

Analysis of the Oxidation State and Oxidation Number by ab Initio Molecular Orbital Calculations: Chlorine and Sulfur Compounds

Keiko Takano,^{1a} Haruo Hosoya,^{*1a} and Suehiro Iwata^{1b}

Contribution from the Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan, Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223, Japan, Institute of Physical and Chemical Research, Wako, Saitama 351, Japan, and Institute for Molecular Science, Okazaki, Aichi 444, Japan. Received August 24, 1981

Abstract: The electron distribution around chlorine and sulfur atoms of various oxidation states in molecules was analyzed in detail with ab initio molecular orbital calculations. The number of electrons $N(R)$ and spherically averaged electron density $\rho_0(R)$ in a sphere with radius R at chlorine and sulfur atoms in two series of chlorine and sulfur compounds were calculated, and the changes $\Delta N(R)$ and $\Delta\rho_0(R)$ from the sum of the component atoms were also examined. The R dependencies of $N(R)$, $\rho_0(R)$, $\Delta N(R)$, and $\Delta\rho_0(R)$ were studied. It was found that the difference spherically averaged electron density $\Delta\rho_0(R)$ around the chlorine and sulfur atoms is linearly related to the classical oxidation number assigned to these atoms. This result was confirmed by checking the basis set dependency, i.e., by use of STO-3G, STO-6G, 4-31G, and 4-31G** functions.

The oxidation number is a classical but useful concept for describing and interpreting the extent of the electron transfer to and from the vicinity of given nuclei in a molecular environment and during the course of a chemical reaction.² A set of signed integers, oxidation numbers, are assigned to the component atoms, with hydrogen (+1) and oxygen (-2) atoms as the standard, so that the sum of them is equal to the total charge of the molecule or ion. Except in a few molecules such as those of the nitrogen oxide family and carbon monoxide, most second-row atoms have their characteristic oxidation numbers. On the other hand, it is usually the case for a heavier atom to have different oxidation numbers in different molecules. For example, the oxidation number of the chlorine atom varies widely from -1 in HCl to +7 in HClO₄. It sometimes happens that different oxidation numbers need to be assigned to different atoms of the same kind in a molecule, such as in F₂S=S.

The question is whether and how the classical concept, the oxidation number, is related to the real electronic state. No crucial theory and/or calculation seem to have been presented. Of course, there have been proposed several quantum chemical approaches, for example, the Mulliken population analysis³ and the contour mapping of electron density.⁴⁻⁶ In the former method, however, the overlap population between a pair of atoms is artificially divided into halves for the paired atoms, and the assignment is made with respect to the origin of the "atomic" functions but not to the real spatial distribution. Only qualitative information can be obtained from the latter method. If the number of electrons in a certain defined space is to be calculated, one has to perform numerical integration,⁷ which, however, is not suitable for obtaining systematic and accurate results within limited computer time.

Recently, one of the present authors obtained analytical expressions for the number and density of electrons in a sphere centered at an arbitrary point, provided that the wave functions are expressed in terms of GTF's.⁸ In this paper two series of

compounds containing chlorine and sulfur are systematically studied by this method in order to elucidate the concept of the oxidation number. The basis set dependency, including d functions, was carefully examined.

From the results obtained so far, we can conclude that the electron distribution around a given atom does not change dramatically as the oxidation number predicts but that a subtle change, if carefully detected, is actually discrete and roughly proportional to the change of the chemically accepted oxidation number. Further, one can assign and compare the various oxidation states of a given atom in different molecules in terms of this newly reinterpreted oxidation number.

Method of Calculation

Let the number of electrons in a sphere with radius R around center C be denoted as $N(R, C)$, which is the sum of the contributions $N(R, C; l, m, n, P)$ from all the component GTF's (l, m, n) as⁸

$$N(R, C; l, m, n, P) = \int_0^R r^2 \rho(l, m, n, P; r) dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad (1a)$$

$$\rho(l, m, n, P; r) = (x - P_x)^l (y - P_y)^m (z - P_z)^n \exp\{-\alpha(\mathbf{r} - \mathbf{P})^2\} \quad (1b)$$

where \mathbf{P} is the position vector of the GTF center. The spherically averaged electron density $\rho_0(R, C)$ is defined as

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

The previous method⁸ to derive the formulas for calculating $N(R, C)$ and $\rho_0(R, C)$ is straightforward but becomes cumbersome when it is extended to d-type functions. The new method begins with simple formulas for $l + m + n = 0$ and 1:

$$N(R, C; 0, 0, 0, P) = (2\pi^{1/2}/\alpha^{3/2})SL(-1)/P \quad (3a)$$

and

$$N(R, C; 1, 0, 0, P) = (\pi/\alpha)^{1/2} P_x / (\alpha^2 P^2) \{CL(0) - SL(-1)/P\} \quad (3b)$$

where the auxiliary functions are defined as

$$CL(2m) \equiv \int_0^\infty \exp(-k^2/4\alpha) (\sin(kR) - kR \cos(kR)) k^{2m-1} \cos(kP) dk \quad (4a)$$

(1) (a) Ochanomizu University. (b) Keio University, Institute of Physical and Chemical Research, and Institute for Molecular Science.

(2) Extensive bibliographies and classical discussions are given in: Jørgensen, C. K. "Oxidation Numbers and Oxidation States"; Springer-Verlag: West Berlin, 1969.

(3) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833-1840, 1841-1846.

(4) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871-2883, and the same series of papers.

(5) Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81-87.

(6) Hilal, R. *J. Comput. Chem.* **1980**, *1*, 348-357, 358-367.

(7) Politzer, P.; Reuther, J.; Kasten, G. T. *J. Chem. Phys.* **1977**, *67*, 2385-2387.

(8) Iwata, S. *Chem. Phys. Lett.* **1980**, *69*, 305-312.

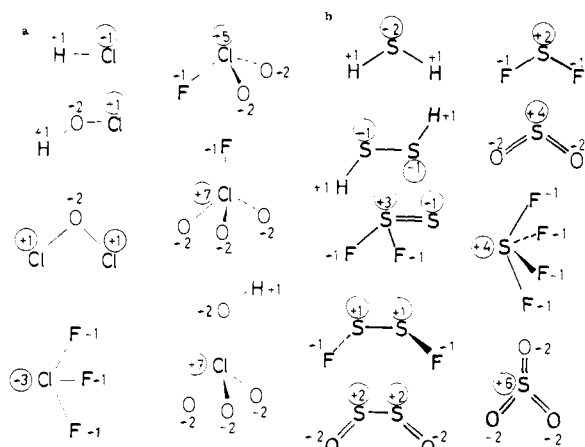


Figure 1. the two series of compounds studied and the oxidation numbers of (a) chlorine and (b) sulfur atoms.

