Theoret. Chim. Acta (Berl.) 63, 511–527 (1983)

THEORETICA CHIMICA ACTA

Valency. II. Applications to Molecules with First-Row Atoms

M. S. Gopinathan* and Karl Jug

Theoretische Chemie, Universität Hannover, Callinstraße 3A, D-3000 Hannover,
Federal Republic of Germany

A quantum chemical definition of valency proposed in Part I is used to calculate the valency of carbon, nitrogen, oxygen, lithium, beryllium and boron in a number of compounds with the SINDO1 method. It is demonstrated that consistency of the basis set is necessary for comparable results. The general features of valency and bonding in these molecules are discussed. The π-electron concept of free valence is generalised to sigma systems and atoms in molecules are classified as subvalent, normal or hypervalent. The relation between valency and natural hybrid occupancy is illustrated. The symmetry properties of natural hybrid orbitals are discussed by means of group theory. A preliminary attempt is made to relate covalency and covalent reactivity. Bond indices and the σ, π character of bonds are obtained by a suitable partitioning and projection of valency into bonding and antibonding contributions.

Key words: Valency of first-row atoms—Free valence—Bond indices—Natural hybrids.

1. Introduction

In Part I of this series [1] we formulated a definition of valency in terms of the appropriate elements of the first-order density matrix of the molecule. Thus the valency V_A of atom A is defined by (Eq. (2.14) of Part I),

$$V_A = \sum_{a}^{A} \sum_{B \neq A} \sum_{b}^{B} p_{ab}^2 \qquad (1.1)$$

---

* Alexander von Humboldt Fellow 1982–83. **Permanent address:** Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

where p_{ab} is the first-order density matrix element between orbitals a on A *and* b on B, the basis set being orthonormal. It was shown that V_A is also given by (Eq. (2.15a) of Part I),

$$V_A = \sum_{a'}^{A} \sum_{B \neq A} \sum_{b'}^{B} p_{a'b'}^2 \tag{1.2}$$

where the primed orbitals refer to the natural hybrid orbitals (NHO). Further V_A is related to the occupancies of the NHO's for closed shell systems by (Eq. (2.15b) of Part I),

$$V_A = \sum_{a'}^{A} 2q_{a'} - q_{a'}^2. \tag{1.3}$$

Valency was also shown to be related to the eigenvalues of the bond orbitals (BO) or of the natural bond orbitals (NBO) as (Eq. (5.10) or (5.12) of Part I),

$$V_A = \sum_{i}^{+ve} \lambda_i^2 \tag{1.4}$$

where λ's are eigenvalues of the BO's or NBO's.

In the present article we use these definitions to calculate and analyse the valencies of the first-row atoms C, N, O, Li, Be and B in a variety of molecules. We show that in most cases the results for valency agree with the chemists' "traditional" values when the latter can be unambiguously stated. We generalise the π-electron concept of free valence [2] and calculate percentage free valences and classify molecules as containing hypervalent, normal or subvalent atoms. We attempt to relate these numbers to the chemical reactivity of molecules. An instructive analysis of valency in terms of the NHO occupancies is carried out. The symmetry properties of the natural hybrid orbitals are also discussed.

The distinction between valency and "bond order" or "bond index" will be clarified. The defect of the Wiberg index [3] that it cannot describe antibonding is remedied by adopting a projection technique proposed earlier by one of us [4]. These modified bond indices and the σ, π character of bonds deduced from these indices in a variety of molecular situations are discussed.

2. Free-, Hyper- and Sub-valence

Coulson introduced the concept of free valence in π-electron molecular orbital theory as a measure of the residual valency of an atom [1]. It is defined as

$$F_r = N_{\max} - N_r \tag{2.1}$$

where $N_{\max}$ the maximum π-bond order of the atom and N_r is the sum of the bond orders of the given atom r to all its neighbours. $N_{\max}$ is usually taken as $\sqrt{3}$, the value for the central carbon in trimethylene methane. F_r has been found to correlate well with the rate of free radical reaction at r in π systems [5].

In generalising this concept to include σ systems, we must consider the following. "Bond order" is a measure of the *net* number of bonding electron pairs, i.e. it gives the difference between the total number of bonding and antibonding pairs of electrons shared between the two atoms concerned. However this is different from valency, which by our definition measures the total extent of sharing including the bonding, nonbonding and antibonding pairs between the atoms. This distinction between bond order and valency is further discussed in section 6, where it is shown, for example, that the valency of Li in LiH is 0.92 whereas the bond index is only 0.81. Hence it appears that if free valence is to measure the ability of an atom to share electrons with a reagent, we must use valency rather than bond order or bond index in its definition. Accordingly we define the free valence of atom A as

$$F_A = V_A^r - V_A. \tag{2.2}$$

Here V_A^r is the "reference" valency of A and V_A is its valency in the molecule under consideration. The reference value is chosen to be the integer value around which the computed valency of A is distributed in a large number of compounds. This turns out to be, as will be seen in Sect. 4, the traditional value of A: for

