The quantum chemistry of valency

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Abstract. It is shown that the chemist's concept of valency can be put in quantum mechanical language. Such a quantification of valency opens up possibilities of new applications which are briefly reviewed. Valency is related to the equilibrium geometry of the molecule through a maximum valency principle. This principle, combined with the idea of molecular orbital valencies, provides a theoretical foundation for the well known Walsh diagrams. Valency can be used as an index of chemical reactivity and valency changes in a reaction can be used to determine the radical nature of intermediates and transition states as well as to indicate the allowed or forbidden nature of reaction paths. Molecular strain may be related to the loss of sigma valency.

Keywords. Valency; maximum valency principle; molecular orbital valency; Walsh diagrams.

1. Introduction

Most theoretical concepts of chemists, like the chemical bond, atomic charge in a molecule, valency, inductive effect and molecular strain, to name only a few, have at best a qualitative basis. The development of quantum chemistry has helped in the quantification of such concepts even though the situation is still far from satisfactory. In this article the highlights of a quantum mechanical treatment of the classical concept of valency attempted by the author's research group is presented. In particular the following topics are discussed:

(a) The quantum chemical definition of valency and its mathematical properties are presented in §2.
(b) A 'maximum valency principle' proposed by us recently is discussed, according to which the molecular valency is a maximum at the equilibrium geometry (§3).
(c) The idea of a valency for each molecular orbital is introduced. This molecular orbital valency is shown to be a measure of the bonding nature of the molecular orbital (§4).
(d) In §5 we show that the molecular orbital valency can, as a consequence of the maximum valency principle, serve as a quantitative ordinate for Walsh diagrams.
(e) Valency can also serve as an index of chemical reactivity. It can be used to determine the radical/biradical nature of species. Molecular orbital valency changes in a reaction reflect the allowed or forbidden nature of the reaction path (§6).
(f) Molecular strain can be quantitatively related to the loss of sigma valency in strained systems (§7).

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2. Definition and properties of valency

A quantum chemical definition of valency (Armstrong *et al* 1973; Semenov 1980; Gopinathan and Jug 1983; Jug 1984; Mayer 1985; Natiello *et al* 1985) should desirably have the classical attributes of valency: (a) its value should be close to traditional integer values like 1 for H, 3 for N and 4 for C, (b) it should have a maximum corresponding to the idea of saturation of valency, and (c) it should be a measure of the degree of electron sharing between atoms in a molecule. It has been shown (Gopinathan and Jug 1983) that these properties are satisfied by the following definition of valency:

Valency V_A of atom A is defined as:

$$V_A^{(GJ)} = \sum_a^A \sum_A \sum_b^B p_{ab}^2,$$

(1)

where P_{ab} is the first order density matrix element between orbital a on atom A and orbital b on atom B. This form of the definition is valid when the basis set orbitals are orthogonal. It can also be defined in a non-orthogonal basis (Mayer 1985; Natiello *et al* 1985). However, it must be realised that definitions of atomic valency in non-orthogonal or different orthogonal bases, even though all formally equivalent, can be numerically different (M S Gopinathan and P Siddarth, unpublished results). This arbitrariness is perhaps unavoidable in any scheme that partitions charge density or its functions into atomic contributions as (1) does. For example, the valency of He in the two-electron system HeH^+ for various types of wavefunctions are (M S Gopinathan and P Siddarth, unpublished results):

(1) 0·719 for non-orthogonal STO-3G functions
(2) 0·223 for cannonically orthogonalised STO-3G functions
(3) 0·329 for Schmidt orthogonalised STO-3G functions and
(4) 0·776 for Löwdin orthogonalised STO-3G functions.

Arguments can be made (M S Gopinathan and P Siddarth, unpublished results) in favour of using the Löwdin orthogonalised wave functions.

Definition of valency for open shell molecules has been controversial (Mayer 1985). We have used (1) for open shell systems also, with $p_{ab} = p_{ab}^\alpha + p_{ab}^\beta$ where p_{ab}^α is the density matrix element for α electrons. Two alternate definitions for open shell systems have been proposed. Thus, Semenov (1980) defines valency as:

$$V_A^{(S)} = \sum_a^A \sum_{B \neq A} \sum_b^B p_{ab}^2 + Q_{ab}^2,$$

(2)

whereas Mayer (1985) and Natiello *et al* (1985) define it as:

$$V_A^{(M)} = 2\sum_a^A p_{aa} - \sum_{a,a1}^A p_{aa1}^2,$$

(3)

where Σ_a^A means summation over orbitals a on atom A.

