Bond Orders and Valences in some Simple Sulphur Compounds

I. MAYER*

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

and M. RÉVÉSZ

Department for Structural Studies, Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, H-1431 Budapest, P.O. Box 117, Hungary

Received August 2, 1983

One of us recently suggested suitable definitions [1] of the bond order (multiplicity) index and of the valence number of an atom in a molecule for the *ab initio* SCF-LCAO-MO method, in order to give a link between the quantum chemical calculations and the genuine chemical concepts. The proposed quantities have integer values equal to those predicted by the classical valence concepts for some diatomics treated at the minimal basis level (*e.g.* H_2, N_2, F_2). For other systems the bond order and valence indices are not strictly integers but are still quite close to the corresponding classical values. These new quantities may to some extent be considered as *ab initio* generalizations of Wiberg indices [2] and valence numbers [3] defined within the framework of the semiempirical CNDO/2 method.

By defining the spinless **P**-matrix as $\mathbf{P} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta}$, where

$$\mathbf{P}^{\sigma} = \sum_{i} \mathbf{c}_i^{\sigma} \mathbf{c}_i^{\sigma +};$$

$\sigma = \alpha$ or β, and $\mathbf{c}_i$ is the column vector of the orbital coefficients of the i-th MO of spin σ, the bond order between atoms A and B may be calculated for the single determinant wave functions as

$$B_{AB} = \sum_{\lambda \epsilon A} \sum_{\omega \epsilon B} (\mathbf{PS})_{\omega\lambda} (\mathbf{PS})_{\lambda\omega} \qquad (1)$$

where **S** is the overlap matrix of the whole AO basis. The total actual valence of atom A is defined as

$$V_A = 2 \sum_{\mu \epsilon A} (\mathbf{PS})_{\mu\mu} - \sum_{\mu, \nu \epsilon A} (\mathbf{PS})_{\mu\nu} (\mathbf{PS})_{\nu\mu} \qquad (2)$$

It can be shown that for the closed shell systems with $\mathbf{P}^{\alpha} = \mathbf{P}^{\beta}$ one has the equality

$$V_A = \sum_{B (B \neq A)} B_{AB},$$

while for the open-shell ones treated at the single determinant UHF level the free valence index of atom A is

$$F_A = V_A - \sum_{B (B \neq A)} B_{AB} \qquad (3)$$

We have performed *ab initio* STO-3G, 3-21G (sp bases for second row atoms) and STO-3G* (spd basis for second row) calculations of above quantities for some simple sulphur compounds. Experimental geometries [4–11] have been used, except for H_2SO and H_2SO_2 for which the geometries obtained in *ab initio* geometry optimization [12] have been applied. The results collected in Table I give an insight into the bonding situation in these molecules and show the importance of including d-type orbitals in the basis in order to treat sulphur atoms with a formal valence of six or four (but not two). The d-orbitals are necessary to accommodate all the electrons forming the (double) bonds and/or lone pairs. The comparison of the STO-3G* and 3-21G results indicates that the inclusion of the d-orbitals *cannot* be substituted by a more flexible sp basis. These conclusions are in complete agreement with our recent results obtained for some sulphonyl chloride molecules at both CNDO/2 and *ab initio* levels [13] (a discussion of the bond order and valence indices obtained for sulphonyl chloride derivatives will be given elsewhere [14]).

According to the above results, we propose the following 'rule of thumb': the inclusion of the d-orbitals in the basis is needed to account for the *qualitative* aspects of the bonding in the given molecule if the bond order and valence indices [eqn. (1) to (3)] obtained in an sp basis are far from the values predicted by the classical valence concepts. In these cases the d-orbitals are not polarization function but true *valence orbitals*.

References

1 I. Mayer, *Chem. Phys. Letters, 97*, 270 (1983).
2 K. A. Wiberg, *Tetrahedron, 24*, 1083 (1968).
3 D. R. Amstrong, P. G. Perkins and J. J. P. Stewart, *J. Chem. Soc. Dalton, 1973*, 838.
4 T. H. Edwards, N. K. Moncur and L. E. Snyder, *J. Chem. Phys., 46*, 2139 (1967).
5 F. J. Marsh and M. S. Gordon, *Chem. Phys. Letters, 45*, 255 (1977).
6 F. J. Lovas, E. Tiemann and D. R. Johnson, *J. Chem. Phys., 60*, 5005 (1974).
7 A. H. Clark, B. Beagley, *Trans. Faraday Soc., 67*, 2216 (1971).

*Author to whom correspondence should be addressed.

0020-1693/83/$3.00

TABLE I. Bond Order and Valence Indices for Some Sulphur Compounds.

