Bond Indices and Valency

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Theory is developed to enable the density matrix results of CNDO self-consistent field molecular orbital calculations to be correlated with chemists' ideas of ' valency. ' Both the valencies of atoms and the anisotropy of an atom in a given environment are derived quantitatively. Examples chosen from carbon, nitrogen, and borane chemistry yield results which are gratifyingly consistent with the chemistry of the system.

In the classical theory of valency, covalence is considered to stem from the sharing of pairs of electrons between atoms, which idea leads naturally to the assignment of integral ' valency ' numbers to atoms, *e.g.*, three for boron and four for carbon.

During the last decade, however, a different view has emerged and this is because new molecular orbital calculations, involving all valence electrons and unrestricted by geometry, have been performed. In these calculations the interactions between all orbitals on all atoms of the molecule have been explicitly included and have been used to construct the spinless electron density matrix for the molecule. A detailed picture of the make-up of all the bonds in the molecule is thereby obtained.

Two features which forcibly emerge are (*a*) interactions, and consequently bond orders, occur between what, in the simple approach, were considered as ' non-bonded ' atoms; (*b*) the individual orbital–orbital bond orders are not usually either integral or associated with a pair of electrons. Of course, neither of these points is completely new but the all-electron calculations carried out before 1960 were too limited in scope and number to bring the points home. The culmination of these ideas is that the concept of an integral number or valency for an atom tends to lose meaning. On the one hand, it seems nonsensical to assign a ' whole ' valency to a single, perhaps small, orbital–orbital bond order (which, moreover, would lead to a wide range of ' valencies ' for atoms with even the simplest chemical behaviour!). On the other hand, such an interaction cannot simply be ignored, as an important chemical or physical consequence may follow from it.

A further difficulty is that frequently the number of electron pair bonds which are known to be equivalent in a given molecule does not correlate in any obvious way with the molecular orbital correlation diagram, *e.g.*, in borane[1] and methane the valence electron configurations $(a'_1)^2(e')^4$ and $(a_1)^2(t_1)^6$ respectively are associated with the three and four two-electron bonds in these molecules. However, a maximum of double- and triple-orbital degeneracy is allowed under the symmetry of these systems and, hence, the two-electron bonds in the molecules appear inequivalent.

In recent years, as a consequence of these kinds of difficulties, the concept of valence has tended to lose ground somewhat. This is truly a pity, since the assumption of the fixed number four for the valency of carbon has undeniably proved an extremely useful tool. Indeed, any theory of real value ought surely to recover, substantiate, and extend such a simple rule. There is clearly, therefore, an urgent need to synthesise and interpret the density matrix results obtained from detailed molecular orbital calculations, so as to generate a simple interpretation of bonding and ' valence.' With this in mind, we have extended the ideas of bond indices suggested by Salem[2] and Wiberg[3] to apply to any chosen atom. Using the new derivation, in the context of the usual limited basis CNDO-based methods, we find that from molecular orbital results we are able to define meaningful ' valencies ' and in ' normal ' compounds such as CH_4, carbon has a ' valency ' of four and hydrogen one. However, in other molecules the ' valency ' deviates from a simple integral number and this can provide a valuable index to the likely reactivity of that particular element in the molecular situation.

THEORY

Atomic Bond Index.—Given an orthonormal matrix of eigenvectors **C** we can construct the density matrix **P**, whose elements are given by equation (1). The sum is

$$P_{\lambda\sigma} = 2\sum_i C_{i\lambda}C_{i\sigma} \tag{1}$$

over all occupied orbitals.

As the eigenvectors are orthogonal, **P** is duodempotent, *i.e.*,

$$2\mathbf{P} = 4\mathbf{C}\mathbf{C}^\dagger = 4\mathbf{C}(\mathbf{C}^\dagger\mathbf{C})\mathbf{C}^\dagger = \mathbf{P}^2 \tag{2}$$

thus

$$2P_{\lambda\lambda} = \sum_\sigma P_{\lambda\sigma}^2 \tag{3}$$

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[1] D. R. Armstrong and P. G. Perkins, *J. Chem. Soc.* (*A*), 1969, 1044.

