PART I

APPROXIMATE MOLECULAR ORBITAL THEORIES : A LOCALISED MO APPROACH.

1.1 Introduction

In order to interprete 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 Huckel method(1-2). With passage of time the Huckel 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 localised MO or Bond orbital approach$^{(8-12,62-65)}$ 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 overemphasised:

(i) The concept of inner shells, lone pairs and bond pairs should not be obscured as in the fully delocalised MO approach where much additional computational labour is needed to construct suitable localised MO's.

(ii) The method should have a strong theoretical basis without being computationally too complex so that information on any molecule 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 hybridisation, 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 σ-bonded systems that we propose to develop in this work.

1.2 The Basic Frame Work of MO 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 algebric 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 minimising 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

$$\Psi = \left| \psi_1(1), \psi_2(2), \cdots\cdots \psi_{2n}(2n) \right| \qquad \ldots (1.1)$$

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

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

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

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

$$= 2\sum_{i} H_{ii} + \sum_{i}\sum_{j} \left(2J_{ij} - K_{ij}\right) \qquad \ldots (1.4)$$

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

$$H^{core} = -\frac{1}{2}\nabla^{2} - \sum Z_A r_A^{-1} \qquad \ldots (1.5)$$

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

$$H_{ii} = \left\langle \phi_i(1) \middle| H^{Core}(1) \middle| \phi_i(1) \right\rangle \qquad \ldots (1.6)$$

$$J_{ij} = \left\langle \phi_i(1)\phi_i(1) \middle| \frac{1}{r_{12}} \middle| \phi_j(2)\phi_j(2) \right. \qquad \ldots (1.7)$$

$$K_{ij} = \left\langle \phi_i(1)\,\phi_j(1) \middle| \frac{1}{r_{12}} \middle| \phi_i(2)\,\phi_j(2) \right. \qquad \ldots (1.8)$$

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

Minimisation 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 equation of the form

$$\mathcal{F}\phi_i = \varepsilon_i \phi_i \qquad \ldots (1.9)$$

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

$$\mathcal{F} = \left[H^{core} + \sum_j \left(2J_j - K_j\right)\right] \qquad \ldots (1.10)$$

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

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

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

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

$$\mathcal{F}\Phi = \varepsilon\Phi \qquad \text{... (1.13)}$$

Hartree-Fock equations are determined within a unitary transformation among the orbitals. These transformation keeps both $\mathcal{F}$ 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

$$\psi_i = \sum_{\mu=1}^{n} C_{\mu i}\,\phi_\mu \qquad \text{... (1.14)}$$

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

$$\Psi = \Phi C \qquad \text{... (1.15)}$$

substituting (1.15) in (1.13) one gets

$$\mathcal{F}\Phi C = \Phi C \varepsilon \qquad \ldots (1.16)$$

$$\Phi^{*}\mathcal{F}\Phi C = \Phi^{*}\Phi C \varepsilon$$

$$\text{or} \quad FC = SC\varepsilon \qquad \ldots (1.17)$$

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

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

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

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

$$S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle \qquad \ldots (1.20)$$

The orthonormality relation of the MO's become

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

The total electronic energy can be written in terms of integrals over atomic orbitals if we substitute the linear expansion of eqn. (1.16) in the molecular orbital integrals. Thus

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

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

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

Similarly we may write

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

$$K_{ij} = \sum_{\mu\lambda\nu\sigma} C^{*}_{\mu i} C^{*}_{\lambda j} C_{\nu i} C_{\sigma j} (\mu\lambda|\nu\sigma) \quad \cdots\cdots \quad (1.24)$$

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

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

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

$$\det (F_{\mu\nu} - \mathcal{E} S_{\mu\nu}) = 0 \quad \cdots\cdots \quad (1.26)$$

The matrix elements of the HF Hamiltonian operator are dependent on the orbital through the elements $p_{\mu\nu}$ and the Roothaan 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 $F_{\mu\nu}$. The diagonalization procedure is effected by standard matrix eigen value techniques and a new matrix of linear expansion coefficients are ibtained. 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 HFR 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

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

where Y_{lm} is the spherical harmonics representing the angular part of the slater function, N_{nl} is the normalisation 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 become much easier with these functions and as such GTO's are now almost exclusively used in ab initio LCAO MO SCF calculations.

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

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

In order to reduce the computational problem to managable proportions, contracted Gaussian functions(20-23) which are linear combinations of Gaussian with fixed coefficients are used. For example, six sets of P-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 representation of slater functions are determined most directly by a least-square fitting procedure which has been extensively used by Pople and co-workers(26,28). A basis in which each slater function is represented by combination of N Gaussians is generally denoted by STO - NG. 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 minimum basis for the inner-shells. For example, in the basis set N - 31G (N = 4 and 6) 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 GTO 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.

1.4 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 multicentre 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 Roby in a series of papers(34-37).

The primary aim of the approximate methods are to provide simple and inexpensive 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 zero differential overlap (ZDO) approximation embodied in eqn. (1.29) and (1.30)$^{(38)}$.

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

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

where δ is the Kronecker delta.

The ZDO approximation follows from the approximate equality

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

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

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

(i) 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 Lowdin basis of orthogonalised atomic orbitals can be transformed to the form

$$\lambda_F . \lambda_C = \lambda_C . \epsilon \qquad \text{... (1.32)}$$

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

and $C = S^{-1/2} \lambda_C$ ... (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) <u>The complete Neglect of the Differential Overlap Method</u>

In this method, developed by Pople et al(40-43), 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 ($\mu|V|\mu$) 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

$$H_{\mu\nu} = (\mu|H^{c}|\nu) = \beta^{\circ}_{\mu\nu} S_{\mu\nu} \qquad \ldots (1.35)$$

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

Using these approximations, the element of F-matrix take the form[17,40-42]

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

(ϕ_μ on atom A)

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

(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.

