CHAPTER - II

ISOVALENT HYBRIDISATION - A CRITICAL ASSESSMENT OF THE BENT'S RULE

II A. Introduction:

In this chapter we shall first discuss the experimental facts which led to the development of Walsh-Bent rule concerning isovalent hybridisation. A critical assessment of the experimental data as a guide to orbital hybridisation is also presented. The inadequacies and limitations of the rule are presented and finally the semiquantitative approach of Majes[1] is discussed to emphasize the factors that one should consider in the development of a quantitative theoretical treatment of isovalent hybridisation.

II B. Walsh's principle:

In order to explain the variation in the properties e.g. bond length, bond energy, reactivity etc. of bonds formed by carbon atom in different molecular environment, Walsh[2] proposed a principle underlying the hybridisation of carbon orbitals from an analysis of experimental facts. The arguments given by Walsh[2] are as follows:

In most of its compounds, carbon uses valencies which may be described as hybrids of its 2s and 2p atomic wave functions. As a result of this hybridisation, a carbon atom in a molecule has an important flexibility. The properties of a carbon valency change as the degree of hybridisation changes.

Thus its electronegativity changes and, with it, changes the strength of the bond formed by the valency. In conformity with the requirement of minimisation of free energy, therefore, a carbon atom adjusts itself to the particular environment in which it lies. The properties of any carbon valency (e.g., the length and direction of the bond it may form) are always specific to a particular valency in a particular atom in a particular molecule.

Considering this along with the fact that the more s-character in a carbon valency, the more electronegative is the carbon atom in that valency, Walsh[2] in 1947 proposed: "if a group X to a carbon is replaced by a more electronegative group Y, then, the carbon valency toward Y has more p-character than it had toward X".

Walsh[2] applied this qualitative rule to explain the observed trends in the properties of carbon bond, e.g., bond polarity, bond strength, bond angle, force constant etc, in different molecular environment.

Thus, the increase in HCH bond angle in methyl halide from the tetrahedral value of 109.5° was attributed to the increase in the s-character of the carbon orbital along the C-H bond due to higher electronegativity of the halogen compared to that of the hydrogen in CH_4. The smaller bending force constant in the methyl halides may also be attributed

to the increased s-character which lowers the resistance towards bending because of spherical symmetry of the s-orbitals.

The gradual decrease in the C-H bending force constant in the series R-CH = CHR with increase in the electronegativity of the substituent R may be readily explained similarly.

Geometries of CH_3, CH_2 and CH radicals were also discussed by Walsh[2] in the light of the above principle and an extension of the principle to the valencies of atoms other than carbon, e.g., phosphorous, was also suggested.

II C. Bent's Rules:

Orbital hybridisation in atoms using s and p orbitals in their valency was more elaborately examined and discussed by Bent[3] in a review published in 1961. Using a vast body of molecular data he examined the dependence of molecular properties on (i) the orbital hybridisation and (ii) the electronegativities of the substituents. This analysis revealed an obvious correlation between the two factors, viz., hybridisation used by an atom and the electronegativity of the substituents connected to it. He stated this correlation as follows:

"Atomic s-character concentrates in orbitals directed towards electropositive substituents".

Before we make a critical assessment of this principle, generally known as the Bent's rule or Walsh-Bent's rule, we shall outline the various factors which were considered by Bent[3] to arrive at this rule. These are given below.

(i) Effect of hybridisation on electronegativity:

As the 2s electrons are more tightly bound to the nucleus than 2p electrons the electronegativity of an atomic valency (hybrid orbital) should increase as the s-character in that valency increases. A carbon sp valency should be more electronegative than a carbon sp^2 valency, which in turn should be more electronegative then carbon sp^3 valency (e.g. Higher acidity of acetylenic hydrogen in comparison to ethylenic hydrogen) supports this.

Organic chemistry provides an extensive evidences as to the effect of hybridisation on the electronegativity. Table 2.1 shows the effect of orbital hybridisation on the acidity of some carboxylic acids. The order of electronegativities determined from the data in table 2.1 is:

$$C(sp, \text{ in cyanide}) > Cl > C(sp^2 \text{ vinyl}) > H > C(sp^3, \text{ methyl})$$

Table 2.1

Effect of orbital hybridisation on Acidity

Acid	$K_a \times 10^5$ [a]
HCOOH	17.12
H_3CCOOH	1.75
H_3CCH_2COOH	1.33
$H_2C = CH.CH_2COOH$	4.62
$N \equiv C.CH_2COOH$	< 369
$ClCH_2COOH$	137.8

a) Ref. 3

The ionisation constants of the following acids: $N \equiv C(CH_2)_2COOH$, $Cl-(CH_2)_2COOH$, $N \equiv C(CH_2)_3COOH$ and $Cl-(CH_2)_3COOH$, whose pk_a are 3.99, 4.08, 4.44 and 4.52 also support the above sequence. Taft[4-5] constants for CN, Cl CH_3CO-, C_6H_5-, H etc. are also consistent with this trend.

Dipole moments provide an additional evidence of the effect of hybridisation on electronegativity. Postulating that single bonds between carbon atoms of different hybridisation have non zero moments and using for carbon-hydrogen bonds

variable bond moments derived from infra red data on CH_4, C_2H_4 and C_2H_2. Petro[6] has obtained the carbon-carbon bond moments given in table 2.2 from a vector model calculation.

Table 2.2

Effect of orbital hybridisation on bond moments

Carbon-carbon bond and polarity	Bond Moment[a] (debyes)
$C^{+}_{sp^3} \longrightarrow C^{-}_{sp^2}$	0.63
$C^{+}_{sp^2} \longrightarrow C^{-}_{sp}$	1.15
$C^{+}_{sp^3} \longrightarrow C^{-}_{sp}$	1.43

a) Ref. 3.

The variation of C-C bond moments with the change of orbital hybridisation of carbon atoms is quite obvious. Thus both chemical and physical evidences appear to support the view that a change in orbital hybridisation may have a powerful effect on the electronegativity of atomic valency.

(ii) Effect of hybridisation on acid-base strength

HCN and C_2H_2 are stronger acids (better proton donors) than ethylene which in turn, is a stronger acid than methane

because in the former compounds the electrons reside in an orbital rich in s-character in the corresponding conjugate base. Aldehydes and ketones are less basic than ethers and alcohols for similar reasons because lone pair resides in $O(sp^2)$ and $O(sp^3)$ type hybrid orbitals.

