Inorg. Chem. **1993**, *32*, 3209–3216

Rigorous Interpretation of Electronic Wave Functions. 2. Electronic Structures of Selected Phosphorus, Sulfur, and Chlorine Fluorides and Oxides

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Received September 10, 1992

Rigorous interpretive tools are used to analyze electronic wave functions of eight molecules and ions that are often believed to possess hypervalent electronic structures. The atomic charges, localized orbitals, and covalent bond orders are calculated in a consistent manner that does not rely on arbitrary references to basis functions as "atomic orbitals". Results of this detailed analysis, in which the first-order density matrices calculated at the MP2/6-311++G** level were employed, clearly show that the ionicity of bonds in the SO_2, SO_3, SO_4^{2-}, PF_5, PF_4^-, SF_4, and SF_6 species is large enough to make it unnecessary to invoke the notion of hypervalency. The only system among the species studied that could possibly be called hypervalent is ClF_4^+.

Introduction

The notion of covalency vs ionicity as applied to chemical bonds and to molecules as a whole is a source of considerable confusion in chemistry. Most textbooks used in freshman chemistry courses that influence the thinking of legions of chemists seem to ignore completely the fact that there are several factors determining whether a given molecule is predominantly ionic or covalent. These include not only the ionicity/covalency of the constituting chemical bonds but also such unrelated factors as the arrangement of atoms, which can greatly influence the electric multipole moments, and the overall molecular shape, which often determines chemical reactivity. For this reason, it is completely unjustifiable to use exclusively the chemical characteristics of a particular species to infer the degree of ionicity/covalency of its chemical bonds. Unfortunately, the oversimplistic view that the propensity toward ionic reactions and electrolytic dissociation are the sole indicators of the presence of ionic bonds not only seems to dominate the thinking of many chemistry lecturers but also is sporadically expressed in research publications. For example, sulfur hexafluoride (SF_6)—a relatively inert gas that does not undergo hydrolysis under normal conditions and does not dissociate into ions in water—is usually called a covalent molecule. Such a description is undoubtedly correct; however, it does not imply that the S–F bonds in SF_6 are covalent and therefore SF_6 is a hypervalent molecule—an assertion that is often found in the chemical literature. In fact, SF_6 possesses bonds that are mostly ionic (as shown in the following sections of this paper) and its volatility is easily explained by its vanishing dipole moment, while its inertness toward hydrolysis and electrolytic dissociation is a simple consequence of its globular structure that hinders the access of solvent molecules to its central atom and the S–F bonds.

One of the most serious consequences of the aforementioned problem is the dispute over the description of bonding in the so-called hypervalent molecules, i.e. molecules in which bonding supposedly violates the octet rule. Over the last 30 years, this dispute has been unnecessarily aggravated by dozens of theoretical papers in which unduly approximate methods, well-known to be incapable of affording clear answers to questions of electronic structure, have been nevertheless used to make claims in favor of one picture of bonding or another. It is not our intention to provide the reader with a more or less complete list of these publications. Instead, we mention that several relevant references can be found in the recent paper by Reed and von Schleyer.[1]

To provide a definitive answer to the question of whether the octet rule[2] is indeed violated in "hypervalent" molecules and ions it is not sufficient to accurately calculate the electronic wave functions of the systems in question. In addition, one has to be able to analyze the computed wave functions in a rigorous manner. This means that the interpretive tools utilized in such an analysis have to employ definitions that are fully independent of the methods used in calculation of the wave functions and the character of the analyzed molecules. This implies that, for example, neither references to basis functions employed in the basis set expansion nor preconceived notions about the location of chemical bonds should be allowed in the definitions of atomic and bond properties.

Although in recent years much evidence has been gathered[1,3] to support the notion that hypervalency is not present in several molecules of sulfur and phosphorus, most of the work done so far has been based upon arbitrary interpretation of electronic wave functions. For example, the ill-posed question of "d-orbital participation" was often considered, despite the fact that atomic orbitals presumed to be eigenfunctions of the angular momentum operator cannot be discerned in molecules that possess no spherical symmetry, unless an obviously fallacious identification of basis functions with atomic orbitals is made.

