Valencies and Bond Indices for the Elements from Hydrogen to Chlorine

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Calculations, within the CNDO framework, have been performed on a wide range of molecules containing elements of the first and second rows of the Periodic Table. By use of the density matrix elements, the valencies of all the atoms are calculated and their significance is discussed. It is found that in many molecules the calculated valencies are essentially the same as the classical ones. Deviations from ' normal ' valencies are discussed in terms of the chemistry of the particular molecule. Anisotropies for some of the atoms and bond indices for the bonds in selected molecules are also calculated and are shown to correlate well with the electronic distribution.

THE concept of valency has, in the past, played a cogent role in the understanding of chemistry and has enabled chemists to bring order to the immense quantity of accumulated data on molecules. More recently, however, the concept of atomic valency defined as an integer denoting the ' bonding power ' of the atom has experienced difficulty. This is because it is difficult to assign a valency to an atom which is involved in ' partial ' bonding. A good example is furnished by the boron trihalides, where one's estimate of the valency of boron or halogen depends on the degree of delocalisation of the halogen π electrons, or, indeed, whether one counts such intramolecular ' dative' bonds at all. Other examples, even more difficult to resolve, abound. The partial demise of the valency concept has coincided with the emergence of molecular orbital theory as a potent tool for calculating the electronic structures of molecules drawn from all areas of chemistry. Now the ability of the theory to produce a good description of delocalised systems has proved to be of particular value and so, because of the above difficulties, it is natural to try to use the molecular orbital approach as the basis for a revised definition of valency. A new definition ought to recover the simple valency rules as well as rationalise adequately those cases where such simplicity is not forthcoming. We recently discussed [1] the problem in detail and suggested formulae to compute the valency of an atom in a molecule and some associated properties. We now present and discuss the results of calculations on a wide range of molecules containing first- and second-row elements. Using these results, we examine the use of the concepts of ' valency ' and ' bond index ' in interpreting the electronic structure of molecules.

METHODS, RESULTS, AND DISCUSSION

The calculations were performed within modifications of the usual CNDO–MO–SCF framework.[2] For all second-row elements, $3d$ orbitals were included in the basis set. The input parameters are all given in references 2 and 3 and the molecular geometries abstracted from standard compilations.[4] Where the bond lengths or geometries were not known, reasonable assumptions were made.

The element $P_{\lambda\sigma}$ of the density matrix $\boldsymbol{P}$ is given by equation (1) where $C_{i\lambda}$ is the coefficient of the atomic

$$P_{\lambda\sigma} = \sum_{i\ \text{occ.}} 2C_{i\lambda}C_{i\sigma} \qquad (1)$$

orbital λ of the occupied molecular orbital i. We define the valency (V_{A}) of an atom as [1] in equation (2) where

$$V_{\text{A}} = \sum_{\text{B}\neq\text{A}} \sum_{\lambda\ \text{on A}} \sum_{\sigma\ \text{on B}} P_{\lambda\sigma}{}^2 = \sum_{\text{B}\neq\text{A}} B_{\text{AB}} \qquad (2)$$

the B_{IJ} are bond indices. The latter quantities are extensions to those given by Salem [5] and Wiberg.[6]

Initially it is important to confirm that the above expression for valency affords sensible values for simple molecules which satisfy chemical intuition. Accordingly, the hydrides and fluorides of the elements of the first row of the Periodic Table were investigated. The calculated atomic valencies are presented in Table 1 and are seen to be very close to the classical integral value. It is, therefore, satisfying that our definition produces credible values.

TABLE 1

Valencies of the atoms in the hydrides and fluorides of the elements of the first row

	Fluoride	Hydride
Lithium	0·98	0·97
Beryllium	2·17	1·99
Boron	3·10	2·98
Carbon	3·76	3·95
Nitrogen	2·94	2·94
Oxygen	1·96	1·94
Fluorine	1·00	0·94

For a first-row element, s and p valency orbitals are readily available and four is the theoretical maximum valency. This, however, can only occur when each atomic orbital has an occupancy of precisely unity and the whole atom is isotropic. Since, in practice, these conditions are virtually unattainable even for carbon, the valency of the elements of the first row will always be less than four. For any first-row element with Q electrons

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[1] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, **1973**, 838.