(b) The Many-Centre Zero differential Overlap (MCZDO) Method (15,43)

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

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

The inclusion of more integrals in the MCZDO method makes it more reliable compared to the CNDO method.

(c) The Neglect of Diatomic Differential Overlap (NDDO) Method (40)

Most of the serious deficiencies of the CNDO method are removed in the NDDO method by retaining even two centre integrals of the type $(\mu_A \nu_A | \lambda_B \sigma_B)$. 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 ZDO 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.

$$\left| F - S\epsilon \right| = 0 \qquad \ldots (1.38)$$

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

(i) <u>The Mulliken Method</u>(46)

In this method, the two centre one electron and two electron integrals are obtained from the Mulliken approximations(46-48) given by the equations:

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

$$\left(\mu_A \nu_B \middle| \lambda_C \sigma_D\right) = \frac{S_{\mu\nu} S_{\lambda\sigma}}{4}\left[\left(\mu_A \cdot \mu_A \middle| \lambda_C \cdot \lambda_C\right) + \left(\mu_A \mu_A \middle| \sigma_D \sigma_D\right)\right.$$

$$\left. + \left(\nu_B \nu_B \middle| \lambda_C \lambda_C\right) + \left(\nu_B \nu_B \middle| \sigma_D \sigma_D\right)\right] \ldots (1.40)$$

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

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

The interrelationship between the various approximations involved have been discussed by Brown and Roby(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 localised orbitals, orbitals that are localised 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.

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

A linear transformation of the orbitals

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

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

gives a new wavefunction

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

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

$$\Psi = \Psi'(\det. C)^2 \qquad \ldots (1.45)$$

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

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

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

Thus Ψ is invariant to orthogonal transformations of the real AO'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 localisation of molecular orbitals. The most objective localisation 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 localisation would require that the definition of separation be decided upon.

The "Degree of separation" can be measured in a number of ways such as sterio-chemically and energetically. The two most commonly used method 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 Edminston - 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

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

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 localised orbitals from delocalised SCF MO's. These procedures so far discussed are known as "intrinsic localisation".

Problem with the intrinsic localisation procedure is that none of these localisation 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 localised orbitals will be to use the chemical concept of bonds, lone pairs, inner shells etc. This may be achieved by using hybridised atomic orbitals (HAO) that are already localised in a specified region of space. The localised molecular orbital (LMO) representing a chemical bond can then be constructed by making linear combination of the appropriate HAO's. Such a localisation procedure is often termed "the external localisation".

The molecular orbitals can then be written as

$$\Psi_{MO} = \sum_i C_{ij} \phi_i \qquad \dots (1.47)$$

where ϕ_i's are appropriately chosen bond orbital localised at each bond (BMO's).

Lennard - Jones et al$^{(52-55)}$ showed that in symmetrical molecule the set of Ψ_i obtained by LCAO scheme can be transformed by a unitary transformation into another set of equivalent ψ_i's localised 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 LCBO 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(12,56-61,72).

Although the 'Bond orbitals' which are fully localised within the bond (i.e. strictly two centre molecular orbitals) cannot describe the electron distribution in a molecule as accurately as the delocalised 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 parametrisation such methods can give a very good account of many molecular properties with almost insignificant computational labour. This is, perhaps, best illustrated by the Del Re(12) method which has found extensive applications in organometallic chemistry as a simple tool for the interpretation and correlation of chemical and physical properties, such as, reactivity, NMR and NQR data, dipole-moment, Mossbauer spectral data, hybridisation etc(56-60). Because of this, the localised 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 localised 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 LCAO 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 (see 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.

1.6 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 hybrids 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 AO'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)

$$E_{HF} = \frac{1}{2}\sum_{\mu,\nu} P_{\mu\nu}\left(H_{\mu\nu} + F_{\mu\nu}\right) \qquad \text{... (1.49)}$$

$$= \frac{1}{2}\,\mathrm{tr.}\left\{P\left(H + F\right)\right\} \qquad \text{... (1.49)}$$

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

$$\phi' = O\,\phi \qquad \text{... (1.50)}$$

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

$$\rho' = O P O^{-1} \qquad \ldots (1.51)$$

$$H' = O H O^{-1} \qquad \ldots (1.52)$$

$$F' = O F O^{-1} \qquad \ldots (1.53)$$

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 localised 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

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

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 2 x 2 submatrices corresponding to MO's given by eqn. (1.54) and diagonal 2's representing lone pairs as shown below:

$$P_{Loc} = \begin{array}{c} \\ \mu \\ \nu \\ \lambda \\ \sigma \\ \vdots \end{array} \begin{array}{c} \begin{array}{ccccc} \mu & \nu & \lambda & \sigma & \cdots \end{array} \\ \left[\begin{array}{cccccc} P_{\mu\mu} & P_{\mu\nu} & 0 & 0 & 0 & \cdots \\ P_{\mu\nu} & P_{\nu\nu} & 0 & 0 & 0 & \cdots \\ 0 & 0 & P_{\lambda\lambda} & P_{\lambda\sigma} & 0 & \cdots \\ 0 & 0 & P_{\lambda\sigma} & P_{\sigma\sigma} & 0 & \\ 0 & 0 & 0 & 0 & \ddots & \\ \vdots & \vdots & \vdots & \vdots & & 2 \end{array}\right] \end{array} \qquad \ldots (1.55)$$