(iii) Effect of hybridisation on bond angle and bond strength

Table 2.3 shows the variation of bond angle with the orbital hybridisation. Clearly, the bond angle increases with the increase in the s-character of bonds.

Table 2.3

Orbital designation	Abbreviations	Percent s-character in hybrid orbital	Inter orbital angle
Tetrahedral	sp^3	25	$109^o28'$
Trigonal	sp^2	33	120^o
Digonal	sp	50	180^o

Table 2.4 shows the variation of C-C bond length with the change of hybridisation of carbon orbitals forming C-C bond.

Table 2.4

Effect of atom hybridisation on bond lengths of carbon-carbon bonds.

Description	Bond length[a] (A^0)
$\rightarrow C_{sp^3} - C_{sp^3} \leftarrow$	1.54
$\rightarrow C_{sp^3} - C_{sp^2} \leftarrow$	1.50
$\rightarrow C_{sp^3} - C_{sp} \equiv$	1.46
$\gg C_{sp^2} - C_{sp^2} \ll$	1.46
$\gg C_{sp^2} - C_{sp} \equiv$	1.42
$\equiv C_{sp} - C_{sp} \equiv$	1.38
$\rangle C_{sp^2} = C_{sp^2} \langle$	1.34
$\rangle C_{sp^2} = C_{sp} =$	1.31
$= C_{sp} = C_{sp} =$	1.28
$- C_{sp} \equiv C_{sp} -$	1.20

a) Ref. 3.

Larger the s-character of the orbitals shorter is the bond. Again, data listed in table 2.5 shows the gradual shortening of carbon-oxygen bond length as the s-character of carbon orbital or of oxygen orbital increases.

Table 2.5

Effect of hybridisation on the length of the carbon-oxygen double bond.

Molecule	Carbon hybridisation	Carbon-oxygen bond distance [a] (A^0)
HCHO	sp^2	1.223
O = C = O	sp	1.162
H_2C = C = O	"	1.16
HN = C = O	"	1.171
O = C = C = C = O	"	1.16
O ≡ O	"	1.123

a) Ref. 5.

Force constants, bond dissociation energy, bond length etc. also show a gradual variation with hybridisation. Experimental data on some carbon compounds listed in table 2.6 clearly show that the larger the s-content of the bond larger

is the stretching force constant, shorter is the bond length and larger is the bond energy.

Table 2.6

Effect of hybridisation on bond dissociation energy, bond length and force constants.

Molecule	Carbon-carbon bond type	Bond length	Force constant K x 10^{-5}	Bond Dissociation Energy, E
		A^{o}	dynes/cm	K Cal/mole[a]
$CH_3 - CH_3$	$sp^3 - sp^3$	1.54	4.5	83
$CH_3 - C_2H_3$	$sp^3 - sp^2$	1.49	-	92.5
$CH_3 - CN$	$sp^3 - sp$	1.46	5.4	103.0
$C_2H_3 - C_2H_3$	$sp^2 - sp^2$	1.40	-	104.0
$HC - CN$	$sp - sp$	1.38	6.7	112.0

a) Ref. 3

(iv) Effect of hybridisation on $^{13}C-H$ coupling constant

Theoretically, the magnitude of coupling constant should depend on the state of hybridisation of the carbon atom[7-10]. Data given in table 2.7 show that greater the s-character in a carbon valency toward hydrogen the greater the $^{13}C-H$ coupling constant.

Table 2.7

Effect of atom hybridisation on $^{13}C-H$ coupling constants.

Molecule	Hybridisation of carbon	$J\ ^{13}C-H$ (in H_z)[a]
CH_4	sp^3	125
C_2H_4	sp^2	157
C_6H_6	sp^2	159
C_2H_2	sp	248-9
$CH_3.C\equiv CH$	sp	248

a) Ref. 3

The effect of the electronegativity of the substituents on the molecular properties discussed[3] are as follows:

(i) Effect of electronegativity on Bond angles:

In compounds of the type AX_2 and AX_3, the valence angle X-A-X appears to be correlated with the electronegativity of X. In the absence of obvious steric effects, the valence angle generally decreases as the electronegativity of the substituent X increases. Illustrative examples are given in table 2.8. Data given in table 2.8 suggest that as the electronegativity of the substituents increases the central atom (atom A)

diverts increasing amount of s-character to the orbital, or orbitals, occupied by the lone pair electrons, thus decreasing the X-A-X bond angle due to increased p-character in the orbitals towards X.

Table 2.3

Effect of electronegativity on bond angles.

X, Y	$\angle XOY^a$
CH_3 CH_3	111^o
CH_3 H	$107 - 109^o$
H H	105^o
F F	103.3^o
X, Y	**$\angle XSX$**
CH_3 H	100^o
H H	92^o
AX_3 compound	**$\angle XAX^a$**
$N(CH_3)_3$	109^o
NH_3	$106^o46'$

Contd..

Table 2.8 (Contd..)

AX_3 compound	$\angle XAX$ [a]
NF_3	$102^{o}30'$
$P(CH_3)_3$	$98^{o}36'$
PH_3	$93^{o}18'$
$As(CH_3)_3$	96^{o}
AsH_3	$91^{o}30$

X,Y, in $CF_2 = CXY$	$\angle FCF$ [a]
H, H	110^{o}
F, F	114^{o}

a) Ref. 3

(ii) Effect of electronegativity on bond length:

In absence of marked steric effects, replacement in the structure X-A-Y of A by an atom more electronegative than X causes the adjacent A-Y bond to become shorter. This effect is particularly noticeable when fluorine is introduced into a molecule (Table 2.9). Again, this shortening may be attributed to the increase in the s-character of the orbital of A

along A-Y bond due to a more electronegative substituent along A-X bond.

Table 2.9

Effect of electronegativity on Bond lengths[a]

Molecule	Bond lengths (Å)[a]
1. Shortening of C-F bond substitution of F for H	
CH_3F	1.391, 1.385
CH_2F_2	1.358
CHF_3	1.332, 1.326
CF_4	1.323
2. Shortening of C-Cl bond substitution of Cl for H	
CH_3Cl	1.734, 1.781
CH_2Cl_2	1.772
$CHCl_3$	1.767, 1.761
CCl_4	1.766
3. Shortening of C-Br bond. Substitution of Br for H	
CH_3Br	1.939
$CHBr_3$	1.930

Contd..

