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Additivity of Bond Energies in the Light of the Maximum Overlap Approximation (MOA) and MINDO/3*

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Optimum parameters are determined for the use of the maximum overlap approximation (MOA) to calculate heats of atomization of a varied set of eleven hydrocarbons. The agreement with experiment is generally good. The reasons for this success are discussed in terms of an analysis by energy partitioning of MINDO/3 calculations for the same hydrocarbons.

INTRODUCTION

While the majority of quantum mechanical calculations in recent years have made use of the molecular orbital (MO) approach, the valence bond (VB) method still has a number of attractions, particularly for the treatment of molecules with »localized« bonds. The VB picture is certainly much closer to the conventional intuitive one in which the bonding in such molecules is represented in terms of two-center bonds formed by sharing of pairs of electrons. There has therefore been a revival of interest recently in VB methods, in particular the simple variant known as the maximum overlap approximation (MOA) which has recently been applied to a large number of hydrocarbons[1].

In the MOA method the hybridization of the AOs used to form two-center bonds is chosen to ensure the maximum overall overlap between the corresponding pairs of AOs in the molecule as a whole. It has been shown[1,2] that the corresponding hybridization parameters can be used successfully to correlate a number of molecular properties in unconjugated hydrocarbons, *e. g.* p. m. r. chemical shifts, n. m. r. coupling constans (J_{CC} and J_{CH}), thermodynamic acidities, and CH stretching frequencies. The overlap integrals between the pairs of AOs used to form bonds have also been correlated with the corresponding bond lengths[3] and bond energies[4].

Although this simple and attractive approach has thus proved remarkably successful, its basis has been essentially intuitive and empirical. It therefore seemed to us of interest to see if a satisfactory theoretical explanation could be given for its success. We also wanted to see how well the MOA method

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could reproduce heats of formation on the assumption that bond energies are related in the manner indicated above to orbital overlap.

An obvious approach seemed to be to compare the results of MOA calculations for hydrocarbons with those from the MINDO/3 method[5]. MINDO/3 is a SCF method, based on the latest version of the MINDO[6] semiempirical SCF MO treatment, equivalent to the INDO method of Pople *et al.*[7] but parametrized to reproduce ground state properties of molecules rather than to mimic the results of *ab initio* SCF calculations. It has two major advantages for the present purpose. First, it gives good estimates of the heats of atomization of molecules. Secondly, the expression for the total energy of a molecule can be dissected into terms representing contributions by individual atoms and bonds by using the Fischer-Kollmar technique of energy partitioning[8].

THEORETICAL APPROACH

Since our concern was with the possible use of the MOA method for calculating heats of atomization, we calculated the hybridization parameters by a procedure that is somewhat different from that used previously[1,2].

We assumed that the bond energy of a given bond in a molecule, *i. e.* the corresponding contribution to the heat of atomization (ΔH_a), is a linear function of the corresponding overlap integral S_{ij}. Thus the bond energy (E_{ij}^{CC}) of a bond between two carbon atoms, formed by interaction of two hybrid AOs Φ_i and Φ_j, is given by

$$E_{ij}^{CC} = K_{CC} S_{ij} + L_{CC} \tag{1}$$

where K_{CC} and L_{CC} are constants. Likewise for CH bonds.

$$E_{kl}^{CH} = K_{CH} S_{kl} + L_{CH} \tag{2}$$

The heat of atomization is then given by:

$$\Delta H_a = K_{CC} \sum_{ij}^{CC} S_{ij} + K_{CH} \sum_{kl}^{CH} S_{kl} + N_{CC} L_{CC} + N_{CH} L_{CH} \tag{3}$$

where the first sum is over the N_{CC} CC bonds and the second over the N_{CH} CH bonds. The AOs are to be chosen in such a way as to minimize the energy of the molecule, *i. e.* to maximize ΔH_a.

The individual atomic orbitals Φ_i of atom m are written as hybrids of corresponding s and p AOs:

$$\Phi_i = a_i s_m + (1 - a_i^2)^{1/2} p_{mi} \tag{4}$$

where s_m is the s AO of atom m while p_{mi} a corresponding p AO with its axis along that of the hybrid AO Φ_i. a_i is the parameter which determines the hybridization of Φ_i. In the case of a hydrogen atom, a_i is of course unity. The AOs of a given atom are required to be orthogonal. Thus if Φ_i and Φ_j are two hybrid AOs of atom m

$$\langle \Phi_i | \Phi_j \rangle = a_i a_j + (1 - a_i^2)^{1/2} (1 - a_j^2)^{1/2} \cos \vartheta_{ij} = 0 \tag{5}$$

where ϑ_{ij} is the interaxial angle between the p AOs Φ_i and Φ_j.