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 maximise 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 localised approximation are usually very small in a properly chosen hybrid basis. Because of this, P_{Loc}, the density matrix obtained by localised 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

$$P' = P_{Loc} + \Delta P \qquad \ldots (1.38)$$

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

We now have,

$$\begin{aligned}
E_{HF} &= \frac{1}{2} tr \left\{ P(H+F) \right\} \\
&= \frac{1}{2} tr \left\{ OPO^{-1}\left(OHO^{-1} + OFO^{-1}\right) \right\} \\
&= \frac{1}{2} tr \left\{ P'\left(H' + F'\right) \right\} \\
&= \frac{1}{2} tr \left\{ P_{Loc}\left(H' + F'\right) \right\} + \frac{1}{2} tr \left\{ \Delta P\left(H' + F'\right) \right\} \\
&= E_{Loc} + \Delta E
\end{aligned} \qquad \text{... (1.57)}$$

where

$$\Delta E = \frac{1}{2} tr \left\{ \Delta P\left(H' + F'\right) \right\} \qquad \text{... (1.58)}$$

$$E_{Loc} = \frac{1}{2} tr \left\{ P_{Loc}\left(H' + F'\right) \right\} \qquad \text{... (1.59)}$$

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

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

$$\text{Or } \delta(E_{Loc} - E_{MO}) = 0$$

$$\text{Or, } \delta E_{Loc} = 0 \qquad \ldots (1.60)$$

Since E_{MO} 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 localised MO's of a molecule. The computational problem for its implementation will be discussed latter.

1.7 (i) 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$^{(6)}$

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

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

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

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

Using this approximation (eqn. 1.63) we have

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

$$= \sum_{\lambda} P'_{\lambda\lambda}(\mu\mu|\lambda\lambda) \qquad \ldots (1.64)$$

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

is Mulliken's gross population(68).

Similarly,

$$\sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\lambda|\mu\sigma) = \sum_{\lambda\sigma} P_{\lambda\sigma}\Big[(\mu\mu|\mu\mu) + (\mu\mu|\sigma\sigma) + (\lambda\lambda|\mu\mu) + (\lambda\lambda|\sigma\sigma)\Big]\frac{S_{\mu\lambda}S_{\mu\sigma}}{4}$$

$$= \frac{1}{2}\sum_{\sigma} P_{\mu\sigma}(\mu\mu|\mu\mu)\, S_{\sigma\mu} + \frac{1}{2}\sum_{\lambda} P_{\mu\lambda}(\mu\mu|\mu\mu)\, S_{\lambda\mu} + O(S^2)$$

$$= P'_{\mu\mu}(\mu\mu|\mu\mu) + O(S^2) \qquad \ldots (1.66)$$

Where,
$$P'_{\mu\mu} = \sum_{\sigma} P_{\mu\sigma} S_{\sigma\mu} \qquad \ldots (1.67)$$

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

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P'_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda} P'_{\lambda\lambda}(\mu\mu|\lambda\lambda) \qquad \ldots (1.68)$$

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:

$$F'C' = C'\epsilon \qquad \ldots (1.69)$$

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

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

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

$$P' = C'.\tilde{C}' = S^{1/2}C.\tilde{C}.S^{1/2} = S^{1/2}PS^{1/2} \qquad \dots (1.71)$$

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

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

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 overlap.

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).

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

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

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P'_{\mu\mu}\gamma_{AA} + \sum_{B}\sum_{\lambda}^{B} P'_{\lambda\lambda}\gamma_{AB} \qquad \ldots (1.74)$$

(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,

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

where the core Hamiltonian operator H is defined by

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

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

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

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

$$U_{\mu\mu} = \langle \mu | \hat{T} + V_A | \mu \rangle \qquad \text{... (1.78)}$$

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

$$U_{\mu\mu} = -\frac{1}{2}\left(I_\mu + A_\mu\right) - \left(Z_A - \frac{1}{2}\right)\gamma_{AA} \qquad \text{... (1.79)}$$

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.,

$$\langle \mu | V_B | \mu \rangle = -Z_B \gamma_{AB} \qquad \text{... (1.80)}$$

where Z_B is the core charge on atom B.

This gives

$$H_{\mu\mu} = -\frac{1}{2}\left(I_{\mu}+A_{\mu}\right)-\left(Z_{A}-\frac{1}{2}\right)\gamma_{AA}-\sum_{B(\neq A)} Z_{B}\gamma_{AB} \quad \ldots (1.81)$$

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

$$F_{\mu\mu} = -\frac{1}{2}\left(I_{\mu}+A_{\mu}\right)+\frac{1}{2}\left(1-P'_{\mu\mu}\right)\gamma_{AA} + \sum_{B}\sum_{\lambda}^{B}\left(P'_{\lambda\lambda}-n_{\lambda}\right)\gamma_{AB} \quad \ldots (1.82)$$

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

$$q_{\lambda} = \left(n_{\lambda}-P'_{\lambda\lambda}\right) \quad \ldots (1.83)$$

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

$$F_{\mu\mu} = \alpha_\mu + \frac{1}{2} q_\mu \gamma_{AA} - \sum_{B} \sum_{\lambda}^{B} q_\lambda \gamma_{AB}$$

$$= \alpha_\mu + \frac{1}{2} q_\mu \gamma_{AA} - \sum_{k} q_k \gamma_{Ak} \qquad \ldots (1.84)$$

where, $$\alpha_\mu = -\frac{1}{2}\left(I_\mu + A_\mu\right) \qquad \ldots (1.85)$$

In equation (1.84), 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_{Ak} 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$^{(67)}$.