Table 2.9 (Contd..)

Molecule	Bond lengths ($\overset{o}{A}$)[a]
4. Shortening of C-Cl bond. Substitution of F for H	
CH_3Cl	1.734
CF_3Cl	1.751
5. Shortening of C-Cl bond. Substitution of F for Cl	
CCl_2F_2	1.77
CF_3Cl	1.751
6. Shortening of C-C bond. Substitution of F for H	
C_2H_6	1.536
C_2F_6	1.51
7. Shortening of C = O bond in XCO.Y	
X Y	C = O distance
H CH_3	1.226
H H	1.225
H C ≡ CH	1.216
H F	1.192
F F	1.17

Contd..

Table 2.9 (Contd..)

Molecule	Bond lengths (Å)[a]
8. Shortening of N-Cl bond. Substitution of Cl for CH_3	
$N(CH_3)_2Cl$	1.77
$N(CH_3)Cl_2$	1.74
9. Shortening of C = C bond. Substitution of F for H	
C_2H_4	1.337
C_2F_6	1.313

a) Ref. 3

(111) Effect of electronegativity on ^{13}C-H coupling constant.

Replacement in the structure X-C-H of X by an atom, or group, more electronegative than X increases the ^{13}C-H coupling constant. The ^{13}C-H coupling constant in the series CH_4, CH_3Cl, CH_2Cl_2 and $CHCl_3$ for example, increases in the order 125, 150, 178, 209Hz[7]. Concomitantly, the carbon hydrogen distance decreases in the order 1.11, 1.0959, 1.082, 1.07 Å[93]. The effect of electronegative groups on ^{13}C-H coupling constants is shown in table 2.10.

Table 2.10

^{13}C-H coupling constants of $CH_{4-n}Cl_n$ ($n \leqslant 3$) and CH_3X type compounds.

Compound	$J_{CH}(Hz)$[a]
CH_4	125-5
CH_3NH_2	133
CH_3NO_2	147
CH_3OH	141
CH_3Cl	151
CH_2Cl_2	178
$CHCl_3$	209

a) Ref. 1,3,7-8

As discussed earlier, increase in ^{13}C-H coupling constant definitely indicates concentration of s-characters of the carbon orbital towards the hydrogen with increase in the electronegativity of the substituent connected to it.

Bent[3] pointed out that the dependence of molecular properties on the electronegativity of the substituents can

be easily explained if one postulates a variation of the orbital hybridisation of an atom with a variation in the electronegativity of the substituents connected to it. He stated this effect as follows:

'Atomic s-character concentrates in orbitals directed towards electropositive (or less electronegative) substituents'.

II D. A critical examination of the foundation of Bent's rule:

The usefulness of this rule has been amply demonstrated by Bent in his original article[3] and therefore needs no further elaboration. While this simple qualitative rule seems to work rather well in a number of cases, the foundation of this rule is not as strong as it is generally believed to be. This is because most of the molecular properties which were considered by Bent in formulating his rule are complicated functions of many factors other than the s-character in the valence orbitals.

Of the many properties used by Bent to ascertain orbital hybridisation, quite a few merit special comment on their reliability as a guide to orbital hybridisation. Some of these are given below.

(i) Bond Angle:

Although large changes in bond angle consequent on a change in molecular geometry, such as the series, $HgCl_2$, C_2H_2 (linear, 180°); BCl_3, $GaCl_3$, C_2H_4 (planar, trigonal,

120°); CH_4, $GeCl_4$, $SiCl_4$ (Tetrahedral, 109°28'); $Ni(CN)_4^{-2}$, $Cu(NH_3)_4^{2}$ (square planar, 90°); $Co(NH_3)_6^{3}$, $Fe(CN)_6^{-3}$ (octahedral) etc. can be explained with sp, sp^2, sp^3, dsp^2 and d^2sp^3 hybridisation respectively, variation of bond angles in many compounds have been explained by considering only the electron repulsions[11-14]. Similarly bond angles in case of NH_3, NF_3, H_2O etc. have been explained in terms of deviations from tetrahedral geometry due to lone pair-bond pair and bond pair-bond pair repulsions. Bond angles in $TeCl_4$, ClF_3, BrF_3, XeF_2, XeF_4 etc. can also be explained successfully using inter-electron pair repulsions as the determining factor. The importance of non-bonding interactions in determining bond angles have been emphasised by Bartell[11,12]. In fact evidences have gradually accumulated to show that the substituents often do not follow the axis of the hybrid orbitals and chemical bonds are more often bent than not[11-14].

That the bond angle often deviates considerably from the angle between the bonding hybrids may be shown as follows:

As already mentioned, ^{13}C-H coupling constants in a molecule is theoretically related to the s-character of the carbon orbital[7,8,9]. It has been shown that the s-character, ρ_{CH}, of the carbon orbital towards the C-H bond is related to the ^{13}C-H coupling constant, J, by the relation[7,8],

$$J = 500 . \rho_{CH} \qquad \ldots (2.1)$$

S-character may, therefore, be computed from the experimental coupling constant data. The angle between the hybrid orbitals, θ , along the C-H bonds in CH_2XY type compounds can be calculated from the relation[15]

$$\theta = \cos^{-1}\left[- \rho_{CH}/(1- \rho_{CH})\right] \qquad \ldots (2.2)$$

Combining eqn. (2.1) and (2.2) we get

$$\theta = \cos^{-1}\left[- J/500-J\right] \qquad \ldots (2.3a)$$

Similarly for CH_{4-nX_n} type compound (n = 2,3) the inter orbital angle, θ , between the C-X hybride is given by

$$\theta = \cos^{-1}\left[- \frac{250 - J}{250 + J} \right] \text{ for } n = 2 \qquad \ldots (2.3b)$$

and $$\theta = \cos^{-1}\left[- \frac{500 - J}{1000 + J} \right] \text{ for } n = 3 \qquad \ldots (2.3c)$$

Table 2.11 shows a comparison between the inter orbital angle computed from eqn. $(2.3)_{\wedge}^{along}$ with experimental bond angles in a number of molecules. The result clearly shows that bond angle is an unsatisfactory guide to orbital hybridisation. In fact, it is now generally agreed that electronic repulsions

play an important role in determining the bond angles.