Definitions (1) to (3) can be related to the trace of the matrix P^2 which contains all electron-sharing terms, i.e. terms quadratic in bond order. It is then possible to show (M S Gopinathan and P Siddarth, unpublished results) that (a) definition (1) which we have employed in all our studies include all interatomic terms in trP^2, as it should, since valency measures the extent of electron sharing between atoms, (b) definition (2) implicitly involves the assumption that $2p_{ab}^\alpha p_{ab}^\beta = p_{ab}^{\alpha2} + p_{ab}^{\beta2}$ which is true only for the

closed shell case, and (c) definition includes the number of unpaired electrons on the atom as contributing to valency. A consequence of this is that Mayer's definition (3) gives, for instance, valencies of 3, 4 and 4 for CH_2, CH_3 and CH_4 species, respectively, whereas our definition (1) would give the values 2, 3 and 4. The latter set of values are closer to the chemist's view and more useful from the point of view of the application of valency as will be evident from the following sections. It may be noted that all three definitions reduce to the same form as (1) for closed shell systems.

For a given definition, valency values are not sensitive to the quality of the wave function at the minimal basis set level. Table 1 shows that valency values obtained using semiempirical and *ab initio* wave functions are very similar. These values are close to the classical integer values in most cases.

Further properties of valency established (Gopinathan and Jug 1983, p. 497) are the

Table 1. Comparison of valency values obtained from different wavefunctions.

Molecule		SINDO[a]	STO-3G[b]	STO-6G[b]
Li_2		1·000	1·007	1·007
N_2		3·000	3·000	3·000
LiH				
	Li	0·919	1·000	1·000
	H	0·919	1·000	1·000
HF				
	H	0·930	0·977	0·974
	F	0·930	0·977	0·974
CO				
	C	2·57	2·613	2·605
	O	2·57	2·613	2·605
H_2O				
	H	0·980	0·983	0·981
	O	1·960	1·967	1·963
NH_3				
	H	0·990	0·989	0·988
	N	2·970	2·967	2·964
HCN				
	H	0·960	0·990	0·990
	C	3·960	3·984	3·983
	N	3·000	3·014	3·014
CO_2				
	C	3·740	3·966	3·964
	O	2·130	2·391	2·388
HCHO				
	H	0·890	0·999	0·999
	C	3·910	3·966	3·964
	O	2·130	2·153	2·150
CH_4				
	H	1·000	0·998	0·999
	C	4·000	3·993	3·992

[a] values from Gopinathan and Jug 1983; [b] values from Ravimohan (1984)
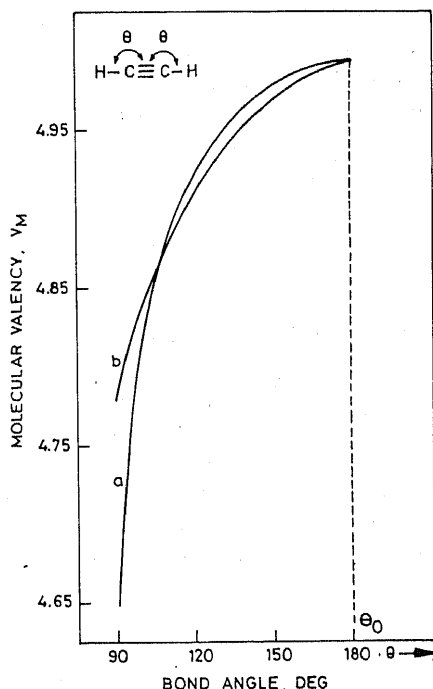
Figure 2. Illustration of the maximum valency principle. Plot of molecular valency in acetylene for (a) symmetric *cis* variation of the HCC angle, and (b) symmetric *trans* variation of the HCC angle.

trans distortions. Clearly in these cases V_M attains its maximum at the equilibrium bond angle. Studies on a variety of molecules have shown (Gopinathan *et al* 1986; Ravimohan 1984) the general validity of the maximum valency principle. However the principle has not been established analytically and efforts are under way towards this end. An important application of the maximum valency principle is that it provides a quantitative ordinate for the famous Walsh diagrams as we describe in §5 below.