[2] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc.* (*A*), 1971, 3674.

[3] K. A. Levison and P. G. Perkins, *Theoret. Chim. Acta*, 1969, **14**, 206.

[4] ' Tables of Interatomic Distances and Configuration in Molecules and Ions,' Chemical Society Special Publication No. 11, London, 1958.

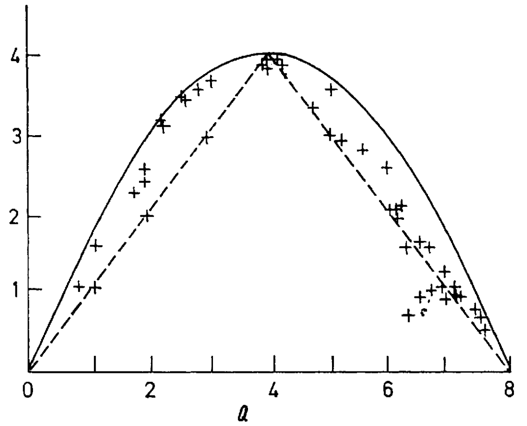
[5] L. Salem, ' Molecular Orbital Theory of Conjugated Systems,' Benjamin, New York, 1966, p. 39.

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

in the valence shell, the maximum valency, $V_{\text{max.}}$, possible for this element is given by equation (3). A graph of

$$V_{\text{max.}} = \left(2Q - \frac{Q^2}{4}\right) \qquad (3)$$

$V_{\text{max.}}$ against Q yields a parabola with a maximum at $Q = 4$ (Figure). The valencies expected from simple valence-bond arguments are found to be, in general, less than the calculated valencies whilst, by definition, the calculated valencies must lie on or inside the parabola. Exceptions to the former statement occur when Q lies between 6 and 7, *e.g.*, oxygen in the ions XO_m^{n-} where oxygen is highly anisotropic.



Relation between valency and number of outer-shell electrons: —— theoretical valency limit; ---- classical valency; + calculated valencies

First-row Atoms.—Valencies. Having established that the calculations afford sensible and meaningful results and having defined the effective limits for first-row valencies, we now proceed to investigate molecules containing first- and second-row atoms. This is so that we can start to build up an overall picture of valencies. In this section we deal with molecules from the former series. The systems were chosen to illustrate how aspects of the chemistry of the molecule can be correlated with the valencies, and associated properties, of constituent atoms. However, the data and discussion presented here are by no means exhaustive: we expect that the tables can be used much more extensively. We have selected aspects of chemistry which are of interest to us, *e.g.*, in the case of lithium, beryllium, and boron we are mainly concerned with the co-ordination compounds of these elements; whilst for the elements on the right-hand side of the Periodic Table, the chemistry of the XO_m^{n-} anions are of particular interest. Table 2 presents results for some familiar molecules and ions containing first-row elements.

Although in the hydrides of lithium, beryllium, and boron essentially the classical valencies are exhibited, formation of complexes is accompanied by an increase in valency for these atoms. A natural consequential question is: what is the highest valency that these atoms can attain? For boron and beryllium, the answer appears to be four (BH_4^-) and three [$(BeCl_2)_2$] respectively, whereas for lithium in the complex $(LiMe)_4$ the low value 1·6 is found. The comparatively small value for lithium reflects somewhat the inability of this element to act as