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

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

$$= \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu|\lambda\lambda) \qquad \ldots (1.68)$$

because

$$\sum_{\lambda}\sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda} = \sum_{\lambda} (\mu\mu|\lambda\lambda) \sum_{\sigma} P_{\lambda\sigma} S_{\sigma\lambda}$$

$$= \sum_{\lambda} P'_{\lambda\lambda} (\mu\nu|\lambda\lambda) \qquad \ldots (1.67)$$

similarly,

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

$$= \frac{1}{2} P'_{\mu\mu} (\mu\mu|\mu\nu) + \frac{1}{2} \sum_{\lambda} P_{\mu\lambda} S_{\lambda\mu} (\lambda\lambda|\mu\nu)$$

$$= P'_{\mu\mu} (\mu\mu|\mu\nu) + \frac{1}{2} \sum_{\lambda} P_{\mu\lambda} S_{\lambda\mu} \Big[(\lambda\lambda|\mu\nu)$$

$$- (\mu\mu|\mu\nu) \Big]$$

$$= P'_{\mu\mu} (\mu\mu|\mu\nu) + O(S^3) \qquad \ldots (1.68)$$

$$\approx P'_{\mu\mu}(\mu\mu|\mu\nu) \qquad \ldots (1.89)$$

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 (1.89) we, therefore, have

$$\begin{aligned}
\sum_{\lambda}\sum_{\sigma} P_{\lambda\sigma}(\mu\lambda|\nu\sigma) &= \sum_{\lambda} P_{\mu\lambda}(\mu\lambda|\mu\nu) + \sum_{\sigma} P_{\nu\sigma}(\mu\lambda|\nu\sigma) \\
&\quad + P_{\mu\nu}(\mu\mu|\nu\nu) + \Big[\sum_{\lambda}\sum_{\sigma(\neq\mu,\nu)} P_{\lambda\sigma}(\mu\nu|\lambda\sigma) \\
&\quad - P_{\mu\nu}(\mu\nu|\mu\nu)\Big] \\
&\simeq P'_{\mu\mu}(\mu\mu|\mu\nu) + P'_{\nu\nu}(\mu\nu|\nu\nu) \\
&\quad + P'_{\mu\nu}(\mu\mu|\nu\nu) \qquad \ldots (1.90)
\end{aligned}$$

Again, only the second order terms in S 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. (1.62), (1.86) and (1.90) we have

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu|\lambda\lambda) - \frac{1}{2} P'_{\mu\mu}(\mu\mu|\mu\nu) - \frac{1}{2} P'_{\nu\nu}(\nu\nu|\mu\nu) - \frac{1}{2} P'_{\mu\nu}(\mu\mu|\nu\nu)$$

$$= \beta_{\mu\nu} - \frac{1}{2} P'_{\mu\nu}(\mu\mu|\nu\nu) \qquad \text{... (1.91)}$$

where

$$\beta_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} P'_{\lambda\lambda}(\mu\nu|\lambda\lambda) - \frac{1}{2} P'_{\mu\mu}(\mu\mu|\mu\nu) - \frac{1}{2} P'_{\nu\nu}(\nu\nu|\mu\nu) \qquad \text{... (1.92)}$$

Now,

$$H_{\mu\nu} = \left(\mu \middle| \hat{T} + V_A + V_B \middle| \nu\right) + \sum_{C(\neq A,B)} \left(\mu \middle| V_C \middle| \nu\right)$$

$$= \frac{1}{2}\Big[\left(\nu \middle| \hat{T} + V_A \middle| \mu\right) + \left(\mu \middle| \hat{T} + V_B \middle| \nu\right)$$

$$+ \left(\mu \middle| V_A \middle| \nu\right) + \left(\nu \middle| V_B \middle| \mu\right)\Big]$$

$$+ \sum_{C(\neq A,B)} \left(\mu \middle| V_C \middle| \nu\right) \qquad \ldots (1.93)$$

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. (1.78) along with Mulliken approximation for the charge distribution $\phi_\mu\phi_\nu$ in eqn. (1.93), we have

$$H_{\mu\nu} = \frac{1}{2}\Big[\left(U_{\mu\mu} + U_{\nu\nu}\right) S_{\mu\nu} - \left(\mu \middle| V_A \middle| \nu\right)$$

$$- \left(\nu \middle| V_B \middle| \mu\right)\Big] - \sum_{C(\neq A,B)} \left(\mu \middle| V_C \middle| \nu\right) \qquad \ldots (1.94)$$

Use of Goeppert-Mayer, Sklar procedure$^{(71)}$ for the estimation of the nuclear attraction integrals ($\mu|V_c|\nu$) then gives

$$\left(\mu\middle| V_c \middle|\nu\right) = -\left[\left(\mu\middle|V_c^{0}\middle|\nu\right) + \sum_{\lambda}^{C}\left(\mu\nu\middle|\lambda\lambda\right)\right] \quad \ldots (1.95)$$

