$$

$$\approx - (1 - \gamma_{\mu}^2)^{-1/2} \gamma_{\mu} \frac{\Delta}{|2F_{uv}|} \quad \dots (A9)$$

Since γ_{μ} is generally quite small and also $|\Delta| \ll |2F_{uv}|$, $\frac{\partial P_{uv}}{\partial \rho_{us}}$ are very small compared to the last term in eqn. (1.158) and can be neglected. Though $\frac{\partial P_{uv}}{\partial \rho_{us}}$ turns out to be somewhat larger than $\frac{\partial P_{uv}}{\partial \rho_{us}}$ (about 3% of the major term in eqn. (1.158)) this may also be neglected. In fact, actual computation shows that retention or neglect of this two terms does not affect the convergence of the iteration process or the final results.