The overlap integrals in equation (2) are calculated using Slater-Zener AOs. Here a problem arises because it is well known that the optimum orbital exponents are not the same for orbitals in free atoms as for the correspoding orbitals in atoms that are chemically combined. In the latter case it is also necessary to distinguish between p AOs used to form σ bonds and those used to form π bonds. In the case of hydrocarbons there are four exponents to be determined; that for hydrogen (ζ_H), that for carbon 2s (ζ_{Cs}), that for carbon 2p used in a σ bond ($\zeta_{Cp\sigma}$) and that for carbon 2p used in a π bond ($\zeta_{Cp\pi}$).

The heat of atomization of a hydrocarbon is therefore a function of the hybridization parameters of the various carbon atoms (a_i in aquation (4)), the quantities K_{CC}, L_{CC}, K_{CH}, and L_{CH} in equation (3), and the orbital exponents ζ_H, ζ_{Cs}, $\zeta_{Cp\sigma}$, and $\zeta_{Cp\pi}$.

The values of the parameters were determined in the following way, using a set of hydrocarbons whose geometries and heats of atomization are known experimentally. Assuming the molecule to have the observed geometry, and assuming values for the various parameters, we can calculate a corresponding heat of atomization (E_μ) for each molecule μ using equation (3). If the corresponding experimental value is $\Delta H_{\mu a}$, the error in our estimate is ($E_\mu - \Delta H_{\mu a}$). The parameters are chosen to minimize the sum (F) of the squares of the errors,

$$F = \sum^{\mu} (E_{\mu} - \Delta H_{\mu a})^2 \tag{6}$$

In practice we assumed values for ζ_H and determined the others by minimizing F with respect to the other parameters by the SIMPLEX method[9]. The results for various values of ζ_H are listed in Table I. The optimum value

TABLE I

Optimized MOA Parameters for Hydrocarbons

Parameter	Orbital exponent (ς_H) for hydrogen					Slater[a]	C.-R.[b]
	1.0	1.1	1.2	1.3[c]	1.4		
ζ_{2s}	1.8552	1.8641	1.9056	1.9165	1.9399	1.625	1.6083
$\zeta_{2p\sigma}$	1.4420	1.4476	1.5147	1.5238	1.5450	1.625	1.5679
$\zeta_{2p\pi}$	1.3429	1.3399	1.3877	1.3904	1.4062	1.625	1.5679
$\frac{K_{CH}}{\text{kcal mol}^{-1}}$	124.3790	124.6198	129.7255	131.0757	133.0290	47.6242	49.2009
$\frac{L_{CH}}{\text{kcal mol}^{-1}}$	— 5.2594	— 4.9222	— 5.3480	— 5.5006	— 5.4604	41.4797	39.4439
$\frac{K_{CC}}{\text{kcal mol}^{-1}}$	117.4559	119.9258	121.5427	123.7983	126.0898	54.3402	70.1049
$\frac{L_{CC}}{\text{kcal mol}^{-1}}$	19.2780	17.7197	19.3773	19.4334	20.3682	65.0215	53.4141
$\frac{\text{SD}^{d}}{\text{kcal mol}^{-1}}$	3.09	2.98	2.92	2.87	2.84	5.35	5.23

(2) Slater[10] exponents except $\zeta_H = 1.2$
(b) Clementi-Raimondi[11] exponents except $\zeta_H = 1.2$
(c) Values used for the calculations in Table II
(d) Standard deviation of calculated ΔH_a from observed ΔH_a for the hydrocarbons listed in Table II, except cyclobutene and cyclopentane

for ζ_H is clearly near 1.3. For comparison, values are also listed for standard Slater exponents[10] and for the modified exponents recommended by Clementi and Raimondi[11]. The results indicate very clearly the need for using different exponents for free atoms and for atoms in molecules and also indicate that little is gained by using the Clementi-Raimondi exponents in place of Slater ones.

RESULTS AND DISCUSSION

Table II shows the optimum MOA estimates of heats of atomization for the chosen set of eleven hydrocarbons. It will be seen that the agreement is quite close for most of them; note in particular the good results for ethane, ethylene, and acetylene, implying that the MOA approximation holds for bonds of all types from single to triple, and for cyclopropane and cubane, both highly strained compounds. On the other hand the errors are larger for two of the eleven compounds (cyclobutene; error, — 14.8 kcal*/mol; and cyclopentane; error, — 29.2 kcal/mol). Evidently the parallel between overlap integrals and bond energies is not at all universal. On the contrary it seems liable to break down for no obvious reason, neither cyclobutene nor cyclopentane possessing features that are absent in the other nine hydrocarbons.