Table 2.11

^{J}CH and calculated bond angle for a number of molecules along with observed angle.

Molecule	J_{CH} Hz	Inter orbital Angle(Å) ∠HCH	∠XCX	Exptl.[a] ∠HCH	∠XCX
CH_3Cl	151	115.6		110.6	
CH_2Cl_2	178	123.6	99.7	113	111.8
$CHCl_3$	209		103.9		110.4
CH_3F	149	115.1			
CH_2F_2	186	126	98.6	111.9	108.8
CHF_3	238		102.2		108.8
CH_3Br	152	115.9		111.2	
$CHBr_3$	206		104.1		110.8
CH_3OH	141	113.1		109.8	
CH_3NH_2	133	111.2		109.5	

a) Ref. 1-5,7-8.

(ii) Bond length:

Although bond distances between two atoms vary with the s-character of the combining orbitals, it is by no means

the only factor. Pauling in his classic book[16] has discussed the various factors that influence bond lengths. The main factors are : (i) Resonance effects (ii) hyperconjugative effects (iii) Double bond - no-bond resonance. The role of these factors are so well known and examples are so numerous that no further comment is required. Thus bond length, like bond angle, is not a very reliable guide to the orbital hybridisation. For example, s-characters of the carbon orbital bonded to the hydrogen atom in CH_4 and CH_3Cl are 0.25 and 0.30 (calculated from eqn. (2.1) respectively, the C-H bond distance in the two compounds are virtually constant).

The dependence of C-C bond length on the bond-order[17] in conjugated molecules where all the carbon atoms are supposed to be sp^2 - hybridised is well known.

In view of this, the use of the bond angle or bond length data as a guide to orbital hybridisation in molecules is open to question.

(iii) Ionisation Potential:

The gradual decrease in the ionisation potential in the series NH_3 (10.15) > CH_3NH_2 (8.97) > $(CH_3)_2NH$ (8.78) > $(CH_3)_3N$ (7.82) or the series H_2O (12.59) > CH_3OH (10.85) > $(CH_3)_2O$ (10.00) and in similar series of molecules has been cited by Bent to illustrate the decrease in the s-character

of the lone pair orbital with increasing methyl substitution.

The idea that the ionization potential would decrease with decreasing s-character is an over simplification of a complex process where the energy change is determined not only by the structure of the initial molecule/radical, but also by the structure of the resulting ion. That such an over simplification may often by very misleading is illustrated by the following examples.

Ionization of oxygen atom leading to the process $O \longrightarrow O^+$ definitely involves removal of an electron from p orbital whereas ionization of H_2O must involve an orbital which is likely to have s-character around 25%, yet, the ionization potential of oxygen, O (13.61 ev) is greater than that of water (12.59). Similarly, the ionization potential of nitrogen (14.54 ev) is far greater than that of NH_3 (10.15 ev) though the latter must involve an orbital with significant amount of s-character.

In fact, chemical shift data on some boron complexes[13] suggests the co-ordination ability in methyl amines follows the sequence $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$ which goes against the organic chemist's concept of an electron releasing methyl group.

Since the ability to form a coordinate link by a base is very likely to be influenced by the ease of electronic

displacement from the lone pair orbital, it should be a much better measure of the orbital hybridisation (increasing s-character will tend to decrease the coordinating ability of the base due to tighter binding of the s-electrons to the nucleus) than the ionisation potential since the former does not require a complete removal of electrons and therefore correspond more closely to the situation pertaining in the neutral molecule.

It is therefore more likely that the s-character of nitrogen lone pair orbital in methyl amines increases in the sequence: $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ as suggested by NMR data[7,18], rather than the opposite sequence suggested by the ionization potential.

The complexities of factors that determine the other molecular quantities e.g. force constant, bond moment, acid-base strength etc. are so well recognised that one can conclude with sufficient justification that the molecular quantities used by Bent[3] for assessing orbital hybridisation in molecules are generally unsatisfactory.

Having thus shown the weaknesses of the basic foundations of the Bent's rule we shall now discuss some of the examples where experimental data definitely contradict the predictions of Walsh-Bent's rule.

II B. Cases where Bent's rule fail

(a) As discussed earlier, ^{13}C-H coupling constants depend almost explicitly on the s-character of carbon orbital directed towards the hydrogen atom. According to Bent's rule, the s-character of a carbon orbital along the C-H bond (ρ_{CH}) should decrease with increasing methyl substituents. Therefore, the expected trend in ρ_{CH} in the following compounds (the carbon atom considered is marked with an asterik)

$$*CH_4\ ,\ *CH_3{\cdot}*CH_3,\ CH_3{\cdot}*CH_2CH_3$$

should decrease along the series from left to right. The $J(^{13}C\text{-}H)$ values are: 125-5, 126, 128 Hz respectively. The coupling constant data in propane definitely indicates a concentration of s-character in the methylene CH orbital compared to that in CH_4 and $CH_3{\cdot}CH_3$. This is clearly contrary to the prediction from Bent's rule.

(b) On the basis of electronegativity of halogens, Bent's rule predicts a decrease in s-character in the carbon C-H orbital along the series $CH_3F > CH_3Cl > CH_3Br > CH_3I$. Both the ^{13}C-H coupling constant and HCH bond angle in these compounds indicate a slight increase from the fluoride to the iodide (Table 2.12).

Table 2.12

^{13}C-H coupling constant and HCH bond angle in methyl halides.

Compound	$J(^{13}C-H)$ Hz [a]	HCH bond angle [b]
CH_3F	148.9	
CH_3Cl	151	110.6°
CH_3Br	152	111.2°
CH_3I	151	111.4°

a) Ref. 1,7-8 (b) Ref. 16

(c) Such anomalies are found not only in carbon compounds but also in some organometallic compounds. For example, $J(^{13}C-H)$ values in the tetramethyl compounds of group IV (table 2.13) follows the order $(CH_3)_4C > (CH_3)_4Si < (CH_3)_4Ge < (CH_3)_4Sn < (CH_3)_4Pb$[1]. This order is in direct contradictions to Bent's electronegativity considerations. This clearly shows that factors other than electronegativity should be considered in estimation of hybridisation of carbon atom in its organometallic derivatives. If the increase in $J(^{13}C-H)$ values is attributed to d-orbital participation, it is difficult to understand the decrease of $J(^{13}C-H)$ in the silicon compounds

Table 2.13

^{13}C-H coupling constants of tetramethyl compound of group IV elements.