$$SL(2m-1) \equiv$$

$$\int_0^{\infty} \exp(-k^2/4\alpha) (\sin(kR) - kR \cos(kR)) k^{2m-2} \sin(kP) dk \quad (4b)$$

which are expressed in terms of Hermite polynomials except for $m = 0$, where the error function is required. To obtain the formulas for $l + m + n \geq 2$, the derivative of the electron density with respect to P_x

$$\begin{aligned} \partial \rho(l, m, n, \mathbf{P}) / \partial P_x &= -l(x - P_x)^{l-1} (y - P_y)^m (z - P_z)^n \exp\{-\alpha(\mathbf{r} - \mathbf{P})^2\} + 2\alpha(x - P_x)^{l+1} (y - P_y)^m (z - P_z)^n \exp\{-\alpha(\mathbf{r} - \mathbf{P})^2\} \\ &= -l\rho(l-1, m, n, \mathbf{P}) + 2\alpha\rho(l+1, m, n, \mathbf{P}) \end{aligned} \quad (5)$$

is used. As $N(R, C; l, m, n, \mathbf{P})$ is an integration of $\rho(l, m, n, \mathbf{P})$, a recurrence formula

$$N(R, C; l+1, m, n, \mathbf{P}) = \frac{1}{2\alpha} [lN(R, C; l-1, m, n, \mathbf{P}) + \frac{\partial}{\partial P_x} N(R, C; l, m, n, \mathbf{P})] \quad (6)$$

can be proved. In addition, the derivatives of the auxiliary functions as

$$\frac{\partial}{\partial P_x} SL(2m-1) = \frac{P_x}{P} CL(2m) \quad (7a)$$

$$\frac{\partial}{\partial P_x} CL(2m) = -\frac{P_x}{P} SL(2m+1) \quad (7b)$$

Therefore all the necessary formulas for $N(R, C; l, m, n, \mathbf{P})$ ($l + m + n \geq 2$) can easily be constructed from eq 5 and 6. They are given in Appendix A.

Similar recurrence formulas for the spherically averaged electron density $\rho_0(R, C; l, m, n, \mathbf{P})$ and its derivative $d\rho_0(R, C; l, m, n, \mathbf{P})/dR$ can be derived from eq 6 for $N(R, C)$. To write down the analytical expression for $\rho_0(R, C)$, the auxiliary functions

$$DSL(2m-1) = \frac{d}{dR} SL(2m-1) = \frac{R}{2} (-1)^m \alpha^m (\alpha\pi)^{1/2} \times [\exp\{-\alpha(R-P)^2\} H_{2m} \{\alpha^{1/2}(R-P)\} - \exp\{-\alpha(R+P)^2\} H_{2m} \{\alpha^{1/2}(R+P)\}] \quad (8a)$$

$$DCL(2m) = \frac{d}{dR} CL(2m) = \frac{R}{2} (-1)^m \alpha^{m+1} \pi^{1/2} [\exp\{-\alpha(R-P)^2\} H_{2m+1} \{\alpha^{1/2}(R-P)\} + \exp\{-\alpha(R+P)^2\} H_{2m+1} \{\alpha^{1/2}(R+P)\}] \quad (8b)$$

are necessary, but for $d\rho_0(R, C)/dR$ no new functions are needed,

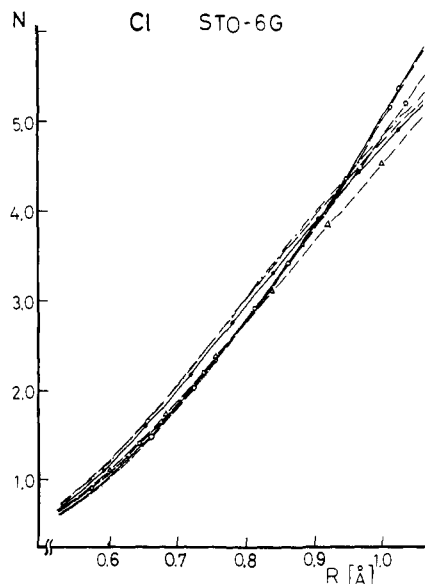


Figure 2. Number of electrons $N(R)$ around the chlorine atom in the series of chlorine compounds calculated with the STO-6G basis. The symbols for the chlorine compounds (oxidation numbers in parentheses) are as follows: (---) HCl (-1); (----) HOCl (+1); (●) Cl₂O (+1); (---Δ---) ClF₃ (+3); (---□---) ClFO₂ (+5); (---○---) ClFO₃ (+7); (---○---) HClO₄ (+7).

because the relations

$$\frac{d}{dR} \frac{DSL(2m-1)}{R^2} = -SL(2m+1)/R^2 \quad (9a)$$

$$\frac{d}{dR} \frac{DCL(2m)}{R^2} = -CL(2m+2)/R^2 \quad (9b)$$

can be used. Thus, coding and computation of both $\rho_0(R, C)$ and its derivative require only a little more labor.

By using basis sets of four different grades, i.e., STO-3G, STO-6G, 4-31G, and 4-31G**,⁹ we performed ab initio molecular orbital calculations for the ground states of the following two series of molecules (see Figure 1): (i) HCl (-1), HOCl (+1), Cl₂O (+1), ClF₃ (+3), ClFO₂ (+5), ClFO₃ (+7), and HClO₄ (+7); (ii) H₂S (-2), H₂S₂ (-1), S₂F₂ (-1, +3), FS₂F (+1), S₂O₂ (+2), SF₂ (+2), SO₂ (+4), SF₄ (+4), and SO₃ (+6). Here the integer in parentheses is a tentatively assigned oxidation number for the central atom concerned.

All the calculations were carried out for the ground-state geometries, which were experimentally obtained by electron diffraction, from the microwave spectrum, or from the infrared spectrum.¹⁰ The input data for their geometries are listed in Tables VI and VII. The calculated total and orbital energies of 4-31G** are given in Tables VIII and IX. Although some interesting discussion can be made on these results, it is left at the readers' disposal, because of limited space in this paper.

From the wave functions obtained, the number of electrons in a sphere, $N(R)$, the spherically averaged electron density, $\rho_0(R)$, and its derivative were calculated and analyzed.

Computations in this work were performed on HITAC M180 and HITAC M200 computers (at the Institute for Molecular Science (IMS)) and a FACOM M 180 IIAD computer (at the Institute of Physical and Chemical Research (IPCR)). The computer program for obtaining the ab initio wave functions is the IPCR version of GAUSSIAN 70 at IPCR and IMS. The sub-routine programs for the electron number analysis, including d functions, were coded for the present work.¹¹

(9) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664.

(10) Landolt-Börnstein, "Structure Data of Free Polyatomic Molecules"; Springer-Verlag: West Berlin, 1976; New Series, II-7.

(11) They will be distributed upon request. A small blank magnetic tape should be sent to the first author.