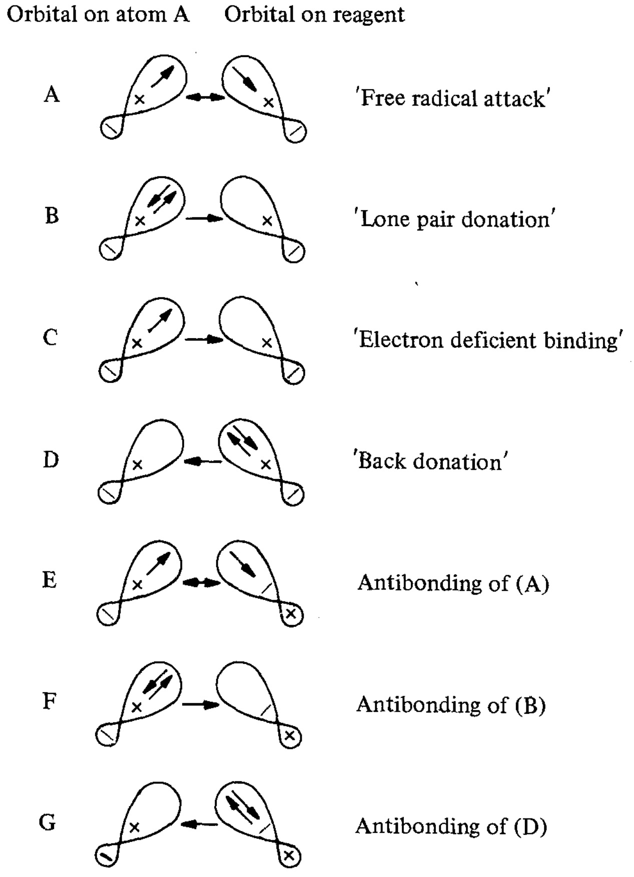


Fig. 1. Schematic representation of the modes of valency enhancement in chemical reactions.

example, 1 for H, 4 for C, 3 for N, 2 for 0 and so on. According to Eq. (2.2), $F_A = 0$ when the atom has its "normal" or reference valency. F_A is positive if the valency is not fully satisfied and we may call this situation as *subvalent.* Similarly F_A is negative when V_A exceeds the reference valency and the atom may then be said to be *hypervalent.* Valency is of course still limited by the inequalities derived in Part I (see Eqs. (3.3) and (3.4) of Part I). We shall see in section 6 that reactivity of atoms is governed by a tendency to change its sub- or hyper-valency to the normal value.

Valency as we showed in Part I, is a measure of the capacity of the atom to engage in covalent sharing of electrons with a reagent. Thus the atom may not have any unpaired electron, but can still share its lone pair or receive electrons from the reagent and thus increase its valency. We may schematically represent such situations as in Fig. 1. Since the generalised Eq (2.2) covers all these situations, F_A *can be considered as a general index of the residual covalent binding capacity of the atom A.* We report F_A in percentage defined as,

$$F_A = (V'_A - V_A) \times 100 / V'_A. \tag{2.3}$$

3. Dependence of Valency on Wavefunction

The accuracy of the density matrix depends on the quality of the wavefunction and hence valency values are also expected to change accordingly. In this section we compare *ab initio* and semiempirical calculations on valency at the minimal basis set level and also compare some *ab initio* values for extended basis sets. We have chosen the molecules C_2 and N_2 for this purpose because they are crucial for the general trend and were already discussed in the context of bond orders [6].

Table 1 presents valency data for C_2 and N_2 for the semiempirical SINDO1 [7] as well as for several *ab initio* wavefunctions. Clearly for both these molecules the semiempirical and the best *ab initio* results are virtually identical at the minimal basis set level showing that the SINDO1 approximations have little

Table 1. Dependence of valency on wavefunction

	Valency	
Wavefunction[a]	N_2	C_2
Minimal basis set:		
Ransil (Slater type)	3.00	3.60
Ransil (best atom)	3.00	3.65
Ransil (best molecular)	3.00	3.35
SINDO1	3.00	3.26
Extended basis set:		
Ahlrichs (DZ)	3.97	3.90
Ahlrichs (TZ)	4.11	3.89

[a] For specification of wavefunctions see Ref. [6]

effect on valency. Extension of the basis set is found to increase valency considerably, since the additional functions open new degrees of freedom for sharing. Valency is, of course, still limited by the inequalities discussed in Part I. To preserve consistency the present discussion of valency, the reference valency and consequently free valences are in the context of the minimal basis set at the SINDO1 level only.

4. Valency of First-row Atoms

4.1. Carbon

Table 2 gives the calculated valency and free valence of C in a number of molecules. It is clear that in most "normal" compounds the valency of carbon is close to the traditional value of 4, which we take as the reference V^r_C. Carbon has in fact its highest valency of 4 in CH_4 and C_2H_6. Valency decreases and free valence increases slightly as C is unsaturated or "strained" (see entries 3–5, 7, 9, 10–12, 15 and 16 in Table 1). It is of particular interest that in compounds like CLi_6 with 10 valence electrons, the valency of carbon is only 3.88. In other words, *there is no hypervalency and the octet rule is not violated in these compounds*, contrary to what is sometimes thought [8]. In CLi_6 the bond index for the C–Li bond is only 0.48 (see Sect. 6 and Table 10) so that C forms only $0.48 \times 6 = 2.88$ electron pair bonds with Li! The "extra" two electrons occupy the HOMO with only 0.2 electrons on C, the rest being involved in considerable Li–Li bonding with a Li–Li valency of 0.19 and a Li–Li bond index of 0.18. Thus carbon is far from being hypervalent in CLi_6; neither does it violate the octet rule. The analogous bonding in the "hyperlithiated" system OLi_4 is discussed in section 4c.