[2] L. Salem, 'Molecular Orbital Theory of Conjugated Systems,' Benjamin, New York, 1966, p. 39.

[3] K. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

This equation has previously been used in the context of π-bond indices by Salem [2] and by Wiberg.[3]

If we now extend the concept and consider its application to atoms, we can define the quantities V_{A}', an atomic bonding index, and B_{AB}, which are related by equation (6).

$$V_{\mathrm{A}}' = \sum_{\text{all } \lambda \text{ on A}} 2P_{\lambda\lambda} \tag{4}$$

$$B_{\mathrm{AB}} = \sum_{\text{all } \lambda \text{ on A}} \; \sum_{\text{all } \sigma \text{ on B}} P_{\lambda\sigma}{}^2 \tag{5}$$

$$\sum_{\mathrm{B}} B_{\mathrm{AB}} = V_{\mathrm{A}}' \tag{6}$$

But the definition of V_{A}' contains redundant terms which describe the bonding of atom A with itself. Hence, from V_{A}' we can subtract B_{AA}, giving equations (7) and (8). But the sum of all orbital densities on atom A is equal to P_{A}, hence equation (9). The quantities V_{A} and B_{AB} are rotationally invariant. By analogy with equation (6), we have equation (10). The quantity V_{A} is essentially the valency of the atom.

$$V_{\mathrm{A}} = V_{\mathrm{A}}' - B_{\mathrm{AA}} \tag{7}$$

$$V_{\mathrm{A}} = \sum_{\text{all } \lambda \text{ on A}} 2P_{\lambda\lambda} - \sum_{\text{all } \lambda \text{ on A}} \; \sum_{\text{all } \sigma \text{ on A}} P_{\lambda\sigma}{}^2 \tag{8}$$

$$V_{\mathrm{A}} = 2P_{\mathrm{A}} - \sum_{\lambda \text{ on A}} \; \sum_{\sigma \text{ on A}} P_{\lambda\sigma}{}^2 \tag{9}$$

$$\sum_{\mathrm{B} \neq \mathrm{A}} B_{\mathrm{AB}} = V_{\mathrm{A}} \tag{10}$$

Anisotropy.—An interesting extension of the idea is to consider the disposition of electron density in space around the atom in similar terms. Local anisotropy in the environment of atoms L_{A} can be represented by equation (11). This expression is derived in the Appendix.

$$L_{\mathrm{A}} = \sum_{\lambda \text{ on A}} \; \sum_{\sigma \text{ on A}} P_{\lambda\sigma}{}^2 - \sum_{l=0}^{k} \left(\sum_{\lambda = l^2 + 1}^{\lambda = (l+1)^2} P_{\lambda\lambda} \right)^2 \times \frac{1}{2l+1} \tag{11}$$

Thus, V_{A} can be dissected into two parts, one of which is the sum of all bonds to other atoms and the other is a measure of the anisotropy in the environment of the atom. This is a valuable addition to the theory, since the local anisotropy of the electron density round an atom enables assessment of the unshielding of the nucleus in any particular direction. Thus, we can associate the anisotropy term with the lability of an atom in a particular environment, and this is obviously important for detailed studies of reaction mechanisms. Now it follows that

$$\sum_{\mathrm{AB}} B_{\mathrm{AB}} = \sum_{\lambda\sigma} P_{\lambda\sigma}{}^2 = \mathrm{tr}\mathbf{P}^2 = \mathrm{tr}2\mathbf{P} = 2N \tag{12}$$

where N is the total number of electrons; B_{AB} can therefore be regarded as a measure of the total number of electrons in the bond between atoms A and B. Thus, by taking the summation over all AB we are counting all bonds twice. Hence, we can consider that the electrons in a molecule can be divided into those which are ' on the atoms ' and those ' in the bonds ' thus:

$$\text{Electrons on atoms} = \tfrac{1}{2}B_{\mathrm{AA}} = \tfrac{1}{2} \sum_{\substack{\lambda \text{ on A} \\ \sigma \text{ on A}}} P_{\lambda\sigma}{}^2 \tag{13}$$

$$\text{Electrons in bonds} = B_{\mathrm{AB}} = \sum_{\substack{\lambda \text{ on A} \\ \sigma \text{ on A}}} P_{\lambda\sigma}{}^2 \tag{14}$$

B_{AB} could be taken as a measure of the ' covalency ' of the bond AB; a ' purely ionic ' bond would have $B_{\mathrm{AB}} = 0$ and a purely ' covalent-two-electron-bond ' would have $B_{\mathrm{AB}} = 1$. In fact, for a homonuclear diatomic molecule, B_{AB} assumes integer values.

