

VARIABLE HYBRIDISATION - A SIMPLE MODEL OF COVALENT BONDING

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Abstract - Extensive evidence is presented which conclusively shows that variable hybridisation is a simple, pictorial and very useful model of covalent bonding. The noninteger hybridisation parameters calculated by the iterative maximum overlap approach are very rich in chemical information. They can be successfully correlated with a number of physico-chemical gross molecular properties which encompass heats of formation, heats of hydrogenation, strain energies etc. They reflect also local properties like spin-spin coupling constants across one bond, C-H stretching frequencies, thermodynamic proton acidities, intrinsic bond energies etc. In addition, the iterative version of the maximum overlap method provides quite reliable estimates of molecular shapes and sizes. Properties which are completely determined by molecular geometry such as diamagnetic contributions to the magnetic susceptibility and nuclear magnetic shielding are well reproduced being in nice agreement with experimental data and rigorous ab initio results.

INTRODUCTION

Pauling's idea about the mixing of pure atomic orbitals (Ref. 1) is one of the most important single contributions to the quantum theory of covalent bonding. The local hybrid orbitals reflect two most important features of the charge reorganisation accompanying molecular formation:

- (a) charge build-up in the regions between the bonded atoms and its decrease in the rest of the space, and
- (b) directional properties of covalent bonding which lead to wonderful molecular architecture.

The hybrids also have sufficient flexibility to describe two additional properties:

- (c) contraction of orbitals in the bonding direction and
- (d) intramolecular charge transfer, which is achieved by changing the screening factors of the hybrid orbitals and by varying their occupation numbers, respectively.

It is clear that local hybrid orbitals give a simple intuitive physical picture of chemical bonding and many outstanding scientists including Slater (Ref. 2), Coulson (Ref. 3) and Mulliken (Ref. 4) have discussed their interpretative power. A posteriori, we can say that variable hybridisation is capable of describing a large number of molecular properties which are related to coupled electron pairs. They are particularly useful if a trend of changes along the series of related compounds is desired.

In principle one can determine hybridisation parameters in an ab initio fashion minimizing the energy of a molecule. However, to keep the model as simple as possible other criteria are needed. One of such procedures is described below.

THE ITERATIVE VERSION OF THE MAXIMUM OVERLAP METHOD

The hybrids involving mixing of s and p atomic orbitals are of a form:

$$\Psi_{A\mu} = c_{A\mu} (ns) + (1 - c_{A\mu}^2)^{1/2} (np_{\mu})_A \quad (1)$$

where A denotes the host nucleus. The hybridisation parameters are sometimes determined by the local symmetry. However, if the latter is low, one can em-

ploy the maximum overlap criterion discussed by Pauling (Ref. 5), Slater (Ref. 2), Mulliken (Ref. 6), Murrell (Ref. 7), Lykos and Schmeising (Ref. 8) and others. In our approach (Refs. 9, 10), the weighted maximum overlap concept is adopted

$$S_W = \sum_{AB} k_{AB} S_{AB} \quad (2)$$

where the summation goes over all bonds in a molecule. It should be mentioned that the number of empirical weighting factors k_{AB} is kept at minimum. They differ only in widely different chemical bonds. Thus in hydrocarbons two parameters k_{CC} and k_{CH} are employed. In addition, the following plausible constraints are imposed:

- (a) hybrids placed on the same nucleus are orthogonal
- (b) perfect orbital following for all C-H and acyclic C-C bonds is assumed. The early applications of the weighted maximum overlap method were based on the use of standard bond distances (Refs. 9, 10). This is not quite justified because it introduces unnecessary bias in the calculation since "standard" bond distances are somewhat arbitrary particularly in strained systems. Therefore a procedure capable of providing reasonable estimates of molecular geometries was highly desirable. It was found in the form of the iterative maximum overlap method (IMOM). The backbone of the iterative procedure consists of conditions (c) and (d):
- (c) the bond-orbital overlaps are forced to be consistent with bond distances calculated by the predetermined linear relations of the type:

$$d(AB) = K_{AB} S_{AB} + L_{AB} \quad (3)$$

- (d) the effect of the π -electron delocalization is taken into account by the Lykos-Schmeising (Ref. 8) maximum overlap molecular orbitals approach according to the empirical formula

$$d_C^\pi(AB) = -0.266 P_{\mu\nu} S_{\mu\nu} \quad (4)$$

where $P_{\mu\nu}$ and $S_{\mu\nu}$ are bond orders and bond overlaps of the mobile π -electrons. Subscript c and superscript π refer to the correction caused by π -electrons.

The resulting hybridisation and structural parameters are obtained by the iterative procedure. One starts the calculation with an arbitrary set of internuclear distances and optimizes the sum of weighted overlaps (2). Then a new array of bond distances is deduced from the linear relations (3) corrected perhaps by the formula (4) if π -electrons are present. The whole procedure is repeated until full consistency, compatible with preconceived tolerance, is attained. More detail can be found elsewhere (Refs. 11, 12).

RESULTS AND DISCUSSION

Hybridisation

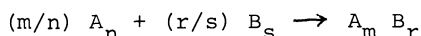
The calculated hybrid orbitals have some remarkable features. Their deviation angles from the straight lines joining neighbouring nuclei are as small as possible. Furthermore, optimal overlapping is attained when deviation angles of two coupled hybrid orbitals assume the same value (Ref. 13). The same conclusion holds for their s -characters (Ref. 14). Thus a pair of strongly overlapping hybrids tend to achieve similar deviation angles and s -characters. Another striking feature of the variable hybridisation model is that mixing parameters generally take noninteger values. Canonical sp^3 , sp^2 and sp^1 hybridisation states are more an exception than a rule. For example, the hybrid orbitals for CH and CC bonds in acetylene are of the $sp^{1.25}$ and $sp^{0.80}$ composition, respectively. Similarly, in ethylene they assume the form of $sp^{2.16}$ and $sp^{1.72}$ again for CH and CC bonds respectively. These two molecules illustrate rather nicely the flexibility of the variable hybridisation to conform to local symmetries of atoms in chemical moieties. Intermediate hybrid compositions are most frequently found in strained cyclic and polycyclic molecules. In such cases hybrid orbitals exhibit large deviation angles forming well known bent bonds (Refs. 15, 16), a fact which has a number of important chemical consequences to mention only strain (vide infra). The hybrid orbitals are to a high degree transferable if a given fragment is repeated in a series of molecules. This feature can save a lot of computational effort when complex

systems are considered. Sometimes the calculation is not even necessary if the hybridisation parameters of similar compounds are known. It should be strongly pointed out that hybridisation parameters do not have an absolute meaning, because their particular values depend on the method employed. However, if the same method is consistently applied, then a meaningful picture emerges. A large number of molecular properties can be correlated with the hybridisation parameters yielding results which are generally in good accordance with experimental findings. Thus hybridisation is a useful index of covalent bonding which is valid within the framework of the adopted theoretical model. Some of these correlations are discussed in the following sections. In particular, we shall consider energetic, structural and some magnetic properties of hydrocarbons.

GLOBAL MOLECULAR PROPERTIES

Heats of formation

The standard heat of formation ΔH_f of a compound $A_m B_r$ is defined as the change in heat content for the synthesis from the corresponding elements



where the process is carried out isothermally at 25°C. Elements A_n , B_s and the final product $A_m B_r$ are assumed to be in their standard thermodynamic states. It turns out that ΔH_f values of hydrocarbons possessing single bonds are successfully correlated by a relation of the form (Ref. 17):

$$\Delta H_f = k_{CC}^{\sigma} \sum S_{CC}^{\sigma} + k_{CC}^{\pi}(b) \sum S_{CC}^{\pi}(b) + k_{CH} \sum S_{CH} + n_{CC} l_{CC} + n_{CH} l_{CH}$$