In the 8-valence electron system CH_5^+, the valency of C is only 3.78. Thus we must rightly call C in CH_5^+ as *hypercoordinated* and not as hypervalent.

Carbon is found, not unexpectedly, to be highly subvalent in C_2, CO, HNC, BeC, CH_2 and LiC. We discuss in general the reactivity of subvalent systems in Sect. 6.

4.2. Nitrogen

The valency of N in the "normal" compounds in Table 3 is close to 3 and hence V^r_N is taken as 3 to compute free valence. Accordingly N exhibits large hypervalency in HNO_3 and NO_3, for example. This is in accord with normal expectations since traditionally N^+ can attain a valency of 4 and N in HNO_3 and NO_3 have charges of +0.66 and 0.63 with valencies of 3.75 and 3.72 respectively. However, hypervalency is not always related to a high positive charge on N. For example, N in HNC is negatively charged (−0.24), but still hypervalent with a free valence of −18%. Similarly N in NO_2 has a large positive charge of +0.55, but has little hypervalency ($V_N = 3.04$; $F_N = -1.3\%$). NO, NH_2, BN and NH are naturally highly subvalent species.

Table 2. Valency of carbon

Molecule	Valency	Free valence (in %)	Atomic charge
1. CH_4	4.00	0.00	0.01
2. C_2H_6	4.00	0.00	0.07
3. $H_2C=CH_2$	3.99	0.25	0.01
4. $C^aH_3C^bH=C^cH_2$	4.00(a)	0.00	0.07
	3.98(b, c)	0.50	0.05(b) −0.04(c)
5. C_6H_6 (benzene)	3.98	0.50	0.02
6. $C^a(C^bH_3)_4$	3.98(a)	0.50	0.10
	3.96(b)	1.00	0.05
7. $HC\equiv CH$	3.97	0.75	−0.10
8. $(CH_3)_2O$	3.96	1.00	0.33
9. C_4H_4 (cyclobutadiene)	3.96	1.00	0.01
10. C_8H_8 (cubane)	3.96	1.00	0.05
11. HCN	3.96	1.00	0.16
12. C_3H_6 (cyclopropane)	3.95	1.25	0.05
13. CH_3OH	3.95	1.25	0.34
14. $H_2C^a=C^bLi_2$	3.93(a)	1.75	0.02
	3.39(b)	15.25	−0.47
15. C_2H_4O (ethylene oxide)	3.92	2.00	0.21
16. C_4H_4 (tetrahedrane)	3.91	2.25	−0.02
17. H_2CO	3.91	2.25	0.44
18. CLi_4	3.91	2.25	−0.57
19. CLi_6	3.88	3.00	−0.59
20. $HCONH_2$	3.87	3.25	0.60
21. HCOOH	3.84	4.00	0.66
22. CH_5^+	3.78	5.50	0.01
23. $H_2C^b=C^aO$	3.75(a)	6.25	0.49
	3.72(b)	7.00	−0.35
24. CO_2	3.74	6.50	0.70
25. $C^a(C^bH_2)_3$ (trimethylene methane)	3.74(a)	6.50	0.05
	3.21(b)	19.75	0.01
26. CH_2Li_2	3.74	6.50	−0.50
27. C_2	3.26	18.50	0.00
28. HNC	2.70	32.50	0.02
29. CO	2.57	35.75	0.12
30. BeC	2.08	48.00	−0.18
31. CH_2 (triplet)	1.91	52.25	−0.02
32. LiC	0.94	76.50	−0.29

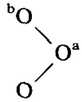
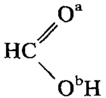
4.3. Oxygen

Oxygen exhibits valencies ranging from 2.80 in O_3 to 1.19 in NO_3 (Table 4). The reference value is taken to be 2. Accordingly we have a large hypervalence of −40% for the central O in O_3 and a high subvalence of +40% in NO_3. Oxygen in CO is hypervalent: $V_O=2.57$, $F_O=-28\%$; however in CO_2, it is almost normal: $V_O=2.13$, $F_O=-6.5\%$.

Table 3. Valency of nitrogen

Molecule	Valency	Free valence (in %)	Atomic charge
1. HNO_3	3.75	−25.00	0.66
2. NO_3	3.72	−24.00	0.63
3. H_3NO	3.67	−22.33	0.23
4. NH_4^+	3.64	−21.33	−0.20
5. HNC	3.54	−18.00	−0.24
6. $B_3N_3H_6$ (borazine)	3.17	−5.67	−0.52
7. NO_2	3.04	−1.33	0.55
8. $HCONH_2$	3.04	−1.33	−0.32
9. N_2	3.00	0.00	0.00
10. HCN	3.00	0.00	−0.13
11. NH_3	2.97	1.00	−0.29
12. NO	2.13	29.00	0.07
13. NH_2	1.99	33.67	−0.12
14. BN	1.87	37.67	−0.20
15. NH	0.99	67.00	−0.03