In the case of a molecule which has an open-shell ground state, then $\mathbf{P}^2 \neq \mathbf{2P}$ and $\sum_{\mathrm{B} \neq \mathrm{A}} B_{\mathrm{AB}} \neq V_{\mathrm{A}}$. In this case the quantity $V_{\mathrm{A}} - \sum_{\mathrm{B} \neq \mathrm{A}} B_{\mathrm{AB}}$ should be a measure of the reactivity of the atom.

Atom valency and anisotropy

	Valencies	Anisotropies	Degrees of bonding ' B_{AB} '
CH_4	C, 3·949; H, 0·997	C, 0·000	C–H, 0·987
C_2H_6	C, 3·972; H, 0·999	C, 0·001	C–C, 1·023; C–H, 0·981
C_2H_4	C, 3·993; H, 0·998	C, 0·012	C–C, 2·032; C–H, 0·979
C_2H_2	C, 3·961; H, 0·978	C, 0·071	C–C, 2·989; C–H, 0·964
HCHO	C, 3·982; O, 2·057	C, 0·163; O, 0·633	C–O, 1·997; C–H, 0·918
NH_3	N, 2·943; H, 0·991	N, 0·428	N–H, 0·981
BH_3	B, 2·982; H, 1·000	B, 0·765	B–H, 0·994
BCl_3	B, 3·419; Cl, 1·261	B, 0·015; Cl, 0·151	B–Cl, 1·140
$B_6H_6{}^{2-}$	B, 3·696; H, 0·989	B, 0·061	B–B, 0·681, B–H, 0·970
$B_{12}H_{12}{}^{2-}$	B, 3·668	B, 0·049	B–B, 0·538; B–H, 0·964
$B_{20}H_{20}{}^{4-}$	B, 3·815	B, 0·024	B–B, 0·675; B–H, 0·806
$B_6Cl_6{}^{2-}$	B, 3·659; Cl, 1·167	B, 0·082; Cl, 0·142	B–B, 0·625; B–Cl, 1·183
$B_{12}Cl_{12}{}^{2-}$	B, 3·663; Cl, 1·035	B, 0·025; Cl, 0·032	B–B, 0·528; B–Cl, 0·930

Examples.—For atoms in ' saturated ' compounds our derivation should, in general, yield integral values for the defined valencies: deviation of V_{A} from these, particularly to low values, should be indicative of reactivity. Bonding data are given in the Table for a series of ' normal ' and ' non-classical ' species. These data were derived from the full spinless density matrices for the systems which were, in turn, obtained from self-consistent field calculations [4] including all valence electrons and electronic interaction. Full analyses of

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[4] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S129; D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc.* (*A*), 1971, 3674.

the results for the cage boranes are to be published elsewhere.[5]

In all the carbon compounds this element exhibits a valency close to four, whilst in all these cases hydrogen has unit valency. The ' single,' ' double,' and ' triple ' nature of the C–C bonds in ethane, ethylene, and acetylene emerge in a way which shows gratifyingly well the consistency and applicability for carbon of simple valence ideas. The decrease in the degree of C–H bonding (B_{CH}) over the series CH_4, C_2H_6, C_2H_4, and C_2H_2 is interesting and could be related to the increasing ' acidic ' nature of the H atoms in the compounds. The anisotropies for the carbon atoms are small for all the hydrocarbons but the trend to greater values from methane to acetylene is significant and reflects on the increased reactivity of this atom over the series. In formaldehyde, carbon has a valency close to four and the oxygen atom is divalent. In keeping with this, the C–O link in this compound shows up as a ' double bond.' It will also be noticed that the anisotropy of both atoms is large. These observations are consistent with the known lability of the C–O group in this compound. It would be interesting to apply the analysis further to other aldehydes, in order to ascertain whether the calculated quantities can rationalise the known differences between the chemistry of formaldehyde and higher homologues in the series.