TABLE 2

Valencies and anisotropies in compounds of elements of the first row

Species	Valency	Anisotropy
	Lithium	
LiMe	1·22	0·12
$(LiMe)_4$	1·61	0·01
LiF_2^-	1·60	0·00
LiF_3^{2-}	1·83	0·01
Li_2	1·00	0·26
	Beryllium	
BeH_2	1·99	0·53
$BeMe_2$	2·58	0·08
$BeCl_2$	2·59	0·03
$(BeCl_2)_2$	2·66	0·02
BeO	2·41	0·01
	Boron	
BCl_3	3·42	0·01
BF_4^-	3·17	0·00
BH_4^-	3·90	0·00
BO_3^{2-}	3·78	0·00
$BF_3{\cdot}NH_3$	3·17	0·01
$BH_3{\cdot}CO$	3·76	0·11
$B_3O_6^{3-}$	3·56	0·03
	Carbon	
CN^-	2·94	0·74
$CN{\cdot}$	3·45	0·26
CO	2·61	0·82
HCHO	3·98	0·16
CO_2	3·86	0·00
CO_3^{2-}	3·93	0·02
C_2H_2	3·96	0·07
C_2H_4	3·99	0·01
C_2H_6	3·97	0·00
CH_3OH	3·94	0·04
$(CH_2)_\infty$	3·98	0·00
$(CH)_\infty$	4·00	0·00
$BH_3{\cdot}CO$	3·53	0·25
	Nitrogen	
NH_3	2·94	0·43
NH_4^+	3·60	0·00
$NO{\cdot}$	3·00	0·68
NO^+	2·84	0·63
$CN{\cdot}$	3·44	0·22
CN^-	2·94	0·51
NF_3	2·94	0·74
$BF_3{\cdot}NH_3$	3·35	0·22
$P_3N_3F_6$	3·14	0·37
	Oxygen	
BO_3^{3-}	1·47	0·32
CO	2·61	0·31
CO_3^{2-}	1·50	0·61
$NO{\cdot}$	2·54	0·44
NO^+	2·84	0·39
SO_2	2·25	0·52
SO_3	2·18	0·26
SO_4^{2-}	1·65	0·61
H_2O	1·94	0·74
$HCO{\cdot}\mathit{O}H$	2·12	0·19
$BH_3{\cdot}CO$	2·55	0·31
$HC\mathit{O}{-}OH$	2·05	0·37
HCHO	2·06	0·63
PO_4^{3-}	1·56	0·47
ClO_2^-	1·29	1·25
ClO_3^-	1·44	1·12
ClO_4^-	1·54	1·03

Table 2 (*continued*)

Species	Valency		Anisotropy
	Fluorine		
HF	0·94		0·43
LiF	0·98		0·01
NF_3	1·03		0·54
CF_4	1·05		0·37
AlF_6^{3-}	0·55		0·02
SiF_4	1·06		0·09
SiF_6^{2-}	0·78		0·05
PF_5	1·16	(axial)	0·13
	1·21	(equat.)	0·17
SF_6	1·20		0·18
ClF	1·22		0·43
ClF_3	1·15	(axial)	0·45
	1·27	(equat.)	0·23
ClF_3	1·27	(axial)	0·36
	1·19	(equat.)	0·46

an acceptor for nucleophiles. This suggestion is borne out in the hypothetical linear and trigonal anions LiF_2^- and LiF_3^{2-}, where the valency of lithium is restricted to 1·6 and 1·8 respectively. It is of further interest to note that the valency of the central atom is low in complexes which are somewhat ' ionic,' *e.g.*, BF_4^- and $NH_3{\cdot}BF_3$.

The valency of carbon in most of the compounds studied is calculated to be *ca.* 3·9: notable exceptions are the cyanide ion and carbon monoxide, where the values are 2·9 and 2·6 respectively. The latter values and their tendency to increase account for the donor properties of these species and their ability to form complexes with transition-metal ions. It is noteworthy that both the nitrogen and oxygen atoms in these species have high valencies. Hence the mode of attachment of CO in metallic carbonyls is also not surprising.

