

density of these "doorway" states in the energy region of interaction decreases from $\Delta\nu = 5$ to $\Delta\nu = 9$.

Presumably the same mechanism would be operative in the fluorobenzenes. Even given the levels of line-width uncertainty, the present data suggest an earlier onset of bandwidth narrowing than in benzene, perhaps due to a change in the relative frequencies of CH stretching and the CCH in-plane wag. It would be of great interest to extend these preliminary line-width results to higher overtones.

E. $\Delta\nu = 2$ of the Tetrafluorobenzenes. A doublet was observed in the $\Delta\nu = 2$ spectrum of 1,2,4,5-tetrafluorobenzene (Figure 6). The spectra of the other two tetrafluorobenzenes at $\Delta\nu = 2$ are broader and asymmetric. From the observed splitting between the symmetric and antisymmetric fundamentals,²⁷ the expected splitting between the $|2,0\rangle_+$ and $|2,0\rangle_-$ states can be calculated on the basis of the local mode description.²⁸ This calculated splitting is too small to account for the observed spacing between the doublet components of 1,2,4,5-tetrafluorobenzene at $\Delta\nu = 2$. Also, the frequencies of the lower frequency modes make it unlikely that one of the doublet components arises from a combination of the type observed in the dihalomethanes.²⁸

The most likely origin of this splitting, and of the asymmetry in the spectra of the other two tetrafluorobenzenes, is traces of rotational structure.

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V. Conclusions

Peaks due to inequivalent CH bonds are resolved in the overtone spectra of fluorinated benzenes. CH bond lengths from the frequency shifts of the peak positions in these spectra agree with those from geometry-optimized ab initio molecular orbital calculations. In particular, agreement with calculations at the 4-21G level is excellent. These calculations predict the small changes in bond lengths better than calculations at the STO-3G level. Overtone spectra and this type of analysis would appear to provide the best available technique for determining CH bond lengths in molecules of this size.

Substituent-induced charge redistribution can be modelled by an electron population parameter, which describes a CH bond in simple terms of "ionic" and "covalent" parts. Changes in such a parameter correlate very well with changes in CH bond lengths. Moreover, the parameter provides a simple physical explanation of bond-length changes with substitution.

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Registry No. Fluorobenzene, 462-06-6; 1,3-difluorobenzene, 372-18-9; 1,2-difluorobenzene, 367-11-3; 1,4-difluorobenzene, 540-36-3; 1,3,5-trifluorobenzene, 372-38-3; 1,2,3,4-tetrafluorobenzene, 551-62-2; 1,2,4,5-tetrafluorobenzene, 327-54-8; 1,2,3,5-tetrafluorobenzene, 2367-82-0.

Quantum Chemical Interpretation of Oxidation Number as Applied to Carbon and Oxygen Compounds. Numerical Analysis of the Electron Distribution with ab Initio Molecular Orbital Wave Functions

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Abstract: To get quantum chemical interpretation of the oxidation states and oxidation numbers of various atoms, the electron distribution around the carbon, oxygen, and fluorine atoms was analyzed for three series of compounds (i) CH₄, CH₃OH, HCHO, HCOOH, and CO₂, (ii) H₂O and H₂O₂, and (iii) F₂O and F₂O₂ by the ab initio molecular orbital calculations. The difference spherically averaged electron density, $\Delta\rho_0(R) = \rho_0(R) - \sum_i^{\text{atom}} \rho_{0i}(R)$, on a sphere with radius R centered at the atom concerned, was calculated with various qualities of basis sets. The present analysis, together with those previously obtained for sulfur and chlorine compounds, shows that (i) the oxidation states around the carbon atom change stepwise from CH₄ to CO₂ a little less than in the case with the S and Cl compounds, (ii) the oxygen atom can retain the same oxidation state in molecules except in H₂O₂ and fluorine oxides, and (iii) the fluorine atom is the most electronegative but the difference from oxygen is less than generally accepted. These conclusions are almost consistent with the formally assigned classical oxidation numbers.

Introduction

One of the main purposes of the ab initio calculations of molecular electronic states is to elucidate the nature of the chemical bond in terms of quantum chemically defined quantities, so that one can reinterpret traditionally used chemical concepts. With the development of computational techniques and the accumulation of wave functions of high quality, detailed three-dimensional analysis of the electronic distribution over a whole molecule,²⁻⁵

instead of the conventional population analysis,⁶⁻⁸ becomes possible.

The classical concepts of the oxidation state and oxidation number are usually introduced in most textbooks of inorganic chemistry and are even favorably used in the research area of inorganic chemistry.¹⁰ On the other hand, in organic chemistry,

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although the oxidation–reduction reactions play one of the most important roles, the concept of the oxidation number is rarely used. During the oxidation of CH_4 to CO_2 , however, a fairly large change in electron distribution around the carbon atom is actually detected from ESCA studies.¹¹ A possible reason for the neglect of the oxidation number concept in organic chemistry might be that this concept is not duly defined, and accordingly there is an ambiguity in assigning the oxidation numbers, if formal, to the atoms involved in highly covalent bonds such as C–H and C–O bonds.