In ammonia the data are consistent with its chemistry, as here co-ordinate bond formation with acceptor moieties increases the valency of the nitrogen atom. The three N–H links in ammonia are ' single bonds ' and the valency of nitrogen is three, as expected. The anisotropy at this atom is seen to be large, and this is due essentially to the ' lone pair ' electrons.

Study of the series of boron compounds produces revealing results. In the borane, BH_3, the ' classical ' valency rules are upheld (valencies of boron and hydrogen are three and one respectively and each B–H bond is ' single '). A large anisotropy is found at the boron atom, however, and this fits well with the known facility of the compound for dimerisation. In boron trichloride, π-bonding between boron and chlorine markedly reduces the anisotropy (although some is transferred to chlorine). The B–Cl bond is multiple and the valency of boron becomes greater than three. This compound does not dimerise, although the valency of boron can be expanded to four in a well known series of co-ordination compounds.

The boron cage anions exhibit some interesting features. First, in all cases, the valency of boron is substantially greater than three whilst that of the terminal atoms (H or Cl) is in the region of one. This fits in with the general tendency of boron to expand its valency to four. Hence the view that the electron acceptor property of a boron atom is internally partially satisfied in cage boranes is valid and is borne out well by our calculations. These features, together with the generally low anisotropies and an even charge distribution on boron atoms in the cages help to account for the great thermal stability of these ions and their lack of reactivity towards reagents which are normally degrading.

The pentagonal dodecahedral anion $B_{20}H_{20}{}^{n-}$ is as yet unknown but it belongs to the icosahedral point group. Our calculation of the ground state indicates that the simplest closed-shell formulation yields $n = 4$, and it seems that it should fit into the general valence scheme for the other anions. However, preliminary calculations of the excited states [5] for this species indicates that the closed-shell formulation may not be the most stable and further study is being undertaken.

APPENDIX

Anisotropy.—Let an atom have valence atomic orbitals specified by angular quantum numbers $l = 0, \ldots k$; $k = 0$ for s only, 1 for s and p and 2 for s, p, and d. Now for each shell to have spherical symmetry in electron density, all orbitals in that shell must have equal occupancy. Furthermore, since the product of two shells is non-spherical, all off-diagonals of the density matrix for one atom between shells must be zero. A spherical atom having configuration $s^p p^q d^r$ would have

$$B_{AA} = p^2 + \frac{q^2}{3} + \frac{r^2}{5}$$

or, in general,

$$B_{AA} = \sum_{l=0}^{k} \left(\sum_{\lambda=l^2+1}^{(l+1)^2} P_{\lambda\lambda} \right)^2 \times \frac{1}{2l+1}$$

Any deviation of the atom from spherical symmetry will lower B_{AA}. Since, in general, the atoms are non-spherical,

$$B_{AA} = \sum_{\substack{\text{all } \lambda \text{ on A} \\ \text{all } \sigma \text{ on A}}} P_{\lambda\sigma}{}^2$$

and the difference is a measure of the anisotropy in electron distribution. Now, $L_A = B_{AA}$ (in molecule) $= B_{AA}$ (ideal), *i.e.*

$$L_A = \sum_{\substack{\text{all } \lambda \text{ on A} \\ \text{all } \sigma \text{ on A}}} P_{\lambda\sigma}{}^2 - \sum_{l=0}^{k} \left(\sum_{\lambda=l^2+1}^{(l+1)^2} P_{\lambda\lambda} \right)^2 \times \frac{1}{2l+1}$$

The larger the anisotropy L_A, the more labile we would expect an atom to be.

The derivation clearly applies only to cases where one principal quantum number is associated with each l number, *e.g.*, a configuration $2s^2,2p^3,3d^1$ is accounted for, but not $2s^2,2p^3,3s^1$.

We thank the S.R.C. for a Maintenance Grant to J. J. P. S.

[2/2139 *Received*, 13*th September*, 1972]

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[5] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1973, 627.