

PART - III

RESULTS AND DISCUSSION

3.1 Charge distribution in different molecules.

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

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

Table 3.1

net atomic charges in different molecules

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Del Re ^(a)	CNDO/2 ^(b)	STO-3G ^(c)
1.	CH ₄	C	-0.0538	-0.006	-0.0500	-0.0730
		H	0.0147	0.0015	0.0125	0.0150
2.	C ₂ H ₂	C	-0.0609		-0.0580	-0.0280
		H	0.0203		0.0030	0.0030

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			our work	Del Re (a)	OH20/2 (b)	OH2-30 (c)
3	¹ C ² H $\text{CH}_3\text{CH}_2\text{CH}_3$	1 C	-0.0506			
		H	0.0217			
		2 C	-0.0516			
		H	0.0233			
4	¹ C ² H $\text{CH}_3\text{CH}(\text{CH}_3)$ CH_3	1 C	-0.0581			
		H	0.0229			
		2 C	-0.0610			
		H	0.0331			
5	¹ C ² H $(\text{CH}_3)_4$	1 C	-0.0563			
		H	0.0239			
		2 C	-0.0592			
6	HF	F	-0.2571		-0.2300	-0.2230
		H	0.2371		0.2330	0.2230
7	CH_3F	C	0.0377		0.1570	0.1630
		H	0.0795		0.0919	-0.0040
		F	-0.2722		-0.1830	-0.1270

Contd..

Table 5.1 (Contd..)

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

Contd..

Table 3.1 (Contd..)

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

Contd..

Table 3.1 (Contd..)

Sl. No.	Molecule	Atom	Net atomic charge			
			Our work	Pol Re ^(a)	CMO/2 ^(b)	320-36 ^(c)
17	CH ₃ NH ₂	C	-0.0440	0.0690	0.0790	0.1130
		N	0.0330	0	-0.0210	-0.0130
		H	-0.1838	-0.2400	-0.2040	-0.4020
		H	0.0594	0.0830	0.0730	0.1510
18	(CH ₃) ₂ NH	C	-0.0466			
		N	0.0363			
		H	-0.1636			
		H	0.0539			
19	¹ CH ₃ ² OH _B	¹ C	-0.0532			
		H	0.0276			
		² O	-0.0424			
		H	0.0414			
		H	-0.1836			
		H	0.0535			

Contd..

Table 3.1 (Contd..)

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

Contd..

Table 3.1 (Contd.)

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

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

3.2 s-characters in optimised hybrid orbitals

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

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

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

Table 3.2

Calculated s-character of hybrid orbitals in different molecules

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

Contd..

Table 3.2 (Contd..)

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

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	s-Character of orbital on atoms	
			A	B
9	$\overset{1}{\text{C}}-\overset{2}{\text{C}}-\overset{3}{\text{N}}$ $\text{CH}_3\text{CH}_2\text{NH}_2$	$\overset{1}{\text{C}}-\text{H}$	0.2645	1
		$\overset{1}{\text{C}}-\overset{2}{\text{C}}$	0.2070	0.2347
		$\overset{3}{\text{N}}-\text{H}$	0.2360	1
		$\text{C}-\text{H}$	0.1914	0.1661
		$\text{N}-\text{H}$	0.1992	1
10	CH_3OH	$\text{C}-\text{H}$	0.2774	1
		$\text{C}-\text{O}$	0.1679	0.1703
		$\text{O}-\text{H}$	0.2076	1
		$\text{O} (\text{LP})$	0.3120	
11	CH_3OCH_3	$\text{C}-\text{H}$	0.2765	1
		$\text{C}-\text{O}$	0.1706	0.1698
		$\text{O} (\text{LP})$	0.3532	
12	$\overset{2}{\text{C}}-\overset{1}{\text{C}}-\overset{3}{\text{N}}$ $\text{CH}_2(\text{OCH}_3)_2$	$\overset{1}{\text{C}}-\text{H}$	0.2773	1
		$\overset{1}{\text{C}}-\text{O}$	0.1680	0.1701
		$\overset{1}{\text{C}}-\overset{2}{\text{C}}$	0.1906	0.1909
		$\overset{3}{\text{N}}-\text{H}$	0.3151	1

Contd..