Recently, we found from the systematic electron number analysis with the ab initio wave functions that the change of the spherically averaged electron density in a sphere with radius R , $\Delta\rho_0(R)$ (the spherically averaged deformation density), is proportional to the formally assigned oxidation number both for the series of sulfur and chlorine compounds.¹² This means that by a careful inspection of the $\Delta\rho_0(R)$ either by changing R or by choosing a fixed R value, we can detect subtle but stepwise changes of the electron distribution around the specified atom as proportional to the classical oxidation number. In some cases we could also assign the otherwise undecided oxidation numbers by the $\Delta\rho_0(R)$ analysis.

In this paper the same analysis was performed for a series of carbon compounds, i.e., CH_4 , CH_3OH , HCHO , HCOOH , and CO_2 , to study in detail how the oxidation state around the carbon atom changes with the stepwise oxidation reaction. In addition, to check the standardizability of the oxygen atom in assigning the oxidation number, the $\Delta\rho_0(R)$ analysis was performed also for the oxygen atoms in the series of carbon compounds, H_2O , H_2O_2 , and F_2O_2 . In the last two compounds the more electronegative fluorine atoms are thought to make the formal oxidation number of the oxygen atoms positive. Several relevant molecules were also studied. We can conclude from this systematic analysis that during the stepwise oxidation reaction of CH_4 to CO_2 the $\Delta\rho_0(R)$ values around the carbon atom also change stepwise as proportional to the formally assigned oxidation number just as in the case of the inorganic sulfur and chlorine compounds, whereas, except in a few cases, the oxidation state of the oxygen atom stays unchanged as assumed in the classical assignment of the oxidation number. It was found that oxygen is actually oxidized by fluorine, but a clear-cut assignment of the oxidation number for those cases is difficult.

Method of Calculation

The spherically averaged electron density $\rho_0(R)$ and its increment relative to the summed-up values of the component atoms, $\Delta\rho_0(R)$, were defined in the previous papers^{12,13} as

$$\rho_0(R) = \frac{dN(R)}{dR} / 4\pi R^2$$

$$\Delta\rho_0(R) = \rho_0(R) - \sum_i \rho_{0i}(R)$$

where $N(R)$ is the number of electrons in a sphere with radius R , and the subscript i refers to the contribution of the component free atom i .

In this work the electron density for the ground state of the following three series of molecules, with varying radius R around the key atoms, was mainly studied: (i) CH_4 , CH_3OH , HCHO , HCOOH , CO_2 ; (ii) H_2O , H_2O_2 ; and (iii) F_2O , F_2O_2 . Calculations for C_2H_6 , C_2H_4 , and C_2H_2 were also performed. The formally assigned oxidation numbers of carbon in series (i) and oxygen in series (ii) are given in Figure 1. For series (iii) the oxidation numbers of oxygen are assigned, respectively, as +2 and +1 with –1 of fluorine taken as the standard.

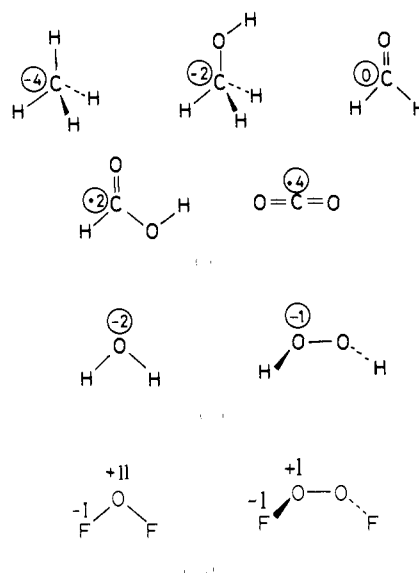


Figure 1. Three series of compounds studied and the formally assigned oxidation numbers for carbon, oxygen, and fluorine atoms in the series (i), (ii), and (iii).

Table I. Input Geometries^a

compd	symmetry	bond distance, Å	bond angle, deg
CH_4	T_d	C–H 1.0940	H–C–H 109.5
CH_3OH	C_s	C–O 1.4246	C–O–H 108.6
		C–H 1.0936	H–C–H 108.5
		O–H 0.9451	
		C=O 1.2078	H–C–H 116.5
HCOOH	C_s	C–H 1.1161	
		C=O 1.202	O=C–O 124.9
		C–O 1.343	H–C=O 124.1
		C–H 1.097	C–O–H 106.3
		O–H 0.972	
CO_2	$C_{\infty h}$	C=O 1.1598	O=C=O 180.0
H_2O	C_{2v}	O–H 0.9575	H–O–H 104.51
H_2O_2	C_2	O–O 1.475	H–O–O 94.8
		O–H 0.950 ^b	120.0 ^c
		O–H 1.4053	1–O–1 103.07
F_2O	C_{2v}	O–O 1.217	1–O–O 109.5
F_2O_2	C_2	O–O 1.575	O–1 87.5 ^c
		O–1 1.575	

^a Reference 16. ^b Assumed value. ^c Dihedral angle.