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

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

Using the partial charge defined by

$$q_\lambda = \left(1 - P'_{\lambda\lambda}\right) \qquad \text{... (1.37)}$$

eqn. (1.36) may be rearranged to give

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

$$+ (\mu|V_A^0|\nu) + (\mu|V_B^0|\nu) - q_\mu(\mu\mu|\mu\nu)$$

$$- q_\nu(\nu\nu|\mu\nu)\Big] - \sum_\lambda q_\lambda(\mu\nu|\lambda\lambda)$$

$$+ \sum_{C(\neq A,B)}(\mu|V_C^0|\nu)$$

$$\simeq \frac{1}{2}\Big[\left(U_{\mu\mu} + U_{\nu\nu}\right)S_{\mu\nu} + \sum_{\lambda(\neq\mu,\nu)}^{A,B}(\mu\nu|\lambda\lambda)$$

$$+ (\mu|V_A^0|\nu) + (\mu|V_B^0|\nu)\Big] \qquad \text{... (1.38)}$$

The three centre penetration integrals ($\mu|V_C^{\circ}|\nu$) are always small (of the order of S^2 or less) and have been neglected in deriving eqn. (1.98). Further, the term $\sum_{\lambda} q_{\lambda}(\mu\nu|\lambda\lambda)$ is also small, not only because $q_{\lambda} \ll 1$, but because of the electrical neutrality condition

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

gives

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

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 S and are dropped.

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

$$\beta_{\mu\nu} = \frac{1}{2}\Big[(U_{\mu\mu} + U_{\nu\nu}) + \frac{1}{2}\Big\{\sum_{\lambda(\neq\mu,\nu)}^{A,B}(\mu\mu|\lambda\lambda) + \sum_{\lambda(\neq\mu,\nu)}^{A,B}(\nu\nu|\lambda\lambda) + (\mu|V_A^{\circ}|\mu) + (\nu|V_B^{\circ}|\nu)\Big\}\Big] S_{\mu\nu} \qquad \ldots (1.99)$$

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

$$\beta_{\mu\nu} = \frac{1}{2}\Big[U_{\mu\mu} + U_{\nu\nu} + \frac{1}{2}\Big\{(Z_A - 1)\gamma_{AA} + (Z_B - 1)\gamma_{BB} + (Z_A + Z_B - 2)\gamma_{AB} + (\mu|V_A^{\circ}|\mu) + (\nu|V_B^{\circ}|\nu)\Big\}\Big]\delta_{\mu\nu} \qquad \ldots (1.100)$$

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 A_μ with appropriate sign.

Further, using the relations

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

and

$$A_{\mu} = I_{\mu} - \gamma_{AA} \qquad \ldots (1.102)$$

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

$$\beta_{\mu\nu} = -\frac{1}{4}\Big[3(I_{\mu}+I_{\nu}) + (Z_A - 2)\gamma_{AA}$$

$$+ (Z_B - 2)\gamma_{BB} - (Z_A + Z_B - 2)\gamma_{AB}\Big] S_{\mu\nu} \ldots (1.103)$$

$$= \beta^{\circ}_{\mu\nu}\, S_{\mu\nu} \qquad \ldots (1.104)$$

where

$$\beta^{\circ}_{\mu\nu} = -\frac{1}{4}\Big[3(I_{\mu}+I_{\nu}) + (Z_A - 2)\gamma_{AA}$$

$$+ (Z_B - 2)\gamma_{BB} - (Z_A + Z_B - 2)\gamma_{AB}\Big] \ldots (1.105)$$

Since most of the semiempirical SCF MO methods, such as CNDO, INDO, MNDO methods use $\beta^{\circ}_{\mu\nu}$ as a parameter invariant to hybridisation thereby making $\beta^{\circ}_{\mu\nu}$ 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. (1.106) into eqn. (1.105)

$$I_{average} = \left(I_s + 3\,I_p\right)/4 \qquad \ldots (1.106)$$

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

This gives

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

$$= \frac{1}{2}\left(\beta^{\circ}_A + \beta^{\circ}_B\right) \qquad \ldots (1.107)$$

Where,

$$\beta^{\circ}_{A} = -\frac{1}{2}\Big[3I_A + (Z_A - 2)\gamma_{AA} - (Z_A - 1)\gamma_{AB} \quad \ldots (1.108)$$

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 $\beta_{\mu\nu}$ used in CNDO, INDO or MNDO 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 x 2 blocks corresponding to the bonds. The secular equation, therefore, reduces to a number of equations of order 2. A general 2 x 2 block can be represented as

$$\begin{vmatrix} F_{\mu\mu} - E & F_{\mu\nu} \\ F_{\mu\nu} & F_{\nu\nu} - E \end{vmatrix} = 0 \qquad \text{... (1.109)}$$

where the MO, $\Psi_{\mu\nu}$, is constructed from the orbitals ϕ_μ and ϕ_ν and expressed as

$$\Psi_{\mu\nu} = C_\mu \phi_\mu + C_\nu \phi_\nu \qquad \text{... (1.110)}$$

The normalisation condition,

$$C_\mu^2 + C_\nu^2 = 1 \qquad \text{... (1.111)}$$

ensures 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

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

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

$$= \frac{F_{\mu\mu} - F_{\nu\nu}}{D_{\mu\nu}} \qquad \ldots (1.112)$$

where,

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

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.

$$F_{\mu\mu} = \alpha_\mu + \frac{1}{2}\, q_\mu \gamma_{AA} - \sum_{k} q_k \gamma_{Ak} \qquad \ldots (1.114)$$

$$(\ \phi_\mu \text{ on atom } A\ )$$

Similarly,

$$F_{\nu\nu} = \alpha_\nu + \frac{1}{2} q_\nu \gamma_{BB} - \sum_k q_k \gamma_{Bk} \qquad \ldots (1.115)$$

$$(\phi_\nu \text{ on atom } B)$$

The normalization condition eqn. (1.111) requires

$$q_\mu = \left(1 - 2C_\mu^2\right) = 2C_\nu^2 - 1 = -q_\nu \qquad \ldots (1.116)$$

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

$$F_{\mu\mu} = \alpha_\mu + \frac{1}{2} q_\mu \gamma_{AA} - \sum_{k-l(\text{bond})} q_k \left(\gamma_{Ak} - \gamma_{Al}\right) \qquad \ldots (1.117)$$

where $k-l$ represents a bond.