Compound	J_{CH} [a] (Hz)
$(CH_3)_4C$	124
$(CH_3)_4Si$	118-20
$(CH_3)_4Ge$	124-26
$(CH_3)_4Sn$	128
$(CH_3)_4Pb$	133-36

a) Ref. 1

where d-orbital participation is well recognised. In this context, it is pertinent to point out that this apparently anomalous trend of coupling constant data in this series has been attributed to variations in C-H bond energy by Drago and Matwiyoff[25].

In terms of Taft[4-5] inductive constant (σ^*) methyl group is less electronegative than hydrogen. Bent's use of group electronegativities as given by the Taft constants is questionable since evidences are accumulating to show that methyl groups attached to a sp^3 - centre where π-conjugation is not possible behave as more electronegative than H atom

as expected from the electronegativity of the CH_3 carbon orbital through which 6-bond is formed. In any case, use of electronegativity along with Bent's rule predicts the following sequence for ^{13}C-H coupling constants in methyl amines: $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$. But the experimental data show a reverse trend (Table 2.14).

Table 2.14

^{13}C-H coupling constants of methyl amines

Compounds	$J_{CH}(Hz)^a$
CH_3NH_2	133
$(CH_3)_2NH$	132
$(CH_3)_3N$	131

a) Ref. 7,8

(e) ^{29}Si-C-H coupling constants in $(CH_3)_3SiX$ type compounds given in table 2.15 increase in the sequence X = Me, F, Cl, Br, I. This trend is again opposite to that expected from Bent's rule. Though, this trend has been attributed to the possibility of $d_\pi - p_\pi$ bonding between silicon and the halogen atoms, a similar trend in ^{13}C-H coupling constants

Table 2.15

^{29}Si-C-H coupling constants in CH_3SiX type compounds

Compounds	J_{Si-C-H} (Hz)[a]
$(CH_3)_4Si$	6.78
$(CH_3)_3SiF$	7.00
$(CH_3)_3SiCl$	7.10
$(CH_3)_3SiBr$	7.23
$(CH_3)_3SiI$	7.30

a) Ref. 1

in methyl halides where the possibility of d_π- p_π bonding is ruled out, suggests other factors to be operative in these molecules. Many such experimental data are now available which demonstrate the inadequacies of Bent's rule.

II F. Inadequacies of Bent's Rule: Probable reasons:

It is not difficult to trace the reasons for the failures of the Bent's rule when one examines the basic assumption involved in this rule.

The essence of the principle underlying the rule may be described as follows:

Consider a system X-A-Y. The bond orbitals, ψ_{AX} and ψ_{AY} corresponding to bonds A-X and A-Y respectively, may be represented by

$$\psi_{AX} = C_{AX}\ \phi_A + C_X \cdot \phi_X \qquad \ldots (2.4a)$$

$$\psi_{AY} = C_{AY} \cdot \phi'_A\ \ C_Y \cdot \phi_Y \qquad \ldots (2.4b)$$

where ϕ_A and ϕ'_A, are the two hybrids of A and ϕ_X and ϕ_Y are the orbitals of X and Y respectively; C's are the coefficients which minimize the energy of the MO's.

If the s-characters of the orbital ϕ_A is increased by an amount $\Delta\rho_s$ and that of ϕ_A is decreased by the same amount, then the change in energy is given by first order perturbation as:

$$\Delta\varepsilon = \langle\psi|H|\psi\rangle = -\left(C_{Ax}^2 - C_{AY}^2\right).\Delta\rho_s \qquad \ldots (2.5)$$

According to eqn. (2.5) the transfer of s-character of the hybrid orbital ϕ_A to ϕ'_A would stabilise the system of $C_{Ax}{}^2 > C_{Ay}{}^2$.

Since the square of the coefficient of ϕ_A is a measure of the probability that the electron remain associated with that orbital, C_{Ax}^2 would be greater than C_{Ay}^2 if ϕ_x is less

electronegative than ϕ_y and vice-versa. Therefore, transfer of s-character from an orbital directed towards more electronegative atom or group to an orbital directed towards less electronegative atom or group is expected to stabilise the system. This qualitative picture of bonds led Bent to enunciate the rule:

'Atomic s-character tends to concentrate towards less electronegative atoms/groups'.

It is now obvious that validity of Bent's rule rests on the assumptions that (i) the system can be adequately described by localised orbitals corresponding to bonds and lone pairs. (ii) Change of s-characters of a hybrid orbital affects only the Coulomb energy.

Since the Bent's rule concerns only with σ-orbitals, the first of the two assumptions is a reasonable one. However, the second one is far from true.

The reasons are:

(i) The change in the s-character of any of the two hybrid orbitals ϕ_A and ϕ_B involved in the bond A-B would change the overlap between the two orbitals. Since the resonance integral $\langle \phi_A | H | \phi_B \rangle$ is expressed to be proportional to the overlap, a change in bond energy would certainly occur in addition to the change in the Coulomb energy.

That the change in bond energy is often larger than that of Coulomb energy may be shown as follows.

Although it is difficult to calculate the resonance and Coulomb energies accurately, one may obtain reasonable approximations to these changes through semiempirical methods, e.g. CNDO method[19-20] where parametrization has been standardised by comparison with experimental properties.

For a bond orbital ψ_{AB} given by eqn. (2.6) formed from the orbitals ϕ_A and ϕ_B of A and B respectively, the total energy of the bond is given by eqn. (2.7).

$$\psi_{AB} = c_A \phi_A + c_B \phi_B \qquad \ldots (2.6)$$

$$\varepsilon_{AB} = 2c_A^2 \cdot H_{AA} + 4c_A \cdot c_B \cdot H_{AB} + 2c_B^2 \cdot H_{BB} \qquad \ldots (2.7)$$

where

$$H_{AA} = \langle \phi_A / H / \phi_A \rangle , \quad H_{BB} = \langle \phi_B / H / \phi_B \rangle$$

and $$H_{AB} = \langle \phi_A / H / \phi_B \rangle$$

H is the electronic hamiltonian for the system.

If we write the hybrid orbital ϕ_A as

$$\phi_A = \rho_s^{\frac{1}{2}} \cdot s_A + (1-\rho_s)^{1/2} \cdot p_A \qquad \ldots (2.8)$$

where ρ_s is the s-character of the hybrid orbital and s_A, p_A denote the s and p orbitals of A.

