PART - II

PARAMETERIZATION AND COMPUTATIONAL PROCEDURE.

2.1 Parametrization

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

Because of the complexities involved in the optimisation of hybrid orbitals for localised 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. 1.27) 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

$$\phi_{\mu} = \rho_{\mu}^{1/2} s_A + (1-\rho_{\mu})^{1/2} p_A \qquad \ldots (2.1)$$

$$\phi_\nu = \rho_\nu^{1/2} s_B + (1-\rho_\nu)^{1/2} p_B \qquad \ldots (2.2)$$

where $\rho^{1/2}$'s are the S-character of the hybrid orbitals. The hybrid overlap integrals $S_{\mu\nu}$ is then given by

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

The evaluation of hybrid overlap integral requires ultimately the knowledge of the appropriate slater AO's overlap which are determined using standard technique$^{(1-4)}$.

(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).

$$\gamma_{AB} = \iint s_A(1)\,(r_{12})^{-1}\,s_B(2)\,d\tau_1\,d\tau_2 \qquad \ldots (2.4)$$

where r_{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

$$S_A(r, \theta, \phi) = N_A\, r^{n_a - 1} \exp(-\zeta_a r)\, Y_{l_a m}(\theta, \phi) \ldots (2.5)$$

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

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

Where

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

and

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

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

Using the eqns. (2.6 - 2.8) in eqn. (2.4), two centre integrals γ_{AB} are determined using standard technique(4,6-7).

One centre integral γ_{AA} is determined similarly using the valence s functions.

(iii) Evaluation of α_μ

α_μ 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 CNDO method.

$$\alpha_\mu = -\frac{1}{2}\left(I_\mu + A_\mu\right) \quad \dots (2.9)$$

$$\alpha_s = -\frac{1}{2}\left(I_s + A_s\right) \qquad \ldots (2.10)$$

$$\alpha_p = -\frac{1}{2}\left(I_p + A_p\right) \qquad \ldots (2.11)$$

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

$$\alpha_\mu = \alpha_p + \rho_s \alpha_s \qquad \ldots (2.12)$$

where ρ_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	5.946	9.594	14.051	19.316	25.390	32.272
$-\alpha_p$		1.258	2.563	4.001	5.572	7.275	9.111	11.090

a) Ref. 4 and 9

(iv) Bond resonance parameters.

Evaluation of Bond resonance parameters from eqn. (1.107) requires the knowledge of average ionisation potential, core charge and repulsion integrals. The ionisation 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.

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

Table 2.2

Average ionisation potentials (in electron volts) used to calculate β_A°

	H	Li	Be	B	C	N	O	F
I_{av}	13.60	4.00	6.80	9.74	12.36	16.29	19.99	24.05

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

$$\beta^\circ_A = -\frac{1}{2}\left[3 I_A + (Z_A - 2)\gamma_{AA} - (Z_A - 1)\gamma'_{AA}\right] \quad \ldots (2.14)$$

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 ionization 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

$$\beta^\circ_{BeH} = \frac{1}{2}\left(\beta^\circ_{Be} + \beta^\circ_H\right)$$

Similarly for β_F° we used β_{HF}° in HF molecule, rather than F_2 molecule because of the large lone pair interactions in fluorine molecule.

<u>Table - 2.5</u>

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
$-\beta_A^\circ$	11.89	2.79	6.84	12.71	19.15	20.00	45.67	35.64

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.

$$\beta_A^\circ(\text{corrected}) = K.\,\beta_A^\circ \qquad \ldots (2.15)$$

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

$$\gamma_{AA}^{exp.} = I - A \qquad \ldots (2.16)$$

where I and A are the appropriate values of the ionisation 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

$$K = \frac{U_{av.}^{exp.}}{U_{av.}^{t}} \qquad \ldots (2.17)$$

where

$$U_{av.}^{exp.} = \alpha_{av.} - \left(Z_A - \tfrac{1}{2}\right)\gamma_{AA}^{exp}$$

$$U_{av.}^{t} = \alpha_{av.} - \left(Z_A - 1/2\right)\gamma_{AA}^{t}$$

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	.6103 (BeH)	.7210	.6363	.683	.643	.6511(HF)
$-\beta_A^{\circ}$ (corrected)	10.3	2.3	4.0	9.2	13.2	19.8	29.6	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.