In the present paper, we report the results of a rigorous analysis of the electronic wave functions pertaining to eight molecules and ions that are often believed to be of a hypervalent character. Bonding in individual species is discussed in terms of the atomic charges, covalent bond orders, and localized natural orbitals that are located at atoms (core orbitals and lone pairs) and two-center bonds (bonding orbitals). This line of analysis has been previously employed in an investigation of bonding in sulfoxides and sulfones,[4] yielding unequivocal proof of the absence of hypervalency in these compounds.

Rigorous Interpretation of Electronic Wave Functions

Rigorous analysis of electronic wave functions requires interpretive tools that do not invoke arbitrarily defined mathematical entities, such as basis functions. Of course, even when such rigorous tools are used, the calculated atomic, bond, and molecular indices are expected to depend on the quality of the electronic wave functions being analyzed, not unlike ordinary expectation values such as, for example, total energies or dipole moments.

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(2) Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762.

(3) Magnusson, E. *J. Am. Chem. Soc.* **1990**, *112*, 7940.

(4) Cioslowski, J.; Surjan, P. R. *J. Mol. Struct.* **1992**, *255*, 9.

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However, as the exact wave functions are approached (meaning expanding the number of basis functions, increasing the number of mesh points in numerical calculations, including larger fractions of correlation effects, etc.), both the expectation values and the rigorously defined indices are guaranteed to converge in a smooth manner to well-defined limits. Unfortunately, the same is not true for methods of analysis that are based on a partitioning of the Hilbert space spanned by basis functions. Such methods yield quantities with values that not only fail to enjoy the aforementioned convergence but also can be freely manipulated by the choice of basis sets used in computation of electronic wave functions. This fact renders them incapable of interpreting the results of quantum-chemical calculations without an unnecessary bias.

The quantum-mechanical theory of atoms in molecules, proposed by Bader,[5] makes it possible to define atomic and bond properties without resorting to the unjustified identification of basis functions as "atomic orbitals". The rigorous interpretation of electronic wave functions commences with construction of the reduced first-order density matrices (also known as one-electron density matrices or simply 1-matrices). For quantum-mechanical methods (such as MP2 or CCSD) that do not afford wave functions, it is still possible to obtain the necessary density matrices by calculating the relevant energy derivatives.[6] Once the density matrix $\Gamma(\vec{r},\vec{r}')$ is known, the atomic basins can be delineated by constructing the zero-flux surfaces[5] that stem from the gradient paths in the electron density $\rho(\vec{r}) \equiv \Gamma(\vec{r},\vec{r})$.

Many atomic properties can be calculated directly with the knowledge of atomic basins and the density matrices. In particular, the Bader charge on atom A is given by[5,7]

$$Q_A = Z_A - \int_{\Omega_A} \rho(\vec{r})\, d\vec{r} \tag{1}$$

where Z_A is the nuclear charge of A and Ω_A is its atomic basin. Another important quantity is the atomic overlap matrix (AOM), which is defined by its matrix elements between two orbitals ϕ_i and ϕ_j as

$$\langle i | j \rangle_A = \int_{\Omega_A} \phi_i^*(\vec{r})\, \phi_j(\vec{r})\, d\vec{r} \tag{2}$$

Most of the information about bonding in molecules is provided by tables of localized molecular orbitals (LMOs). Such orbitals maximize the localization sum[8]

$$L = \sum_A \sum_i \nu_i^2 \langle i | i \rangle_A^{\,2} \tag{3}$$

where ν_i is the occupation number of the ith orbital and the first summation runs over all atoms of the molecule in question. In general, the LMOs are related to the natural orbitals by the so-called isopycnic transformations[8] and have the important property of yielding the correct density matrix

$$\Gamma(\vec{r},\vec{r}') = \sum_i \nu_i\, \phi_i(\vec{r})\, \phi_i(\vec{r}') \tag{4}$$

In the case of Hartree–Fock wave functions, the isopycnic transformations become identical with the familiar unitary transformations.

The tables of LMOs usually list the strongly occupied localized orbitals that have large occupation numbers. For each LMO, the atomic occupancies that are given by $\langle i|i \rangle_A$ are displayed. From the values of atomic occupancies, chemical bonding described by individual LMOs can be easily discerned without plotting them or invoking the notion of "atomic orbitals". In addition, some helpful indices can be derived. These indices include the degrees of orbital localization and ionicity. For LMOs localized predominantly at one atom A, such as core and lone pair orbitals, the degree of localization is simply $\langle i|i \rangle_A \cdot 100\%$. For LMOs that span two atoms A and B and therefore describe chemical bonding, the degree of localization equals $(\langle i|i \rangle_A + \langle i|i \rangle_B) \cdot 100\%$ and the degree of ionicity is given by $|(\langle i|i \rangle_A - \langle i|i \rangle_B)/(\langle i|i \rangle_A + \langle i|i \rangle_B)| \cdot 100\%$.