4. Molecular orbital valency

The molecular valency defined by (5) can be decomposed into its molecular orbital (MO) components as (Gopinathan *et al* 1986; Ravimohan 1984):

$$V_M = \sum_i^{mo} v_i,$$

with

$$v_i = \tfrac{1}{2} \sum_A^A \sum_a \sum_{B \neq A}^B \sum_b^{mo} \sum_j n_i n_j \, C_{ia} C_{ib} C_{ja} C_{jb},$$

(6)

where n_i is the occupancy of the ith MO, c_{ia} the coefficient of the ath atomic orbital in the ith MO. We call v_i the molecular orbital valency of the ith MO. v_i measures the extent of

sharing of the n_i electrons (1 or 2) in the ith MO among the various atoms. It can therefore be expected that v_i will be zero for atomic core MO and lone pair MO, close to unity for strongly bonding MO and will have much smaller values for 'nonbonding' and 'antibonding' MO. Extensive comparison (Gopinathan et al 1986) of MO valencies with ESCA spectral information as well as Mulliken overlap population analysis bears this out. Table 2 gives some typical results. The MO valency is thus indeed a quantitative measure of the bonding power of the MO and it can be reliably used for assignment of peaks in the experimental ESCA spectra of molecules.

5.   MO valency as ordinate of Walsh diagrams

Walsh diagrams (Mulliken 1942; Walsh 1953; Coulson and Deb 1971; Stenkamp and Davidson 1973; Buenker and Peyerimhoff 1974) are correlation diagrams of molecular orbital 'binding energies' with molecular geometry. These diagrams have traditionally been used very successfully to explain the shape of molecules. However, Walsh did not define 'binding energies'—the ordinate of the diagram—and his diagrams were drawn based on qualitative arguments regarding atomic overlaps and their relation to MO

Table 2. Molecular orbital valency (STO-3G results).

Molecule	MO(i)	MO valency v_i	Bonding character of MO[*][†] from v_i	from ESCA
N_2	$1\sigma_g$	0·004	n	
	$1\sigma_u$	0·000	n	
	$2\sigma_g$	0·849	s	
	$2\sigma_u$	0·000	n	n
	$1\pi_u$	1·000	s	s
	$3\sigma_g$	0·146	w	w
F_2	$1\sigma_g$	0·000	n	
	$1\sigma_u$	0·000	n	
	$2\sigma_g$	0·140	w	
	$2\sigma_u$	0·000	n	
	$1\pi_u$	0·000	n	b(?)
	$3\sigma_g$	0·859	s	
	$1\pi_g$	0·000	n	a
CO	1σ	0·001	n	
	2σ	0·001	n	
	3σ	0·732	s	
	4σ	0·123	w	w
	1π	0·829	s	s
	5σ	0·096	n(w)	n
CH_4	$1a_1$	0·002	n	
	$1t_2$	1·020	s	s
	$2a_1$	0·990	s	s

[*] n = nonbonding; a = antibonding; b = moderately   bonding; s = strongly bonding. Note that v_i cannot distinguish between a and n since it is always positive.
[†] For reference to ESCA spectral data and for detailed comments on them see Gopinathan et al 1986.

binding energies. Several attempts have been made in the past to formulate a precise theoretical ordinate for these diagrams. Quantities such as MO eigenvalues (Buenker and Peyerimhoff 1974) or their variants (Stenkamp and Davidson 1973) and MO forces (Coulson and Deb 1971) have been tried, but these attempts have only been partially successful. An MO quantity to be successful as the ordinate should have the following properties. It should be a quantitative measure of the bonding power of the MO. Its sum over all occupied MO should yield a molecular quantity that has the extremum value at the equilibrium geometry.

Molecular orbital valency introduced in the previous section satisfies these two requirements. We have seen that MO valency is a quantitative measure of the bonding power of the MO. Further the MO valencies exactly add up to the molecular valency which is a maximum at the equilibrium geometry according to the maximum valency principle. Hence MO valency should serve as the ordinate of Walsh diagrams. This expectation is indeed fulfilled and we have shown that MO valency as the ordinate reproduce the Walsh diagrams quite successfully for several molecules (Gopinathan *et al* 1986; Ravimohan 1984). Figure 3 gives a comparison of the original Walsh diagram and the MO valency diagram for H_2O. In addition to reproducing the qualitative features of the Walsh diagrams, our MO valency diagrams do predict the geometry exactly unlike the original Walsh diagrams. For example, the original Walsh diagram for H_2O predicts a bond angle much less than 90°, whereas the MO valency diagram predicts it as 105°.