Table 4. Valency of oxygen

Molecule	Valency	Free valence (in %)	Atomic charge
1. OH_4^{+2}	2.80	−40.00	−0.18
2. 	2.80(a) 1.75(b)	−40.00 12.50	0.34 −0.17
3. CO	2.57	−28.50	−0.12
4. OH_3^+	2.53	−26.50	−0.16
5. $H_2C{=}C{=}O$	2.32	−16.00	−0.25
6. OLi_4	2.28	−14.00	−0.62
7. NO	2.13	−6.50	−0.07
8. H_2CO	2.13	−6.50	−0.24
9. CO_2	2.13	−6.50	−0.35
10. 	2.08(a) 2.11(b)	−4.00 −5.50	−0.35 −0.31
11. $(CH_3)_2O$	2.09	−4.50	−0.27
12. $HCONH_2$	2.09	−4.50	−0.32
13. OLi_4^{+2}	2.06	−3.00	−0.77
14. CH_3OH	2.02	−1.00	−0.26
15. C_2H_4O (ethylene oxide)	2.00	0.00	−0.21
16. H_2O_2	2.01	−0.50	−0.10
17. H_2O	1.96	2.00	−0.29
19. $H^aON^bO_2$	2.00(a) 1.69(b)	0.00 15.50	−0.22 −0.30
19. LiOH	1.89	5.50	−0.55
20. NO_2	1.78	11.00	−0.23
21. BO_2	1.57	21.50	−0.26
22. O_2	1.50	25.00	0.00

The bonding and valency of oxygen in the "hypercoordinated" species OLi_4 deserves special discussion. Schleyer [8] has presented as one point of view that in this 10 valence electron system oxygen does not violate the octet rule, but rather the extra two electrons are involved mainly in Li–Li bonding similar to the CLi_6 case discussed above. Therefore he could call O in OLi_4 not hypervalent while of course pointing out the lack of a precise definition of hypervalence.

Our semiempirical results are in substantial agreement with Schleyer's *ab initio* calculations. The bonding in OLi_4 can be summarised as follows. O forms four weak O–Li bonds of bond index 0.47 each (see Sect. 7); i.e. in effect $0.47 \times 4 = 1.88$ electron pair bonds. Thus there is nothing unusual about oxygen bonding here and certainly there is no violation of the octet rule. The extra two electrons are in the HOMO which is concentrated on the Li atoms and corresponds to only 0.10 electrons on O. However, the valency of O, which by definition is the total (bonding, nonbonding and antibonding) number of pairs of electrons shared between O and all the Li atoms is 2.28. This is higher than the reference value of 2 and hence by our criteria O is hypervalent in OLi_4 with a free valence of −14%.

Another interesting case is that of O_2, which has only a valency of 1.5 and therefore a high subvalence of 25%. Though this low value of 1.5 contrasts with the conventional value of 2, it is understandable since in O_2 two electrons are actually unpaired and our definition of valency is a measure of the extent of electron pairing.

4.4. Lithium

Results for Li are given in Table 5. Taking the reference value as 1, it is seen that Li is hypervalent in CLi_6, CLi_4, OLi_4, CH_2Li_2, $CH_2=CLi_2$ and C_2Li_2. For example, V_{Li} in OLi_4 is 1.35. Eq. (1.1) shows that we may partition the valency of an atom into contributions from each of the other atoms in the molecule. Thus Li has a valency of 0.57 towards 0 and 0.26 towards each other Li. Note the considerable Li–Li valency in this molecule, which is a common feature of other "hyperlithiated" compounds like CLi_6.

Table 5. Valency of lithium

Molecule	Valency	Free valence (in %)	Atomic charge
1. CLi_6	1.50	−50.0	0.10
2. CLi_4	1.40	−40.0	0.14
3. OLi_4	1.35	−35.0	0.16
4. CH_2Li_2	1.13	−13.0	0.26
5. Li_2	1.00	0.0	0.00
6. LiOH	0.96	4.0	0.46
7. LiC	0.94	6.0	0.29
8. LiH	0.92	8.0	0.28
9. LiF	0.81	19.0	0.55

Li also exhibits subvalence as in LiH and LiF. Valency of Li is reduced from 0.92 to 0.81 in going from LiH to LiF. In this case the reduced covalency is obviously due to the greater charge transfer from Li to F, i.e. due to the increased ionic character of the bond. In the hypothetical case of 100% ionic Li^+F^-, covalency as we have defined would of course reduce to its proper limit of zero.

4.5. Boron

Table 6 gives the valency of B in a few boron compounds. V_B in B_2H_6 is 3.41, a hypervalence of −13.7%, taking V_B^r as 3. This is made up of 0.97 towards each terminal hydrogen atom, 0.485 towards each bridging hydrogen and 0.49 towards the other boron atom. Valency of the terminal H incidentally is 0.98 and that of the bridging H is 1.00.

B in borazine, $B_3N_3H_6$, is slightly hypervalent with a valency of 3.16, which breaks up as 1.10 towards each adjacent N, 0.91 towards the bonded H and the rest 0.05 coming from non-bonded atoms. The bond indices and the σ, π character of the B–N bond are discussed are discussed in Sect. 7.

4.6 Beryllium

Results for a few Be compounds are given in Table 7. It is interesting that there is a small valency of 0.03 for Be in Be_2 even though there is no formal bond, the bond index being zero. This is because there is a bonding valence of 0.015 and an equal amount of antibonding sharing in Be_2.