TABLE II

Calculated and Observed Heats of Atomization of Hydrocarbons

Molecule	Heat of atomization (ΔH_a/kcal mol^{-1}) at 25 °C		
	Observed	MINDO/3	MOA
Methane	397.8	386.7	403.1
Ethane	674.6	672.7	672.5
Propane	954.3	946.6	954.7
Ethylene	537.7	529.2	533.3
Propene	820.4	815.9	820.5
Acetylene	391.8	388.5	393.4
Cyclopropane	812.5	814.0	815.0
Cyclobutane	1094.0	1099.1	1091.6
Cyclopentane	1393.9	1397.3	1364.7
Cyclobutene	958.7	961.1	940.9
Cubane	1635.2	1641.1	1635.8

We have included in Table II heats of atomization given by MINDO/3. In MINDO/3 calculations the geometry is normally calculated by minimizing the energy with respect to all geometrical variables. Here, however, we are concerned with a comparison of MOA with MINDO/3; to facilitate this we have used experimental geometries in both cases. The errors in the MINDO/3 energies are consequently somewhat larger than usual, the heats of atomization tending to be too small.

In an all-valence-electron MO approximation, the total energy E_T of a molecule is given by

$$E_T = E_{el} + E_{nn} \tag{7}$$

where E_{el} is the total electronic energy and E_{nn} is the total core-core repulsion energy. The heat of atomization, ΔH_a, is then given by

$$\Delta H_a = -[E_T - \Sigma E_A] \tag{8}$$

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* 1 kcal = 4.184 kJ

where E_A is the total energy of atom A and the sum is over all the atoms that compose the molecule we are considering. In an approximation of the MINDO type, where electron repulsion integrals involving bicentric overlap are neglected, this can be expanded following the energy partitioning scheme of Fischer and Kollmar[8]:

$$\Delta H_a = T_1 + T_2 + T_3 \tag{9}$$

where

$$T_1 = -\sum_{A<B}^{a} (E_{AB}^{R} + E_{AB}^{V} + E_{AB}^{J} + E_{AB}^{K} + E_{AB}^{N}) \tag{10}$$

$$T_2 = -\sum_{A<B}^{na} (E_{AB}^{R} + E_{AB}^{V} + E_{AB}^{J} + E_{AB}^{K} + E_{AB}^{N}) \tag{11}$$

$$T_3 = -\sum_{A} (E_{A}^{U} + E_{A}^{J} + E_{A}^{K} - E_{A}) \tag{12}$$

Here $\overset{a}{\Sigma}$ implies summation over pairs of adjacent atoms *i. e.* ones that are directly bonded to one another, while $\overset{na}{\Sigma}$ implies summation over nonadjacent pairs. Thus T_1 represents the contribution to ΔH_a of interactions between atoms in forming bonds, T_2 the corresponding nonbonded interactions, and T_3 the changes in energies of atoms, through promotion or transfer of electrons from one atom to another. E_{AB}^{R} denotes one-electron terms, *i. e.* those involving the one-electron core resonance integrals β_{ij}^{C} between AOs of atoms A and B. E_{AB}^{V} is the core-electron attraction between atoms A and B, *i. e.* a sum of the attractive potential energies between the valence electrons of A and the core of B and between the valence electrons of B and the core of A. E_{AB}^{J} and E_{AB}^{K} are the coulombic and exchange interactions between the valence electrons of A and those of B. E_{AB}^{N} is the A—B core repulsion. E_{A}^{U} is the sum of the monocentric kinetic energy of the valence electrons of atom A and the attraction between them and the core of atom A. E_{A}^{J} and E_{A}^{K} are the coulombic and exchange interactions between the valence electrons of atom A. All these quantities can be calculated very simply for the MINDO wave function[12]. The success of the MINDO/3 method suggests that the dissection of ΔH_a into one center, bonded two-center, and nonbonded two-center terms is probably meaningful.

The well known additivity of bond energies in unconjugated molecules implies that ΔH_a can be dissected into bonded two-center contributions. The success of the MOA method implied further that the corresponding bond energies E_{xy} between pairs of atoms X and Y can be expressed in the form (see equation (11)):

$$E_{xy} = K_{xy} \Sigma S_{ij} + nL_{xy} \tag{13}$$

where the sum is over the n pairs of AOs Φ_i and Φ_j used in forming the n bonds between atoms X and Y.

The simplest and intuitively most reasonable quantity to identify with bonding is the nearest-neighbor two-center term T_1 in equation (9). There is indeed quite a good linear relation between T_1 and the experimentally determined heat of atomization ΔH_a (Figure 1). Indeed the least squared line through the points in Figure 1 passes through the origin. The slope of the line (— 1.698) is, however, far from unity. A large part of the bonding must therefore be attributed to the other terms $(T_2 + T_3)$. If therefore T_1 is a measure of bonding, so must also be $(T_2 + T_3)$. There should therefore be a linear relation between T_1 and $(T_2 + T_3)$ and this indeed is the case (Figure 2).