A basic assumption in the construction of the original Walsh diagram is that the MO correlation diagrams are the same for a given molecular symmetry species, like AH_2 for instance, and that the features of the diagram are independent of the number of electrons or the state of ionisation of the molecule. We are currently examining the validity of this assumption for the MO valency diagrams.
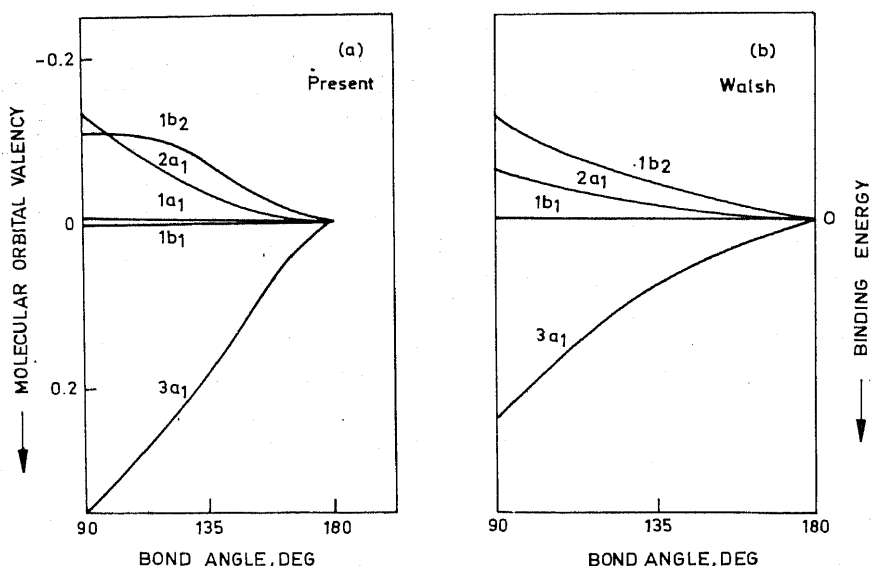

Figure 3. Comparison of the molecular orbital valency diagram (a) for H_2O with the general Walsh diagram, (b) for AH_2 systems.

6. Valency and chemical reactions

The valency concept can be used to determine the reactivity of atoms in a molecule, i.e. to measure the tendency of the atom to form further covalent bonds. The changes in valency of atoms in a chemical reaction can be used very convincingly to determine the radical nature of reaction intermediates and transition states and to predict the allowed or forbidden nature of reaction paths. A beginning has been made (Gopinathan and Jug 1983; Jug and Gopinathan 1986) towards such applications of valency and we merely cite some examples here.

As we saw in §2, computed valency values of atoms are scattered around classical integer values like 3 for N, 4 for C etc. We call these values the *normal* valencies and deviations from them as *free valencies*. That is,

$$F_A = V_A^{normal} - V_A^{actual} \tag{7}$$

If free valence F_A is positive, the atom is called *subvalent*, and if F_A is negative, the atom is termed *hypervalent*. Notice that the free valence of an isolated atom is equal to its normal valency. The reactivity of atoms in molecules can be rationalised by the hypothesis (Gopinathan and Jug 1983, p. 511) that atoms tend to reduce their subvalency or hypervalency, and thus revert to their normal valency by making new bonds or by weakening existing ones respectively. For example, O_2 with a subvalency of 25 % is highly reactive while N_2 with zero free valency is unreactive. In CO, C is subvalent (36 %) and hence reactive, while O with F value of -29 % is hypervalent and hence 'antireactive', i.e. it tends to weaken its existing bonds. This is borne out by the tendency of CO to form metal carbonyls by binding through C.

The course of concerted reactions can be predicted by computing the valency reduction for the transition state. For example (Jug and Gopinathan 1985) in the cyclobutene → butadiene reaction, the Woodward-Hoffmann-allowed conrotatory transition state has a reduction of 0·10 in molecular valency whereas the forbidden disrotatory transition state has a reduction of about 2 units of valency. Generally the path with the minimum reduction in valency is the preferred one. The valency reduction can also be used profitably to determine the radical, biradical or zwitterion nature of transition states and intermediates. The valency method has some advantages (Jug and Gopinathan 1985) over other methods for the determination of radical nature such as the method of Salem and Röwland (1972) based on singlet-triplet energy difference and the method of Döhnert and Koutecky (1980) based on natural orbital occupancies.