Table 6. Valency of boron

Molecule	Valency	Free valence (in %)	Atomic charge
1. B_2H_6 (diborane)	3.41	−13.67	0.32
2. $B_3N_3H_6$ (borazine)	3.16	−5.33	0.63
3. B_2F_4	3.02	−0.67	0.60
4. BF_3	2.80	2.67	1.10
5. BF	1.27	57.67	0.23

Table 7. Valency of beryllium

Molecule	Valency	Free valence (in %)	Atomic charge
1. BeC	2.08	−4.00	0.18
2. BeF_2	1.95	2.50	0.84
3. BeH_2	1.87	6.50	0.50
4. Be_2	0.03	98.50	0.00

5. Valency and Natural Hybrid Occupancy

Eq. (1.3) gives valency in terms of the NHO occupancy. It is instructive to compare the NHO occupancies and valencies of an atom in different bonding situations. Table 8 presents the NHO occupancies of C and O in a few molecules. The reference valency of 2 for O is closely approached in H_2O. Here the NHO's correspond to two lone-pairs of occupancy 2, and two bond hybrids of occupancy approximately equal to 1. See below for comments on the inequivalence of NHO's. When four atoms are available for bonding to O as in OLi_4, the NHO occupancies get suitably readjusted. We no longer have lone-pairs, its occupancy being reduced to about 1.66, thus increasing its binding capacity and the occupancy of the bond NHO's get increased from unity weakening their binding capacity. It is remarkable that by this "judicious" choice of NHO occupancies, oxygen atom "manages" to attain a valency of 2.28, even though the charge on O (−0.61) indicates that it is close to O^- and can have only a valency close to unity according to traditional thinking. The other entries in Table 8 are largely self-explanatory.

The NHO occupancies for carbon in a few typical molecules are also given in Table 8. It is clear from this table how valency reduces from the reference value of 4 as the NHO occupancy departs from 1.

An explanation of the "inequivalence" of the NHO occupancies in Table 8 is in order. Among the four oxygen NHO's in the tetrahedral OLi_4, three are degenerate with occupancy 1.66 each where as the fourth has an occupancy of 1.63. Similar observations may be made about the NHO occupancies in CH_4 and CLi_6.

Another example of the inequivalence of NHO's is the oxygen bond hybrids in H_2O, which have occupancies of 1.13 and 1.17. Previously Foster and Weinhold (FW) [9] have obtained lone-pair NHO's in H_2O which are inequivalent in their occupancy and *s*, *p* character. All these observations can be understood in terms

Table 8. Natural hybrid occupancies and valency of carbon and oxygen

Atom	molecule	NHO occupancy				Total	Charge	Valency
		h_1	h_2	h_3	h_4			
C	CH_4	1.00	1.00	1.00	0.98	3.99	0.01	4.00
	C_3H_6 (cyclopropane)	1.15	1.04	0.92	0.84	3.95	0.05	3.95
	C_2H_4O (ethylene oxide)	1.10	1.04	0.90	0.75	3.79	0.21	3.92
	H_2CO	1.06	0.86	0.83	0.81	3.56	0.44	3.91
	CLi_6	1.29	1.10	1.10	1.10	4.59	−0.59	3.88
O	O_3 (central O)	2.00	1.37	1.20	1.09	5.66	0.34	2.80
	CO	2.00	1.41	1.41	1.30	6.12	−0.12	2.57
	OLi_4	1.66	1.66	1.66	1.63	6.61	−0.61	2.28
	H_2O	2.00	2.00	1.13	1.17	6.30	−0.30	1.96
	O_3 (terminal O)	2.00	1.98	1.46	0.73	6.17	−0.17	1.75

Table 9. Natural hybrid orbitals of Oxygen in H_2O (Molecule in X–Y plane with X-axis along one O–H bond)

Symmetry		a_1	b_2	a_1	b_1
Occupancy		1.126	1.166	2.000	2.000
Coefficients	$2s$	0.40846	0.0	0.91278	0.0
	$2p_x$	−0.55440	0.79441	0.24809	0.0
	$2p_y$	0.72512	0.60738	−0.32449	0.0
	$2p_z$	0.0	0.0	0.0	1.00000

of the symmetry properties of the NHO's. The McWeeny NHO's [10], with which we are concerned, have the symmetry of the irreducible representations of the point group formed by the local electron density distribution around the atom. Thus the NHO's of O in H_2O have the symmetries $2a_1$, b_1 and b_2 of the C_{2v} group (Table 9). The two lone-pairs belong to symmetries a_1 and b_1, one being 100% p and the other having only about 17% p character (which may be compared with the INDO results of 100% p and 36% p respectively, obtained by Foster and Weinhold). In our case the NHO lone-pairs on O are accidentally degenerate. The bond hybrids belong to the a_1 and b_1 representations and are naturally inequivalent with occupancies 1.13 and 1.17. The McWeeny bond NHO's cannot be compared with the FW bond NHO's as the latter are obtained by a different, involved procedure whereas the lone-pair NHO's are obtained by the same method in both cases.