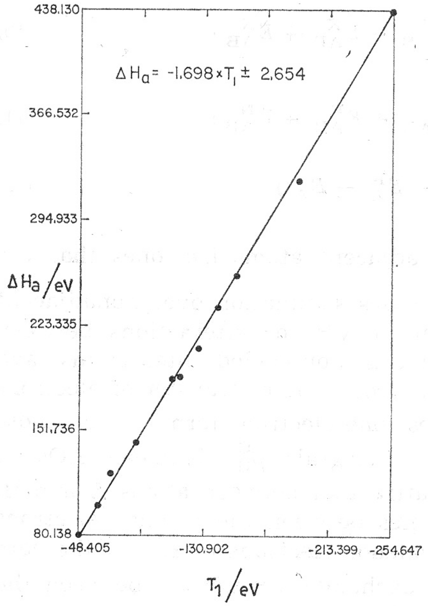

Fig. 1

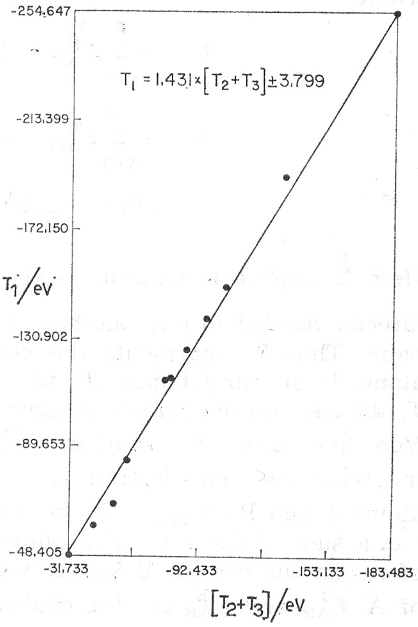

Fig. 2

There is, however, a complication. Although the plots in Figures 1 and 2 look nicely linear, the standard deviations of the points for the best straight lines are in fact very large in a chemical sense (SD for ΔH_a, 2.65 eV; SD for T_1, 3.80 eV). Since MINDO/3 gives heats of atomization that are usually correct to 0.3 eV, it is clear that there must be a remarkable cancellation of the deviations of T_1 with those of $(T_1 + T_3)$.

A further curious point is that the success of the MOA method indicates that ΔH_a is linearly related to the bond overlap integrals. Now according to the Mulliken approximation used in MINDO/3, these in turn are proportional to the one-electron core resonance integrals. It follows that ΔH_a is linearly related not to T_1 but to the one-electron terms in T_1. The deviations form linearity in Figure 1 are due to fluctuations in the two-center terms in T_1 which cancel with analogous fluctuations in $(T_2 + T_3)$.

This of course is in full agreement with the deduction by Ruedenberg that chemical bonding is essentially a function of the one-electron exchange terms. Our analysis suggests a further refinement of this picture. If atoms behaved classically, chemical bonding would be virtually nonexistent. The electron distribution in a set of isolated atoms is such as to minimize their total energy. When the atoms come together, the resulting change in energy can be dissected into a »classical« part corresponding to timple electrostatic interactions and a »nonclassical« part corresponding to the interference effects of orbitals that lead to changes in the one-electron terms. Since the overall change in energy of a set of atoms on combination to form a molecule is only a small fraction of the total energy, the peturbation involved is quite small. Since the classical electrostatic interactions should have a first order effect on the electron distribution but only a second order effect on the energy, their overall contribution to the latter should be small. If, however, we dissect this contribution into individual one-center and two-center interactions, the latter may well be large since they depend on local changes in electron distribution. If added together, however, they must nearly cancel. Thus we can relate bonding energy to the one-electron two-center terms only, *i. e.* those involving the core resonance integrals β_{ij}^{C} , or to the total energy, including all terms, but we cannot relate it to any intermediate dissection. This is probably why the Extended Hückel (Wolfberg-Helmholz) method gives such poor results. In it one tries to identify bonding with a combination of one-center terms and two-center exchange terms. As Figures 1 and 2 indicate, hybrid treatments of this kind may well give results that show general lienar correlations with experiment but they cannot be expected to give quantitative results with chemical accuracy.

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SAŽETAK

Aditivnost energija kemijskih veza u svjetlu aproksimacije maksimalnog prekrivanja i MINDO/3 metode

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Metodom maksimalnog prekrivanja izračunane su topline atomizacije jedanaest karakterističnih ugljikovodika. Postignuto slaganje s eksperimentom prilično je dobro. Rezultati su analizirani i uspoređeni s MINDO/3-računima koji su izvedeni za iste molekule.

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