Interatomic and intraatomic analysis of the density matrix: applications to chlorobenzenes

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Abstract. Bond orders and valence indices have been evaluated employing Mayer's definitions with orthogonalized atomic orbitals (OAO) obtained from Löwdin orthogonalization over an STO-3G basis set in an *ab initio* formalism. It has been observed that the eigenvalues of the submatrices associated with bond order orbitals, natural hybrid orbitals and natural bond orbitals also reproduce the same values of the bond orders and the valence indices which in turn are quite close to the classical values. Bond orders obtained by a similarity transformation of the *ab initio* density matrix differ appreciably in numerical magnitude.

Keywords. Löwdin orthogonalization; bond order orbitals, natural hybrid orbitals and natural bond orbitals; similarity transformation.

1. Introduction

One of the main objectives of the *ab initio* molecular orbital studies of the electronic structure of molecules is to elucidate the nature of the classical chemical bond in terms of quantum chemical parameters. Indices like bond order and valence index are classical concepts which have been long used to parameterize and distinguish different bonding situations. They also represent useful links between the quantum chemical results and classical concepts since their *ab initio* values often closely follow the classical valence theory results. In spite of this important role of these indices, their evaluation from *ab initio* calculations have been rare in the literature.

In a pioneering work (Coulson 1939) introduced a bond order parameter and gave an expression to relate it with the bond lengths for π-electron systems. This relationship has been used with a fair amount of success in both π-electron and all valence electron semiempirical theories to estimate changes in bond lengths (see Yadav *et al* 1972, 1973, 1975, 1987a, for applications to substituted benzenes;

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experimental results are discussed by Cvitas *et al* 1970 and Niu and Boggs 1984). In more recent years, several workers have given other definitions for bond orders in *ab initio* theory (Mayer 1983, 1984; Elliot and Richards 1982; Mcluskie and Richards 1982).

The concept of bond order orbitals (BOO), natural hybrid orbitals (NHO) and natural bond orbitals (NBO) have been introduced by Jug (1977, 1984) and Gopinathan and Jug (1983) in order to define bond order and valence index in another way. These orbitals as originally defined could be generated only when the basis set is orthogonalized and this required the use of a modified density matrix PS in place of P in the formulation. Now PS is not a symmetric matrix (in contrast to P which is symmetric) because P and S do not commute. As in an earlier work therefore, we have preferred to replace PS by the Löwdin (1950) symmetrized density matrix $(S^{1/2} PS^{1/2})$ which is a symmetric matrix. Further since $tr(PS) = tr(S^{1/2} PS^{1/2})$, we hope to retrieve Jug's results. Another way of obtaining useful bond order indices is to use a similarity transformation as described by Mishra and Rai (1972) (see also Singh and Yadav 1986). Earlier studies on fluorobenzenes (Singh and Yadav 1986) have been fairly successful and we felt it worthwhile to see if the same procedure could work for chlorine substituted benzenes. Further, we considered the various procedures suggested by Jug to see if they lead to consistent results.

2. Computational details

The entire symmetrically orthogonalised density matrix P is subdivided into blocks referring to the atoms A, B, C, ... in the molecule as

$$
P_{\mu\nu} = \begin{bmatrix} P^{AA} & P^{AB} & P^{AC} & .... & P^{AL} \\ P^{BA} & P^{BB} & P^{BC} & .... & P^{BL} \\ P^{CA} & P^{CB} & P^{CC} & .... & \\ ... & ... & ... & & \\ P^{LA} & P^{LB} & P^{LC} & .... & P^{LL} \end{bmatrix} \tag{1}
$$

The diatomic blocks P^{AB} are defined as the matrix formed by the elements of $P_{\mu\nu}$ in which μ and ν are the atomic orbitals related to atoms A and B respectively. It is clear that P^{AA} refers to charge and hybridization of atom A while P^{AB} refers to the bond between atoms A and B.