The analytical method for evaluation of $\rho_0(R)$ and $N(R)$ has been given elsewhere.^{12,13} The position of the center of the sphere for calculating these quantities can be varied if necessary. To study the basis set dependency, the following five basis sets of different quality were chosen: STO-6G, 4-31G, and 4-31G** by Pople and his co-workers,¹⁴ and MIDI-4 and MIDI-4** by Tatewaki and Huzinaga.¹⁵ In Table I are listed the input geometries determined experimentally.¹⁶

The computers used in this work were the HITAC-M200H/M180 at the Institute for Molecular Science and the HITAC-M280H/M200H at the University of Tokyo.

Stepwise Change of $\Delta\rho_0(R)$ Values around the Carbon Atom

As in the previous study, we have plotted $N(R)$, the number of the electrons, and $\Delta N(R)$ values, against the radius R of a sphere around the carbon, oxygen, and fluorine atoms for the wave functions of various basis sets. However, in the case of the $N(R)$ plot the contribution from the neighboring atoms was found to overwhelm the subtle difference of electron density in the bonding

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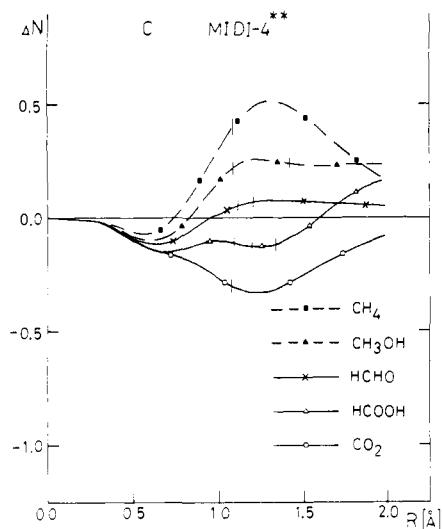


Figure 2. Difference electron number $\Delta N(R)$ around the carbon atom in the series (i) carbon compounds with the MIDI-4** basis. The vertical bars on the curves at around 1.2 Å indicate the positions of the neighboring atoms.

region, making the comparison between, say, around carbon atoms for CO_2 and CH_4 meaningless. On the other hand, the $\Delta N(R)$ plots for the carbon atom in the five compounds of series (i) are found to have almost equal spacings in the bonding region. See the curves at $0.7 < R < 1.2$ Å in Figure 2, where the vertical bars on the curves at around 1.2 Å indicate the positions of the neighboring atoms. This result suggests a stepwise change in the electron distribution around the carbon atom in line with the classical notion of the stepwise oxidation of CH_4 to CO_2 .

We have already shown that among the various quantities relevant to the electron number analysis the $\Delta\rho_0(R)$ (the increment of the spherically averaged electron density relative to the component atoms) is the best for analyzing the oxidation states of the atoms in molecules, and also that the essential feature of the radial dependency of $\Delta\rho_0(R)$ does not change with the quality of the basis set chosen.¹² Since the chemical interpretation of the ab initio calculations is the main purpose of this paper, detailed discussion of the basis set dependency will be given elsewhere. Here we will give the results of the STO-6G (smallest) and MIDI-4** (largest) calculations. In Figure 3 are given the relationships between $\Delta\rho_0(R)$ and R , the radius of the sphere around the carbon atom in series (i) molecules. Let us focus our attention on the clear stepwise change of $\Delta\rho_0(R)$ around the carbon atoms in the bonding region, especially between 0.6 and 1.1 Å.

In both curves a and b in Figure 3, the $\Delta\rho_0(R)$ value of the carbon atom is the most negative for CO_2 , while it is the most positive for CH_4 . Formally, the oxidation numbers of CO_2 and CH_4 are -4 and $+4$, respectively. It should be noted that the curves for HCOOH , HCHO , and CH_3OH lie between those of CO_2 and CH_4 with almost the same spacing. A similar stepwise change of the $\Delta\rho_0(R)$ curves was found in the previous work for sulfur and chlorine compounds, in which the classical oxidation numbers of sulfur and chlorine atoms change from $+6$ to -2 and from $+7$ to -1 , respectively. Thus, if the same criterion is to be applied to the carbon compounds as in the case of inorganic compounds, we may tentatively assign $+4$, $+2$, 0 , -2 , and -4 to the formal oxidation numbers of the carbon atoms in CO_2 , HCOOH , HCHO , CH_3OH , and CH_4 , respectively. At this stage a criticism might arise that in the $\Delta\rho_0(R)$ change we merely count the number of the overlap peaks of CH bonds. However, this possibility can be eliminated from the later discussion of the result of C_2H_6 , C_2H_4 , and C_2H_2 . For each basis set calculation the differences between the $\Delta\rho_0(R)$ curves of the most negative CO_2 and the most positive CH_4 in the bonding region is about as three quarters as those obtained for the cases of sulfur (between SO_3 and H_2S) and chlorine (between HClO_4 and HCl) compounds. Because the oxidation number difference is eight for each pair of these three series of molecules, the above results suggest that