where n_{CC} and n_{CH} are the numbers of CC and CH bonds, respectively. Here k and l are adjustable empirical parameters. It should be mentioned that provision is made for the π -type of interaction in bent bonds represented by the $k_{CC}^{\pi}(b) S_{CC}^{\pi}(b)$ term. In molecules involving strained double bonds two more weighting factors are needed (Ref. 17). Resulting ΔH_f values for a small sample of characteristic compounds are compared with experimental and MINDO/3 (Ref. 18) results in Table 1. The quality of the correlation is quite good

TABLE 1. Comparison of the heats of formation as calculated by the IMOM procedure with experimental and MINDO/3 results^a

Molecule	ΔH_f (IMOM)	ΔH_f (exp.)	ΔH_f (MINDO/3)
methane	-16.6	-17.9	-6.3
ethane	-20.7	-20.24	-19.8
propane	-26.8	-24.82	-26.5
ethylene	13.2	12.50	19.2
propene	5.8	4.88	6.5
n-butane	-30.6	-30.15	-30.4
n-pentane	-35.5	-35.0	-
cyclopropane	14.6	12.74	8.7
cyclobutane	2.1	6.38	-5.1
norbornane	-9.0	-12.42	8.4
norbornadiene	60.5	59.70	84.5
cubane	148.8	148.70	139.8

^a in kcal/mole

suggesting that a more general bond energy function of the form

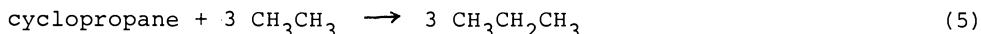
$$E_{AB} = f(S_{AB}) = k_0 + k_1 S_{AB} + k_2 S_{AB}^2 + \dots$$

would lead to excellent results. Once the empirical weighting factors are

known they can be used to calculate ΔH_f values in a predictive manner. For example, one can estimate heats of hydrogenation of olefins which are in fair accordance with observed values (Ref. 17). Similarly one obtains a measure of molecular destabilization called strain.

Strain energies

Strain energy is closely related to molecular reactivity. Although it can not be exactly defined, it represents a useful index of molecular (in)stability. Strain is probably best estimated by an adequate homodesmotic chemical reaction (Ref. 19). The latter is a hypothetical reaction exhibiting two important features: (a) the number of CC bonds (single, double etc.) classified according to the coordination numbers of participating carbon atoms is conserved, (b) there are equal numbers of C atoms with zero, one, two and three H atoms attached to them in reactants and products (Refs. 14, 19). For example, the strain energy of the cyclopropane is given by the negative enthalpy change of the gedanken homodesmotic reaction



The estimated strain energies (refs. 14, 20) for some three and four membered ring compounds are presented in Table 2. Since the strain energy is ob-

TABLE 2. Comparison of the IMOM strain energies with MINDO/3, experimental or ab initio values (in kcal/mole)

Molecule	IMOM	MINDO/3	EXPTL. OR AB INITIO*
cyclopropane	32.9	28.8	28.7* : 26.5
cyclopropene	53.2	52.0	57.6* : 52.5
1,2-dimethylcyclopropene	46.8	43.8	47.5
cyclobutane	24.6	21.7	24.8
methylcyclobutane	25.2	14.5	22.0
methylenecyclobutane	28.8	14.8	27.9
cyclopentane	7.1	5.6	4.6

tained as a difference of several ΔH_f values, the IMOM results are in satisfactory agreement with experiment or more accurate ab initio predictions. The MINDO/3 method yields less satisfactory strain energies due to troubles with bulky alkyl groups (Ref. 21). Finally, it is noteworthy that deviation of hybrid orbitals from the straight lines passing through bonded nuclei offers a simple physical picture of the angular strain (Ref. 22).