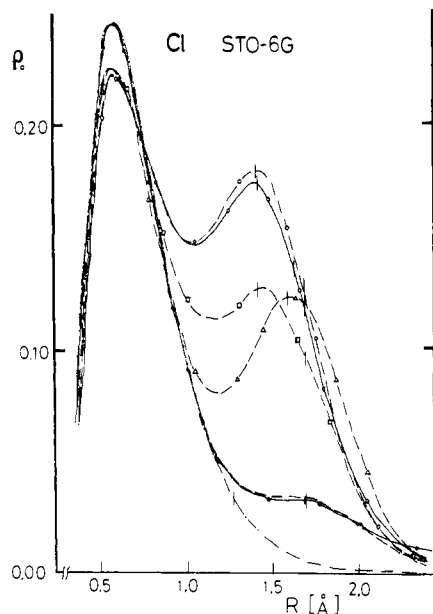


Figure 3. Spherically averaged electron density $\rho_0(R)$ around the chlorine atom in the series of chlorine compounds calculated with the STO-6G basis. The vertical bars represent the position of the neighboring atom. The symbols for the compounds are the same as those in Figure 2.

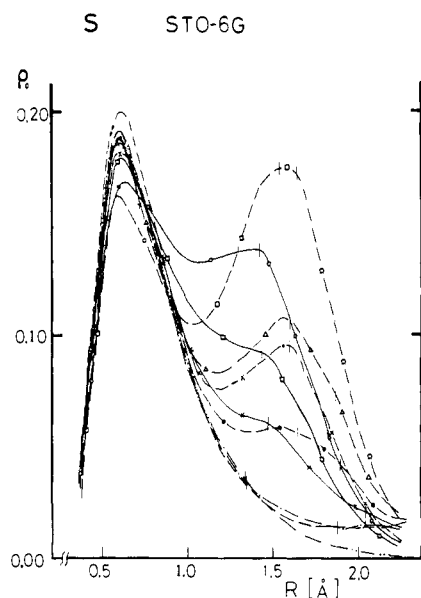


Figure 4. Spherically averaged electron density $\rho_0(R)$ around the sulfur atom in the series of sulfur compounds calculated with the STO-6G basis. The symbols for the sulfur compounds (oxidation numbers in parentheses) are as follows: (---) H_2S (-2); (- - -) H_2S_2 (-1); (---) S_2F_2 (-1); (- - - -) FS_2F (+1); (-x-) S_2O_2 (+2); (- - x - -) SF_2 (+2); (- - Δ - -) S_2F_2 (+3); (-□-) SO_2 (+4); (- - □ - -) SF_4 (+4); (-○-) SO_3 (+6). Solid lines are used for oxides, broken lines for fluorides, and dotted lines for hydrides.

Number of Electrons and the Spherically Averaged Electron Density in a Sphere with Radius R

The distribution of the core electrons is tight in space and is expected not to be influenced by chemical bonding. This was actually confirmed by a test calculation. As our main interest is the analysis in the bonding region, the electron distribution of the valence electrons in this region was studied in most cases.

Figure 2 shows the number of electrons $N(R)$ in a sphere with radius R around a chlorine atom in the series of molecules calculated with the STO-6G basis. Since the results of the STO-3G basis calculations are not substantially different from those of STO-6G, the former will not be referred to in the following

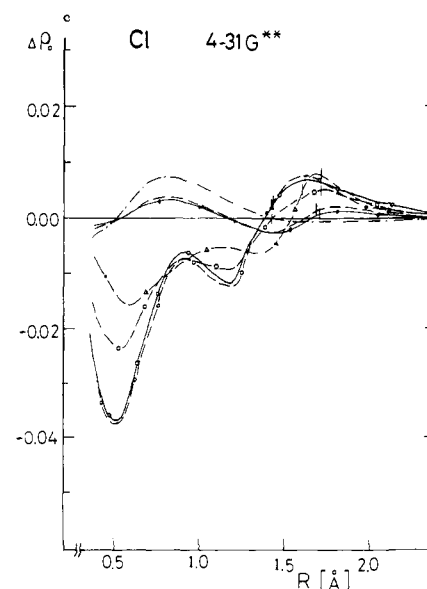
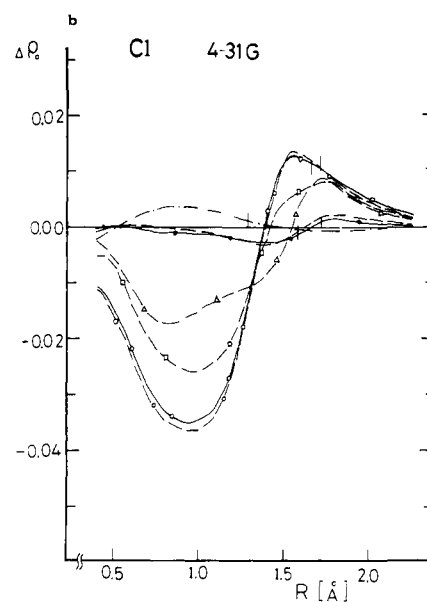
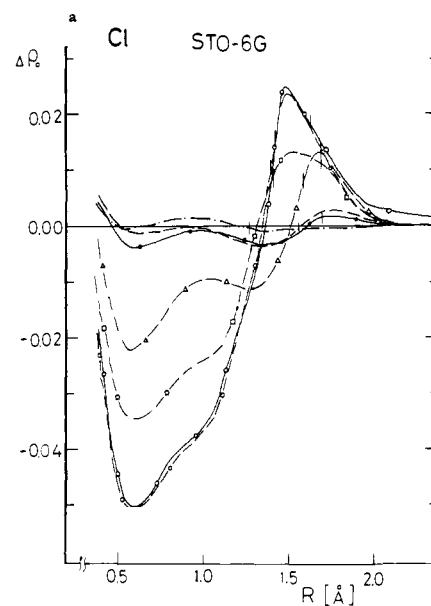


Figure 5. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the chlorine atom in the series of chlorine compounds: (a) STO-6G basis; (b) 4-31G basis; (c) 4-31G** basis. For the symbols see Figure 2.

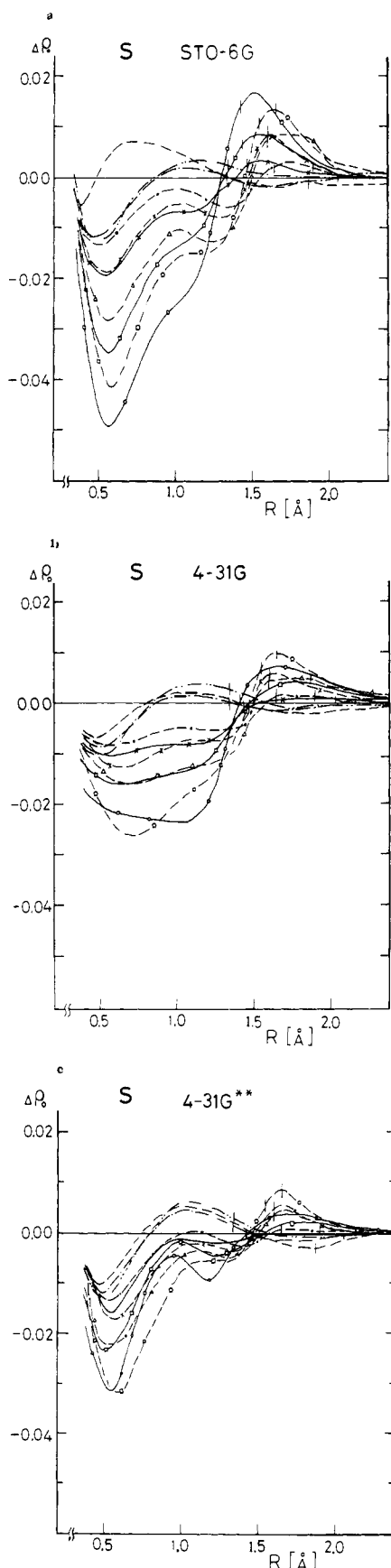


Figure 6. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the sulfur atom in the series of sulfur compounds: (a) STO-6G basis; (b) 4-31G basis; (c) 4-31G** basis. For the symbols see Figure 4.