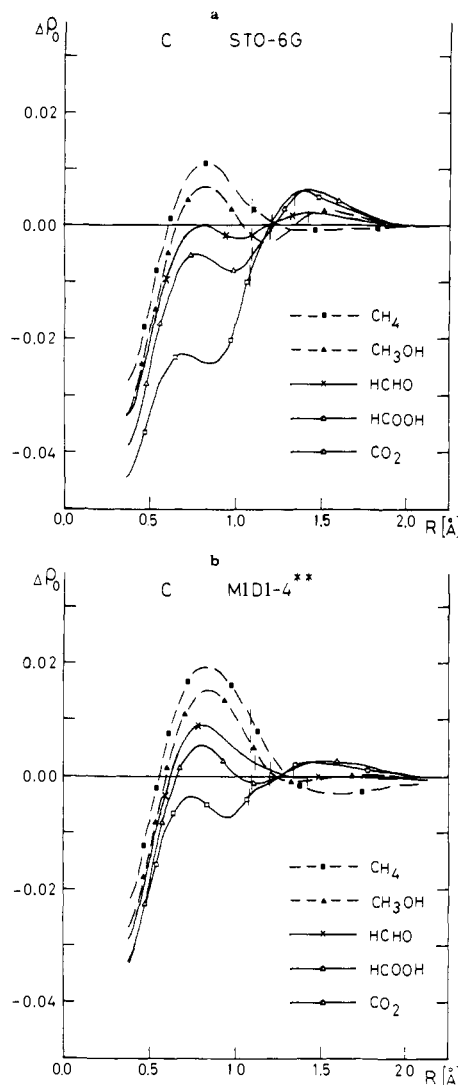


Figure 3. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the carbon atom in the series (i) carbon compounds with the following two basis sets: (a) STO-6G and (b) MIDI-4**.

Table II. Square Roots of the Expectation Values of r^2 for Free Atoms: $(\langle r^2 \rangle)^{1/2}$, Å

basis set	C	O
STO-6G	0.636	0.540
4-31G	0.723	0.585
MIDI-4 ^a	0.702	0.590

^a $(\langle r^2 \rangle)^{1/2}$ for MIDI-4** is almost equal to that of MIDI-4.

the degree of the overall change of charge distribution in carbon compounds is not so different from that of the inorganic compounds. In the case of carbon compounds, as is evident from Figure 3, the stepwise change in $\Delta\rho_0(R)$ is much more regular than in the case of the sulfur and chlorine compounds. This can also be clearly seen in Figure 4, where the $\Delta\rho_0(R)$ value at the radius $(\langle r^2 \rangle)^{1/2}$, the square root of the expectation value of r^2 taken for all the electrons around a free atom, changes linearly with the classically assigned oxidation number of the carbon atom. All of the different basis sets give almost the same trend. In Table II are given the square roots of the expectation values of r^2 of carbon and oxygen atoms obtained from the various basis sets. The $\Delta\rho_0(R)$ values at the conventional atomic radii for single and double bonds were also analyzed for comparison. Discussion of the choice of the representative $\Delta\rho_0(R)$ values will be given later. Although there remains some arbitrariness in choosing this type of index, the $\Delta\rho_0(R)$ value at $(\langle r^2 \rangle)^{1/2}$ will be shown to be rather convenient for discussing the chemical relevance of the quantum chemical oxidation number. It is clear that the oxidation number,

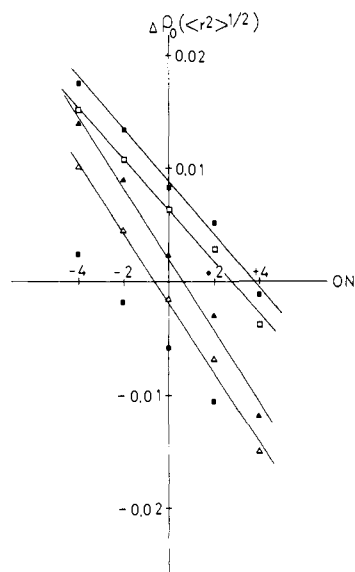


Figure 4. The plots of the formally assigned oxidation numbers (ON) vs. the $\Delta\rho_0(R)$ values at $R = \langle r^2 \rangle^{1/2}$ (in Å) around the carbon atom in the series (i) carbon compounds with each basis set. The symbols for the basis sets are as follows: (●) STO-6G; (▲) 4-31G; (■) 4-31G**; (△) MIDI-4; (□) MIDI-4**.

Table III. The $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ Values with MIDI-4** and Assumed Oxidation Numbers for the Carbon Atoms

compd	$\Delta\rho_0(0.702 \text{ \AA})$	assumed oxid. no. for C		
		a	$a = 1$	$a = 0.5$
CH ₄	0.0151	$-4a$	-4	-2
CH ₃ OH	0.0107	$1 - 3a$	-2	-0.5
HCHO	0.0063	$2 - 2a$	0	+1
HCOOH	0.0028	$3 - a$	+2	+2.5
CO ₂	-0.0039	+4	+4	+4
C ₂ H ₆	0.0128	$-3a$	-3	-1.5
C ₂ H ₄	0.0119	$-2a$	-2	-1
C ₂ H ₂	0.0113	$-a$	-1	-0.5

in whatever meaning it has, increases equally stepwise in the order of CH₄, CH₃OH, HCHO, HCOOH, and CO₂.