Nitrogen has a valency of nearly three in most of its compounds. The deviation from three occurs in molecules in which the nitrogen is co-ordinated to Lewis acids, *e.g.*, in $NH_3{\cdot}BF_3$ and NH_4^+, where the valency of the nitrogen rises significantly above three. An interesting case is the NO· molecule; here the valency definition goes somewhat awry because the molecule does not possess a closed-shell ground state. This was predicted from the equations given in ref. 1; when the odd electron is removed, to give NO^+, the valencies of the atoms are sensible.

In neutral species an oxygen atom is approximately bivalent in character. In anions of the type XO_m^{n-}, however, the valency of the oxygen drops to a value between 1·3 and 1·7. (This is even lower when *d* orbitals are not included on the central atom.) The excess of unused bonding power of oxygen can presumably be used to interact covalently with cations, as in the formation of sulphato-complexes and in sequestering agents. A similar phenomenon is observed with the complex fluoride anions, where the normal valency (*ca.* 1) is reduced on anion formation.

Anisotropies. The anisotropy of an atom in a molecule or ion is a measure of the non-spherical distortion of its electronic environment.[1] This distortion commonly manifests itself as lone pairs when sufficient valency electrons are available. Good examples (Table 2) of this situation are furnished by nitrogen in NH_3 and NO·, oxygen in H_2O, and carbon in CO. Here the named atoms are highly anisotropic. In general, however, in polyatomic molecules the atoms are only feebly anisotropic. The importance of anisotropy in chemistry is that it can afford a measure of the reactivity of an atom in a molecule. From its definition it implies changes in electron screening in different directions in space and, hence, is related to the ease of chemical attack on the atom from a given direction. Clearly, the development of this idea could be of some importance in reaction mechanism theory and the formation and mode of decomposition of transition states.

Further, in a donor-acceptor reaction such as (4) there

$$BF_3 + NH_3 \longrightarrow BF_3{\cdot}NH_3 \qquad (4)$$

will be a decrease in anisotropy on going from left to right of the equation. The essence of this is that changes in anisotropy constitute a quantitative measure of a tendency to ' gain electronic symmetry '.

A third noteworthy point is that the co-ordinative behaviour of the ligands NO·, CN^-, and CO can all be understood in terms of the large anisotropies of nitrogen in NO· and carbon in CN^- and CO. This anisotropy is decreased on formation of a complex, *e.g.*, in $BH_3{\cdot}CO$ the anisotropy of carbon is reduced to 0·25.

An interesting final example is provided by monomeric BeH_2. Here the loss of electron density from the *p* orbitals of Be leads to a high anisotropy for that atom. This can obviously be relieved by coupling of monomers to produce a BeH_2 polymer in which each ' internal ' Be will have zero anisotropy.

Elements of the Second Row.—While the elements of the first row are limited to four valence orbitals, the elements of the second row can exploit the 3*d* orbitals in bonding, giving rise to a total of nine valency orbitals. The valencies of second-row atoms in various environments are shown in Table 3. It can be seen that the atomic 3*d* population rises (*a*) with atomic number, *i.e.*, with increasing valency orbital ionisation potential, and (*b*) with increase in co-ordination number. Now in highly co-ordinated covalent complexes the central atom must have a high valency of four or more then, of necessity, it must have a significant *d*-electron population. It is gratifying to find that the calculated valencies of phosphorus, sulphur, and chlorine in their fluorides PF_5, SF_6, ClF_5, are 4·9, 5·9, and 4·8, respectively. In general, the valencies of the central atoms assume non-integral values arising from the presence of the *partial* double bonds which occur in the majority of molecules. In the fluorides and hydrides of the first row, the double-bonding character is negligible.

As with the first-row atoms, the valency of the second-row atoms varies in a parabolic fashion with respect to the number of valence electrons, if *d* orbitals are neglected. However, an added effect in these atoms is the increase in *d*-orbital participation as the number of valency electrons increases. This phenomenon is very marked for phosphorus-, sulphur-, and chlorine-containing species where high co-ordination numbers are the rule. Hence the defined valency of a second-row element can have a wide range of values, depending on the co-ordination number of the second-row element.