Table 3.2 (Contd..)

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

Contd..

Table 3.2 (Contd..)

Sl. No.	Molecule	Bond A-B	s-character of orbital on atom	
			A	B
17	$\begin{array}{c} 1 \quad 2 \\ \text{CH}_3 \text{OH}(\text{CH}_2) \\ \\ \text{F} \end{array}$	1 C-H	0.2673	1
		1 2 C-O	0.1900	0.2607
		2 C-H	0.3141	1
		2 C-F	0.1646	0.1987
18	$\begin{array}{c} 1 \quad 2 \\ \text{CH}_3 \text{OH} \\ 3 \quad 4 \end{array}$	1 C-H	0.2732	1
		1 2 C-O	0.1799	0.3023
		2 C-H	0.3505	1
		3 C-O	0.1736	0.1852
19	$\begin{array}{c} 2 \quad 1 \\ \text{C}(\text{CH}_3)_4 \end{array}$	1 C-H	0.2631	1
		1 2 C-C	0.3107	0.25
20	HF	H-F	1	0.2266
		F (1P)	0.2573	
21	H ₂ O	O-H	0.2100	1
		O (1P)	0.2640	

Contd..

Table 3.2 (Contd..)

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

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

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

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

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

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

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

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

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

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

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

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

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

For sp^3 configuration we have

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

where Q_c is the net charge on the carbon atom.

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

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

which gives

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

Thus, the relation

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

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

Table 3.3

Molecule	P_c	Calculated J_{13C-H} (Hz)		Experimental (a)
		Using eqn(3.2)	Using eqn (3.8)	
CH_4	0.25	119.788	121.244	125
C_2H_6	0.262	127.428	127.469	126

Contd..

Table 3.3 (Contd..)

Molecule	ρ_0	Calculated $\delta_{150-H} (\text{Hz})$		Experimental (a)
		Using eqn(3.2)	Using eqn(3.3)	
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.265	128.665	128.001	128
CH_3F	0.237	143.347	144.237	143
CH_2F_2	0.341	177.730	179.108	175
CHF_3	0.431	233.036	233.636	233
CH_3OH	0.277	136.979	133.244	141
CH_3OCH_3	0.277	136.979	136.742	133
$\text{CH}_2(\text{OCH}_3)_2$	0.330	164.359	161.463	162
$\text{OH}(\text{OCH}_3)_3$	0.367	194.293	189.189	186
CH_2NH_2	0.272	133.796	133.364	133
$(\text{CH}_3)_2\text{NH}$	0.271	133.159	132.720	132
$(\text{CH}_3)_3\text{N}$	0.271	133.159	132.720	131
CH_3CF_3	0.280	139.339	139.746	139

a) Ref. 6, 36-41.

3.3 Dipole moments

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

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

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

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

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

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

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

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

For a single determinant wave function

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

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

and

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

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

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

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

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

where ρ_s is the s-character of hybrid A0.

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

$$\Psi_{MO} = c_A \phi_u + c_B \phi_v \quad \dots (3.14)$$

(u on atom A and v on atom B)

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

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

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

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

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

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

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

$$\mu_{\text{charge}} = Z_{\mu} e R_A + Z_{\nu} e R_B \dots (3.18)$$

Simplifying eqn. (3.18) and using standard technique⁽²³⁾, dipole moment due to net charges can be written in terms of debye unit as

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

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

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

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

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

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

where subscript λ indicates lone pair orbital.

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

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

Table 3.4

Calculated dipole moments for different molecules
(in Debye unit)

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

Contd..

Table 3.4 (Contd..)