Oxidation State of Carbon Atoms in Hydrocarbons

To get finer details of the oxidation state of the carbon atom, analysis was also performed for a series of hydrocarbons, C₂H₆, C₂H₄, and C₂H₂, in which less distinctive redox change is expected. In Table III the MIDI-4** $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ values of the carbon atoms are compared with those for series (i) molecules. Contrary to the case of series (i) molecules, the $\Delta\rho_0$ values around the carbon atoms in these hydrocarbons are not so much different from each other, lying in between those of CH₄ and CH₃OH. This is possibly due to the similar electronegativity values of carbon and hydrogen. If a conventional assignment is taken, the carbon atoms in C₂H₂ have higher oxidation number (-1) than that (-2) in CH₃OH. However, it is not the case, and apparently the $\Delta\rho_0$ value is not a simple function of the number of the attached hydrogen atoms.

We could get a systematic assignment of the oxidation states of the carbon atoms in those compounds by assuming the following oxidation numbers: (1) -2 for oxygen in all cases; (2) +1 for hydrogen attached to oxygen; (3) $+a$ ($0 < a \leq 1$) for hydrogen attached to carbon, whose value is to be determined so as to reach the electroneutrality of the molecule. Thus the oxidation numbers of carbon atoms are given as $-4a$, $1 - 3a$, $2 - 2a$, $3 - a$, $+4$ for CH₄, CH₃OH, HCOOH, and CO₂, and $-3a$, $-2a$, $-a$ for C₂H₆, C₂H₄, and C₂H₂, respectively. Figure 5 shows how the assigned oxidation numbers change with the value of a . Note that our standpoint is not to get such simple numbers as to "correct" the classically assigned oxidation number. However, the results obtained with MIDI-4** basis in Table III can tell rather quantitative features of the various oxidation states of the carbon atom.

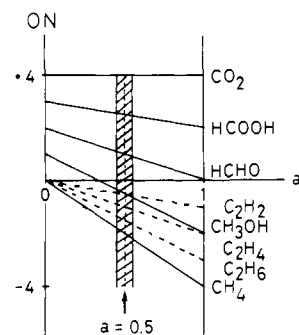


Figure 5. Variation of the oxidation number of carbon against parameter a .

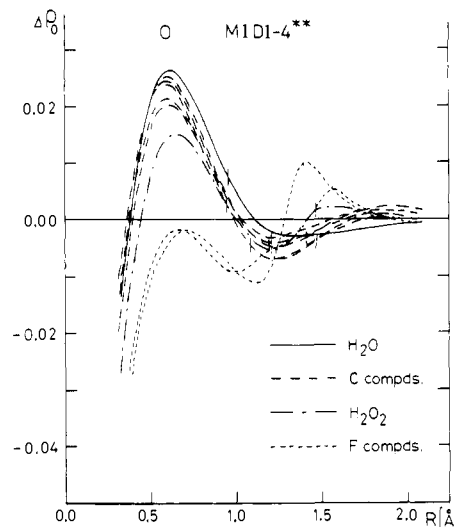


Figure 6. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the oxygen atom in the series (i), (ii), and (iii) with the MIDI-4** basis.

Namely, if, for example, we assume $a = 0.5$ rather than 1.0 as used in more polar inorganic molecules, the relative magnitudes of all the $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ values can be understood quite well. The oxidation states of the carbon atoms of almost all the hydrocarbons lie between those of methane (-2) and methanol (-0.5), e.g., -1.5 for C₂H₆, -1.0 for C₂H₄, and -0.5 for C₂H₂. Note also that whatever the actual a value is, the relative magnitudes of the oxidation numbers for the carbon atoms in series (i) molecules do not change at all as seen in Figure 5.

The half-way value of $a = 0.5$ for hydrogen in the hydrocarbons seems to be reasonable, where the degree of the deformation of charge density in CH bonds is smaller than the polar bonds in inorganic molecules as inferred from the overall change of $\Delta\rho_0$ values from CH₄ to CO₂ (vide supra). Thus, for organic molecules containing oxygen and/or other electronegative atoms, the oxidation numbers and $\Delta\rho_0$ values for the carbon atoms are determined by the balance of all the neighboring atoms. These findings may suggest one of the reasons why the concept of the oxidation number has not long been used favorably in organic chemistry.

Reference Oxygen and Fluorine Atoms

It is generally accepted that the classical oxidation number of all oxygen atoms is assigned as -2 with the following exceptions; (H¹)₂(O⁻¹)₂, (F⁻¹)₂(O¹)₂, and (F⁻¹)₂O¹¹, while the most negative fluorine atom is always given the standard value of -1 except in F₂.

