

***Ab initio* evaluation of oxidation numbers in some substituted benzenes**

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Abstract. Giambiagi's definition of oxidation number of an atom in a molecule has been applied successfully in the *ab initio* SCF theory to calculate oxidation numbers using STO-3G and 4-31G basis sets for some substituted benzenes involving –F, –OH, –CH₃ and –NH₂ as substituents. The present study suggests that the oxidation numbers also seem to be indicative of their orientational behaviour like the net atomic charges.

Keywords. Oxidation numbers; substituted benzenes; *ab initio* SCF theory.

1. Introduction

In our earlier papers (Singh and Yadav 1985, 1986, 1987), we have evaluated ground state properties such as ionization potentials, dipole moments, orbital populations, net charges, bond-orders and valence indices for several substituted benzenes using different basis sets. Another useful classical concept for describing and interpreting the extent of electron transfer to or from the vicinity of a given nucleus in a molecular environment and during the course of a chemical reaction is the oxidation number. Unfortunately, no reliable theory is as yet available for direct evaluation of the oxidation number and only qualitative quantum chemical approaches based on population analysis (Mulliken 1955) or electron density distribution (Bader 1980; Collins and Streitwiser 1980; Hilal 1980) are available. In order to calculate the number of electrons in a certain defined space, one has to perform numerical integration (Politzer *et al* 1977), which, however, is not suitable for obtaining systematic and accurate results within limited computer time.

Recently, Iwata (1980) obtained analytical expressions for the number and density of electrons in a sphere centred at an arbitrary point, provided that the wave functions are of the Gaussian type. Using this method, Takano *et al* (1982, 1984) have systematically studied two series of compounds containing chlorine and sulphur atoms in order to elucidate the concept of oxidation number associated

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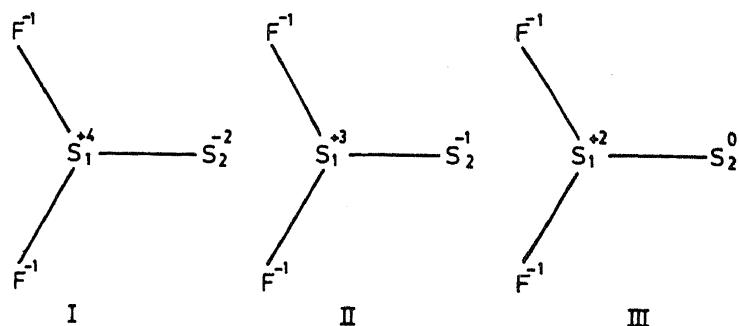


Figure 1. The three possibilities for oxidation numbers in S_2F_2 .

with the *ab initio* spherically averaged electron density around the atoms but some ambiguities still exist. For example, in the case of S_2F_2 , there exists some perplexity as to which of the three possibilities shown in figure 1 should be preferred. The authors give arguments supporting structure II, although they also say that chemical intuition could favour I or III. On the other hand, Giambiagi *et al* (1984) have defined oxidation number in terms of bond order indices and this number has been found very useful for neutral species. This definition often leads to dramatic changes in the oxidation numbers, as happens classically. In view of the above facts, it was thought worthwhile to apply Giambiagi's method to some of these molecules. A calculation on the same lines for some isomeric chlorobenzenes has already been presented by Yadav *et al* (1987). The present paper deals with the *ab initio* evaluation of oxidation numbers of some substituted benzenes.

2. Method of calculation

According to Giambiagi *et al* (1984), the oxidation number Ξ_A of an atom A is defined as

$$\Xi_A = (|Q_A|/Q_A) \sum_{A \neq B} B_{AB}$$

where Q_A is the net charge on A and the sum is carried out over the atoms with polarity different from that of atom A. B_{AB} is the bond order index between atoms A and B. In order to incorporate the above suggestion of Giambiagi, we have used the Gaussian 82 (Binkley *et al* 1983) programme to facilitate the calculation of these indices. Except for the molecule containing $-CH_3$ group, all the other molecules have been assumed to be planar with the benzene ring a regular hexagon (all ring angles 120°). The geometry of the benzene ring is assumed to be unaffected by the substitution. The successive substituents' ground state geometry has been taken from the Landolt-Bornstein Table (*Structure data of free polyatomic molecules* 1976). The C-C (ring), C-F, C-O ($-OH$), C-N ($-NH_2$), C-C ($-CH_3$), C-H, N-H, O-H and C-H ($-CH_3$) bond lengths have been taken as 1.397, 1.350, 1.380, 1.420, 1.540, 1.084, 1.040, 0.940 and 1.100 Å, respectively. The angles H-N-H, H-O-C and C-C-H on NH_2- , OH- and CH_3- substituted molecules, respectively, are taken to be 107, 105 and 109.5° .