Therefore

$$H_{AA} = \langle \phi_A / H / \phi_A \rangle$$

$$= \rho_s \langle s_A / H / s_A \rangle + (1 - \rho_s) \cdot \langle p_A / H / p_A \rangle$$

$$= H_{pp} + \rho_s \cdot (H_{ss} - H_{pp}) \qquad \ldots (2.9)$$

Therefore the change in the coulomb integral due to a change in ρ_s is given by

$$H_{AA} = (H_{ss} - H_{pp}) \cdot \Delta \rho_s \qquad \ldots (2.10)$$

In terms of CNDO approximations, the resonance integral H_{AB} is given by

$$H_{AB} = \beta^{\circ}_{AB} \cdot S_{AB} \qquad \ldots (2.11)$$

where β°_{AB} is the bond resonance parameter and S_{AB} is the value of the overlap integral (ϕ_A / ϕ_B). Therefore, we have,

$$\Delta H_{AB} = \beta^{\circ}_{AB} \cdot \Delta S_{AB} \qquad \ldots (2.12)$$

Therefore, the total change in the energy of the bond orbital H_{AB} associated with a change in the s-character of one of the orbitals, say, ϕ_A is given by

$$\Delta \mathcal{E} = 2C_A^2 \cdot \Delta H_{AA} + 4C_A \cdot C_B \cdot \Delta H_{AB} \qquad \ldots (2.13)$$

Unless the bond is highly polar, both the orbital population ($2P_A^2$) and the bond order ($2P_AC_B$) is close to unity, so that for our purpose we may write eqn. (2.13) as

$$\begin{aligned}\Delta\mathcal{E} &\doteq \Delta H_{AA} + 2.\Delta H_{AB} \\ &= (H_{ss} - H_{pp}).\Delta\rho_s + 2.\beta^0_{AB}.\Delta S_{AB} \\ &= -(I_s - I_p).\Delta\rho_s + 2\beta^0_{AB}.\Delta S_{AB}\end{aligned} \qquad \ldots (2.14)$$

The difference in Coulomb energy has been replaced by the s-p promotion energy of A, which may be regarded as the difference in the ionisation potentials of s and p electrons.

The change in the energy associated with redistribution of s-character in some typical systems calculated from eqn. (2.14), using CNDO parameters[19-20] are shown in tables (2.16a-c).

Table 2.16a

Change in energy, $\Delta\mathcal{E}$, of C_{sp^3}-H bond as a function of the change in the s-character ($\Delta\rho_s$) of carbon orbital.

$\Delta\rho_s$	$-2\Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta\mathcal{E}^*_{AB}$
0.00	0.00	0.00	0.00
0.01	0.088	0.088	0.176

Contd..

Table 2.16a (Contd..)

$\Delta \rho_s$	$-\lambda \Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta \varepsilon^*_{AB}$
0.02	0.173	0.175	0.348
0.03	0.254	0.263	0.517
0.04	0.332	0.351	0.683
0.05	0.406	0.439	0.845
0.06	0.477	0.526	1.003
0.07	0.545	0.614	1.159
0.08	0.610	0.702	1.312
0.09	0.672	0.789	1.461
0.1	0.732	0.877	1.609
0.11	0.788	0.965	1.753
0.12	0.842	1.052	1.894
0.13	0.893	1.140	2.033
0.14	0.942	1.228	2.17
0.15	0.988	1.316	2.304
0.16	1.032	1.403	2.435
0.17	1.074	1.491	2.565
0.18	1.113	1.579	2.691
0.19	1.149	1.666	2.815
0.20	1.183	1.754	2.937
0.21	1.216	1.842	3.058

Contd..

Table 2.16a (Contd..)

$\Delta \rho_s$	$-2 \Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta \varepsilon^*_{AB}$
0.22	1.246	1.929	3.175
0.23	1.273	2.017	3.290
0.24	1.30	2.105	3.406
0.25	1.322	2.193	3.515
0.26	1.343	2.280	3.623
0.27	1.362	2.368	3.73
0.28	1.379	2.455	3.834
0.29	1.393	2.543	3.936
0.30	1.405	2.631	4.036

* eV.

Table 2.16b

Change in energy, $\Delta \varepsilon$, of $C_{sp^3} - C_{sp^3}$ bond as a function of the change in the s-character ($\Delta \rho_s$)

$\Delta \rho_s$	$-2 \Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta \varepsilon^*_{AB}$
0.00	0.00	0.00	0.00
0.01	0.088	0.088	0.176
0.02	0.172	0.175	0.347

Contd..

Table 2.16b (Contd..)

$\Delta\rho_B$	$-\lambda \Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta \varepsilon_{AB}{}^*$
0.03	0.252	0.263	0.515
0.04	0.327	0.351	0.678
0.05	0.398	0.439	0.837
0.06	0.465	0.526	0.991
0.07	0.529	0.614	1.143
0.08	0.588	0.702	1.290
0.09	0.644	0.789	1.433
0.10	0.697	0.877	1.574
0.11	0.746	0.965	1.711
0.12	0.792	1.052	1.844
0.13	0.835	1.140	1.975
0.14	0.874	1.228	2.102
0.15	0.910	1.316	2.226
0.16	0.944	1.403	2.347
0.17	0.974	1.491	2.465
0.18	1.001	1.579	2.58
0.19	1.025	1.666	2.692
0.20	1.047	1.754	2.801
0.21	1.065	1.842	2.907

Contd..

Table 2.16b (Contd..)

$\Delta\rho_s$	$-2\Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta \varepsilon^*_{AB}$
0.22	1.091	1.929	3.018
0.23	1.093	2.017	3.110
0.24	1.103	2.105	3.208
0.25	1.110	2.193	3.303
0.26	1.114	2.280	3.394
0.27	1.116	2.368	3.484
0.28	1.114	2.456	3.57
0.29	1.110	2.543	3.653
0.30	1.103	2.631	3.734

* ev.

Table 2.16c

Change in energy, $\Delta\varepsilon$, of N_{sp^3} - H bond as a function of the change in the s-character ($\Delta\rho_s$) of carbon orbital.

