CROATICA CHEMICA ACTA CCACAA **69** (3) 933–940 (1996)

ISSN-0011-1643
CCA–2352
Original Scientific Paper

On the Definitions of Bond Index and Valence for Correlated Wave Functions

Robert Ponec,[a] *Filip Uhlik,*[a] *David L. Cooper,*[b] *and Karl Jug*[c]

[a]*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague 6, Suchdol 2, 165 02, Czech Republic*

[b]*Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, UK*

[c]*Theoretische Chemie, Universität Hannover, Am Kleinen Felde 30, Hannover, D 3000, Germany*

Received November 6, 1995; revised January 7, 1996; accepted January 9, 1996

Definitions of bond index and valence for *correlated* wave functions are discussed. The utility of renormalizing Wiberg bond indices is investigated for a series of simple molecules at the spin-coupled level of theory.

INTRODUCTION

Continuing progress both in mathematical methodology and in computer technology means that it is becoming routine to generate reliable correlated wave functions for systems of real chemical interest. In general, such complicated wave functions do not lend themselves easily to direct interpretation. Thus, in order to make the physical content more transparent, chemists tend to rely on various simply defined quantities that are related to classical chemical concepts such as bond order (bond index), valence, and so on.

The concept of bond order, introduced in the now classical study of Coulson,[1] has found numerous applications in various fields of chemistry. In addition to providing rationalizations of static molecular properties as in, for example, various forms of bond order – bond length relationships,[2] this concept has also proved useful in the field of chemical reactivity.[3] The original definition of bond order has found its greatest use within the framework of π electron theory. It has since been generalized for more sophisticated semiempirical approaches by various authors.[4–10] A critical summary of existing definitions appropriate to SCF wave functions can be found in a recent review.[11] The concept of bond order or bond index is also closely related to the classical concept of valence.[12]

The importance attached to the electron pair in Lewis' model of the chemical bond has inspired studies linking bond multiplicity to quantities obtained using the so-called pair population analysis.[13,14] Within that approach it was possible to demonstrate that the 'effective' pair populations are indeed closely related to classical chemical bonds.[15]

There is as yet no consensus as to the most useful approaches for the generalization of the concepts of bond order and valence to correlated (post-SCF) wave functions. One aim of the present study is to examine some of the existing proposals and, based on our findings, to put forward a new scheme. A further aim is to generalize the concept of valence so as to be consistently applicable at post-SCF levels of theory.

THEORY

The starting point of many modern approaches to the problem of bond order is the so-called bond index introduced some time ago by Wiberg[5] at the level of semiempirical MO methods with orthogonal basis sets, but which was subsequently generalized for *ab initio* SCF wave functions.[16,17] This bond index is defined according to

$$B_{\mathrm{AB}} = \sum_{\mu \in \mathrm{A}} \sum_{\nu \in \mathrm{B}} (PS)_{\mu\nu}(PS)_{\nu\mu} = W_{\mathrm{AB}} \tag{1}$$

in which μ,ν label basis functions, A,B label nuclei, and $\boldsymbol{P}$ and $\boldsymbol{S}$ are one-particle density and overlap matrices, respectively. Such an expression arises in a Mulliken-like partitioning of the normalization condition for the one-particle density. A similar approach has been pursued recently by Cioslowski and Mixon[18] within the framework of Bader's theory of atoms in molecules.[19] In their scheme, the bond index is defined in terms of integrals over the atomic basins Ω_{A} and Ω_{B}:

$$B_{\mathrm{AB}} = 2 \sum_{i}^{\mathrm{occ}} \langle \phi_i | \phi_i \rangle_{\mathrm{A}} \langle \phi_i | \phi_i \rangle_{\mathrm{B}} \tag{2}$$

where the summation runs over occupied MOs. Such a heuristic generalization is not entirely satisfactory and so we propose instead

$$B_{AB} = -2F(\Omega_A,\Omega_B) \tag{3}$$

in which the »inter-loge correlation« $F(\Omega_A,\Omega_B)$, introduced by Bader,[20] is calculated from the pair density according to

$$F(\Omega_A,\Omega_B) = 2\left(\int_{\Omega_A} dr_1 \int_{\Omega_B} \rho_2(r_1,r_2)dr_2\right) - \left(\int_{\Omega_A} \rho_1(r_1)dr_1\right)\left(\int_{\Omega_B} \rho_1(r_1)dr_1\right). \tag{4}$$