The above symmetry properties of the NHO's are further illustrated in the case of C in CH_4 where one has triply degenerate NHO's of t_2 symmetry (p_x, p_y and p_z orbitals) with occupancy of 1.0004 each and the non-degenerate a_1 NHO ($2s$ orbital) with occupancy 0.9773. It may be pointed out that the NHO's for an atom not on the principal axis of the group will not have the symmetry of the group, but will span the symmetry group, if any, of the local density around the atom.

6. Valency and Chemical Reactivity

In this section we attempt a *qualitative* correlation between the generalised free valence of atoms in molecules and their affinity for covalent formation with other reagents. To accomplish this we adopt the following hypothesis. *In chemical reactions, an atom in a molecule would make further covalent bond(s), or break or weaken existing bond(s) so as to convert its sub- or hyper-valency to its normal valency.* In other words, an atom having zero free valence would be unreactive; one with high subvalence would be reactive. If the atom has a high hypervalence, i.e. large negative free valence, it would be, say, "antireactive" in the sense that it would not normally form further covalent bonds, but would tend to reduce its hypervalency by breaking or weakening the existing bonds.

This hypothesis can be supported by considering the reactivity and calculated free valence of a few typical molecules, given in Table 10. O_2 with a high

Table 10. Valency and covalent chemical reactivity

Molecule	Atom	Free valence (%) Hyper	 Normal	 Sub	Predicted affinity for covalent formation
O_2	O			25	Highly reactive
N_2	N		0		Unreactive
CO	C			36	Highly reactive
	O	−29			"Antireactive"[a]
H_2CO	C			2	Unreactive
	O	−6			Unreactive
CO_2	C			7	Unreactive
	O	−7			Unreactive
H_2O	O			2	Unreactive
O_3	O (central)	−40			"Antireactive"
	O (terminal)			13	Reactive
NO	N			29	Highly reactive
	O	−6			Unreactive
NO_2	N	−1			Unreactive
	O			11	Reactive

[a] See text

subvalence of 25% is predicted to be highly reactive whereas N_2 with zero free valence must be unreactive, in agreement with the well known properties of these two molecules. C in CO is predicted to be highly reactive whereas O in this molecule is antireactive. Thus in metal carbonyls, for instance, it is C that binds to the metal. As a crude model of what happens to the valencies of C and O when CO is bound, we may consider H_2CO. We note from Table 10 that the free valence of C is now reduced close to the normal value of zero and the hypervalence of 29% for O in CO is reduced considerably to 6% in H_2CO. Similar comments can be made about the valency of N and O in NO and NO_2.

It must be remembered that we are dealing with reactivity as a tendency for covalent bond formation. Nucleophilic or electrophilic reactivity is thus excluded. For instance, the existence of R–NO_2 does not contradict the predicted unreactivity at N in NO_2, since nitration involves either NO_2^- or NO_2^+ ions and not NO_2. Also the dimer N_2O_4 involves [11] a very weak NN bond with a dissociation energy of about 12 kcals mole^{-1} and thus there is no pronounced covalent chemical reactivity at N in NO_2. Similar considerations apply to other systems with covalent unreactive sites like Be in BeF_2, where electrophilic attack can occur at the highly positively charged Be atom (Table 7).

The free valence of O in O_3 is interesting. The terminal O is subvalent and hence reactive whereas the central O is highly antireactive with a hypervalence of 40%. This prediction is supported, for example, by the fact that in ozonolysis of alkenes, it is the terminal oxygens that bind to the carbon atoms to form the intermediate malozanide [12]. Further, calculations on the reaction $O_3 + F \rightarrow O_2 + OF$ has shown [13] that the approach of F to the central O is repulsive whereas F binds to the terminal O. Oxygen in water is predicted to be unreactive whereas, as noted above, O_2 is highly reactive. This can be further supported, for instance, by comparing the strength of the crystal fields produced by H_2O and O_2 in their complexes with metals. Thus H_2O produces a weak field whereas O_2 produces a strong field in the complex with the ferrohaemoglobin ion as evidenced by the high spin value of 2 for the H_2O complex and the low spin value of zero for the O_2 complex [14].

The above examples have been selected at random and are not intended to be a systematic or quantitative correlation of free valence and reactivity. Nevertheless they seem to provide sufficient evidence in support of the present hypothesis linking the generalised free valence and covalent binding. More extensive and quantitative studies in this direction appear to be worthwhile.

7. Valency and Bond Indices

We have already remarked that valency as defined presently is a measure of the total extent of electron sharing of the atom, including bonding, antibonding and nonbonding pairs. It is necessary and often useful to distinguish valency from the "bond indices" of the atom. The quantity $\sum_a \sum_b p_{ab}^2$ appearing in the definition of valency, Eq. (1.1) is the orthogonal analogue of the "bond index" between atoms A and B, introduced by Wiberg [3]. Even though this quantity yields reasonable bond indices in many cases [3, 11], it has the defect that the Wiberg index is always positive by definition and is thus incapable of describing antibonding situations. We therefore take the view that a "bond index" must be a measure, *not* of the total extent of electron pairing between the two given atoms as the Wiberg index is, but it must be a measure of the difference: number of bonding pairs minus that of antibonding pairs. This definition is closer to the traditional definition of bond order in simple molecular orbital theory where it is simply (1/2) × (number of electrons in bonding MO's—number of electrons in antibonding MO's). Such a definition would have the desirable property that the bond index would be negative when antibonding exceeds bonding.