Another important quantity is the AOM-derived covalent bond order.[9] The bond order between atoms A and B is defined as[9]

$$P_{AB} = \sum_i \nu_i^2 \langle i | i \rangle_A \langle i | i \rangle_B \tag{5}$$

where the sum runs over localized natural orbitals. So-defined covalent bond orders do not rely on "atomic orbitals" and therefore are largely independent of the basis sets used, provided enough variational flexibility is present in the basis functions to assure accurate approximation of the electronic wave function being analyzed. For this reason, the AOM-derived covalent bond orders are an ideal tool for assessing the degree of covalent bonding between two atoms and as such they have already been proven useful for several molecules.[9,10]

Finally, it should be mentioned that an alternative method for estimating atomic charges, which is based on the derivatives of dipole moments with respect to nuclear displacements, is provided by the GAPT (generalized atomic polar tensors) definition.[11]

Rigorous Definition of Hypervalent Molecules

Results of the aforedescribed analysis of electronic wave functions cannot be used to distinguish hypervalent molecules from the "normal" ones until a rigorous definition of hypervalency is given. Traditionally, hypervalent molecules are defined as those possessing hypervalent atoms, i.e. atoms with more than an octet of valence electrons. It is therefore obvious that the notion of electron count is central to the definition of hypervalency.

The idea of counting electrons (or electron pairs) is deeply rooted in the concepts first articulated by Lewis.[2] According to these concepts, two-electron bonds in molecules span a spectrum ranging from those being purely covalent to those that are 100% ionic. The purely covalent bond between atoms A and B corresponds to an equal sharing of the electron pair and is usually denoted by A:B. The other extreme, which is a fully ionic bond, corresponds to the electron pair belonging to only one atom (say A) and is denoted by $A:^- B^+$. Although bonding between A and B is obviously present in both cases, the purely covalent bonding has very different consequences for the electron count and the atomic charges than its purely ionic counterpart. As far as calculation of atomic charges is concerned, the purely covalent bond results in one electron on atom A and one electron on atom B. However, for the purpose of the electron count invoked in the octet rule, the electron pair of the purely covalent bond is counted *twice* ("shared") and contributes two electrons to both A and B. On the other hand, because no sharing of the electron pair is involved, the contribution of the purely ionic bond to *both* the atomic charges and the electron count is two electrons to atom A and no electrons to atom B.

The above line of reasoning is easily generalized to bonds of a mixed character. A bond with the degree of ionicity of w (or $w \cdot 100\%$; see the preceding section) is traditionally described within

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the language of the valence-bond (VB) theory as a superposition of two VB (Lewis) structures, with the weight of $(1 - w)\cdot 100\%$ assigned to the A:B covalent structure and the remaining $w\cdot 100\%$ assigned to its ionic counterpart. Therefore, such a polarized bond contributes $(1 - w)\cdot 2 + w\cdot 2 = 2$ electrons to the electron count of atom A and $(1 - w)\cdot 2 + w\cdot 0 = 2 - 2w$ electrons to atom B. For a bond with the A^+B^- polarity, the electron count is $2 - 2w$ and 2, respectively.

In light of the above discussion, it is clear that the knowledge of atomic charges and bond ionicities is important, as they determine the validity of the octet rule as applied to a particular chemical system. In particular, the requirement for a molecule not to be hypervalent actually imposes lower bounds on bond ionicities and the magnitudes of atomic charges. For example, bonding in the HF molecule can be described without violating the octet rule as either H^+F^- (a fully ionic bond) or H–F (a fully covalent bond), and therefore, the bond ionicity can span the entire range between 0 and 100%. On the other hand, in order to conform with the octet rule, bonding in the ClF_3 species has to be described as a superposition of three Lewis structures, each with two lone pairs on the chlorine atom, together with two fully covalent and one fully ionic Cl–F bonds. This corresponds to the degree of ionicity equal to 33.3% and the atomic charges of –0.333 on each of the fluorines and 1.000 on the central chlorine atom. Obviously, replacing the fully covalent bond by partially polarized ones does not result in violation of the octet rule, meaning that the above numbers are actually lower limits for the bond ionicity and atomic charges. Therefore, should electronic structure calculations on ClF_3 afford bond ionicities smaller than 33.3%, ClF_3 would justifiably be called hypervalent. On the contrary, calculated bond ionicities greater than 33.3% would indicate that the octet rule is not violated in ClF_3.

