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Relationship between valency and heat of atomisation of molecules

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Abstract. A numerical correlation between quantum-chemically calculated bond valency and experimental heat of atomisation of molecules is reported. It is shown that bond valency is a reliable measure of bond multiplicity in a variety of molecules including cases where these are ambiguous classically.

Keywords. Bond valency; heat of atomisation; bond multiplicity.

1. Introduction

Valency V_A of an atom in a molecule has been defined quantum-chemically (Armstrong *et al* 1973; Semenov 1980; Gopinathan and Jug 1983) as,

$$V_A = \sum_{B \neq A} V_{AB} = \sum_{B \neq A} \sum_{a}^{A} \sum_{b}^{B} P_{ab}^2, \tag{1}$$

where P_{ab} is the orthogonalised density matrix between atomic orbitals a on atom A and b on atom B and V_{AB} is the bond valency between atoms A and B. Various structural applications of this valency definition studied in recent years (Gopinathan *et al* 1986; Jug *et al* 1986; Siddarth and Gopinathan 1986, 1987, 1988) indicate that valency and molecular energy may be closely related. Establishing an analytical relation between valency and energy is difficult, since the functional dependence of energy on density is as yet undetermined (Bamzai and Deb 1981). In this paper, we attempt a numerical correlation between bond valency as defined by (1) and the experimental heat of atomisation of molecules.

2. Formalism

The bond valencies V_{AB} in a number of diatomic and polyatomic molecules calculated at their STO–3G optimised geometries using Lowdin-orthogonalised wavefunctions are given in table 1. For open shell systems, unrestricted Hartree–Fock formalism was used (table 1). The conventional single bonds in H_2, Li_2, F_2, LiH, HF, H_2O, NH_3, and CH_4 all have bond valencies equal to or close to 1; while the double bonds in CO_2, HCHO and C_2H_4 and the triple bonds in HCN and C_2H_2 have valency values close to 2 and 3 respectively. The present bond valencies therefore constitute a reliable measure

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Table 1. Bond valencies in diatomic and ployatomic molecules.

Molecule/bond	Bond valency[b]	Molecule/bond	Bond valency[a]
$H_2(^1\Sigma_g^+)$	1·000	$H_2O(^1A_1)$(O–H)	0·986
		(H–H)	0·000
$Li_2(^1\Sigma_g^+)$	0·990	$NH_3(^1A_1)$(N–H)	0·988
		(H–H)	0·003
$B_2(^1\Sigma_g^-)$	1·801 (1·301, 0·500)	$CH_4(^1A_1)$(C–H)	1·002
		(H–H)	0·000
$C_2(^1\Sigma_g^+)$	2·252 (1·002, 1·250)	$C_2H_6(^1A_g)$(C–C)	1·020
		(C–H)	0·994
		(H–H)	0·001
$N_2(^1\Sigma_g^+)$	3·000 (1·000, 2·000)	$C_2H_4(^1A_g)$(C–C)	2·004 (1·001, 1·003)
		(C–H)	0·992
		(H–H)	0·000
$O_2(^3\Sigma_g^-)$	1·499 (1·000, 0·499)	$C_2H_2(^1\Sigma_g^+)$(C–C)	2·995 (0·997, 1·998)
		(C–H)	0·984
		(H–H)	0·000
$F_2(^1\Sigma_g^+)$	9·989	$CO_2(^1\Sigma_g^+)$(C–O)	2·995 (1·001, 0·994)
		(O–O)	0·225
$LiH(^1\Sigma^+)$	1·000	$HCHO(^1A_1)$(C–O)	2·022 (0·995, 1·027)
		(C–H)	0·957
		(O–H)	0·004
$BH(^1\Sigma^+)$	0·986	$HCN(^1\Sigma^+)$(C–N)	3·005 (0·994, 2·011)
		(C–H)	0·984
$CH(^2\pi)$	1·000	$H_2S(^1A_1)$(S–H)	0·995
		(H–H)	0·000
$NH(^3\Sigma)$	0·972	$PH_3(^1A_1)$(P–H)	0·984
		(H–H)	0·002
$OH(^2\pi)$	0·993		
$FH(^1\Sigma^+)$	0·997		
$ClH(^1\Sigma^+)$	0·998		
$LiF(^1\Sigma^+)$	1·536 (0·576, 0·960)		
$BF(^1\Sigma^+)$	1·566 (0·757, 0·809)		
$CF(^2\pi)$	1·118 (0·902, 0·216)		
$CO(^1\Sigma^+)$	2·572 (0·950, 1·622)		
$NO(^2\pi)$	1·559 (0·977, 0·582)		

[a] Values in parentheses give the σ and π contributions respectively for multiple bonds.

of bond multiplicity. It may also be noted that for compounds like C_2, CO, NO, BF and CF for which bond multiplicities are ambiguous classically, it is now possible to determine the bond valencies. Further in table 1, we have also given the valencies between nonbonded atoms. These are generally small, of the order of 0·002, except in the case of CO_2 where the O–O valency is 0·225.