The bond index must be distinguished from bond order. The former is a function of the *square* of the density matrix elements whereas the latter is defined in terms of the density matrix elements themselves. The bond index, as we have noted, is a measure of the electron pairs shared between the two atoms concerned, the sharing being counted *exclusively*. In the usual definitions of bond order, on the other hand, the bonding interaction seems to be counted *inclusively* as is indicated by the large sum of bond orders of an atom [15]. For instance, the total π bond index for the central carbon in trimethylene methane is 0.836 only (Table 10) whereas the total π bond order is 1.815 according to Ref. [15] or 1.732 according to the Hückel theory.

The bond index is presently obtained as follows. We may write Eq. (1.1) as,

$$V_A = \sum_{B \neq A} \sum_a^A \sum_b^B p_{ab}^2 = \sum_{B \neq A} V_{AB}. \qquad (7.1)$$

Here V_{AB} is the valency between atoms A and B. In part I we related valency to the eigenvalues λ_i's of the bond orbitals (Eq. (5.10) of Part I) as

$$V_A = \sum_{B \neq A} \sum_{i}^{+ve} \lambda^2_{i(AB)}. \tag{7.2}$$

Comparing Eqs. (7.1) and (7.2) gives

$$V_{AB} = \sum_{i}^{+ve} \lambda^2_{(i(AB)} \tag{7.3}$$

Previously one of us has used a vector projection technique [4] to project λ_i into its bonding and antibonding components. If we write the bond orbital $\boldsymbol{b}_i$ as

$$\boldsymbol{b}_i = \boldsymbol{g}_i + \boldsymbol{h}_i$$

where $\boldsymbol{g}_i$ and $\boldsymbol{h}_i$ are components of $\boldsymbol{b}_i$ on A and B, the projection factor f_i is given by the cosine of the angle between $\boldsymbol{g}_i$ and $\boldsymbol{h}_i$ which are now considered to be vectors in a Hilbert space. Thus

$$f_i = \cos \phi_i = \boldsymbol{g}_i \cdot \boldsymbol{h}_i / |\boldsymbol{g}_i||\boldsymbol{h}_i|.$$

Presently we use the same projection factor to project λ_i^2 also, so that we can write for the bond index b_{AB} between atoms A and B,

$$b_{AB} = \sum_{i}^{+ve} f_i \lambda^2_{i(AB)}. \tag{7.4}$$

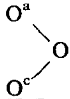
If all f_i's are +1, i.e. if all electron pairing is fully bonding, then it is obvious that the valency V_{AB} of Eq. (7.3) and the bond index b_{AB} of Eq. (7.4) are identical. However in many cases f_i is far from unity making valency and bond index different.

The bond index b_{AB} can be transformed into σ (along the internuclear axis A–B) and π (perpendicular to the A–B axis) components by transforming the two-centre density matrix to a local coordinate system [15]. The bond indices and their σ, π components for a few selected molecules are given in Table 11.

In CH_4 we have the highest C–H bond index of unity. The C–C bond index in ethane, ethylene and acetylene are close to the traditional values of 1, 2 and 3. The well known bent nature of the C–C bond [16] in the strained ring systems such as cyclopropane, tetrahedrane and cubane is evident from the large π contribution to the bond index. The C–O bond in ethylene oxide is also considerably bent.

It is interesting that the C–N bond in formamide, $HCONH_2$, which is considered to be a "partial double bond" because of the observed [17] restricted rotation about this bond, has only a bond index of 0.99. But the bond is seen to have a π bond index of 0.10, which explains the restricted rotation. Similarly the B–N bond in borazine, $B_3N_3H_6$, also has only a bond index of 1.11, but 0.30 of it is π.

Table 11. Bond indices and the σ–π character of bonds

	Bond	Bond index	σ–π	Character
Molecule	AB	b_{AB}	σ	π
1. CH_4	CH	1.00	1.00	0.00
2. C_2H_6	CH	0.99	0.99	—
	CC	1.04	1.00	0.04
3. $H_2C=CH_2$	CC	2.04	1.00	1.04
4. $HC\equiv CH$	CC	2.98	0.98	2.00
5. C_6H_6 (benzene)	CC	1.43	0.96	0.47
6. C_4H_4 (cyclobutadiene)	C^1C^2	0.94	0.84	0.10
	C^1C^4	1.96	0.96	1.00
7. $C(CH_2)_3$ (trimethylene methane)	CC	1.24	0.96	0.28
8. C_3H_6 (cyclopropane)	CC	0.99	0.83	0.16
9. C_4H_4 (tetrahedrane)	CC	0.97	0.78	0.19
10. C_8H_8 (cubane)	CC	0.97	0.72	0.25
11. CLi_4	CLi	0.92	0.55	0.37
12. CLi_6	CLi	0.48	0.23	0.25
	LiLi (adj.)	0.18	0.15	0.03
	LiLi (diag.)	0.08	0.05	0.03
13. HCN	CN	2.90	0.91	1.99
14. HNC	CN	2.54	0.76	1.78
15. $HCONH_2$	CN	0.99	0.89	0.10
	CO	1.91	0.93	0.98
16. CO	CO	2.57	0.91	1.66
17. CO_2	CO	1.79	0.89	0.90
	OO	−0.25	−0.02	−0.23
18. $(CH_3)O$	CO	0.99	0.93	0.06
19. C_2H_4O (ethylene oxide)	CO	0.91	0.68	0.23
20. H_2CO	CO	2.05	0.97	1.08
21. O_2	OO	1.50	1.00	0.50
22. 	O^aO^b	1.38	0.88	0.50
	O^aO^c	−0.32	−0.04	−0.28
23. H_2O_2	OO	1.01	1.00	0.01
24. LiOH	OLi	0.89	0.50	0.39
25. OLi_4	OLi	0.47	0.19	0.28
	LiLi	0.26	0.25	0.01
26. NO	NO	2.13	0.98	1.15
27. N_2	NN	3.00	1.00	2.00
28. $B_3N_3H_6$ (borazine)	BN	1.11	0.81	0.30
29. B_2H_6 (diborane)	BB	0.49	0.32	0.17
	BH (terminal)	0.97	0.97	—
	BH (bridge)	0.49	0.49	—
	HH (bridge)	−0.02	−0.02	—
30. Li_2	LiLi	1.00	1.00	0.00
31. LiH	LiH	0.81	0.81	—
32. LiF	LiF	0.78	0.45	0.33
33. HF	HF	0.93	0.93	—