discussion. All the curves for the chlorine and sulfur (not shown here) compounds monotonously and uniformly increase with R ,

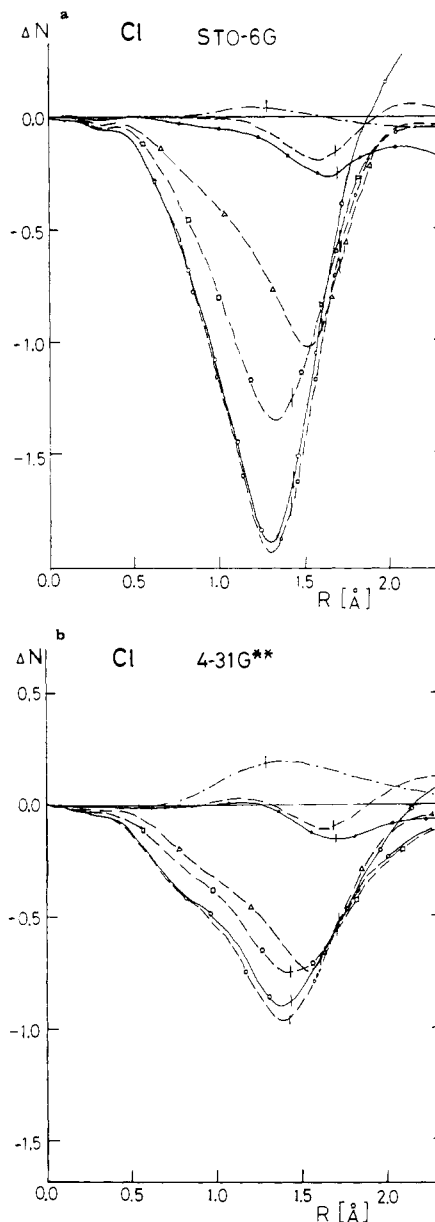


Figure 7. Difference electron number $\Delta N(R)$ around the chlorine atom in the series of chlorine compounds: (a) STO-6G basis; (b) 4-31G** basis.

and it is difficult to draw meaningful conclusions from the analysis of the $N(R)$ curves.

The spherically averaged electron density $\rho_0(R)$ seems to be more suitable to see the change of electron distribution around the atom, as shown in Figures 3 and 4 for the chlorine and sulfur compounds, respectively. It is clearly seen that in these figures the radius R_m at the first peak of $\rho_0(R)$ is almost independent of the oxidation state for each series of compounds. The peak position can easily be obtained from the derivative $d\rho_0/dR$. The basis set dependency of R_m is found to be very small among the examined basis sets. Irrespective of the oxidation state and hybridization, R_m is likely a constant for each atom, $R_m \approx 0.570 \pm 0.025$ Å for chlorine and $R_m \approx 0.625 \pm 0.010$ Å for sulfur. The currently adopted covalent radii of Cl and S are, respectively, 0.99 and 1.04 Å; R_m is about 60% of the covalent radius. The vertical bars on the curves in these figures at about 1.5 Å indicate the positions of the neighboring atoms, around where the second peak of $\rho_0(R)$ is found.

The sulfur compounds examined can be grouped into three groups: hydrides, oxides, and fluorides. In each group the larger the oxidation number, the smaller the $\rho_0(R)$ value at R_m . This

Table I. Difference Spherically Averaged Electron Density $\Delta\rho_0(R)$ Values for the Chlorine Compounds

compd	ON ^a	STO-6G		4-31G		4-31G**	
		R_m	$\langle r^2 \rangle^{1/2}$	R_m	$\langle r^2 \rangle^{1/2}$	R_m	$\langle r^2 \rangle^{1/2}$
		0.57 Å	0.78 Å	0.57 Å	0.85 Å	0.57 Å	0.85 Å
HCl	-1	-0.0001	+0.0010	+0.0013	+0.0035	+0.0022	+0.0071
HOCl	+1	-0.0011	-0.0008	+0.0003	-0.0004	+0.0007	+0.0031
Cl ₂ O	+1	-0.0039	-0.0023	-0.0002	-0.0010	+0.0006	+0.0026
ClF ₃	+3	-0.0224	-0.0160	-0.0108	-0.0171	-0.0159	-0.0090
ClFO ₂	+5	-0.0344	-0.0306	-0.0128	-0.0250	-0.0224	-0.0080
ClFO ₃	+7	-0.0504	-0.0447	-0.0222	-0.0358	-0.0340	-0.0082
HClO ₄	+7	-0.0503	-0.0435	-0.0213	-0.0345	-0.0325	-0.0071

^a Oxidation number assigned in this study. ^b Calculated with the valence orbitals.

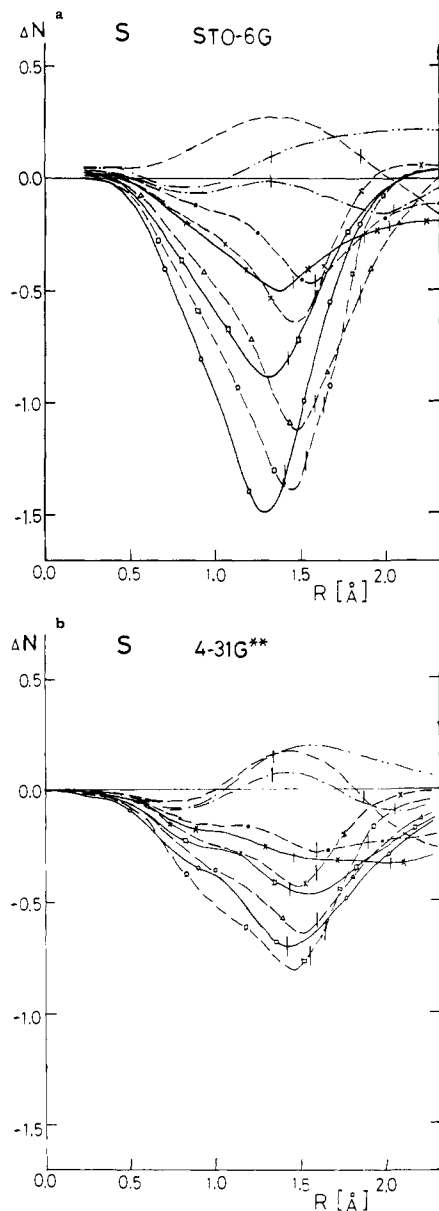


Figure 8. Difference electron number $\Delta N(R)$ around the sulfur atom in the series of sulfur compounds: (a) STO-6G basis; (b) 4-31G** basis.

trend is found in all four basis set calculations. This is consistent with our chemical intuition. For the chlorine compounds studied here, grouping is less clear.