Correlation diagrams of the Woodward-Hoffmann type but employing the molecular orbital valency as the ordinate instead of energy, can be constructed (Siddarth 1984) to display the allowed and forbidden paths of concerted reactions. For instance, figure 4 shows the variation of the homo valency for the conrotatory and disrotatory cyclisation of butadiene to cyclobutene. Clearly, for the forbidden disrotatory path there is drastic reduction in homovalency, whereas for the allowed path the mo valency change is insignificant. Application of this concept to other chemical reactions is now under study.

7. Valency and molecular strain

Molecular strain has been attributed to the bent nature of bonds (Coulson and Moffitt (1949)). Therefore we can expect strain to be related to the reduction in valency of bent
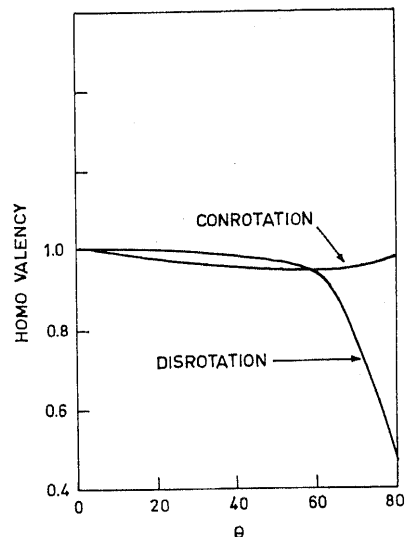
Figure 4. Variation of HOMO valency for the forbidden disrotatory and for the allowed conrotatory cyclisation of butadiene to cyclobutene.

bonds. A bent bond can be considered as consisting of a σ and a π component. The reduction in σ valency in a bent bond compared to that in a strain free bond results in loss of binding energy. This is partly, but not fully, compensated for by the formation of the π component. The net loss in binding energy is the strain energy. We now illustrate this method. The total C–C valency in cyclopropane is 0·99 which can be decomposed into (M S Gopinathan and P Siddarth, unpublished results) a σ valency of 0·83 and a π valency of 0·16. We can view the situation as a loss of 0·17 (= 1 − 0·83) σ valency and a gain of 0·16 π valency, compared to a strain free C–C bond of σ valency 1 and π valency 0. Taking the binding energy of a σ C–C bond to be 85 k cal. mole^{-1} and that of a π C–C bond to be half of the σ bond (since σ and π overlap for carbon p orbitals are roughly in this ratio), we find that the loss in energy is $3 \times (0·17 \times 85 − 0·16 \times 85/2)$ = 23 k cal. mole^{-1}. This may be compared with the 'experimental' strain energy of 28 k cal. mole^{-1} for cyclopropane. Inclusion of 'strain' from the C–H bond, which in the present formalism means, a reduction in the valency of the bond compared to that in alkanes, improves the calculated strain close to 28 k cal mole^{-1}.

What is remarkable is that this rather crude approach to strain gives strain energies in surprising agreement with experimental estimates. For example (M S Gopinathan and P Siddarth, unpublished results) we have for cyclobutane 24 (27); cyclopentane 9 (7); cyclopropene 41 (54); cyclobutene 29 (31); cubane 176 (166); here the first quantity is the strain energy estimated from valency and that in paranthesis is the experimental value, all in k cal mole^{-1}.

Controversial issues such as whether strain is due to the bent nature of bonds, or due to nonbonded C–C repulsions (Wiberg *et al* 1976) due to H–H repulsions (Baud and Cessac 1977), can hopefully also be settled by studying the valency between nonbonded atoms in the strained molecules. Such detailed studies remain to be undertaken.

8. Conclusions

The classical concept of chemical valency can be translated into quantum mechanical language and quantified. This results in a deeper understanding of the fundamental role valency plays in chemical phenomena. We have shown that apart from being a measure of the degree of electron sharing between atoms, which has been its meaning classically, valency determines the shape of molecules through the maximum valency principle; it affords a quantitative measure of the bonding nature of molecular orbitals; it provides the quantitative ordinate for the Walsh diagrams; it can be used: as an index of the chemical reactivity of atoms and of their radical and diradical nature in reactions; to construct correlation diagrams which exhibit the allowed or forbidden nature of reaction paths; and, to estimate the values and to discuss the origin of molecular strain. These various avenues of applications of the valency concept which we have explored remain to be studied in more detail and hopefully new applications await discovery. It is indeed remarkable that the intuitive concept of chemists when quantified and put in a quantum chemical language can go a long way in our understanding of the structure and behaviour of molecules.

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