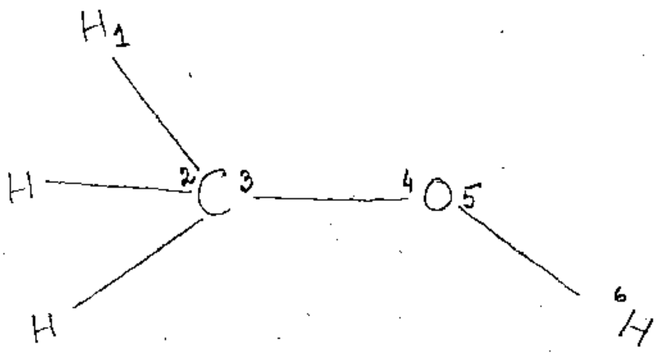
2.2 Computational Procedure

Having fully specified the parametrization we shall now consider the details of the computational procedure for obtaining the optimised 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_μ. 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 2s and three 2p 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 flourine atom which forms single covalent bond, the calculation with initial ρ as 0.25 led to a large correction in the s-character ($\sim$ .10) and therefore in all calculations $\rho=0.15$ was used as initial s-character for flourine 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 1.8 . We shall illustrate the procedure with an example.

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



(I)

Since the C – H bonds are equivalent, the system consists of only three non-equivalent bonds, viz., C-H, C-O and O-H 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 O-H bond.

We also note

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

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

The simultaneous equations for charges become (eqn. 1.120)

$$\epsilon_{12} q_1 + 2 q_1 (\gamma_{CC} - \gamma_{CH}) - q_3 (\gamma_{CC} - \gamma_{CO}) = \alpha_H - \alpha_C \quad \ldots (2.13a)$$

$$\epsilon_{34} q_3 - 3 q_1 (\gamma_{CC} - \gamma_{CH}) - q_5 (\gamma_{OO} - \gamma_{OH}) = \alpha_C - \alpha_O \quad \ldots (2.13b)$$

$$\epsilon_{56} q_5 - q_3 (\gamma_{OO} - \gamma_{CO}) = \alpha_O - \alpha_H \quad \ldots (2.13c)$$

The charges can be easily obtained provided $\epsilon_{\mu\nu}$'s are computed.

Now, $\epsilon_{\mu\nu}$ is given by (eqn. 1.122)

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

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

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

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

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 charge	
		Using eqn (2.19)	by iterative procedure
(1) CH_4	H-C	0.0147	0.0147
(2) C_2H_6	H-C	0.0174	0.0174
	C-C	0.0022	0.0022

Contd..

Table 2.3 (Contd..)

Molecules	Bond	Calculated charge	
		Using eqn (2.19)	by iterative procedure
(3) NH_3	H-N	0.0316	0.0316
(4) H_2O	H-O	0.1572	0.1561
(5) OF_2	F-O	-0.0653	-0.0652
(6) CH_3NH_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 optimising the hybrids on the different centre and is done according to the procedure developed in section 1.9. 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 optimise the hybrid orbitals. In the example we are considering viz, CH_3OH, 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

(i) Hybrid orbitals connecting C- atom, ϕ_4

(ii) Hybrid orbitals connecting H- atom of O-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

$$2\beta^{\circ}_{CH} P_{12} C'_{22} \Delta\rho_2 + a_c = \rho_c \cdot P_{22} - 2\beta^{\circ}_{CH} P_{12} C_2 \quad \ldots (2.20a)$$

$$2\beta^{\circ}_{CO} P_{34} C'_{33} \Delta\rho_3 + 2\beta^{\circ}_{CO} P_{34} C'_{34} \Delta\rho_4 + a_c = \rho_c \cdot P_{33} - 2\beta^{\circ}_{CO} P_{34} C_3 \quad \ldots (2.20b)$$

$$2\beta^{\circ}_{CO} P_{43} C'_{44} \Delta\rho_4 + 2\beta^{\circ}_{CO} P_{43} C'_{43} \Delta\rho_3 + a_o = \rho_o \cdot P_{44} - 2\beta^{\circ}_{CO} P_{43} C_4 \quad \ldots (2.20c)$$

$$2\beta^{\circ}_{OH} P_{56} C'_{55} \Delta\rho_5 + a_0 = \rho_0 \cdot P_{55} - 2\beta^{\circ}_{OH} P_{56} C_5 \quad \ldots (2.20d)$$

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

$$3\,\Delta\rho_2 + \Delta\rho_3 = 0 \quad \ldots (2.20f)$$

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 hybridisation does not explicitly enter the equations), while the last equation is a result of the condition that the total s-character remains constant.