The B–B bond in diborane, B_2H_6, has an index of 0.49 and the same value for the B–H bond with the bridge hydrogen. There is a slight anti-bonding interaction of −0.02 between the two bridge hydrogens. Considerable antibonding interaction exists between the oxygen atoms in CO_2 as well as between the terminal oxygen atoms in ozone. The "hyperlithiated" compounds CLi_6 and OLi_4 exhibit notable Li–Li bonding. It is also noteworthy that the rather weak covalent bond in LiF with a bond index of 0.78 has a high π character of 0.33.

8. Conclusions

Calculations on valency are only comparable when a consistent basis set is used. Valencies of first-row atoms calculated with SINDO1 minimal basis set are in accordance with normal chemical expectations. The concept of generalised free valence introduced here enables atoms in molecules to be classified as being normal, hypervalent or subvalent. The study of correlations of chemical reactivity with the generalised free valence appears promising. The traditional view that valency of an atom is directly related to the atomic charge is found to be invalid. Valency of an atom, on the other hand, is found to be determined by the way the electrons on the atom are distributed among its natural hybrid orbitals. In other words, valency is determined by the occupancies of individual natural hybrid orbitals and not by the sum of these orbital occupancies which of course is the total number of electrons on the atom.

The natural hybrid orbitals of an atom are not necessarily directed along internuclear axes, but they have the symmetries of the irreducible representations of the point group formed by the local electron density around the atom.

We have called the bonding part of valency obtained by a suitable projection as the bond index. The study of the bond index and its σ, π components in a variety of molecules shows that the bond index as presently defined is a good measure of the multiplicity of electron pair bonds between atoms. Chemical concepts such as unsaturation, bent bonds and antibonding interactions can be quantitatively discussed in terms of these indices and their components. For example, a quantitative correlation has been established [18] between the values of bond index components and the strain energy of molecules.

Acknowledgement. One of us (MSG) wishes to thank the Alexander von Humboldt Stiftung for the award of a fellowship that made possible his visit to the Federal Republic of Germany. The computations reported here were performed with a CYBER 76 at Universität Hannover.

References

1. Gopinathan, M. S., Jug, K.: Theoret. Chim. Acta (Berl.), this Vol., preceding paper
2. Coulson, C. A.: Trans. Faraday Soc. **42**, 265 (1946)
3. Wiberg, K. B.: Tetrahedron **24**, 1083 (1968)
4. Jug, K.: Theoret. Chim. Acta (Berl.) **51**, 331 (1979)

5. Salem, L.: The molecular orbital theory of conjugated systems. New York: W. A. Benjamin, Inc. 1966
6. Jug, K., Bussian, B. M.: Theoret. Chim. Acta (Berl.) **52**, 341 (1979)
7. Nanda, D. N., Jug, K.: Theoret. Chim. Acta (Berl.) **57**, 95 (1980)
8. For a discussion see Schleyer, P. von R. in: New Horizons of Quantum Chemistry, p. 95ff, Ed. P. O. Löwdin, B. Pullman, Reidel: Dordrecht 1983
9. Foster, J. P., Weinhold, F.: J. Am. Chem. Soc. **102**, 7211 (1980)
10. McWeeny, R.: Rev. Mod. Phys. **32**, 335 (1960)
11. Kishner, S., Whitehead, M. A., Gopinathan, M. S.: J. Am. Chem. Soc. **100**, 1365 (1978)
12. Roberts, J. D., Caserio, M. C.: Basic principles of organic chemistry. New York: W. A. Benjamin, Inc. 1965
13. Müller-Remmers, P. L.: private communication
14. Van Vleck, J. H.: Pure Appl. Chem. **24**, 235 (1970)
15. Jug, K.: J. Am. Chem. Soc. **100**, 6581 (1978)
16. Newton, M. D. in: Applications of electronic structure theory, Ed. Schaefer III, H. F. New York: Plenum Press, 1977
17. Bovey, F. A.: Chem. Eng. News **43**, 98 (1965)
18. Gopinathan, M. S.: unpublished results

Received November 30, 1982/April 6, 1983