This leads to

$$F_{\mu\mu} - F_{\nu\nu} = \left(\alpha_\mu - \alpha_\nu\right) + \frac{1}{2} q_\mu \left(\gamma_{AA} + \gamma_{BB}\right) - \sum_{k-l} q_k \left[\left(\gamma_{Ak} - \gamma_{Al}\right) - \left(\gamma_{Bk} - \gamma_{Bl}\right)\right] \qquad \ldots (1.118)$$

Using eqn. (1.113) this becomes

$$\left(D_{\mu\nu} - \frac{\gamma_{AA}+\gamma_{BB}}{2}\right) q_{\mu} + \sum_{k-l} q_k \left[\left(\gamma_{Ak} - \gamma_{Al}\right) - \left(\gamma_{Bk} - \gamma_{Bl}\right)\right] = \alpha_{\mu} - \alpha_{\nu} \qquad \ldots (1.119)$$

Each bond μ-ν 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. (1.119) is quite simple and involves only two centre repulsion integrals of the type $(ii|jj)$, their number can also be further reduced by neglecting all the terms in the summation except those arising out of bonds 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 bond μ-ν then, takes the simple form

$$\epsilon_{\mu\nu} q_{\mu} + \sum_{k-l(\neq \mu,\nu)} q_{k}\left(\gamma_{AA}-\gamma_{Al}\right) - \sum_{k-l(\neq \mu,\nu)} q_{k}\left(\gamma_{BB}-\gamma_{Bl}\right)$$

$$= \alpha_{\mu} - \alpha_{\nu} \qquad \text{... (1.120)}$$

Where, $$\epsilon_{\mu\nu} = D_{\mu\nu} + \frac{\gamma_{AA}+\gamma_{BB}}{2} - 2\gamma_{AB} \qquad \text{... (1.121)}$$

One advantage of this simplification is that each bond K-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,

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

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

Now,

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

$$\simeq \left| 2 F_{\mu\nu} \right| \quad , \text{ because } \left(F_{\mu\mu} - F_{\nu\nu} \right)^2 \ll 4 F_{\mu\nu}^{\,2}$$

$$\simeq \left| 2 \beta_{\mu\nu} - \gamma_{AB} \right| = 2 \left| \beta_{\mu\nu} \right| + \gamma_{AB} \qquad \ldots (1.122)$$

Since,

$$P_{\mu\nu} = 2 C_\mu C_\nu = \left(1 - q_\mu^{\,2} \right)^{1/2} \underset{\left(q_\mu^2 \ll 1 \right)}{\simeq} 1$$

With this approximation we have

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

$$= 2 \left| \beta_{\mu\nu} \right| + \frac{\gamma_{AA} + \gamma_{BB}}{2} - \gamma_{AB} \qquad \ldots (1.123)$$

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 equation 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 Optimisation of hybridisation

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

$$\delta \varepsilon = 0 \qquad \ldots (1.124)$$

where ε is the electronic energy calculated in the localised 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

$$\phi_\mu = \sum_{i}^{A} C_{\mu i} \chi_i \qquad \ldots (1.125)$$

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 function 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:

$$\phi_{\mu} = \sum_{i}^{A} \rho_{\mu i}^{1/2} \chi_{i} \qquad \ldots\ldots (1.126)$$

Where $\rho_{\mu i} \left(= C_{\mu i}^{2}\right)$ denotes χ_{i} character of the hybrid.

For optimisation of the hybrid orbitals we must minimise the calculated electronic energy with respect to variation in the $\rho_{\mu i}$'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

$$\sum_{i}^{A} C_{\mu i} C_{\nu i} = \delta_{\mu\nu} \qquad \ldots (1.127)$$

and

$$\sum_{\mu}^{A} C_{\mu i} C_{\mu j} = \delta_{ij} \qquad \ldots (1.128)$$

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

$$\sum_{i} \rho_{\mu i} = 1 \qquad \ldots (1.129)$$

and

$$\sum_{\mu}^{A} \rho_{\mu i} = 1 \qquad \ldots (1.130)$$

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

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

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

$$G = \mathcal{E} + \sum_{A,i,\mu} a_i^A \rho_{\mu i} \qquad \ldots (1.132)$$

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

$$\frac{\partial G}{\partial \rho_{\lambda i}} = \frac{\partial \mathcal{E}}{\partial \rho_{\lambda i}} + a_i^A = 0 \; ; \left. \begin{array}{l} \lambda = 1, 2 \cdots n_i^A \\ A = 1, 2 \cdots n \end{array} \right\} \ldots (1.133)$$

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, $\frac{\delta\varepsilon}{\delta\lambda_i}$'s are themselves function of $\rho_{\mu i}$'s , the set of equations obtained from eqn. (1.133) cannot be used to calculate the optimised 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

$$\frac{\delta\varepsilon}{\delta\rho_{\lambda i}} = \left(\frac{\delta\varepsilon}{\delta\rho_{\lambda i}}\right)_0 + \sum_{i,j} \frac{\delta^2\varepsilon}{\delta\rho_{\sigma j}\,\delta\rho_{\lambda i}} \Delta\rho_{\sigma j}$$

$$+ \text{ higher order terms} \quad \ldots (1.134)$$

where $\left(\frac{\delta\varepsilon}{\delta\rho_{\lambda i}}\right)_0$ 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

$$\sum_{i,j} \frac{\delta^2\varepsilon}{\delta\rho_{\sigma j}\,\delta\rho_{\lambda i}} \nabla\rho_{\sigma j} + a_i^A = -\left(\frac{\delta\varepsilon}{\delta\rho_{\lambda i}}\right)_0 \quad \ldots (1.135)$$