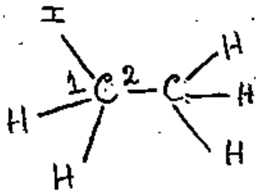
The elements of the matrix representing the simultaneous equation in $\Delta\rho$'s are determined using the formulae given in section 1.9 and the parametrisation procedure outlined in section 2.1.

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-characters with accuracy of 4 digits. This is illustrated in a few representative cases in table 2.6.

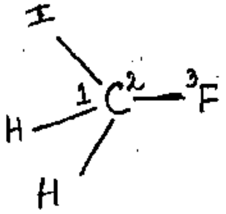
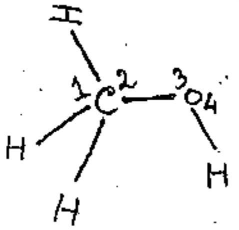
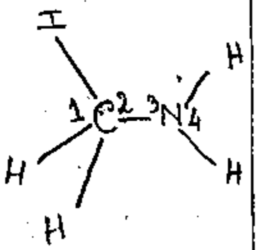
Table 2.6

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
$\mathrm{H-\overset{1}{O}-H}$	ρ_1	0.25	0.2172	0.2161	0.2159	0.2159
	ρ_2(LP)	0.25	0.2826	0.2839	0.2841	0.2841
$\mathrm{H-\overset{1}{N}-H}$ | H	ρ_1	0.25	0.1956	0.1933	0.1936	0.1936
	ρ_2(LP)	0.25	0.4132	0.4051	0.4042	0.4042
	ρ_1	0.25	0.2625	0.2624	0.2623	0.2623
	ρ_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 Iteration	2nd Iteration	3rd Iteration	Last Iteration
	ρ_1	0.25	0.2960	0.2888	0.2870	0.2870
	ρ_2	0.25	0.1119	0.1359	0.1389	0.1391
	ρ_3	0.25	0.1525	0.1683	0.1691	0.1689
	ρ_4(LP)	0.25	0.2825	0.2772	0.2769	0.2170
	ρ_1	0.25	0.2914	0.2773	0.2775	0.2773
	ρ_2	0.25	0.1580	0.1630	0.1630	0.1630
	ρ_3	0.25	0.1520	0.1692	0.1701	0.1701
	ρ_4	0.25	0.2091	0.2036	0.2079	0.3079
	ρ_5(LP)	0.25	0.3100	0.3110	0.3110	0.3110
	ρ_1	0.25	0.2743	0.2719	0.2722	0.2723
	ρ_2	0.25	0.1770	0.1844	0.1835	0.1831
	ρ_3	0.25	0.1445	0.1620	0.1655	0.1657
	ρ_4	0.25	0.1972	0.1997	0.1994	0.1992
	ρ_5(LP)	0.25	0.4613	0.4360	0.4339	0.4359

(*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_2O	O	-0.3144	-0.2896	-0.2888	-0.2888
	H	0.1572	0.1448	0.1444	0.1444
NH_3	N	-0.2454	-0.1965	-0.1989	-0.1992
	H	0.0818	0.0655	0.0663	0.0664
C_2H_6	C	-0.0507	-0.0612	-0.0609	-0.0609
	H	0.0169	0.0204	0.0203	0.0203
CH_3F	C	0.0649	0.0275	0.0334	0.0337
	H	0.0708	0.0823	0.0800	0.0795
	F	-0.2773	-0.2744	-0.2734	-0.2722
CH_3NH_2	C	-0.0258	-0.0490	-0.0446	-0.0440
	H	0.0322	0.0367	0.0373	0.0380
	N	-0.2263	-0.1841	-0.1881	-0.1888
	H	0.0777	0.0615	0.0604	0.0594

Contd..

Table 2.7 (Contd..)

Molecule	Atom	Net atomic charge			
		1st iteration	2nd iteration	3rd iteration	Last iteration
CH_3OH	C	-0.0055	0.0229	0.0101	0.0176
	H	0.0471	0.0336	0.0553	0.0336
	O	-0.2908	-0.2651	-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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