3. Results and discussions

The calculated oxidation numbers have been presented in table 1. This definition, appropriate for neutral species, ensures that oxidation numbers in a molecule add up to zero. Despite the difficulty which arises in the balance of oxidation-reduction equations, it permits assignment of an oxidation number in ambiguous cases. A close inspection of this table indicates that the fractional values obtained in our calculations are equal (at least close) to the integers predicted in classical approaches. A set of signed (positive or negative) values are assigned to individual atoms so that their sum equals the total charge on the molecule or ion. The carbon atoms attached to the substituents acquire high positive values while other carbon atoms are observed to show negative values in all the molecules of the present study except toluene in which the carbon atom attached to the substituent group ($-\text{CH}_3$) in the 4-31G basis set attains a very small negative value while in the STO-3G basis the same atom attains a high positive value almost equal to its valence number. As this carbon atom has the same polarity in the 4-31G basis set as the other ring carbons as well as the carbon atom of the substituent $-\text{CH}_3$, its oxidation number is practically zero, with only very small contributions from bond order values corresponding to nonbonded atoms. Small variations of electronic densities (0.045 e in toluene in going from STO-3G to 4-31G) may switch the polarities and yield very different oxidation numbers. Although, this dramatic change in the oxidation numbers

Table 1. Oxidation numbers and net atomic charges of the atoms in some molecules

Molecules	Atoms	Oxidation numbers and net atomic charges*	
		STO-3G	4-31G
Monofluorobenzene	C_1	+3.900(+140)	+3.554(+410)
	C_2	-2.371(-086)	-2.329(-220)
	C_3	-0.985(-053)	-0.906(-178)
	C_4	-1.096(-069)	-1.029(-196)
	F_1	-1.023(-134)	-0.721(-460)
	H_2	+0.987(+071)	+0.937(+217)
	H_3	+0.984(+068)	+0.929(+205)
	H_4	+0.989(+064)	+0.932(+198)
<i>o</i> -Difluorobenzene	C_1	+2.565(+119)	+2.184(+384)
	C_3	-2.375(-078)	-2.276(-202)
	C_4	-1.090(-060)	-0.998(-185)
	F_1	-1.066(-127)	-0.764(-441)
	H_3	+0.982(+076)	+0.929(+232)
	H_4	+0.984(+069)	+0.923(+212)
<i>m</i> -Difluorobenzene	C_1	+3.905(+150)	+3.569(+429)
	C_2	-3.757(-110)	-3.683(-251)
	C_4	-2.471(-093)	-2.419(-223)
	C_5	-0.982(-044)	-0.873(-169)
	F_1	-1.033(-129)	-0.734(-452)
	H_2	+0.985(+079)	+0.938(+243)

(Continued)

Table 1. (continued)