$\Delta\rho_s$	$-2\Delta H^*_{AB}$	$-\Delta H^*_{AA}$	$-\Delta\varepsilon^*_{AB}$
0.00	0.00	0.00	0.00
0.01	0.104	0.124	0.228
0.02	0.204	0.248	0.452

Contd..

Table 2.16c (Contd..)

$\Delta \rho_s$	$-\lambda \Delta H_{AB}^{*}$	$-\Delta H_{AA}^{*}$	$-\Delta \varepsilon_{AB}^{*}$
0.03	0.300	0.372	0.672
0.04	0.392	0.496	0.888
0.05	0.480	0.62	1.100
0.06	0.566	0.743	1.309
0.07	0.648	0.867	1.515
0.08	0.727	0.991	1.718
0.09	0.802	1.115	1.917
0.10	0.875	1.239	2.114
0.11	0.945	1.363	2.308
0.12	1.012	1.487	2.499
0.13	1.077	1.611	2.687
0.14	1.138	1.735	2.873
0.15	1.197	1.858	3.056
0.16	1.254	1.982	3.236
0.17	1.308	2.107	3.414
0.18	1.359	2.230	3.589
0.19	1.408	2.354	3.762
0.20	1.454	2.478	3.932
0.21	1.5	2.602	4.101

Contd..

Table 2.16c (Contd..)

$\Delta\rho_s$	$-2\Delta H_{AB}^{*}$	$-\Delta H_{AA}^{*}$	$-\Delta\mathcal{E}_{AB}^{*}$
0.22	1.540	2.726	4.266
0.23	1.580	2.850	4.430
0.24	1.617	2.974	4.591
0.25	1.652	3.098	4.75
0.26	1.685	3.221	4.906
0.27	1.715	3.345	5.06
0.28	1.743	3.469	5.212
0.29	1.769	3.593	5.362
0.30	1.792	3.717	5.509

* ev.

It is clear from the data given in tables (2.16a-c), that the variation in the resonance energy is considerable and in no case, it can be neglected. In view of this it is surprising how Bent's[3] rule predicts the correct trend in rehydridisation of atomic orbitals so often. One reason for the apparent success of Bent's rule that emerged from the present study (to be discussed more fully in the later chapters) is that the change in the resonance interactions of two bonds

A-X and A-Y in a system X-A-Y is often proportional to the electronegativity difference of X and Y as is also the change in the Coulomb integrals. It is precisely those cases where change in total resonance interaction of the system does not follow the electronegativity difference of the substituents X and Y that Bent's rule fails.

(ii) Another factor that may be of considerable importance in atoms with lone pair electrons is the change in the inter electronic repulsions due to change in hybrid orbitals. Since inclusion of such changes are possible only at the level of INDO or MNDO approximations[21-23] which are beyond the scope of the present work, this point will not be further considered.

II G. Modifications of the Bent's rule.

In order to have a more quantitative approach to isovalent hybridisation which includes the changes in Coulomb as well as resonance energy, Majee[1] put forward a simple treatment. His treatment is as follows:

Let us consider a molecule Y-A-X. Let the bonding AOs of A directed towards X and Y be represented by ϕ_{AX} and ϕ_{AY} (which are hybrids of s and p orbitals) respectively. The localised bond orbitals for the AX and AY bonds may be written as

$$\psi_{AX} = c_{AX}\,\phi_{AX} + c_{X}\,\phi_{X} \qquad \ldots (2.15)$$

$$\psi_{AY} = c_{AY} \cdot \Phi_{AY} + c_Y \cdot \Phi_Y \qquad \ldots (2.16)$$

and the total energy, E, of the molecule is given by

$$E = 2 \cdot [(c_{AX}^2 \cdot H_{AA}^X + c_X^2 H_{XX} + 2c_{AX} \cdot c_X \cdot \beta_{AX}) + (c_{AY}^2 \cdot H_{AA}^Y + c_Y^2 \cdot H_{YY} + 2c_{AY} \cdot c_Y \cdot \beta_{AY})] \qquad \ldots (2.17)$$

where

$$H_{AA}^X = \langle \Phi_{AX} | H | \Phi_{AX} \rangle \qquad \ldots (2.18)$$

and

$$\beta_{AX} = \langle \Phi_{AX} | H | \Phi_X \rangle \qquad \ldots (2.19)$$

With similar expressions for H_{AA}^Y and β_{AY}.

The hybrid orbitals Φ_{AX} and Φ_{AY} may be written in terms of the s and p orbitals of A (s_A and p_A) as in eqn. (2.20). The coulomb integrals is then given by (2.21) where P_{sp} is the s-p promotion energy of the atom A.

$$\Phi_{AX} = \rho_{AX}^{\frac{1}{2}} \cdot s_A + (1 - \rho_{AX})^{\frac{1}{2}} \cdot p_A \qquad \ldots (2.20)$$

$$\begin{aligned} H_{AA}^X &= \rho_{SX} \cdot E_s + (1 - \rho_{SX}) \cdot E_p \\ &= E_p + \rho_{SX} \cdot (E_s - E_p) \\ &= E_p + P_{sp} \cdot \rho_{SX} \end{aligned} \qquad \ldots (2.21)$$

The resonance integrals may be similarly approximated by eqn. (2.22) [Balhausen - Gray Scheme] :

$$\beta_{AX} = K.\left[H^{X}_{AA} \cdot H_{XX}\right]^{\frac{1}{2}} \cdot S_{AX} \qquad \ldots (2.22)$$

Where K is a proportionately constant and S_{AX} is the overlap integral between ϕ_{AX} and ϕ_X. Similar expressions for A-Y bond may be written.