Geometry of hydrocarbons

Sizes and shapes of hydrocarbons are well reproduced by the IMO method. Performance of our approach is discussed in great detail in a review article (Ref. 23). Briefly, one can say that structural parameters calculated by the IMOM procedure are similar to those obtained by the ab initio STO-3G method (Ref. 24). If there are discrepancies with measurements, there are usually good reasons for them. For example, differences between the calculated bond distances in spiro(2,4)-hepta-4,6-diene and microwave data indicate significant interaction of the HOMO of the cyclopropyl ring with the LUMO of the cyclopentadiene fragment (Ref. 13). Perusal of the results obtained for a large number of molecules shows that bond distances are strongly affected by the s-characters of the hybrid orbitals participating in a bond. Further, it should be kept in mind that bond distance is not identical with bond length in strained systems if the latter is defined as a segment of a curve passing through points of the maximum electron density (Refs. 13, 25, 26). To conclude, the hybrid orbitals rationalize a great deal of organic stereochemistry.

Diamagnetic part of the magnetic susceptibility

The temperature independent part of magnetic susceptibility consists of two contributions (Ref. 27):

$$\chi_{aa} = \chi_{aa}^d + \chi_{aa}^p \quad (6)$$

where χ_{aa}^d is Langevin's diamagnetic term and χ_{aa}^p is van Vleck's paramagnetic term. We have shown that the first term may be expressed conveniently by a point charge approximation as

$$\chi_{aa}^d \cong (Ne^2/4mc^2) \sum_A Z_A (b_A^2 + c_A^2) + \sum_p k_p n_p \quad (7)$$

where a_A , b_A and c_A are coordinates of the nucleus A and constants have their usual meanings. The second term is isotropic and can be obtained by the simple additivity rule (Ref. 28). Other diagonal elements of the χ^d tensor are obtained by the cyclic permutation of coordinates. It should be noted that the intramolecular charge transfer is neglected in the formula (7) and the atomic number Z_A measures electron density associated with the nucleus A.

Thus it appears that Langevin's term is easily calculated if the atomic coordinates are known. We have computed χ^d values for a number of hydrocarbons utilising geometries provided by the IMO method (Ref. 29). Results presented in Table 3 are in fine agreement with experimental data and/or ab initio results. It is interesting to mention in passing by that the "neutral atom approach" implied by the formula (7) works well even in heteroatomic molecules (Ref. 30). The effect of intramolecular charge transfer should be taken into account only if atoms of highly different electronegativities are involved, e.g. alkali halides (Ref. 31). A survey of the data in table 3 shows that Langevin's diamagnetism is easily calculated by pencil and paper in a satisfactory manner if molecular geometries are known.

TABLE 3. Comparison of diamagnetic contributions to magnetic susceptibilities of some hydrocarbons as calculated by the IMO method employing formula (7) with the experimental results and ab initio values.

Molecule	Axis	IMO method	exptl. or ab initio*
methane	aa	29.0	-27.8*
ethane	aa	-54.7	-52.6*
	bb	-103.9	-103.0
	cc	-103.9	-103.0
ethylene	aa	-38.4	-39.6*
	bb	-72.5	-72.8
	cc	-87.2	-84.1
cyclopropane	aa	-113.5	-112.4*
	bb	-113.5	-112.4
	cc	-149.3	-149.3
cyclopropene	aa	-82.5	-82.3 ± 0.3
	bb	-94.9	-100.4 ± 0.3
	cc	-130.7	-133.3 ± 0.3
methylene-cyclopropane	aa	-123.9	-115.9
	bb	-233.8	-240.6
	cc	-285.9	-284.3
cyclobutene	aa	-155.8	-154.1
	bb	-159.4	-160.8
	cc	-244.8	-242.8

* Ab initio results are denoted by an asterisk (in $10^{-6} \text{ cm}^3/\text{mole}$).