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

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

3.4 Heat of atomisation

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

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

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

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

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

where

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

and

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

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

Using the net atomic charges Q_A and Q_B , given by

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

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

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

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

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

Further,

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

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

Eqn (3.24) then reduces to

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

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

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

Therefore, the stabilization due to molecule formation is

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

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

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

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

We get

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

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

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

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

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

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

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

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

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

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

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

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

Table 3.5

Calculated observed heats of atomization of different compounds.

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

Contd..

Table 3.8 (Contd..)

Sl. No.	Compound	Heat of atomisation in (e.v)	
		Calculated	Experimental (a)
7	$\text{CH}_3 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot$ $\text{CH}(\text{CH}_3) \cdot \text{CH}_3$	30.633	30.152
8	$(\text{CH}_3)_4^{\ominus}$	66.133	65.011
9	$\text{CH}_3 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3)_3$ CH_3	102.942	102.313
10	Cyclo- C_3H_6	48.121	47.650
11	Cyclo- C_5H_{10}	61.120	60.473
12	Cyclo- C_6H_{12}	73.253	72.670
13	NH_3	10.215	12.132
14	$\text{H}_2^{\ominus} \cdot \text{NH}_2$	19.949	17.312
15	CH_3NH_2	24.027	23.633
16	$\text{C}_2\text{H}_5\text{NH}_2$	36.230	36.016
17	H_2O	7.415	9.694
18	CH_3OH	23.334	21.107
19	HF	1.376	6.906
20	CH_3F	19.261	17.921
21	CH_2F_2	20.537	13.225

Contd..

Table 3.5 (Contd..)

Sl. No.	Compound	Heat of atomisation in (e.v.)	
		Calculated	Experimental (a)
22	CHF_3	20.404	19.292
23	CF_4	16.922	20.533
24	$\text{CHF}_2 \cdot \text{CH}_3$	32.143	30.755
25	CH_3CF_3	32.775	31.720
26	$(\text{CF}_3)_2\text{CHF}$	43.242	41.695
27	C_2F_6	34.408	33.632

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

3.8 Molecular geometry : Bond angle and s-characters

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

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

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

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

lone pair - lone pair interactions.

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

Table 3.6

Molecule	Angle	Bond angles	
		Calculated	Experimental (a)
NH_3	HNH	104.4	107.3 ± 2
H_2O	HOH	105.9	$104.5 \pm .1$
NF_3	FNF	96.4	102.2
H_2O_2	HOH	98.9	96.9
F_2O	OFF	98.4	103.2 ± 1
CH_3F	HCH	113.7	110.0
	HCF	104.8	103.3
CH_2F_2	HCH	121.1	111.0 ± 4
	HCF	103.2	
	FCF	109.9	109.3 ± 1

Contd..

Table 3.6 (Contd..)

Molecule	Angle	Bond Angles	
		Calculated	Experimental (a)
CH_2F_2	FCF	102.2	$108.8 \pm .8$
CH_2OH_2	HCH	110.9	$109.3 \pm .8$
	HOC	106.1	
CH_3NH_2	HCH	111.9	109.5 ± 1
	HON	106.6	
	NNH	104.4	
	ONH	102.6	
CH_3OH	HCH	112.5	$109.3 \pm .8$
	HCO	104.6	$107 - 109$
	COH	100.3	
$(\text{CH}_3)_4\text{O}$	HCH	110.9	
	HCO	107.9	
	OCO	109.5	
$(\text{CH}_3)_3\text{N}$	HCH	111.6	
	HON	106.9	
	CNC	101.2	103 ± 4

Contd..

Table 3.6 (Contd..)

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

(a) Reference -52

3.6 Conclusion

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

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APPENDIX

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

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

From eqn. (1.118) we get

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

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

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

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

... (A1)

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

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

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

Differentiating eqn. (A2) we get

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

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

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

Since α_μ can be written as

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

where,

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

we have

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

which gives

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

Therefore,

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

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

Differentiation of eqn. (A8) gives

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

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

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