The valency for multiple bonds can be broken into σ and π contributions as

$$V_{AB} = V^{\sigma}_{AB} + V^{\pi}_{AB}, \tag{2}$$

with

$$V^{\sigma}_{AB} = \sum_{a}^{\sigma A} \sum_{b}^{\sigma B} P^2_{ab},$$

where the summation is over only the σ orbitals of A and B. A similar expression holds for V^{π}_{AB}. These σ and π contributions to multiple bonds are also indicated in table 1.

A relation between bond valency V_{AB} and bond energy E_{AB} may be established by the following qualitative arguments.

In the context of the zero differential overlap theories (Pople and Beveridge 1970), the resonance integral β_{AB} is related to the overlap integral S_{AB} through the "core integrals" U_{AA} and U_{BB} as

$$\beta_{AB} = K[(U_{AA} + U_{BB})/2]S_{AB}, \tag{3}$$

where K is a proportionality constant (Wolfsberg and Helmholz 1952). It is customary (Pople and Segal 1966) to obtain the core integrals U from the electronegativities χ.

The resonance integral β_{AB} is a measure of the lowering of the energy when two atomic orbitals on A and B combine to form a bonding molecular orbital. For example, in a Hückel type of theory, it is easy to show that for a homonuclear diatomic molecule, the lowering of energy is given by β. Therefore, in analogy with (3), we propose that the bond energy E_{AB} and the bond valency V_{AB} can be related as

$$E_{AB} = k[(\chi_A + \chi_B)/2]V_{AB} + l, \tag{4}$$

with parameters k and l. Here, S_{AB} in (3) has been replaced by the bond valency V_{AB}, since the latter is a good measure of the bond multiplicity.

Generalising (4) to polyatomic molecules with more than one bond, we have

$$E = \sum_{A-B}^{\text{bond pairs}} E_{AB} = k \sum_{A-B}^{\text{bond pairs}} [(\chi_A + \chi_B)/2]V_{AB} + L \tag{5}$$

where the energies of all the bonds in the molecule are added up to give the atomisation energy E of the molecule. In writing (5), we have assumed that k is a universal constant applicable to all bonds. We have also neglected the nonbonded valencies which are in any case small. This is also in the spirit of the assumption in thermochemical studies that the heat of atomisation is given by the sum of the bond energies alone.

In multiply bonded systems, the electronegativities for the σ orbitals are considerably larger than that for the π orbitals (Hinze and Jaffe 1962). Hence using (2), (5) may be written more generally as

$$\begin{aligned} E &= k \sum_{A-B}^{\text{bond}} \{V^{\sigma}_{AB}[(\chi^{\sigma}_A + \chi^{\sigma}_B)/2] + V^{\pi}_{AB}[(\chi^{\pi}_A + \chi^{\pi}_B)/2]\} + L \\ &= kE' + L \end{aligned} \tag{6}$$

where E' is the energy quantity obtained by the summation.

E given by (6) provides in principle a theoretical estimate of the experimental heat of atomisation of the molecule ΔH_a. Therefore, identifying E with ΔH_a, we can write (6) as

$$\Delta H_a = kE' + L. \tag{7}$$

3. Results and discussion

Presently, we have calculated E' values for a number of diatomic and polyatomic molecules from the STO–3G bond valencies and the electronegativity values of Hinze and Jaffe (1962). For hydrocarbons and other molecules where hybridisation is of importance, the appropriate orbital electronegativities have been used. The calculated values of E' are then plotted against the literature values of ΔH_a (Weast and Astle 1979) in figure 1 for the molecules listed in table 1. A remarkable linear correlation, with a correlation coefficient of 0·981 and a mean deviation of 1·0 eV is obtained indicating that the assumptions underlying the derivation of (7) are indeed valid. The straight line in figure 1 corresponds to the values $k = 0{\cdot}257$ and $L = 0{\cdot}44$ eV.

It is noted from figure 1 that the largest deviation to the correlation between E' and ΔH_a occurs for F_2. The exceptional behaviour of F_2 may perhaps be attributed to the relatively large number of pairwise interactions between nonbonded (lone pair) electrons, which makes the heat of atomisation considerably lower than that estimated by (7). We recall that (7) was based on qualitative reasoning of the Hückel type which does not explicitly consider electron–electron repulsion. For the same reason, (7) may not be valid for systems with multiple-bonded O and N atoms.