We have plotted in Figure 6 the $\Delta\rho_0(R)$ curves around the oxygen atoms for all the molecules in series (i)-(iii) with MIDI-4** wave functions. In Figure 7 are plotted the $\Delta\rho_0(R)$ curves around the fluorine atoms for series (iii) molecules and various sulfur fluorides studied before.¹²

In Figure 6 all the curves for the oxygen-containing carbon compounds (dashed lines) and of water (bold line) almost collapse to each other. They also coincide with the majority of the curves

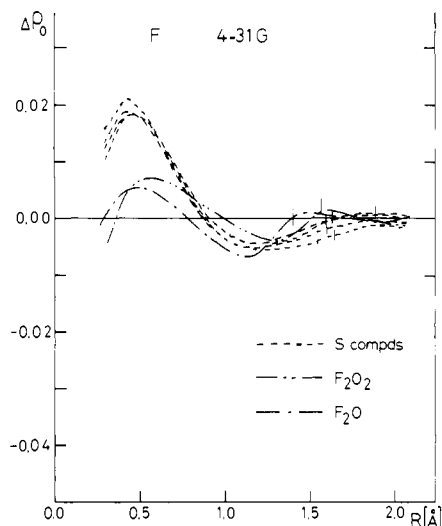


Figure 7. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the fluorine atom in the series (iii) fluoro oxides and in the sulfur compounds studied before (ref 12).

Table IV. The $\Delta\rho_0((r^2)^{1/2})$ Values for the Oxygen Atoms in H_2O and H_2O_2 Calculated with Various Basis Sets

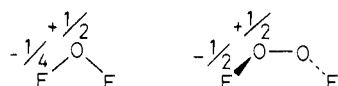
basis set	H_2O	H_2O_2	$\text{H}_2\text{O}/\text{H}_2\text{O}_2$
STO-6G	0.0175	0.0087	2.01
4-31G	0.0190	0.0103	1.84
4-31G**	0.0234	0.0138	1.70
MIDI-4	0.0197	0.0111	1.77
MIDI-4**	0.0260	0.0138	1.88

of sulfur and chlorine compounds reported in the previous paper.¹² The oxidation number for the oxygen atoms of these compounds are undoubtedly assigned as -2 . On the other hand, the amplitude of the curve in the bonding region for H_2O_2 is almost half of the above group, indicating the oxidation number of -1 just as the classical assignment. The ratio of $\Delta\rho_0(R)$ at $(r^2)^{1/2}$ for the two oxygen atoms of H_2O_2 and H_2O was actually found to be about 1:2 for all the five basis sets of different quality (see Table IV).

The third group consists of F_2O and F_2O_2 , whose $\Delta\rho_0(R)$ curves in the bonding region are below the zero line, indicating that these oxygen atoms are undoubtedly "oxidized" to the same amount. Although from this result one cannot assign quantitatively the oxidation number of the oxygen atoms of these two molecules, one may well estimate it somewhere between 0 and $+1$, say, around $+1/2$. The plots of other basis set calculations lead to the same conclusion, although addition of d-type functions seems to shift the $\Delta\rho_0(R)$ curves upward for all the molecules as in the case of carbon atoms.

The oxidation states of the fluorine atoms are found to be almost the same as exemplified for the various sulfur fluorides in Figure 7 except for F_2O and F_2O_2 . The oxidation number of F_2O and F_2O_2 seems to be rather small in magnitude compared to the majority of the fluorine compounds. Besides, the amplitudes of the curve for F_2O are about half those of F_2O_2 not only with the 4-31G basis set but also with other basis sets.

Thus by combining these results one can tentatively assign the oxidation numbers of F and O atoms in F_2O and F_2O_2 as



Although these values differ from the classically assigned oxidation numbers, they can reasonably be understood from the small difference between the electronegativities of fluorine and oxygen. Note also that our quantum-chemically reinterpreted oxidation number is deduced from the $\Delta\rho_0(R)$ analysis and thus is different from the classical and formal book-keeping number.

Table V. Calculated Charge per Unit Volume in a Sphere Spanning the C-C Bonds

molecules	formal bond order	$r_{\text{C-C}/2}$, Å	$N(r_{\text{C-C}/2})$	charge per unit volume	
$\text{H}_3\text{C}-\text{CH}_3$	1	0.766	3.85	2.05	<i>a</i>
		0.772	3.8849	1.9950	<i>b</i>
$\text{H}_2\text{C}=\text{CH}_2$	2	0.670	3.45	2.74	<i>a</i>
		0.677	3.5909	2.7628	<i>b</i>
$\text{HC}\equiv\text{CH}$	3	0.602	3.32	3.63	<i>a</i>
		0.601	3.3417	3.6750	<i>b</i>

^a Our work with MIDI-4**. ^b Reference 2c, with STO-3G. There is some inconsistency among the set of three figures for ethane given in ref 2c.