The magnitude of $F(\Omega_A,\Omega_B)$ is related to the number of pairs which can be formed between electrons in Ω_A and those in Ω_B.[20] In the special case of a closed-shell SCF wave function, the pair density is given by

$$\rho_2(r_1,r_2) = \frac{1}{2}\rho_1(r_1)\rho_1(r_2) - \frac{1}{4}\rho_1(r_1,r_2)\rho_1(r_2,r_1) \tag{5}$$

and so Eqs. (3) and (4) reduce to

$$B_{AB} = 4\sum_i^{\text{occ}}\sum_j^{\text{occ}} \langle\phi_i|\phi_j\rangle_A\langle\phi_j|\phi_i\rangle_B\,. \tag{6}$$

We note that this last definition, unlike that of Cioslowski and Mixon,[18] reduces to W_{AB} if the integration over atomic basins is replaced by Mulliken-like restrictions on the summations over basis functions.

Eq. (6) is a special case of Eq. (2.18) of Ref. 21

$$B_{AB} = \sum_i^{\text{occ}} n_i \sum_j^{\text{occ}} n_j\ \langle\phi_i|\phi_j\rangle_A\langle\phi_j|\phi_i\rangle_B \tag{7}$$

which is valid for configuration interaction (CI) wavefunctions composed of double excitations among molecular orbitals ϕ_i. A form of Eq. (7) is valid for general CI wavefunctions only if ϕ_i the are natural orbitals.[22] The molecular orbital or natural orbital occupancies n_i are generally noninteger numbers.

A principal concern of correlated bond indices is whether the definition is to be based on inherently pair quantities or whether a satisfactory scheme can be developed from just one-electron quantities, as in the SCF case. Intuitively, a pair density approach is preferable because of the importance of the electron pair in models of chemical bonding. An obvious candidate for further study is the definition embodied in Eqs. (3) and (4). In the present work, we have decided to replace the integrals over atomic basins by appropriate restrictions on the summations over basis functions (as in Eq. (1)) so that:

$$B_{AB} = 2 \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\kappa} \sum_{\lambda} \frac{1}{2} [P_{\mu\nu} P_{\kappa\lambda} - D(\mu\nu|\kappa\lambda)] S_{\mu\kappa} S_{\nu\lambda} \tag{8}$$

in which $D(\mu\nu|\kappa\lambda)$ is an element of the (spin-less) pair density matrix. Such a definition was proposed some time ago by Giambiagi[23] and Mayer.[24] Mayer has also investigated this scheme for the simple case of the dissociation of H_2 and concluded that the resulting values of B_{AB} are too small to be considered a realistic measure of bond order. It seems useful to carry out a few further numerical tests, to discover if this finding is a general one. With this in mind, we examined the ground states of H_2, LiH, H_2O and CH_4 at equilibrium geometry, taking *ab initio* correlated pair densities from the spin-coupled (SC) calculations described in detail in Ref. 25. The corresponding SCF calculations are also described in Ref. 25. The resulting values of B_{AB} are collected in Table I.

TABLE I

Comparison of pair-density bond indices, derived from Eq, for *ab initio* SCF and spin-coupled (SC) wave functions

Molecule	SCF	SC
H_2	1.000	0.526
LiH	0.911	0.477
CH_4	0.980	0.568
H_2O	0.909	0.610

The key observation from Table I is that although the classical bond multiplicities are well represented by the SCF bond orders, the values derived from the correlated pair density are far too small. It seems that Mayer's finding for H_2 is quite general and we may conclude that Eq. (8) does not represent a useful basis for defining post-SCF bond orders. It is likely that direct integration over atomic basins, as in Eqs. (3) and (4), would lead to analogous conclusions. Nonetheless, we still recommend further investigation of Eq. (6) for SCF wave functions.