Thus we can inspect the electron distribution around an atom in molecules more clearly through the spherically averaged electron density $\rho_0(R)$ than through the number of electrons $N(R)$. However, it is still difficult to draw meaningful and useful conclusions only from Figures 3 and 4 without recourse to chemical knowledge on each compound.

Difference Electron Number and Difference Electron Density

In order to examine in detail the change of the electron distribution in molecules, the difference electron number $\Delta N(R)$ in a sphere and the difference spherically averaged electron density $\Delta\rho_0(R)$ are defined as

$$\Delta N(R) = N(R) - \sum_i^{\text{atom}} N_i(R) \quad (10)$$

$$\Delta\rho_0(R) = \rho_0(R) - \sum_i^{\text{atom}} \rho_{0i}(R) \quad (11)$$

where the subscript i refers to the contribution of the component free atom i . The $\Delta\rho_0(R)$ and $\Delta N(R)$ values are respectively plotted against R in Figures 5 and 6 and Figures 7 and 8. In these figures the core electron contribution is included, although almost identical curves are obtained without it.

Molecular dependency of the electron distribution around the chlorine and sulfur atoms now becomes evident in these difference curves. The R dependency of the difference electron density $\Delta\rho_0(R)$ shows an interesting trend in that all the curves of both STO-3G and STO-6G are almost parallel in the region $0.3 < R < 1.3$ Å, giving a fairly clear-cut assignment of the oxidation state of the Cl and S atoms in each compound. On the other hand, the 4-31G curves seem to be a little distorted and entangled. However, as long as compounds in the same family (oxide, fluoride, etc.) are compared, the parallelism of the curves is still preserved. The pattern of the $\Delta\rho_0(R)$ curves calculated with the 4-31G** basis, which includes d functions, closely resembles that of STO-6G rather than 4-31G, except that in the 4-31G** curves the humps around 0.8–0.9 Å are steeper than in the STO-6G curves. The split-shell (4-31G) basis set seems somewhat unbalanced around the bonding region.

In Tables I and II $\Delta\rho_0(R)$ values at R_m and at $R = \langle r^2 \rangle^{1/2}$ are given, where $\langle r^2 \rangle$ is the calculated expectation value of r^2 for the valence electrons of the corresponding free atom in each basis set calculation (see Table III).

A quantitative relationship between the oxidation number and $\Delta\rho_0(R)$ is found for the region $0.5 < R < 1.3$ Å. For instance, the ratios of $\Delta\rho_0(R)$ at $R = 0.57$ Å by the STO-6G calculation for ClF₃, ClFO₂, ClFO₃, and HClO₄ are 1:1.54:2.25:2.25, respectively, which parallel the ratios of the widely accepted oxidation numbers (3:5:7:7 = 1:1.67:2.33:2.33). A similar trend is also found in the other basis set calculations. The $\Delta\rho_0(R)$ curves for ClFO₃ and HClO₄ in Figure 5 are almost indistinguishable and show the largest amplitude in all four basis set calculations, revealing that the Cl atoms in both compounds are in the same and highest oxidation state: they both have an oxidation number of +7. Among the chlorine compounds examined, only the chlorine in HCl is said to have a negative oxidation number (-1), which is reflected in Figure 5, where the $\Delta\rho_0(R)$ curve of HCl alone takes positive, though small, values for $0.6 < R < 1$ Å. This trend means that there is an increase of electron density around the Cl atom. The results of HOCl and Cl₂O with the 4-31G** basis set are the only exceptions that predict a sign opposite to that of chemical intuition for the oxidation number of the Cl atom. For these compounds the $\Delta\rho_0(R)$ is so small that its sign is rather sensitive to the choice of the standard free atom contributions.

Table II. Difference Spherically Averaged Electron Density $\Delta\rho_0(R)$ Values for the Sulfur Compounds

compd	ON ^a	STO-6G		4-31G		4-31G**	
		R_m 0.63 Å	$\langle r^2 \rangle^{1/2}$ ^b 0.73 Å	R_m 0.63 Å	$\langle r^2 \rangle^{1/2}$ 0.84 Å	R_m 0.63 Å	$\langle r^2 \rangle^{1/2}$ 0.84 Å
H ₂ S	-2	-0.0092	-0.0040	-0.0076	+0.0004	-0.0080	+0.0020
H ₂ S ₂	-1	-0.0083	-0.0046	-0.0065	-0.0002	-0.0071	+0.0015
S ₂ F ₂	-1 ^c	+0.0062	+0.0070	-0.0037	+0.0008	-0.0051	+0.0028
FS ₂ F	+1	-0.0106	-0.0070	-0.0080	-0.0062	-0.0112	-0.0030
S ₂ O ₂	+2	-0.0175	-0.0129	-0.0010	-0.0084	-0.0129	-0.0035
SF ₂	+2	-0.0168	-0.0120	-0.0126	-0.0101	-0.0159	-0.0068
S ₂ F ₂	+3 ^d	-0.0268	-0.0208	-0.0156	-0.0169	-0.0208	-0.0098
SO ₂	+4	-0.0323	-0.0256	-0.0160	-0.0148	-0.0192	-0.0055
SF ₄	+4	-0.0399	-0.0319	-0.0255	-0.0242	-0.0312	-0.0164
SO ₃	+6	-0.0467	-0.0399	-0.0219	-0.0230	-0.0258	-0.0068

^a Oxidation number assigned in this study. ^b Calculated with the valence orbitals. ^c Terminal S atom. ^d Central S atom.

Table III. Root-Mean-Square Values of the Electrons of Various Atoms^a

atom	basis set	electrons		
		all	valence	core
S	STO-6G	0.555	0.727	0.509
	4-31G	0.718	0.844	0.513
Cl	STO-6G	0.586	0.775	0.492
	4-31G	0.627	0.854	0.466
O	STO-6G	0.540	0.650	0.121
	4-31G	0.585	0.688	0.122
F	STO-6G	0.495	0.572	0.107
	4-31G	0.540	0.623	0.108
H	STO-6G	0.739		
	4-31G	0.896		

^a $\langle r^2 \rangle^{1/2}$.