Radial Dependency

The basis set dependency of the $\Delta\rho_0(R)$ curve (see Figures 3, 6, and 7) is very large, particularly in the region of R below 0.6 Å, whereas essentially the same parallelism among the curves of different compounds can be seen in the range of $0.6 < R < 1.2$ Å. The largest discrepancy among the $\Delta\rho_0(R)$ curves is seen in the region around 0.1–0.2 Å. If one compares with each other the radial parts of the 1s, 2s, and 2p AO wave functions χ , χ^2 , or $r^2\chi^2$ of a carbon atom obtained with various basis sets, the largest discrepancy can be found at this very region where the 2s wave function changes its sign. The discrepancy gradually decreases with the increase of R , and in the region of $0.7 \approx R < 1.1$ Å these curves almost collapse to one curve, and again the deviation, though small, begins to take place. It is interesting to note that in the whole region of R all these curves seem to wind in and out along the Clementi's near Hartree-Fock, wave functions. One can infer that the concordant behavior of the $\Delta\rho_0(R)$ curves in the "bonding region" obtained with the various basis set wave functions is due to this fortuitous "stability" of the conventional GTF's in this region. Thus the relative $\Delta\rho_0(R)$ values for a certain atom in different compounds are thought to reflect faithfully the difference in the oxidation state.

The next problem is: can we select a proper radius at which the $\Delta\rho_0(R)$ value is used as some index for the newly reinterpreted oxidation number and the "electron population" on the atom? We have chosen three different radii around the carbon atom, namely, $r_{\text{C-X}}$ (covalent radius of a single bond C-X), $r_{\text{C=X}}$ (of a double bond C=X), and $(r^2)^{1/2}$ (root-mean-square of the expectation value of the position of the electrons around the key atom). Of course, there are some other candidates for this specified R value, such as $(r^2)^{1/2}_{\text{val}}$ (averaged over valence electrons) and bond critical point by Bader et al.⁴ We recommend the use of $(r^2)^{1/2}$, since it takes account of the basis set dependency and covers the range where the $\Delta\rho_0(R)$ takes fairly large values. Our main standpoint is, however, not to select a "point-information", such as the classical oxidation number and electron population, but to grasp a "space-information", such as the $\Delta\rho_0(R)$ curve, on the change of electron distribution around the specified atom upon the oxidation-reduction reactions.

Comparison with Other Studies

Richards and his co-workers proposed a new method for calculating the number of electrons in a sphere and applied it to the elucidation of the concept of the bond order in organic molecules.^{2c} They took account only of one center and neighboring atom contributions and obtained the results in concordance with the naive assignment of the bond order. We have performed similar analyses for C_2H_6 , C_2H_4 , and C_2H_2 , and compared the results with that of Richards. In Table V are compared the results of these two methods on the number of electrons in a sphere, which is centered at the midpoint of the C-C bond and with the radius equal to half the bond length, and charge per unit volume ($N/(4/3)\pi R^3$) for the single, double, and triple bonds. These results agree well with other, particularly on the charge per unit volume, and have a good correlation with the formal bond order. Thus, these two methods are shown to be equally applicable to the study of bulk quantities such as the bond order. The charge per unit

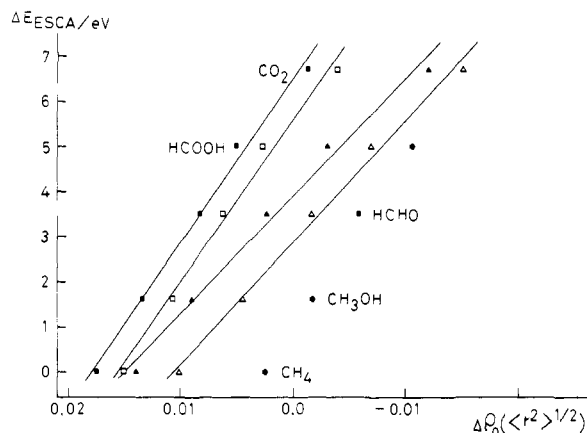


Figure 8. The plot of the $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ values around the carbon atom with each basis set vs. $\Delta E_{\text{ESCA}}(1s)$ in eV relative to CH_4 for the series (i) molecules. The symbols for the basis sets are as follows: (●) STO-6G; (▲) 4-31G; (■) 4-31G**; (△) MIDI-4; (□) MIDI-4**.

volume by Richards is obtained by averaging the approximate charge over a defined sphere. On the other hand, our method can calculate the $\rho_0(R)$ value averaged over a spherical surface analytically, and one can easily obtain its radial dependency. One can treat the homopolar bonds by calculating the charge per unit volume around the bonds, but there arise several ambiguities for heteropolar bonds, e.g., on the location of the center and the choice of the radius of the sphere. Thus the method chosen here is more suitable for studying local properties of electron distribution, such as the oxidation state.

The next problem is to find available experimental data which reflect the oxidation state or the electron density around the specified nucleus reasonably well to be compared with our calculations. Detailed analysis of the X-ray diffraction data can tell the deformed electron density $\Delta\rho(r) = \rho_{\text{mol}}(r) - \sum_i \rho_{\text{atom}}^i(r)$ over the whole region in the molecular domain in crystals.¹⁷ There is, however, some ambiguity in choosing the unperturbed atomic wavefunction for calculating the $\rho_{\text{atom}}^i(r)$ term. Further, there are no available data for isolated molecules to be compared with the series of molecules studied here.