A rehybridisation at A in which the s-characters of ϕ_{AX} and ϕ_{AY} are changed by $\Delta\rho_{SX}$ and $\Delta\rho_{SY}$ respectively, will change the total energy approximately by the amount:

$$\Delta\varepsilon = 2\left[\left(C_{AX}^{2}\frac{\partial H^{X}_{AA}}{\partial \rho_{SX}} + C_{AX}.C_{X}.\frac{\partial \beta_{AX}}{\partial \rho_{SX}}\right).\Delta\rho_{SX}\right.$$

$$\left. + \left(C_{AY}^{2}.\frac{\partial H^{Y}_{AA}}{\partial \rho_{SY}} + 2.C_{AY}.C_{Y}.\frac{\partial \beta_{AY}}{\partial \rho_{SY}}\right).\Delta\rho_{SY}\right] \qquad \ldots (2.23)$$

From eqn. (2.21) one gets

$$\left(\partial H^{X}_{AA}/\partial \rho_{SX}\right) = \left(\partial H^{Y}_{AA}/\partial \rho_{SY}\right) = P_{s} \qquad \ldots (2.24)$$

Neglecting the change in overlap due to rehybridisation one obtains

$$\frac{\partial \beta_{AX}}{\partial \rho_{SX}} = \frac{1}{2}.K.\frac{H_{XX}^{\frac{1}{2}}}{H^{X}_{AA}V_{sp}}.\frac{\partial H^{X}_{AA}}{\partial \rho_{SX}}$$

$$= \frac{P_{s}.\beta_{AX}}{2H^{X}_{AA}} \qquad \ldots (2.25)$$

and $$\frac{\delta \beta_{AY}}{\delta \rho_{SY}} = \frac{P_A \cdot \beta_{AY}}{2 H^{Y}_{AA}} \qquad \ldots (2.26)$$

Further, normalisation condition requires

$$\sum_A \Delta \rho_S = 0 \text{ , or } \quad \Delta \rho_{SX} + \Delta \rho_{SY} = 0 \qquad \ldots (2.27)$$

From eqns. (2.21) - (2.27) we obtain

$$\Delta \mathcal{E} = \mathfrak{P}_A \left[\alpha (C_{AX}^2 - C_{AY}^2) + \left(\frac{C_{AX} \cdot C_X \cdot \beta_{AX}}{H^{X}_{AA}} - \frac{C_{AY} \cdot C_Y \cdot \beta_{AY}}{H^{Y}_{AA}} \right) \right] \cdot \Delta \rho_{SX} \qquad \ldots (2.28)$$

For wave functions correctly representing the equilibrium configuration of the molecule $\delta E/\delta \rho_S$ would be zero. However, if the calculation ~~are~~ is carried with some assumed regular hybridisation at A (e.g. sp, sp^2, sp^3 etc) as is the usual practice in simple MO calculations the bond orbitals will not represent the true equilibrium and the right hand side of eqn. (2.28) will not be zero. The magnitude of this quantity is, therefore, expected to be proportional to the deviation of the assumed hybridisation from the optimum hybridisation required for energy minimisation. Therefore a rehybridisation, which is equivalent to transfering s-character from an orbital must occur till $\delta E/\delta \rho_S$ becomes zero.

On the basis of this argument, transfer of s-character from A-Y bond to A-X bond is expected to be proportional to ΔE, that is,

$$\Delta \rho_{sx} \propto \Delta E \propto 2P.\left[\left(C_{AX}^2 - C_{AY}^2\right) + \left(C_{AX}.C_X.\beta_{AX} - C_{AY}.C_Y.\beta_{AY}\right)/H_{AB}\right] \quad \ldots (2.29)$$

Since, $H_{AA}^X = H_{AA}^Y = H_{AA}$; for regular hybridisation. It is easy to show that the same conditions apply to compounds of the general type X_nAY_n' also.

Use of Del Re approximations[24] [Chapter (V)] for the localised bond orbitals then gives,

$$\begin{aligned} 2C_{AX}^2 - 2C_{AY}^2 &= (1-Q_{AX}) - (1-Q_{AY}) \\ &= (Q_{AX} - Q_{AY}) \end{aligned} \quad \ldots (2.30)$$

where Q_{AX} and Q_{AY} are the bond polarities of A-X and A-Y bonds respectively. Further

$$2C_{AX}.C_X = (1-Q_{AX}^2)^{\frac{1}{2}} \doteq 1 \quad \ldots (2.31a)$$

$$2C_{AY}.C_Y = (1-Q_{AY}^2)^{\frac{1}{2}} \doteq 1 \quad \ldots (2.31b)$$

Since Q_{AX}^2 and Q_{AY}^2 are always very small.

In terms of Del Re parameters[24] and bond charges, the change in s-character is then given by

$$\Delta P_{SX} = K_1 \cdot (Q_{AY} - Q_{AX}) + K_2 \cdot (\epsilon_{AX} - \epsilon_{AY}) \qquad \ldots (2.32)$$

where the proportionality constant K_1 and K_2 include promotion energy (P_N), valence state ionisation energies (H_{AA}) etc; ϵ's are the Del Re resonance parameters[1,24].

If the resonance integrals for A-X and A-Y bonds are nearly equal which happens when A-X and A-Y bond energies are roughly equal, the second term of eqn. (2.32) may be neglected. Further (Q_{AY}-Q_{AX}) will be roughly proportional to electronegativity difference. When this condition is fulfilled, the decrease in the s-character of the A-Y orbital, consequently the increase in the s-character along A-X bond in a series $X_nAY_{n'}$ will be proportional to the electronegativity of the substituent Y. Thus Bent's rule is only a special case of more general rule embodied in eqn. (2.32) which may be stated as follows.

In a molecule of the type $X_nAY_{n'}$, the increase in the s-character along the A-X bond and consequent increase in p-character along A-Y bond is proportional to (a) the difference in the polarities of the two bonds and (b) the difference in the resonance integrals of the two bonds (roughly bond energies). In other words, s-character will be transferred from a more polar bond to a less polar bond if the bond energies

are nearly equal and from a less strong bond to a more strong bond if the bond polarities are nearly equal.

The superiority of this general rule over Walsh-Bent's rule and quantitative correlations of coupling constants in a large number of systems using Del Re calculations have been reviewed in detail by Majee[1] and needs no further elaboration.

Although this treatment represents an important advance in the right direction, it is far from satisfactory due to following reasons:

(i) The formulation of the eqn. (2.32) is based on qualitative argument.

(ii) The parameters K_1 and K_2 appearing in eqn. (2.32) are to be determined empirically.

(iii) Eqn. (2.32) can not be used in cases where more than two different substituents are connected to the same atom.

(iv) In a poly atomic molecule any change in hybridisation at a given atom would result in readjustment of hybridisations in all the atoms. This effect has not been considered in this model.

In view of the advantage of using valence-bond concept in the description of molecules which retains the chemist's concept of a bond, it is worthwhile to develop a more quantitative and satisfactory approach for the description of orbital hybridisation in molecules.

We shall therefore attempt to develop a more quantitative theoretical approach to orbital hybridisation in the subsequent chapters of the present work.

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