We turn instead to definitions based only on one-electron quantities. Ángyán, Loos and Mayer[26] have recently proposed:

$$B_{AB} = 2 \left(\int_{\Omega_A} dr_1 \int_{\Omega_B} \rho_1(r_1,r_2)\, \rho_1(r_2,r_1) dr_2 \right). \tag{9}$$

If the integrations over atomic basins are replaced by restricted summations over basis functions, then this last equation reduces to the same general form as Eq. (1), but now with $\boldsymbol{P}$ calculated from the correlated wave function. In order to test the utility of such a scheme, we collect in Table II values of B_{AB} calculated according to Eq. (1) for the same systems as in Table I. It is clear that these new values, labeled 'unscaled', are chemically much more reasonable as a measure of bond order than are those calculated from Eq. (8). Nevertheless, it does seem worthwhile to consider a further modification to this definition. Because of the idempotency of the SCF one-particle density matrix, the corresponding indices satisfy the useful normalization condition

TABLE II

Comparison of unscaled and renormalized bond indices (derived from W_{AB}) for SC wave functions

Molecule	unscaled	renormalized
H_2	0.956	0.979
LiH	0.878	0.897
CH_4	0.951	0.969
H_2O	0.876	0.892

$$\frac{1}{2}\sum_{\mathrm{A}} W_{\mathrm{AB}} + \sum_{\mathrm{A}<B} W_{\mathrm{AB}} = N \tag{10}$$

whereas

$$\frac{1}{2}\sum_{\mathrm{A}} W_{\mathrm{AB}}^{\mathrm{corr}} + \sum_{\mathrm{A}<B} W_{\mathrm{AB}}^{\mathrm{corr}} = \tilde{N} \tag{11}$$

in which the quantity $\tilde{N}$ is in no simple relation to the number of electrons N, except that $\tilde{N} \leq N$. An obvious procedure, as was also proposed some time ago by Bochicchio,[27] is to rescale the correlated bond indices by a factor of $(N/\tilde{N})$. The corresponding values for our test molecules are reported in Table II. One side effect of this rescaling is that the post-SCF indices approach even more closely the SCF values. In addition to this useful result there is yet another interesting consequence of rescaling the correlated bond indices. This consequence concerns the concept of atomic valence. The first attempt at introducing these quantities is due to Jug[21,22] who based his approach on

CI wavefunctions. Here we propose a slight modification of this approach which takes into account the rescaling of the bond indices, *i.e.*

$$V_{\mathrm{A}}^{\mathrm{corr}} = (N/\tilde{N}) \sum_{\mathrm{B} \neq A} W_{\mathrm{AB}}^{\mathrm{corr}} . \tag{12}$$

Taken together with the various (re)normalization conditions, this last expression suggests an alternative definition, namely:

$$V_{\mathrm{A}}^{\mathrm{corr}} = 2q_{\mathrm{A}} - (N/\tilde{N})\, W_{\mathrm{A}}^{\mathrm{corr}} \tag{13}$$

in which q_{A} is the Mulliken population on center A.

Atomic valencies calculated from (rescaled) bond indices are collected in Table III for our test systems. Taking account of electron correlation tends to reduce the values of W_{A}, so that the atomic valencies derived from correlated densities are smaller than the SCF values. We note in passing that *ab initio* SCF valencies calculated with flexible basis sets may exceed the classical limits (*e.g.* $V_{\mathrm{A}}^{\mathrm{SCF}}(\mathrm{C}) > 4$) and that a procedure has been proposed to remedy this inconvenience.[28] It now seems that such rather artificial corrections may turn out to be redundant for correlated wave functions of sufficient quality.

TABLE III

Atomic valencies (V_{A}) from SCF and SC wave functions

Molecule	atom	SCF (Eq. 1)	SC (Eq. 12)	SC (Eq. 13)
H_2	H	1.000	0.979	0.979
LiH	Li	0.911	0.897	0.860
	H	0.911	0.897	0.934
CH_4	C	3.920	3.876	3.865
	H	0.951	0.937	0.940
H_2O	O	1.818	1.784	1.772
	H	0.909	0.891	0.897

Finally, we report in Table IV the variation of atomic valence, $V_{\mathrm{A}}(\mathrm{H})$, with bond length, R, for the simple case of H_2, using the same SC wave functions as in Ref. 25 and renormalized bond indices. Around the equilibrium geometry, the atomic valence of H is close to its classical limit of unity, suggesting that the atoms are completely engaged in bonding. $V_{\mathrm{A}}(\mathrm{H})$ decreases monotonically with increasing R, reaching zero at complete dissociation. It