The ¹³C NMR shift reflects the total electron density around the carbon atom and a good collection of these data have been contributing to the elucidation of molecular structures of fairly large size.¹⁸ However, the shift value is so sensitive to the anisotropic field gradient and, of course, to the molecular surroundings including the solvent and/or neighboring molecules. This means that this technique is suitable for getting the information consistent within a molecule and among the molecules with similar structure, but not for the analysis of the properties among those series of molecules as studied here.

Correlation between the charge distribution and ESCA shift has been studied extensively.¹⁹ Among a series of studies by Richards and his co-workers on the electron density analysis they found a good linear correlation between the ESCA shifts of the 1s electron of nitrogen atoms and the calculated charge within a sphere of covalent radius centered on the nitrogen atom in a series of nitrogen compounds.^{2a}

(17) Coppens, P. "Electron Distributions and the Chemical Bond", Coppens, P.; Hall, B. H., Ed.; Plenum Press: New York, 1982; pp 61-92.

(18) For example: (a) Breitmaier, E.; Voelter, W. "¹³C NMR Spectroscopy"; Verlag-Chemie: Weinheim, New York, 1978. (b) American Petroleum Institute Research Project 44: "Selected ¹³C Nuclear Magnetic Resonance Spectral Data"; Thermodynamics Research Center and the American Petroleum Institute: Texas, 1975-1978, Vol. 1-3.

(19) Siegbahn, K. et al. "ESCA Applied to Free Molecules"; North-Holland: Amsterdam, 1971.

We have compared the spherically averaged electron density, $\Delta\rho_0(R)$ value, for the carbon atom with the ESCA 1s shifts ΔE_{ESCA} , in eV relative to CH_4 of the carbon atom in the series (i) molecules. The results are shown and compared in Figure 8, where roughly linear relationships between ΔE_{ESCA} and the $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ calculated with any of the five different basis sets are found except for CO_2 with the STO-6G basis. It is remarkable that the linear relationship gets better as the quality of the basis set improves. Although there is no a priori reason for the linearity between $\Delta E_{\text{ESCA}}(1s)$ and the density distribution spherically averaged over the core and valence electrons, the results obtained here ensure that the easily calculable quantity $\Delta\rho_0(\langle r^2 \rangle^{1/2})$ especially from the 4-31G** and MIDI-4** bases can be used to assign the ESCA shift, and discussion can also be done vice versa. This means that both the experimental ΔE_{ESCA} and theoretical $\Delta\rho_0(R)$ values are useful for predicting the change in the oxidation state around a specified atomic species within a molecule or in a series of molecules. The classically assigned index, the oxidation number, gains its legitimate meaning in this context.

Concluding Remarks

We have demonstrated that the subtle but stepwise change in the $\Delta\rho_0(R)$ value around the carbon atom in the series of compounds, CH_4 , CH_3OH , HCHO , HCOOH , and CO_2 , really reflects the decrease of the electron distribution in the bonding region as proportional to the change in the classically assigned oxidation number irrespective of the existence of less polar CH bonds. On the other hand, the electron distribution around the oxygen atom in a series of compounds stays almost constant except for a few cases and thus supports the idea that the oxygen atom can be used as one of the reference atoms with respect to the oxidation-reduction reactions.

Fluorine is slightly more electronegative than oxygen, but the difference is found to be smaller than what is widely expected. One more important finding is that the concept of the oxidation number, if it is modified as proposed in the present study, can equally be applicable to the organic compounds.

The Mulliken population analysis for the series of compounds studied here also gave a similar but less distinctive correlation with the oxidation number.²⁰ This is, however, a fortuitous result. There is a growing accumulation of those documents of ab initio calculations which lead to conclusions opposite to that predicted by the population analysis.⁹ Wiberg and Wendoloski²¹ and Bader et al.⁴ pointed out that, based on the numerical integration over the atomic basin, the hydrogen atoms in typical aliphatic molecules are negatively charged, contrary to the widely accepted chemical notion. If this statement is taken literally the carbon atom is oxidized in methane. More careful and systematic calculation is necessary for judging whether or not this is the case. The present work also demonstrated the usefulness of the $\Delta\rho_0(R)$ plots, which is a one-dimensional view of the electron distribution in the molecule. By discarding the information on the deformation from a spherical atom, we can more easily compare the electron distribution change in various molecules than the two- and three-dimensional views, because we can simply use the numbers in the comparison. This does not mean that the deformation from the spherical distribution is less significant.

Registry No. CH_4 , 74-82-8; CH_3OH , 67-56-1; HCHO , 50-00-0; HCOOH , 64-18-6; CO_2 , 124-38-9; H_2O , 7732-18-5; H_2O_2 , 7722-84-1; F_2O , 7783-41-7; F_2O_2 , 7783-44-0; carbon, 7440-44-0; oxygen atom, 17778-80-2.

(20) The plot of the net atomic charge on the carbon atom by the Mulliken population analysis against the oxidation number was similar to Figure 4. Although the plots for each basis set give a straight line with positive tangent, the slope of each line varies from basis set to basis set.

(21) Wiberg, K. B.; Wendoloski, J. J. *J. Comput. Chem.* **1981**, *2*, 53-57.