The diatomic portion of $P_{\mu\nu}$ matrix represented by

$$
P_{\mu\nu}^{AB} = \begin{bmatrix} 0 & P^{AB} \\ \hline P^{BA} & 0 \end{bmatrix} \tag{2}
$$

is now diagonalised to get the eigenvalues λ_i and eigen vectors of this matrix. From the structure of the matrix P^{AB}, it follows that the eigenvalues appear in pairs and there are $|n_A - n_B|$ vanishing eigenvalues if n_A and n_B are the number of atomic

orbitals on A and B respectively. Gopinathan and Jug (1983) define the bond order between the atom A and B as

$$B_{AB} = \sum_i^{+ve} \lambda_i^2(AB) \tag{3}$$

and the valence index of atom A as

$$V_A = \sum_{B \neq A} \sum_i^{+ve} \lambda_i^2(AB). \tag{4}$$

Similarly the diagonalization of the intraatomic portion P^{AA} of the density matrix yields eigenvalues and eigenvectors which may be related to the occupancies and to the hybridization of atomic orbitals. These eigenvalues can again be used to define the valence index and the hybridized orbitals can be interpreted as natural hybrid orbitals (NHO) which are basic to an understanding of the steric arrangement of the atoms in the molecule.

The valence index V_A is computed by

$$V_A = \sum_{a'} (2q_{a'} - q_{a'}^2), \tag{5}$$

a' being the number of the atomic orbitals centered on A and the q's are the respective occupancies.

Lastly, the eigenvalues obtained from a diagonalization of the complete off-diagonal sub-matrix $P^{AB\cdots L}$ defined by

$$P^{AB\cdots L} = \begin{bmatrix} 0 & P^{AB} & P^{AC} & \cdots & P^{AL} \\ P^{BA} & 0 & 0 & \cdots & 0 \\ P^{CA} & 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdot \\ P^{LA} & 0 & 0 & \cdots & 0 \end{bmatrix} \tag{6}$$

are associated with natural bond orbitals (NBO) and determine the valence index of atom A given by the relation

$$V_A = \sum_i^{+ve} \xi_i^2, \tag{7}$$

where ξ_i are the eigenvalues of $P^{AB\cdots L}$ (These eigenvalues also appear in pairs). To calculate the bond orders under the similarity transformation procedure (Mishra and Rai 1972; Singh and Yadav 1986), the carbon atoms are assumed to retain their sp^2 hybridized state. The σ-bond orders are evaluated pair to pair after proper rotational transformation of the axes while the π bond orders are directly taken from the P matrix since these are unaffected by such transformations.

All the molecules have been considered as planar with all the bond angles 120°. The bond lengths of C–C, C–H and C–Cl bonds have been taken as 1·397, 1·084 and 1·723 Å respectively. The Gaussian 76 program of Binkley *et al* (1977) has

been extended to accommodate the suggestions of Mayer (1983, 1984), Jug (1977) and Mishra and Rai (1972).

3. Results and discussions

3.1 *Bond orders*

Table 1 lists the bond orders and valence indices as defined by Mayer (1984) for mono and dichlorobenzenes. The bond orders as well as the population in the various hybrids (the numbering follows that given in figure 1) obtained by the similarity transformation method are also given in the table. These values are in reasonable agreement with earlier results (Yadav *et al* 1987b). It is noteworthy that bond orders for the C–Cl and C–C bonds as calculated by Mayer's formula are significantly smaller than those obtained by the similarity transformation method, while for the C–H bonds the reverse holds good. This perhaps is due to the forced retention of the sp^2-trigonal hybridization in the similarity transformation method. Mayer's value for the bond order is reproduced when one uses the definition (3).

3.2 *Valence indices*

Table 1 also lists the calculated valence indices of the atoms employing Mayer's definition using the elements of the density matrix. These values are also consistent with our previous results (Yadav *et al* 1987b) and are also close to the integer values required by the classical concepts. It is more interesting to see that exactly the same values are obtained if one uses the eigenvalues of (BOO), (NHO) and (NBO) in the appropriate equations, (4), (5) and (7).

The diagonalization of the various parts of the density matrix as mentioned in §2 yields different indices e.g. bond order orbitals and associated eigenvalues, natural hybrid orbitals and associated eigenvalues and natural bond orbitals and their associated eigenvalues. These quantities have also been evaluated for all the molecules included in this study (the values are not reported in order to save space). As expected from general considerations the eigenvalues associated with the bond orbitals and the natural bond orbitals both appear in +ve and −ve pairs. The positive eigenvalues associated with the bond orbitals are five in number for both the carbon-carbon and the carbon-chlorine atoms and only one for the carbon-hydrogen bonds. This last eigenvalue is in each case close to unity but in the case of the C–C and the C–Cl bonds only one eigenvalue is close to unity. For C–Cl bonds the rest of the eigenvalues (4 in number) are less than 0·2 while for C–C bonds 3 are less than 0·2 and one is close to 0·66. This is reminiscent of the qualitative description of a C–Cl bond as a σ-bond with bond order 1 and of aromatic C–C bond as composed of a σ and a π bond (total bond order 1·66). The positive eigenvalues associated with the natural bond orbitals are characteristic of each individual atom and their values suggest that in the carbon atoms the $1s$ orbital remains unaffected by molecule formation while $2s$, $2p_x$, $2p_y$, $2p_z$ each participates equally in the formation of bonds with neighbouring atoms. The Cl atom again retains its unhybridized state and only one eigenvalue is close to unity (only one of