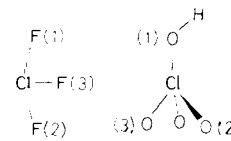
Table IV. Values of Difference Electron Number $\Delta N(R)$ at the Root-Mean-Square Value $\langle r^2 \rangle^{1/2}$ of Valence Electrons of Chlorine Compounds

compd	ON	STO-6G 0.78 Å	4-31G 0.85 Å	4-31G** 0.85 Å
HCl	-1	+0.005	+0.028	+0.038
HOCl	+1	-0.006	-0.001	-0.005
Cl ₂ O	+1	-0.034	-0.009	-0.015
ClF ₃	+3	-0.236	-0.244	-0.263
ClFO ₂	+5	-0.405	-0.298	-0.315
ClFO ₃	+7	-0.593	-0.460	-0.448
HClO ₄	+7	-0.590	-0.429	-0.440

Table V. Values of Difference Electron Number $\Delta N(R)$ at the Root-Mean-Square Value $\langle r^2 \rangle^{1/2}$ of Valence Electrons of Sulfur Compounds


compd	ON	STO-6G 0.73 Å	4-31G 0.84 Å	4-31G** 0.84 Å
H ₂ S	-2	-0.033	-0.088	-0.080
H ₂ S ₂	-1	-0.052	-0.077	-0.085
F ₂ S ₂	-1	+0.081	-0.040	-0.048
FS ₂ F	+1	-0.077	-0.121	-0.145
S ₂ O ₂	+2	-0.137	-0.151	-0.170
SF ₂	+2	-0.127	-0.185	-0.205
F ₂ S ₂	+3	-0.226	-0.247	-0.287
SO ₂	+4	-0.275	-0.250	-0.243
SF ₄	+4	-0.343	-0.394	-0.405
SO ₃	+6	-0.430	-0.370	-0.336

For the sulfur compounds, when compared within the oxide and fluoride families, the $\Delta\rho_0(R)$ values show a remarkable correlation with the chemically accepted oxidation numbers. For oxides the ratios of $\Delta\rho_0(R)$ at $R_m = 0.63$ Å (see Table II) in STO-6G and those of the oxidation number for S₂O₂, SO₂, and SO₃ are respectively 1:1.85:2.67 and 1:2:3. The ratios for FS₂F, SF₂, S₂F₂ (central S), and SF₄ are 1:1.58:2.53:3.76 and 1:2:3:4, respectively, if +3 is assigned to the central S of S₂F₂ (vide infra). In both cases

Table VI. Input Geometries of Chlorine Compounds^a


compd	bond distance, Å		bond angle, deg	
	HCl	H-Cl	1.27459	
HOCl	O-Cl	1.6895	H-O-Cl	102.48
	O-H	0.975		
Cl ₂ O	O-Cl	1.7004	Cl-O-Cl	110.86
ClF ₃	Cl-F(1)	1.698	F(1)-Cl-F(3)	87.5
	Cl-F(3)	1.598		
ClFO ₂	Cl-F	1.697	O-Cl-O	115.23
	Cl-O	1.418	F-Cl-O	101.72
ClFO ₃	Cl-F	1.619	O-Cl-O	116.6
	Cl-O	1.404	F-Cl-O	100.8
HClO ₄	Cl-O(2)	1.408	O(2)-Cl-O(3)	112.8
	Cl-O(1)	1.635	O(2)-Cl-O(1)	105.8
	H-O(1)	0.9451 ^b	Cl-O(1)-H	120.0 ^c

^a Reference 10. ^b O-H (in CH₃OH). ^c H is assumed to be trans to O(3).

Table VII. Input Geometries of Sulfur Compounds^a


compd	bond distances, Å		bond angles, deg	
H ₂ S	S-H	1.3356	H-S-H	92.12
H ₂ S ₂	S-S	2.055	S-S-H	91.33
	S-H	1.327	H-S-S-H	90.60 ^b
S ₂ F ₂	S-S	1.860	S-S-F	107.5
	S-F	1.598	F-S-F	92.5
FS ₂ F	S-S	1.888	S-S-F	108.3
	S-F	1.635	F-S-S-F	87.9 ^b
S ₂ O ₂	S-O	1.458	O-S-S	112.7
	S-S	2.0245		
SF ₂	S-F	1.59208	F-S-F	98.197
SO ₂	S-O	1.43076	O-S-O	119.33
SF ₄	S-F	1.545	F-S-F	101.6
	S-F'	1.646	F'-S-F'	186.9
SO ₃	S-O	1.4198		

^a Reference 10. ^b Dihedral angle.

a linear relation is found between $\Delta\rho_0(R)$ and the oxidation number. As in HCl, the $\Delta\rho_0(R)$ values at $R \approx 1$ Å for the sulfur atoms with supposedly negative oxidation numbers are positive in HSH (-2), HSSH (-1), and S₂F₂ (-1, terminal S) (see Figure 6a-c).

There often arises some arbitrariness in the assignment of oxidation numbers. For example, there is no definite rule for

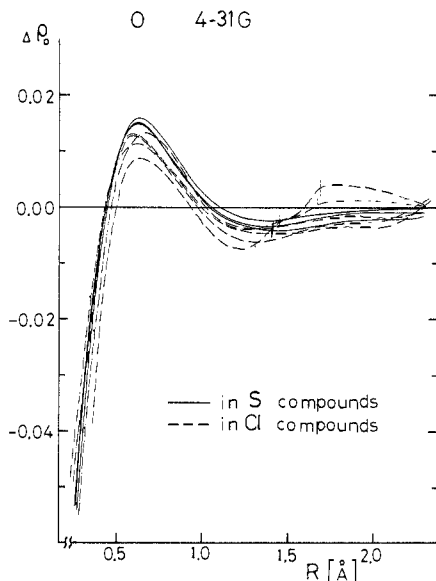
Table VIII. Total Energy and Orbital Energies of the Lowest Unoccupied (LUMO) and Higher Occupied Orbitals of Chlorine Compounds

molecule symmetry ^a	HCl C _{∞v}	HOCl C _s	Cl ₂ O C _{2v}	ClF ₃ C _{2v}	ClFO ₂ C _s	ClFO ₃ C _{3v}	HClO ₄ C _s
total energy, au ^b	-459.60649	-534.31911	-992.68257	-756.75155	-707.58856	-782.26506	-758.29981
LUMO, eV	6σ 5.00	11a' 3.49	10a ₁ 1.66	12a ₁ 1.37	15a' 1.40	11a ₁ 2.54	18a' 3.20
HOMO, eV	2π -12.61 5σ -16.67 4σ -30.04	3a'' -11.79 10a' -12.45 9a' -16.07 2a'' -16.41 8a' -19.25 7a' -28.55	3b ₁ -11.93 8a ₂ -12.74 9a ₁ -13.08 2b ₂ -13.45 8a ₁ -17.49 7a ₂ -17.93	4b ₁ -14.25 11a ₁ -14.41 10a ₁ -16.96 6a ₂ -16.98 1b ₂ -17.68 3b ₁ -18.58	14a' -13.76 7a'' -14.75 6a'' -15.43 13a' -16.00 12a' -18.20 5a'' -18.46	1a ₂ -14.93 7e -15.85 10a ₁ -17.04 6e -17.49 5e -20.00 4e -22.74	8a'' -13.94 7a'' -14.65 17a' -14.91 16a' -15.89 6a'' -16.49 15a' -16.66

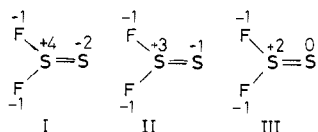
^a See Tables VI and VII. ^b 4-31G** basis.