Molecules	Atoms	Oxidation numbers and net atomic charges*	
		STO-3G	4-31G
<i>p</i> -Difluorobenzene	H ₄	+0.986(+079)	+0.935(+224)
	H ₅	+0.979(+074)	+0.919(+220)
<i>p</i> -Difluorobenzene	C ₁	+3.803(+134)	+3.462(+408)
	C ₂	-2.366(-077)	-2.294(-208)
	F ₁	-1.033(-133)	-0.733(-456)
	H ₂	+0.981(+077)	+0.929(+231)
Phenol	C ₁	+3.907(+129)	+3.610(+358)
	C ₂	-2.370(-084)	-2.341(-195)
	C ₃	-0.987(-051)	-0.903(-173)
	C ₄	-1.093(-076)	-1.028(-208)
	C ₅	-0.985(-051)	-0.909(-169)
	C ₆	-2.370(-101)	-2.327(-246)
	O ₁	-1.967(-300)	-1.573(-763)
	H ₂	+0.987(+071)	+0.939(+213)
	H ₃	+0.984(+067)	+0.927(+200)
	H ₄	+0.990(+060)	+0.933(+191)
	H ₅	+0.985(+065)	+0.927(+198)
	H ₆	+0.986(+053)	+0.946(+188)
	H(OH)	+0.935(+219)	+0.797(+405)
Aniline	C ₁	+3.896(+135)	+3.675(+350)
	C ₂	-2.365(-091)	-2.337(-227)
	C ₃	-0.988(-051)	-0.899(-166)
	C ₄	-1.091(-084)	-1.033(-221)
	N ₁	-2.916(-413)	-2.556(-984)
	H ₂	+0.987(+056)	+0.950(+185)
	H ₃	+0.985(+062)	+0.929(+191)
	H ₄	+0.990(+055)	+0.930(+181)
	H ₁ (N ₁ H)	+0.941(+176)	+0.855(+355)
Toluene	C ₁	+3.951(+014)	-0.070(+031)
	C ₂	-2.410(-072)	-0.956(-197)
	C ₃	-0.987(-060)	-0.931(-182)
	C ₄	-1.107(-067)	-0.938(-199)
	C ₅	-0.987(-061)	-0.930(-182)
	C ₆	-2.420(-071)	-0.960(-200)
	C ₁ (CH ₃)	-3.941(-173)	-2.868(-447)
	H ₂	+0.985(+059)	+0.934(+189)
	H ₃	+0.985(+061)	+0.934(+189)
	H ₄	+0.990(+060)	+0.934(+187)
	H ₅	+0.985(+061)	+0.934(+189)
	H ₆	+0.987(+059)	+0.933(+189)
	H ₁ (CH ₃)	+0.990(+064)	+0.946(+168)
	H ₂ (CH ₃)	+0.989(+061)	+0.951(+160)
	H ₃ (CH ₃)	+0.990(+064)	+0.946(+168)

* Oxidation numbers and net atomic charges of the other atoms can be obtained by symmetry. Values of the net atomic charges are in the parenthesis and are represented in units of 10^{-3} electrons.

favours its classical behaviour, the terrible discrepancy in the two different values of the oxidation numbers of the same atom in a molecule with different basis sets is an artifact of the calculational methods. However, the oxidation numbers of the carbon atom attached with the substituent in toluene reveals that this atom strongly discourages electrophilic substitution in both the basis sets although their polarities are different. Even then if such uncertainties arise, the question should certainly be settled through more rigorous calculations and more generalized definition. It is to be noted that positive and negative signs of the oxidation numbers are correlated with the signs of the net atomic charges and therefore unable to describe the subtle balance in σ and π effects.

In the STO-3G calculation the fluorine atoms show an oxidation number which is more than their classical valence number, but the 4-31G calculations yield values smaller than their corresponding valence numbers. It is to be noted that the calculated STO-3G valence index corresponding to this atom is higher than its classical valence index while this is reversed in the 4-31G basis set (Singh and Yadav 1985a, 1987) and this somewhat smaller numerical value of the valence index obtained with 4-31G basis may be related with the known "overpolarization" of the bonds characteristic of this split valence basis set. This error can be minimized by taking the polarization functions into account (Singh and Yadav 1985a).

Further, because of very small variations in their electronic charges, all the ring hydrogen atoms have approximately the same oxidation number which is also equal to the classical valence of hydrogen. The hydrogen atoms in the $-\text{OH}$ and the $-\text{NH}_2$ groups, however, have somewhat smaller values of oxidation numbers as compared to the ring hydrogens. The oxidation number of the oxygen atom in phenol is found to have a value very close to its valence index. This is because the oxygen atom has a polarity different from that of the other two atoms (i.e. $\text{H}(\text{OH})$ and C_1) attached to it and thus its valence coincides with the oxidation number. Similar results hold good for the other substituent atoms namely, nitrogen and carbon in the $-\text{NH}_2$ and the $-\text{CH}_3$ groups, respectively. Due to the negative oxidation number of the substituent atoms, the ring is left with a positive charge as a whole which in turn discourages any further electrophilic substitution. However, electron distribution in the highest occupied orbital has been proposed to be a significant factor in the outcome of the electrophilic substitution reactions (Fukui *et al* 1952).

4. Concluding remarks

Besides various well-known properties of the oxidation number viz. in enabling one to tell whether a substance taking part in a chemical reaction is oxidized or reduced, in the balancing of chemical equations, and in calculating the equivalent weights of oxidizing and reducing agents etc., the oxidation number, like the net charges, may be used as reactivity index upto some extent. However, in general, the present study confirms the validity of the statement of Cotton and Wilkinson (1979), "Since the only thing that is physically and chemically important is the actual electron distribution, it seems that in essentially covalent bonding situations, ionic formulations with their attendant necessity for, or consequence of, assigning oxidation numbers are best avoided".

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