Diamagnetic part of the chemical shift

Another property which can be calculated on the back of an envelope is the diamagnetic part of the chemical shift. Ramsey has shown (Ref. 32) that magnetic screening of the nucleus A in a molecule is given by

$$\sigma_{av.} = \sigma_{av.}^d + \sigma_{av.}^p \quad (8)$$

where spherical averaging is implied. Superscripts d and p refer to diamagnetic and paramagnetic contributions. The former is our concern here and as Flygare and Goodisman (Ref. 33) have shown, it can be calculated to good accuracy in the point charge approximation neglecting intramolecular charge transfer

$$\sigma_{av.}^d = (e^2/3mc^2) \langle 0 | 1/r | 0 \rangle \approx \sigma_{av.}^d(FA) + (e^2/3mc^2) \sum Z_A/r_A \quad (9)$$

where the first term is equal to the free atom value. Consequently, diamagnetic shielding is completely determined by the geometry of the molecule. By using structural parameters computed by the IMO method diamagnetic shieldings of hydrocarbons are easily obtained. They are favourably compared with ab initio values (Ref. 34). Some of the results are presented in Table 4 for the sake of illustration.

TABLE 4. Comparison between the IMOM diamagnetic shielding values for carbon atoms and the corresponding ab initio double ξ results*.

Molecule	IMOM	AB INITIO
methane	294.8	296.7
ethane	335.7	337.2
ethylene	328.9	330.1
propylene		
C(1)	357.1	355.5
C(2)	371.1	369.5
C(3)	356.7	355.8
cyclopropane	268.7	370.7
cyclopropene		
C(1)	362.3	360.4
C(2)	363.6	360.4

* In ppm. Ab initio free atom value for C atom of 260.7 ppm is taken from the paper: G. Malli and C. Froese, Int. J. Quant. Chem., 15, 95 (1967).

LOCAL MOLECULAR PROPERTIES

The coupled-hybrid-orbitals model described above is the simplest form of the VB method. It is, therefore, not surprising that variable hybridisation reflects a number of local properties which will be only briefly discussed due to the limitation of space. More details can be found in the original papers.

Intrinsic bond energies may be considered as a local property because the effect of the molecular relaxation upon the bond rupture is excluded (Ref. 35). The experimentally estimated intrinsic bond energies of CC bonds can be very successfully correlated with corresponding bond overlap integrals (Ref. 36).

A sensitive measure of electron density distribution in the neighbourhood of bonded nuclei is provided by the spin-spin coupling constants. In hydrocarbons the most important contribution to $^1J(CC)$ and $^1J(CH)$ constants is generally the Fermi contact term which in turn is proportional to the product of s-characters (Refs. 37-40). Hybrid orbitals evaluated by the maximum overlap method have proved useful in discussing changes of coupling constants for a large variety of hydrocarbons (Ref. 37). Similar conclusion holds for

$^1J(C-Si)$ and $^1J(Si-H)$ couplings in silanes but the quality of the correlations is lower presumably due to significant contributions of other terms apart the Fermi contact interaction (Ref. 41).

Finally, it should be mentioned that s-characters of hybrid orbitals reflect changes of proton thermodynamic acidity (Ref. 42), C-H stretching frequencies (Ref. 43) and influence proton isotropic hyperfine coupling constants in planar radicals (Ref. 44).

CONCLUSION

There are several widespread misconceptions concerning hybridisation of atomic orbitals. The hybridisation indices are sometimes regarded as artifacts (Ref. 45) or at best as a convenient transformation of the basis set which can be possibly used for interpretative purposes. This common fallacy is a consequence of the invariance of the MO Slater determinants to all orthogonal transformations. In this connection it is worthwhile to mention that one can define s-character-like quantities even within the MO framework (Refs. 46, 47). More importantly, as we have conclusively shown, noninteger hybridisation is a simple VB model of covalent bonding capable of rationalizing a large body of molecular data. Since it is efficient and conceptually appealing it is not obsolete or outmoded. On the contrary, we feel quite confident that forthcoming semiempirical methods will be based on suitably orthogonalized hybrid basis sets (Refs. 48, 49).

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