the $3p$ orbitals plays a major role in bond formation). Similar conclusions are reached from the analysis of the eigenvalues of the natural hybrid orbitals.

3.3 *Hybrid populations*

Hybrid populations in the different hybrids of the atoms (see figure 1 for numbering scheme) are listed in table 1. The $1s$ and the $2s$ orbitals of the chlorine

Table 1. Calculated values of bond orders, valence indices and hybrid populations for some chlorobenzenes using an STO-3G basis set

Molecule	Bonds*	Bond orders[a]	Atoms*	Valence indices	Hybrid* No.	Hybrid Population
Monochloro-benzene	C_1-C_2	1·421(1·639)	C_1	3·968	1	0·889
	C_2-C_3	1·444(1·623)	C_2	3·998	2	1·024
					3	0·984
	C_3-C_4	1·443(1·616)	C_3	3·998	4	1·048
	C_1-Cl_7	0·992(1·248)	C_4	3·999	5	1·009
	C_2-H_8	0·979(0·963)	Cl_7	1·026	6	0·996
	C_3-H_9	0·980(0·965)	H_8	0·998	7	1·042
	C_4-H_{10}	0·980(0·963)	H_9	0·999	8	1·006
			H_{10}	0·999	9	1·003
					10	1·041
Ortho-dichloro-benzene	C_1-C_2	1·394(1·655)	C_1	3·972	1	0·904
	C_2-C_3	1·420(1·642)	C_3	3·997	2	1·005
	C_3-C_4	1·443(1·620)	C_4	3·998	5	1·029
	C_4-C_5	1·440(1·611)	Cl_7	1·097	6	0·977
	C_1-Cl_7	1·005(1·260)	H_9	0·997	7	1·053
	C_3-H_9	0·978(0·967)	H_{10}	0·998	8	1·010
	C_4-H_{10}	0·980(0·967)			9	0·995
					10	1·046
					11	1·004
Meta-dichloro-benzene	C_1-C_2	1·421(1·643)	C_1	3·972	1	0·896
	C_3-C_4	1·420(1·636)	C_2	3·997	2	1·016
	C_4-C_5	1·442(1·619)	C_4	3·997	3	0·989
	C_1-Cl_7	1·002(1·259)	C_5	3·998	4	1·060
	C_2-H_8	0·976(0·964)	Cl_7	1·092	8	1·025
	C_4-H_{10}	0·978(0·964)	H_8	0·997	9	0·983
	C_5-H_{11}	0·979(0·969)	H_{10}	0·998	10	1·053
			H_{11}	0·998	11	1·008
					12	0·997
					13	1·048
Para-dichloro-benzene	C_1-C_2	1·420(1·636)	C_1	3·971	1	0·894
	C_2-C_3	1·444(1·627)	C_2	3·997	2	1·023
	C_1-Cl_7	1·002(1·257)	Cl_7	1·091	3	0·986
	C_2-H_8	0·978(0·967)	H_8	0·997	4	1·054
					5	1·001

*Values for other bonds, atoms and hybrids can be estimated by symmetry.
[a]Bond orders calculated by the similarity transformation method are given in parentheses.