Molecule	Bond orders				Valences			
	Atoms	STO-3G	3-21G	STO-3G*	Atom	STO-3G	3-21G	STO-3G*
H_2S	S–H	0.9883	0.9479	0.9953	S	1.9966	1.8957	1.9907
	H...H	0.0007	−0.0176	0.0001	H	0.9990	0.9303	0.9954
SO (triplet)	S–O	1.4037	1.2037	1.7630	S	2.3302 (0.9265)[a]	2.2288 (1.0251)[a]	3.0852 (1.3222)[a]
					O	2.4864 (1.0827)[a]	2.2139 (1.0101)[a]	2.5049 (0.7419)[a]
SO (singlet)	S–O	1.9367	1.7117	2.1824	S	1.9367	1.7117	2.1824
					O	1.9367	1.7117	2.1824
OSSO	S–O	1.6687	1.5048	1.9600	S	2.0394	1.5560	3.7154
	S–S	0.3168	0.0096	1.5015	O	1.9457	1.7001	2.2942
	S...O	0.0538	0.0417	0.2539				
	O...O	0.2231	0.1537	0.0803				
SO_2	S–O	1.4628	1.4633	2.1558	S	2.9252	2.9266	4.3116
	O...O	0.5037	0.3035	0.2153	O	1.9663	1.7668	2.3711
SO_3	S–O	1.2598	1.3926	2.0773	S	3.7795	4.1777	6.2319
	O...O	0.3057	0.1729	0.1406	O	1.8713	1.7383	2.3586
H_2SO	S–H	0.8440	0.7340	0.8937	S	2.6546	2.5455	3.5520
	S–O	0.9666	1.0775	1.7646	H	0.9989	0.9378	0.9872
	H...H	0.0482	0.0787	0.0331	O	1.1801	1.3279	1.8854
	O...H	0.1067	0.1252	0.0604				
H_2SO_2	S–H	0.7144	0.6607	0.8814	S	3.6989	3.8614	5.8483
	S–O	1.1351	1.2700	2.0427	H	0.9995	0.9190	0.9902
	H...H	0.0395	0.0480	0.0213	O	1.5305	1.5728	2.2220
	O...O	0.1495	0.0924	0.0918				
	O...H	0.1228	0.1052	0.0437				
Cl_2SO_2	S–O	1.3043	1.3196	2.1170	S	3.7342	3.8956	6.1036
	S–Cl	0.5628	0.6282	0.9348	O	1.8877	1.6757	2.3892
	Cl...Cl	0.0684	0.0661	0.0651	Cl	0.9987	0.9312	1.1775
	O...O	0.2159	0.1191	0.0945				
	O...Cl	0.1838	0.1185	0.0888				
$(CH_3)_2SO$	S–O	1.1855	1.2587	1.9396	S	2.9258	2.6895	3.9205
	S–C	0.8562	0.7227	0.9589	O	1.4498	1.4539	2.0727
	C–H	0.9781	0.8913	0.9741	C	3.9399	3.4995	3.9566
		0.9833	0.9096	0.9772	H	0.9937	0.8947	0.9938
		0.9784	0.8862	0.9740		0.9945	0.9033	0.9948
	C...C	0.0174	0.0100	0.0104		0.9914	0.8836	0.9918
	O...C	0.1220	0.0746	0.0579				
$(CH_3)_2SO_2$	S–O	1.2176	1.2809	2.2431	S	3.8271	4.0745	6.3735
	S–C	0.6850	0.7526	0.9121	O	1.8007	1.5426	2.4290
	C–H	0.9824	0.9069	0.9707	C	3.9284	3.5386	3.9598
		0.9811	0.9043	0.9773	H	0.9955	0.9117	0.9957
	O...O	0.2900	0.1569	0.0672		0.9956	0.9095	0.9962
	C...C	0.0185	−0.0079	0.0173				
	O...C	0.1380	0.0371	0.0512				

[a] Free valence indices F_A are given in parentheses.

8 A. Kaldor and A. G. Maki, *J. Mol. Struct., 15,* 123 (1973).
9 I. Hargittai, *Acta Chim. Acad. Sci. Hung., 57,* 403 (1968); *ibid., 60,* 231 (1969).
10 W. Typke, *Z. Naturforsch., 33a,* 847 (1978).
11 M. Hargittai and I. Hargittai, *J. Chem. Phys., 59,* 2513 (1973).
12 A. Schmiedekamp, D. W. J. Cruickshank, S. Skaarup, P. Pulay, I. Hargittai and J. E. Boggs, *J. Am. Chem. Soc., 101,* 2002 (1979).
13 I. Mayer, M. Révész and I. Hargittai, *Acta Chim. Acad. Sci. Hung.,* in press.
14 I. Mayer, M. Révész and I. Hargittai, to be published.