The set of simultaneous equations generated by eqn. (1.135) may be written in more convenient matrix form

$$\left|\varepsilon''\right| \left|\Delta\rho, a\right| = \left|\varepsilon'\right| \qquad \ldots (1.136)$$

where $\left|\varepsilon''\right|$ represents the matrix whose elements are $\frac{\delta^2\varepsilon}{\partial\rho_{\sigma j}\partial\rho_{\lambda i}}$'s and 1's corresponding to the Lagrangian multipliers a_i^A's ; $\left|\Delta\rho, a\right|$ is the matrix of $\Delta\rho$'s and a_i^A's which are to be determined and $\left|\varepsilon'\right|$ is a column matrix consisting of $\left(\frac{\delta\varepsilon}{\partial\rho_{hi}}\right)_0$. $\Delta\rho$ and a's can then be easily obtained from eqn. (1.136) by standard procedure and a new set of ρ's given by

$$\rho = \rho_{initial} + \Delta\rho \qquad \ldots (1.137)$$

will be obtained. The new set may then be used to generate the next approximations to ρ's and the process may iterated till $\Delta\rho$'s are smaller than a prescribed limit.

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

The total energy, $\mathcal{E}$ of the system in the localised approximation is given by

$$\mathcal{E} = \sum_{\mu-\nu\,(\mathrm{bonds})} P_{\mu\nu}\left[H_{\mu\nu} + \frac{1}{2}\sum_{\lambda\sigma\,(\mathrm{bond})} P_{\lambda\sigma}\left\{(\mu\nu|\lambda\sigma) - (\mu\lambda|\nu\sigma)\right\}\right] \quad \ldots\ (1.138)$$

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

$$\mathcal{E} = \sum_{\mu-\nu\,(\mathrm{bonds})} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2}\sum_{\mu,\lambda} P_{\mu\mu} P_{\lambda\lambda}\gamma_{\mu\lambda} - \frac{1}{4}\sum_{\mu-\nu\,(\mathrm{bonds})} P_{\mu\nu}^{2}\gamma_{\mu\nu} \quad \ldots\ (1.139)$$

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

$$\frac{\delta\mathcal{E}}{\delta\rho_{\lambda i}} = \sum_{\mu,\nu}\left[\frac{\partial\mathcal{E}}{\delta P_{\mu\nu}}\cdot\frac{\delta P_{\mu\nu}}{\delta\rho_{\lambda i}} + \frac{\delta\mathcal{E}}{\delta H_{\mu\nu}}\cdot\frac{\delta H_{\mu\nu}}{\delta\rho_{\lambda i}} + \frac{\delta\mathcal{E}}{\partial\gamma_{\mu\nu}}\cdot\frac{\delta\gamma_{\mu\nu}}{\delta\rho_{\lambda i}}\right] \quad \ldots\ (1.140)$$

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

$$\frac{\delta \varepsilon}{\delta P_{\mu\nu}} = 0 \qquad \ldots (1.141)$$

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

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

eqn. (1.140) then reduces to

$$\frac{\partial \varepsilon}{\partial \rho_{\lambda i}} = \sum_{\mu,\nu} \frac{\delta \varepsilon}{\delta H_{\mu\nu}} \cdot \frac{\delta H_{\mu\nu}}{\delta \rho_{\lambda i}} = \sum_{\mu,\nu} P_{\mu\nu} \cdot \frac{\partial H_{\mu\nu}}{\partial \rho_{\lambda i}} \qquad \ldots (1.143)$$

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). We, therefore, have

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

$$= \rho_{\mu s}\langle s_A|H|s_A + (1-\rho_{\mu s})\langle p_A|H|p_A\rangle$$

$$= \rho_{\mu s}\cdot H_{ss}^{A} + (1-\rho_{\mu s})\,H_{pp}^{A}$$

$$= H_{pp}^{A} - P_A\cdot\rho_{\mu s} \qquad \ldots (1.144)$$

Where, $P_A = \left(H_{pp}^{A} - H_{ss}^{A}\right),$

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 P_A positive. With spherically averaged core-electron attraction integrals we have (eqn. 1.77)

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

$$H_{pp}^{A} = U_{pp}^{A} - \sum_{B(\neq A)} V_{AB} \qquad \ldots (1.146)$$

where U_{ss} and U_{pp} are given by (see eqn. 1.79)

$$U_{ss} = -\frac{1}{2}\left(I_{s_A} + A_{s_A}\right) - \left(Z_A - \frac{1}{2}\right)\gamma_{AA} \qquad \ldots (1.147)$$

and, $$U_{pp} = -\frac{1}{2}\left(I_{p_A} + A_{p_A}\right) - \left(Z_A - \frac{1}{2}\right)\gamma_{AA} \qquad \ldots (1.148)$$

Therefore,

$$P_A = H_{pp}^{A} - H_{ss}^{A}$$

$$= \frac{1}{2}\left(I_{s_A} + A_{s_A}\right) - \frac{1}{2}\left(I_{p_A} + A_{p_A}\right) \qquad \ldots (1.149)$$

Differentiating eqn. (1.144) w.r.t $\rho_{\mu s}$ we get

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

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

Again,

$$H_{\mu\nu} = \beta^{\circ}_{AB}\, S_{\mu\nu} \;;\; \phi_{\mu} \text{ on } A \;,\; \phi_{\nu} \text{ on } B \qquad \ldots (1.152)$$