atom behave like nonbonding ones and do not appreciably exchange any charge with the ring. Since the p_x orbital of the chlorine atom 'steals' more charge from the ring than the $p_x(\pi)$ donates to the ring, the chlorine atom is negatively charged. The hybrid of the carbon atom which is linked with the substituent loses charge to the substituent while the other hybrids gain charge.
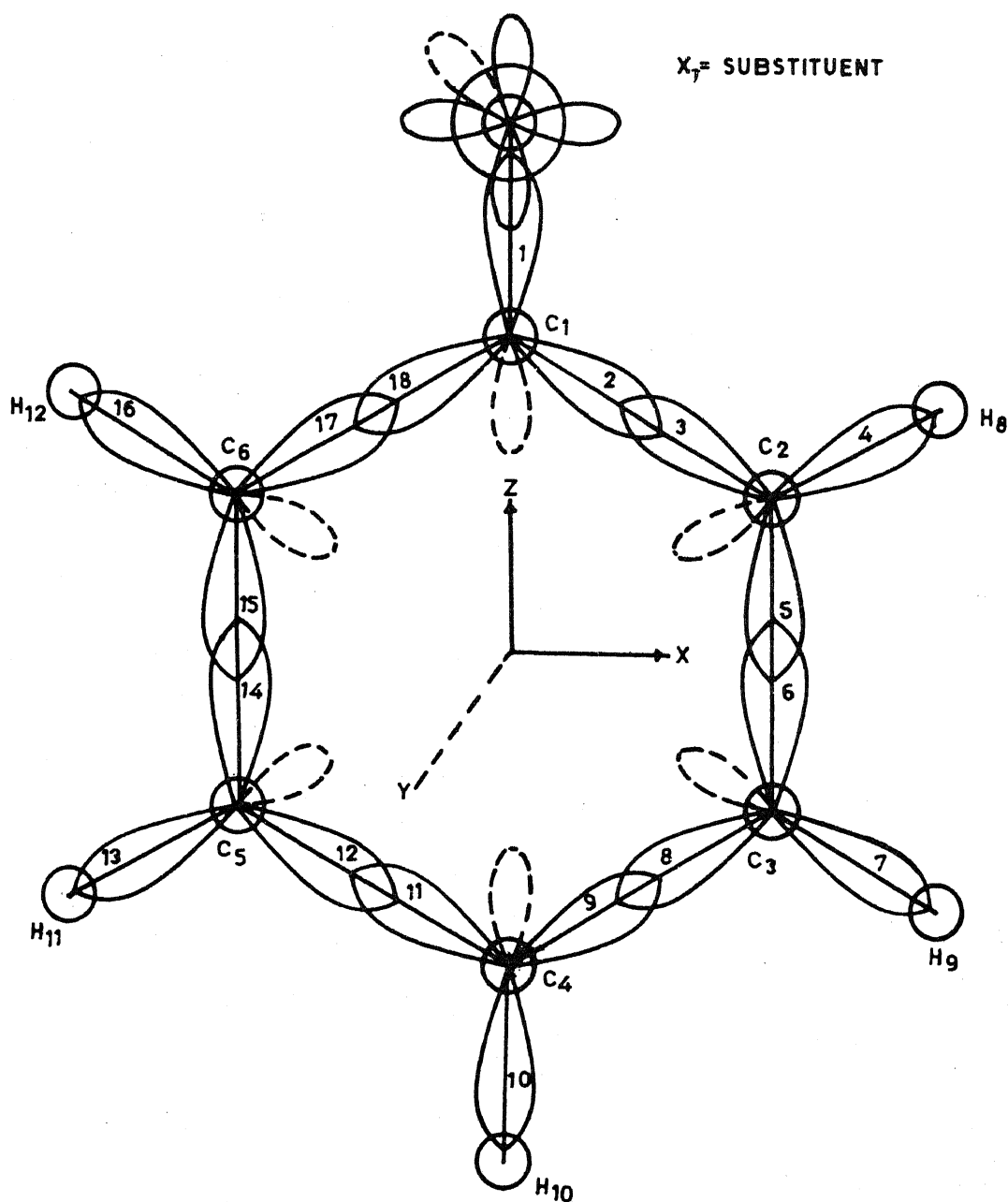

Figure 1 Choice of cartesian axes and atomic and hybrid numbering scheme; Molecular bonding in monosubstituted benzene, overlap of sp^2 hybrids of carbons with atomic orbitals of hydrogens and substituent. Atomic numbering for *o-m-p*-disubstituted benzenes can be obtained by replacing H_8, H_9 and H_{10} by X_8, X_9 and X_{10} respectively.

4. Conclusion

We conclude that Löwdin's symmetric orthogonalisation provides a suitable procedure for obtaining a symmetric density matrix which can be used to determine the various classical valence properties. This procedure also permits the use of a similarity transformation useful in semiempirical theories to *ab initio* studies. The various definitions of the valence parameters as given by Jug (1977, 1984) and by Gopinathan and Jug (1983) are seen to be consistent.

Acknowledgement

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