It is important to note that figure 1 also includes eight molecules namely B_2, C_2, O_2, LiF, BF, CF, CO and NO for which bond multiplicities are ambiguous classically. However, for these molecules, one may assign a bond number N_{AB} from conventional

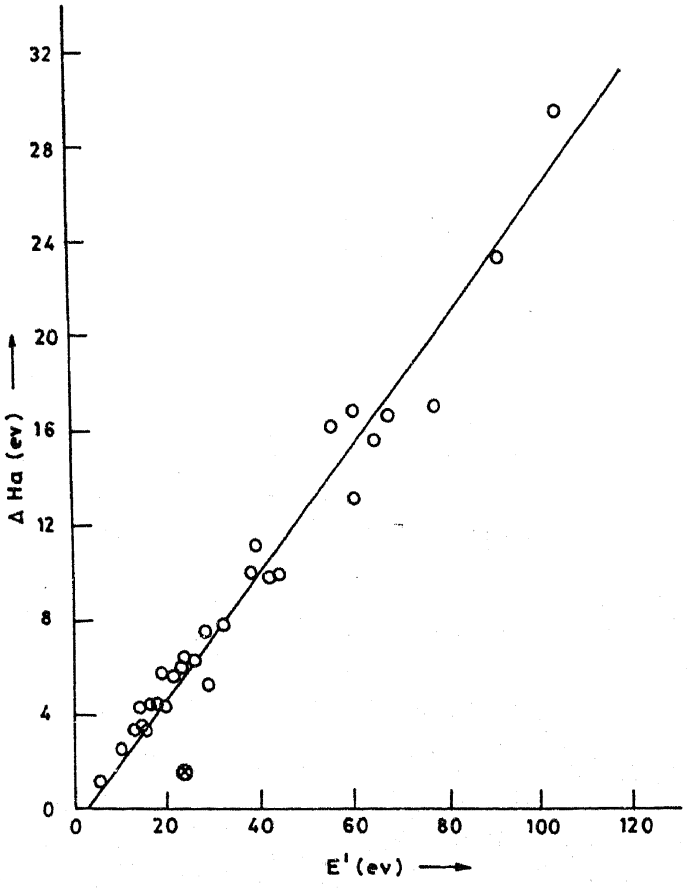

Figure 1. Linear correlation between theoretical energy E' and experimental heat of atomisation ΔH_a for molecules listed in table 1. ⊗ denotes F_2.

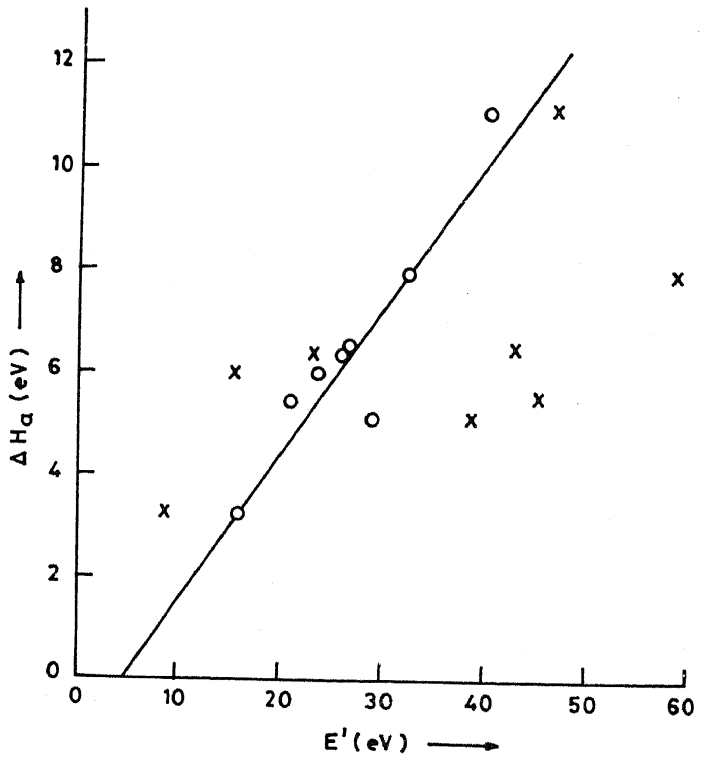

Figure 2. Linear correlation between E' and ΔH_a (O——O) for the molecules B_2, C_2, O_2, LiF, BF, CF, CO and NO using V_{AB}; crosses (×) indicate the E' values evaluated using N_{AB} (see text) instead of V_{AB} in (6) for the same systems.

MO diagrams, N_{AB} being defined as one-half the excess number of bonding electrons over antibonding electrons (McWeeny 1979). Using N_{AB} instead of V_{AB} in (6) leads to a significantly poorer correlation between E' and ΔH_a, as is seen from figure 2. Thus it is clear that the present definition of bond valency is a reliable measure of covalent bond multiplicity. Indeed, the previously reported successful application of bond valency to estimate bond strain quantitatively (Siddarth and Gopinathan 1986) is also a reflection of this property.

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