TABLE 3

Valencies and 3*d*-orbital populations in compounds of second-row elements

	Species	Valency	3*d* population	Anisotropy
Sodium	NaCl	1·07	0·00	0·02
Magnesium	MgF_2	1·63	0·00	0·00
	$MgCl_2$	2·28	0·01	0·01
Aluminium	AlF_6^{3-}	2·85	0·11	0·00
Silicon	SiH_4	4·00	0·06	0·00
	SiF_4	3·71	0·31	0·00
	SiF_6^{2-}	3·95	0·43	0·00
	$SiCl_4$	4·75	0·67	0·00
Phosphorus	PH_3	2·97	0·06	0·12
	PH_4^+	3·84	0·07	0·00
	PCl_3	4·21	0·55	0·80
	PCl_5	5·71	1·04	0·00
	PF_5	4·94	0·69	0·00
	$P_3N_3F_6$	5·21	0·79	0·05
	PO_4^{3-}	5·42	0·80	0·00
Sulphur	SO_2	4·06	0·62	0·75
	SO_3	5·68	1·00	0·30
	SO_4^{2-}	5·89	1·11	0·00
	SF_6	5·92	1·22	0·00
Chlorine	HCl	0·98	0·02	0·56
	PCl_3	1·73	0·15	0·49
	PCl_5	1·74 (axial)	0·17	0·21
		1·90 (equat.)	0·19	0·41
Chlorine	$SiCl_4$	1·69	0·12	0·21
	BCl_3	1·26	0·13	0·15
	ClO_2^-	2·52	0·46	0·28
	ClO_3^-	3·97	0·79	0·38
	ClO_4^-	5·59	1·15	0·00
	ClF	1·22	0·14	1·04
	ClF_3	3·05	0·59	1·01
	ClF_5	4·78	1·06	0·60

Bond Indices.—Table 4 lists the bond-index components for bonds in selected molecules. These refer solely to nearest-neighbour bonds and, although the valency is defined over all atoms in the molecule, the bond index component between non-neighbouring atoms is small in the majority of molecules.

The way in which the valency can be dissected into component bonds builds up gratifyingly well the traditional valency-bond picture of electron-pair bonds. For instance, in the compounds which contain hydrogen, all the bonds to hydrogen have indices close to unity. In the hydrocarbon series C_2H_2, C_2H_4, and C_2H_6, the C–C bond indices are 2·99, 2·03, and 1·02, respectively. Consistent with this trend, the corresponding value in benzene is 1·44. Butadiene is an instructive example, and here the bond indices have the values 1·93 and 1·07 for the outer and inner C–C bonds respectively: this correlates with the ' alternating-double-bond ' nature of the polyenes.

The large bond index in NaCl is at first sight surprising, since this indicates a ' covalent ' bond. However, it must be remembered that the calculation refers to molecular NaCl in which the bond length is shorter than in the solid: this feature enhances covalency. It has been shown [7] that increase in bond length in NaCl induces greater ionic character in the bond. It should be emphasised that the bond indices apply only to covalent bonding situations. Thus, they are inadequate for describing the bonds which are largely ionic in nature, such as those present in crystalline sodium chloride.

In the complexes $BH_3{\cdot}CO$ and $BF_3{\cdot}NH_3$, the donor–acceptor bonds are of interest and in these cases they have a covalent bond index >0·5. The overall view of this bond is completed by adding that there is frequently a degree of charge transfer across the D–A bond.