The aforedescribed considerations provide a rigorous definition of hypervalent molecules, adding quantitative character to the reasoning employed in many of the previous publications, including ref 1. The fact that only the minimal set of VB structures is used does not impair the validity of the above arguments, as in any case the description of molecules in terms of Lewis structures and electron counts is obviously rather naive and oversimplistic. For the same reason, in practice the sharp borderline between the hypervalent and "normal" molecules has to be somewhat blunted. In particular, *small* positive deviations from the octet of electrons on each of the constituting atoms should not necessarily be regarded as manifestations of hypervalency; likewise the respective negative deviations should not be interpreted as the presence of "hypovalent" atoms.

Theoretical Methods

Electronic wave functions were computed at the HF/6-311++G** and MP2/6-311++G** levels with the GAUSSIAN 90 suite of programs.[12] The augmentation of the basis sets by diffuse functions was motivated by the intention to reproduce the orbitals describing lone pairs in an adequate manner. All geometries were fully optimized within the indicated molecular symmetry and theoretical level. In addition, the stationary points on the potential energy hypersurfaces were characterized at the HF/6-311++G** level by the number of imaginary vibrational frequencies. Since the absolute magnitudes of the lowest vibrational frequencies were found to be quite large, we do not anticipate qualitative changes in the character of the stationary points upon inclusion of electron correlation.

Results and Discussion

The calculated total energies are listed in Table I, and the corresponding optimized geometries are given in Table II. The calculations indicate that the ground-state geometries of the SO_2, PF_4^-, SF_4, and ClF_4^+ species have C_{2v} symmetry. In the last three systems, two of the fluorine atoms are almost collinear with the central atom. These fluorines are called axial and denoted by F_a throughout the text. The other two F atoms are called equatorial and denoted by F_e.

Table I. Total HF/6-311++G** and MP2/6-311++G** Energies

molecule	sym	N^a	E_{HF}	E_{MP2}
SO_2	C_{2v}	0	–547.231 448	–547.946 755
SO_3	D_{3h}	0	–622.059 795	–622.989 161
SO_4^{2-}	T_d	0	–696.918 038	–698.071 597
PF_5	D_{3h}	0	–838.196 364	–839.573 538
	C_{4v}	1	–838.188 920	–839.567 511
PF_4^-	C_{2v}	0	–738.747 211	–739.918 517
	C_{4v}	1	–738.728 567	–739.901 353
SF_4	C_{2v}	0	–795.264 153	–796.455 673
ClF_4^+	C_{2v}	0	–856.496 952	–857.658 346
SF_6	O_h	0	–994.152 350	–995.802 497

[a] Number of imaginary frequencies.

Table II. HF/6-311++G** and MP2/6-311++G** Optimized Geometries

molecule	sym	bond length (Å)[a]		bond angle (deg)[a]	
SO_2	C_{2v}	S–O	1.468 (1.408)	O–S–O	119.2 (118.6)
SO_3	D_{3h}	S–O	1.448 (1.397)	O–S–O	120.0 (120.0)
SO_4^{2-}	T_d	S–O	1.517 (1.484)	O–S–O	109.5 (109.5)
PF_5	D_{3h}	$P–F_a$	1.596 (1.567)	$F_a–P–F_e$	90.0 (90.0)
		$P–F_e$	1.561 (1.529)	$F_e–P–F_e$	120.0 (120.0)
	C_{4v}	$P–F_a$	1.543 (1.513)	$F_a–P–F_e$	102.2 (102.2)
		$P–F_e$	1.584 (1.554)	$F_e–P–F_e$	87.4 (87.4)
PF_4^-	C_{2v}	$P–F_a$	1.789 (1.750)	$F_a–P–F_e$	87.1 (86.4)
		$P–F_e$	1.638 (1.601)	$F_e–P–F_e$	99.0 (99.8)
				$F_a–P–F_a$	170.9 (168.7)
	C_{4v}	P–F	1.717 (1.676)	F–P–F	82.4 (82.2)
SF_4	C_{2v}	$S–F_a$	1.689 (1.643)	$F_a–S–F_e$	87.6 (87.1)
		$S–F_e$	1.578 (1.534)	$F_e–S–F_e$	101.8 (102.4)
				$F_a–S–F_a$	172.5 (170.8)
ClF_4^+	C_{2v}	$Cl–F_a$	1.654 (1.591)	$F_a–Cl–F_e$	87.1 (87.1)
		$Cl–F_e$	1.580 (1.528)	$F_e–Cl–F_e$	110.7 (109.3)
				$F_a–Cl–F_a$	169.9 (170.0)
SF_6	O_h	S–F	1.589 (1.548)	F–S–F	90.0 (90.0)