TABLE IV

Change to the atomic valence of H during the course of the dissociation of H_2

R/bohr	V_A(H)	R/bohr	V_A(H)	R/bohr	V_A(H)
0.75	0.995	2.0	0.941	4.6	0.203
0.8	0.994	2.4	0.890	5.0	0.120
1.0	0.991	2.8	0.809	6.0	0.028
1.2	0.986	3.2	0.692	8.0	0.001
1.4	0.979	3.4	0.622	10.0	0.000
1.6	0.970	3.8	0.469		
1.8	0.957	4.2	0.322		

is tempting in the present case to interpret $1 - V_A$(H) as the »free valence« of the hydrogen atom. This free valence is very small around the equilibrium geometry but reaches unity at large R.

REFERENCES

1. C. A. Coulson, *Proc. Roy. Soc* **A169** (1939) 413.
2. L. Salem, *Molecular Orbital Theory of Conjugated Molecules*, W. A. Benjamin, New York, 1961, pp. 165–172.
3. K. Jug, *Croat. Chem. Acta* **57** (1984) 941.
4. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1841.
5. K. B. Wiberg, *Tetrahedron* **24** (1968) 1083.
6. D. R. Armstrong, P. G. Perkins, J. J. Stewart, *J. Chem. Soc.* (1973) 2273.
7. M. A. Natiello, J. A. Medrano, *Chem. Phys. Lett.* **105** (1984) 180.
8. M. Giambiagi, M. S. Giamiagi, D. R. Grempol, C. D. Heymann, *J. Chim. Phys.* **72** (1975) 15.
9. R. S. Boyd, Can *J. Chem.* **51** (1973) 1151.
10. K. Jug, *J. Am. Chem. Soc.* **99** (1977) 7800.
11. A. B. Sannigrah, *Adv. Quant. Chem.* **23** (1992) 301.
12. M. S. Gopinathan, K. Jug, *Theor. Chim. Acta* **63** (1983) 497, 511.
13. R. Ponec, M. Strnad, *Int. J. Quant. Chem.* **50** (1994) 43.
14. R. Ponec, *Coll. Czech. Chem. Commun.* **59** (1994) 505.
15. R. Ponec, F. Uhlik, *Coll. Czech. Chem. Commun.* **59** (1994) 2567.
16. I. Mayer, *Chem. Phys. Lett.* **97** (1983) 270.
17. I. Mayer, *Int. J. Quant. Chem.* **26** (1984) 151.
18. J. Cioslowski, T. S. Mixon, *J. Am. Chem. Soc.* **113** (1991) 4142.
19. R. F. W. Bader, *Chem. Rev.* **91** (1991) 893.
20. R. F. W. Bader, M. E. Stephens, *J. Am. Chem. Soc.* **97** (1975) 7391.
21. K. Jug. *J. Comp. Chem.* **5** (1984) 555.
22. K. Jug, in *Molecules in Physics, Chemistry and Biology Vol. 3*, J. Maruani (Ed.), Reidel, Dordrecht, 1988, p. 149.

23. M. S. Giambiagi, M. Giambiagi, F. E. Jorge, *Theor. Chim. Acta* **68** (1985) 337.
24. I. Mayer, *Int. J. Quant. Chem.* **29** (1986) 73.
25. D. L. Cooper, R. Ponec, T. Thorsteinsson, G. Raos, *Int. J. Quant. Chem.* **57** (1996) 501.
26. J. Angyan, M. Loos, I. Mayer, *J. Phys. Chem.* **98** (1994) 5244.
27. R. Bochicchio, *J. Mol. Struct. (Theochem)* **228** (1991) 227.
28. K. Jug, F. Fasold, M. S. Gopinathan, *J. Comput. Chem.* **10** (1989) 965.

SAŽETAK

O definicijama indeksa veze i valencije za korelirane valne funkcije

Robert Ponec, Filip Uhlik, David L. Cooper i Karl Jug

Prodiskutirane su definicije indeksa veze i valencije za korelirane valne funkcije. Na razini teorije vezanih spinova istražena je korisnost renormaliziranih Wibergovih indeksa veze za niz jednostavnih molekula.