Table IX. Total Energy and Orbital Energies of the Lowest Unoccupied (LUMO) and Higher Occupied Orbitals of Sulfur Compounds

molecule symmetry ^a	H ₂ S C _{2v}	H ₂ S ₂ C ₂	F ₂ S ₂ C _s	FS ₂ F C ₂	
total energy, au ^b	-398.26617	-795.36530	-992.82249	-992.83166	
LUMO, eV	3a ₂ 5.34	9b 3.71	9a'' 2.25	13b 3.41	
HOMO, eV	2b ₂ -10.17 5a ₁ -13.32 2a ₂ -15.81 4a ₁ -26.47	9a -10.19 8b -10.19 8a -12.90 7b -15.02 7a -15.87 6b -23.88	17a' -10.42 8a'' -11.03 16a' -13.82 15a' -17.35 7a'' -18.10 6a'' -19.10	13a -11.33 12b -11.68 12a -13.60 11b -16.69 11a -18.31 10b -18.35	
molecule symmetry ^a	S ₂ O ₂ C _{2v}	SF ₂ C _{2v}	SO ₂ C _{2v}	SF ₄ C _{2v}	SO ₃ D _{3h}
total energy, au	-943.63017	-595.72744	-546.62228	-794.34027	-805.80654
LUMO, eV	3b ₂ -0.81	6a ₂ 3.49	3b ₁ 0.80	7a ₂ 3.47	4a ₂ '' 1.70
HOMO, eV	3b ₁ -9.48 10a ₁ -11.00 9a ₂ -14.36 2b ₂ -15.33 8a ₂ -15.69 2b ₁ -16.89	3b ₁ -10.51 8a ₁ -15.99 5a ₂ -17.68 1b ₂ -18.65 2b ₁ -19.89 7a ₁ -19.93	8a ₁ -13.11 1b ₂ -13.78 5a ₂ -14.42 2b ₁ -17.91 7a ₁ -18.70 4a ₂ -18.73	12a ₁ -11.77 2b ₂ -17.32 6b ₁ -17.42 6a ₂ -17.51 11a ₁ -17.65 5b ₁ -19.59	1a ₂ ' -14.41 1e ₂ ' -15.35 5e' -16.64 4e' -20.25 2a ₂ '' -20.41 5a ₁ ' -23.49

^a See Tables VI and VII. ^b 4-31G** basis.Figure 9. Difference spherically averaged electron density $\Delta\rho_0(R)$ around the oxygen atom in the chlorine and sulfur compounds.

deciding which is the correct formula for S₂F₂ among I–III (or more). Chemical intuition may favor I or III, as it is usually



the case with the sulfur atom to take an even oxidation number. Although the curve of the central S of S₂F₂ in Figure 6 resembles

that of SO₂ in any of the different basis set calculations studied, it is situated just between those of SF₄ and SF₂. Further, there is a close resemblance between the curves of H₂S and S₂F₂ (terminal S). Thus one may conclude that +3 and -1 (see formula II) can be assigned as the oxidation numbers to the central and terminal S atoms, respectively, for S₂F₂.

In order to proceed along this line of reasoning on the oxidation number, one has to check the electron density distribution around the oxygen atom as a reference system in both the chlorine and sulfur compounds. Figure 9 shows the $\Delta\rho_0(R)$ curves of the typical oxygen atoms for the compounds studied here calculated with the 4-31G basis set.¹² Although they do not completely overlap with each other, the deviation is remarkably small if one compares the oxygen curve (Figure 9) with the curves for chlorine (Figure 5b) and sulfur (Figure 6b) at the same level of approximation.¹³

The above examples illustrate the usefulness of the present analysis and at the same time the appropriateness of the use of the concept of the classical oxidation number under certain conditions.

Figures 7 and 8 show the R dependencies of the difference electron number $\Delta N(R)$. The minima are located near the bond "distance" in most cases. It also shows the change of the electron distribution around the chlorine and sulfur atoms with various oxidation numbers. Particularly for the chlorine compounds, $\Delta N(R)$ is related to the assigned oxidation number. Namely, $\Delta N(R)$ is positive for HCl and almost zero for HOCl and Cl₂O, while for the chlorine atom with an oxidation number of +3, +5, or +7, $\Delta N(R)$ takes a large negative value, as seen in Figure 7 and Table IV. Although a general trend is less clear, for the sulfur compounds $\Delta N(R)$ for the atoms with higher oxidation numbers among the fluorides and oxides is large in absolute value. For

(12) The hydrogen atom is not suitable for this purpose, as it is too small relative to the third-row atoms.

(13) The results for other basis set calculations show substantially the same trend.

instance, in Figure 8 compare the three solid lines for S_2O_2 (+2), SO_2 (+4), and SO_3 (+6). The sulfur atom in SO_3 is obviously the most positive (see also Table V).

The importance of adding the polarization functions for the description of the electron distribution is clearly seen in Figures 5-8. The $\Delta\rho_0(R)$ curves with the polarization functions (4-31G**) show more structures, i.e., with more humps, than those without them (4-31G), which suggests, though $\Delta\rho_0(R)$ is spherically averaged, that the radial and angular change of the electron distribution around the atom in molecules is well described by adding the polarization function. The apparent decrease of the absolute value of $\Delta N(R)$ in 4-31G** from those of 4-31G and STO-6G seems rather surprising, but this decrease might be reasonable, since in a smaller basis set the charge transfer among atoms in a molecule is often exaggerated.

Concluding Remarks

The most important conclusion in this study is as follows: There is no dramatic change in the electron number around a specified atom as the classical oxidation number predicts, but a subtle and stepwise change in the electron density $\Delta\rho_0(R)$ relative to the free atom can be detected in parallel with the classical oxidation number. The results obtained by adding d functions, e.g., $\Delta\rho_0(R)$ for 4-31G**, suggest that the effect of d orbitals is significant. Correlation between $\Delta\rho_0(R)$ in all the basis sets and the oxidation number is fairly good. This analysis was made possible by the analytical expressions of the electron number and density for the Gaussian-type wave functions. Further study along these lines is in progress.