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

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

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

Similarly,

$$\frac{\delta S_{\mu\nu}}{\delta \rho_{\nu s}} = \frac{1}{2}\Big[\rho_{\mu s}^{1/2}\Big\{\rho_{\nu s}^{-1/2}\left(s_A | s_B\right) - \left(1-\rho_{\nu s}\right)^{-1/2}\left(s_A | p_B\right)\Big\}$$
$$+\left(1-\rho_{\mu s}\right)^{1/2}\Big\{\rho_{\nu s}^{-1/2}\left(p_A | s_B\right)$$
$$-\left(1-\rho_{\nu s}\right)^{-1/2}\left(p_A | p_B\right)\Big\}\Big]$$
$$= C_\nu \quad (\text{say}) \qquad \ldots (1.155)$$

and,

$$\frac{\delta S_{\mu\nu}}{\delta \rho_{\lambda i}} = 0 \quad ; \quad \lambda \neq \mu, \nu \text{ and } i \neq s \qquad \ldots (1.156)$$

Combining eqn. (1.143) and eqns. (1.150) - (1.156) we get

$$\frac{\delta \mathcal{E}}{\delta \rho_{\mu s}} = - P_A \cdot P_{\mu\mu} + 2 P_{\mu\nu} \cdot \beta^{\circ}_{AB} \cdot C_\mu \qquad \ldots (1.157)$$

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

$$\frac{\delta^2 \mathcal{E}}{\delta \rho_{\lambda s} \cdot \delta \rho_{\mu s}} = - P_A \cdot \frac{\partial P_{\mu\mu}}{\partial \rho_{\lambda s}} + 2 \frac{\delta P_{\mu\nu}}{\delta \rho_{\lambda s}} \cdot \beta^{\circ}_{AB} \cdot C_\mu$$
$$+ 2 P_{\mu\nu} \beta^{\circ}_{AB} \frac{\partial C_\mu}{\delta \rho_{\lambda s}} \qquad \ldots (1.158)$$

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 $\frac{\partial^2 \varepsilon}{\partial \rho_{\mu s}^2}$ and $\frac{\partial^2 \varepsilon}{\partial \rho_{\nu s} \partial \rho_{\mu s}}$.

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

$$\frac{\partial^2 \varepsilon}{\partial \rho_{\lambda s} \cdot \partial \rho_{\mu s}} = 2 P_{\mu\nu} \beta^{\circ}_{AB} \cdot \frac{\partial C_\mu}{\partial \rho_{\lambda s}} \qquad \ldots (1.159)$$

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

$$\begin{aligned}\frac{\delta C_\mu}{\delta \rho_{\mu s}} = -\frac{1}{4} \Big[\rho_{\mu s}^{3/2} \Big\{ \rho_{\nu s}^{1/2} (s_A | s_B) + (1-\rho_{\nu s})^{1/2} (s_A | p_A) \Big\} \\ + (1-\rho_{\mu s})^{-3/2} \Big\{ \rho_{\nu s}^{1/2} (p_A | s_B) \\ + (1-\rho_{\nu s})^{1/2} (p_A | p_B) \Big\} \Big] \\ = C'_{\mu\mu} \ (\text{say}) \qquad \ldots (1.160)\end{aligned}$$

$$\frac{\partial C_\mu}{\partial \rho_{\nu s}} = \frac{1}{4}\Big[\rho_{\mu s}^{-1/2}\Big\{\rho_{\nu s}^{-1/2}(s_A|s_B) - (1-\rho_{\nu s})^{-1/2}(s_A|p_B)\Big\} - (1-\rho_{\mu s})^{-1/2}\Big\{\rho_{\nu s}^{-1/2}(p_A|s_B) - (1-\rho_{\nu s})^{-1/2}(p_A|p_B)\Big\}\Big]$$

$$= C'_{\mu\nu} \quad (\text{say}) \qquad \ldots (1.161)$$

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

$$2P_{\mu\nu}\beta^{\circ}_{AB}\,C'_{\mu\mu}\,\Delta\rho_{\mu s} + 2P_{\mu\nu}\beta^{\circ}_{AB}\,C'_{\mu\nu}\,\Delta\rho_{\nu s} + \alpha_A = P_A \cdot P_{\mu\mu} - 2P_{\mu\nu}\beta^{\circ}_{AB}\,C_\mu \qquad \ldots (1.162)$$

With one such equation for each hybrid ϕ_μ on atom. The remaining equation comes from constraint on the $\rho_{\mu s}$'s as expressed by eqn. (1.150) which give

$$\sum_{\mu}^{A} \Delta \rho_{\mu s} = 0 \qquad \ldots (1.163)$$

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

$$\frac{\partial \varepsilon}{\partial \rho_{\mu s}} = -2 P_A \qquad \ldots (1.164)$$

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

$$\frac{\partial^2 \varepsilon}{\partial \rho_{\lambda s}^2} = 0 \qquad \ldots (1.165)$$

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

$$q_A = 2P_A \qquad \ldots (1.166)$$

The set of equations given by (1.163), (1.165) and (1.166) may then be solved for $\Delta\rho$'s to give a better approximation to $\rho_{\mu s}$'s in the different bonds. This may then be used to generate the new set of equations for a second iteration. The process may be repeated till $|\Delta\rho|$ is less than the prescribed limit. Usually 3 iterations are sufficient to obtain $\rho_{\mu s}$ values correct to 4 digits.

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