Finally, we draw attention to cases where there is a significant index between ' non-bonded ' atoms in a molecule. Two interesting ones occur in the phosphorus series: these are PCl_5 and the triphosphazenes. In the former, the indices for Cl(equat.)–Cl(axial) and Cl(equat.)–Cl(equat.) are 0·22 and 0·11 respectively. This leads to a picture of PCl_5 as a molecule in which a

TABLE 4

Bond indices for some compounds containing first- and second-row elements

Carbon compounds	Bond	Bond index
CO	C–O	2·61
CO_2	C–O	1·93
CO_3^{2-}	C–O	1·31
CH_4	C–H	0·99
C_2H_2	C–C	2·99
C_2H_4	C–C	2·03
C_2H_6	C–C	1·02
	C–H	0·98
trans-C_4H_6	C–C inner	1·07
	C–C outer	1·93
C_6H_6	C–C	1·44
CN^-	C–N	2·94
Me_2Be	C–Be	1·06
$BH_3{\cdot}CO$	C–B	1·00
	C–O	2·38
Other first-row compounds		
$(BeCl_2)_2$	Be–Cl (term.)	0·71
	Be–Cl (bridge)	1·16
BCl_3	B–Cl	1·14
$BF_3{\cdot}NH_3$	B–N	0·52
O_2	O–O	2·00
O_3	O(1)–O(2)	1·26
	O(2)–O(3)	0·17
Compounds of second-row elements		
NaCl	Na–Cl	1·07
SiF_4	Si–F	0·93
SiF_6^{2-}	Si–F	0·66
PCl_3	P–Cl	1·40
PCl_5	P–Cl (axial)	1·00
	P–Cl (equat.)	1·23
	Cl(a)–Cl(e)	0·22
	Cl(e)–Cl(e)	0·11
$P_3N_3F_6$	P–P	0·26
SO_2	S–O	2·03
	O–O	0·22
SO_3	S–O	1·89
SO_4^{2-}	S–O	1·47
SF_6	S–F	0·99
ClO_2^-	Cl–O	1·26
ClO_3^-	Cl–O	1·32
ClO_4^-	Cl–O	1·40

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[7] K. A. Levison and P. G. Perkins, to be published.

phosphorus atom is bonded tightly into a chlorine cage which itself has some intrinsic stability. It has been noted that high P–P *bond orders* occur in cyclic phosphazenes.[8] This is now shown to correlate with a high valency for phosphorus in these rings and the P–P bond index is 0·25.

These ' secondary ' bonds were also revealed in ozone and carboxylic acids; the index of the O–O bond was typically *ca.* 0·2.

Comparison of Valency and Bond Index with Electron Population and Bond Order.—From the foregoing results it should be clear that valency and bond index are informative quantities which are well worth calculating. It is of some further interest to compare them with the corresponding electron population and bond order which are normally calculated to represent electronic distribution. Clearly, the electron density and valency are complementary quantities, as the former yields information on the formal charge of the atoms in the molecule, whereas the latter relates to the bonding of the same electrons. This means that valency will be useful for predicting reactive centres in molecules, whereas the electron population can be developed to provide a picture of the spatial distribution of electronic charge around an atom in the molecule. The relationship is well illustrated by the carbon monoxide and methane molecules. The electron population and valency of carbon in CO are 3·92 and 2·61 respectively and it is only the valency which indicates the reactivity of the molecule. In methane the valency of carbon is 3·95 but this, by itself, provides no information as to the way the charge is distributed about the carbon.

Bond index and bond order both give a measure of bonding between atoms in a molecule. There are usually several bond-order terms between the two atoms and, by themselves, they do not afford a readily comprehensible picture of a two-electron bond.

Indeed, a sensible picture of the interaction can only be obtained through comparison with other related bond-order values. This is well exemplified by the following: the C–C bond order and bond index in a given molecule are 1·88 and 2·99, respectively. The classical triple bonding is immediately revealed by the latter value but the former quantity requires the information in Table 5 before such an appraisal of the bonding can be given. In this respect, the bond index is a more useful and meaningful concept.

TABLE 5

Some C–C bond orders

C_2H_2	C_2H_4	C_2H_6	C_6H_6
1·88	1·32	0·81	1·11

One of us (J. J. P. S.) thanks the S.R.C. for a Maintenance Grant.

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[8] D. R. Armstrong, G. H. Longmuir, and P. G. Perkins, *J.C.S. Chem. Comm.*, 1972, 464.