Appendix

$$\text{Formulas of } N(R,C;l,m,n,P) = N(l,m,n).$$

Notations

$$\begin{aligned} P &= \alpha_1 R_1 + \alpha_2 R_2 & \alpha &= \alpha_1 + \alpha_2 \\ M_x &= P_x/P & M_y &= P_y/P & M_z &= P_z/P \\ (\text{CLSL}) &= \text{CL}(0) - \text{SL}(-1)/P \\ X_{12} &= X_2 - X_1 & Y_{12} &= Y_2 - Y_1 & Z_{12} &= Z_2 - Z_1 \\ R_{12}^2 &= X_{12}^2 + Y_{12}^2 + Z_{12}^2 \\ \text{EXP} &= \exp(-\alpha_1 \alpha_2 R_{12}^2 / \alpha) \end{aligned}$$

Normalization Constants

$$\begin{aligned} N_s(\alpha) &= (2\alpha/\pi)^{3/4} \\ N_{p_x}(\alpha) &= 2^{7/4} \alpha^{5/4} / \pi^{3/4} \\ N_{d_{xx}}(\alpha) &= 2^{11/4} \alpha^{7/4} / (3^{1/2} \pi^{3/4}) \\ N_{d_{yy}}(\alpha) &= 2^{11/4} \alpha^{7/4} / \pi^{3/4} \\ N(l,m,n) & \quad 0 \leq l, m, n \leq 2 \\ & \quad \text{(i) } l + m + n = 0 \\ N(0,0,0) &= (\pi/\alpha)^{1/2} \frac{2\text{SL}(-1)}{\alpha P} \\ & \quad \text{(ii) } l + m + n = 1 \\ N(1,0,0) &= (\pi/\alpha)^{1/2} \frac{M_x(\text{CLSL})}{\alpha^2 P} \\ & \quad \text{(iii) } l + m + n = 2 \end{aligned}$$

$$N(2,0,0) =$$

$$(\pi/\alpha)^{1/2} \frac{1}{\alpha^2} \left\{ \frac{\text{SL}(-1)}{P} + \frac{1 - 3M_x^2}{2\alpha P^2} (\text{CLSL}) - \frac{M_x^2}{2\alpha} \frac{\text{SL}(1)}{P} \right\}$$

$$N(1,1,0) = -(\pi/\alpha)^{1/2} \frac{M_x M_y}{2\alpha^3} \left[\frac{3}{P^2} (\text{CLSL}) + \frac{\text{SL}(1)}{P} \right]$$

$$\text{(iv) } l + m + n = 3$$

$$N(3,0,0) = (\pi/\alpha)^{1/2} \frac{M_x}{2\alpha^3 P} \left\{ 3 \left(P^2 - \frac{3 - 5M_x^2}{2\alpha} \right) \frac{(\text{CLSL})}{P^2} - \frac{3(1 - 2M_x^2)}{2\alpha} \frac{\text{SL}(1)}{P} - \frac{M_x^2}{2\alpha} \text{CL}(2) \right\}$$

$$N(2,1,0) = (\pi/\alpha)^{1/2} \frac{M_y}{2\alpha^3 P} \left\{ \left(P^2 - \frac{3 - 15M_x^2}{2\alpha} \right) \frac{(\text{CLSL})}{P^2} - \frac{1 - 6M_x^2}{2\alpha} \frac{\text{SL}(1)}{P} - \frac{M_x^2}{2\alpha} \text{CL}(2) \right\}$$

$$N(1,1,1) =$$

$$(\pi/\alpha)^{1/2} \frac{M_x M_y M_z}{4\alpha^4 P} \left\{ 15 \frac{(\text{CLSL})}{P^2} + 6 \frac{\text{SL}(1)}{P} - \text{CL}(2) \right\}$$

$$\text{(v) } l + m + n = 4$$

$$N(4,0,0) = (\pi/\alpha)^{1/2} \frac{3}{2\alpha^3} \left\{ \frac{\text{SL}(-1)}{P} + \frac{1 - 3M_x^2}{\alpha} \frac{(\text{CLSL})}{P^2} - \frac{M_x^2}{\alpha} \frac{\text{SL}(1)}{P} \right\} + (\pi/\alpha)^{1/2} \frac{1}{8\alpha^5 P^2} \left\{ 3(-3 + 30M_x^2 - 35M_x^4) \frac{(\text{CLSL})}{P^2} - 3(1 - 12M_x^2 + 15M_x^4) \frac{\text{SL}(1)}{P} - 2M_x^2(3 - 5M_x^2) \text{CL}(2) + P^2 M_x^4 \frac{\text{SL}(3)}{P} \right\}$$

$$N(3,1,0) = -(\pi/\alpha)^{1/2} \frac{3M_x M_y}{4\alpha^4} \left\{ 3 \frac{(\text{CLSL})}{P^2} + \frac{\text{SL}(1)}{P} \right\} + (\pi/\alpha)^{1/2} \frac{M_x M_y}{8\alpha^5 P^2} \left\{ 15(3 - 7M_x^2) \frac{(\text{CLSL})}{P^2} + 9(2 - 5M_x^2) \frac{\text{SL}(1)}{P} - (3 - 10M_x^2) \text{CL}(2) + P^2 M_x^2 \frac{\text{SL}(3)}{P} \right\}$$

$$N(2,2,0) = (\pi/\alpha)^{1/2} \frac{1}{2\alpha^3} \left\{ \frac{\text{SL}(-1)}{P} + \frac{2 - 3M_x^2 - 3M_y^2}{2\alpha} \times \frac{(\text{CLSL})}{P^2} - \frac{M_x^2 + M_y^2}{2\alpha} \frac{\text{SL}(1)}{P} \right\} - (\pi/\alpha)^{1/2} \frac{1}{8\alpha^5 P^2} \left\{ 3(1 - 5M_x^2 - 5M_y^2 + 35M_x^2 M_y^2) \frac{(\text{CLSL})}{P^2} + (1 - 6M_x^2 - 6M_y^2 + 45M_x^2 M_y^2) \frac{\text{SL}(1)}{P} + (M_x^2 + M_y^2 - 10M_x^2 M_y^2) \text{CL}(2) - P^2 M_x^2 M_y^2 \frac{\text{SL}(3)}{P} \right\}$$

$$N(2,1,1) = -(\pi/\alpha)^{1/2} \frac{M_y M_z}{4\alpha^4} \left\{ 3 \frac{(\text{CLSL})}{P^2} + \frac{\text{SL}(1)}{P} \right\} + (\pi/\alpha)^{1/2} \frac{M_y M_z}{8\alpha^5 P^2} \left\{ 15(1 - 7M_x^2) \frac{(\text{CLSL})}{P^2} + 3(2 - 15M_x^2) \frac{\text{SL}(1)}{P} - (1 - 10M_x^2) \text{CL}(2) + P^2 M_x^2 \frac{\text{SL}(3)}{P} \right\}$$

Input Geometries and Energies. Input geometries of the chlorine and sulfur compounds are given in Tables VI and VII, respectively, and the total energy and orbital energies of the lowest unoccupied (LUMO) and higher occupied orbitals of the chlorine and sulfur compounds are given in Tables VIII and IX, respectively.