[a] MP2 values followed by the HF data in parentheses.

The Bader atomic charges and the AOM-derived covalent bond orders are displayed in Table III. It should be noted that in the systems under study inclusion of electron correlation tends to reduce the absolute values of the atomic charges and to increase the covalent bond orders. This is in agreement with the well-known fact that the bond ionicities are exaggerated at the Hartree–Fock level.[11,13] The importance of the fact that the GAPT atomic charges, presented in Table IV, are on average as large as their Bader counterparts should be emphasized here. Because the GAPT atomic charges can be derived from experimentally measured infrared intensities, their qualitative agreement with the Bader charges that arise from partitioning of the Cartesian space into atomic basins strongly reinforces the notion that the bonds in the species under study are indeed highly ionic. Although the GAPT atomic charges were not calculated at the MP2/6-311++G** level due to the substantial cost of their evaluation, we expect them to follow the trends exhibited by their Bader counterparts, i.e. have their magnitudes somewhat reduced.

Because of the aforementioned exaggeration of ionicities at the HF level, only the quantities pertinent to the computed MP2/6-311++G** electronic wave functions are used in the following discussion on electronic structures of the individual molecules. Only the conformers corresponding to the energy minima are discussed. The strongly occupied localized natural orbitals that are displayed in Tables V–X and Figures 1 and 2 are ordered according to increasing negative kinetic energies.

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Table III. HF/6-311++G** and MP2/6-311++G** Bader Atomic Charges and AOM-Based Covalent Bond Orders

molecule	sym	atom	$Q_{\mathrm{Bader}}{}^a$	bond	$P_{\mathrm{cov}}{}^a$
SO_2	C_{2v}	S	2.114 (2.684)	S–O	1.596 (1.404)
		O	−1.057 (−1.342)	O–O	0.294 (0.303)
SO_3	D_{3h}	S	3.313 (4.103)	S–O	1.365 (1.126)
		O	−1.104 (−1.368)	O–O	0.230 (0.251)
SO_4^{2-}	T_d	S	3.658 (4.278)	S–O	0.945 (0.777)
		O	−1.415 (−1.570)	O–O	0.200 (0.215)
PF_5	D_{3h}	P	3.770 (4.036)	P–F_a	0.404 (0.346)
		F_a	−0.766 (−0.818)	P–F_e	0.468 (0.408)
		F_e	−0.746 (−0.800)	F_a–F_e	0.182 (0.186)
				F_e–F_e	0.058 (0.056)
				F_a–F_a	0.008 (0.008)
	C_{4v}	P	3.747 (4.030)	P–F_a	0.464 (0.405)
		F_a	−0.753 (−0.804)	P–F_e	0.447 (0.381)
		F_e	−0.748 (−0.807)	F_a–F_e	0.111 (0.115)
				F_e–F_e	0.200 (0.207)
				F_e–$F_{e'}$	0.010 (0.009)
PF_4^-	C_{2v}	P	2.170 (2.401)	P–F_a	0.553 (0.494)
		F_a	−0.797 (−0.858)	P–F_e	0.558 (0.494)
		F_e	−0.788 (−0.842)	F_a–F_e	0.135 (0.145)
				F_a–F_a	0.026 (0.020)
				F_e–F_e	0.103 (0.102)
	C_{4v}	P	2.128 (2.382)	P–F	0.561 (0.493)
		F	−0.782 (−0.846)	F–F	0.174 (0.186)
				F–F′	0.020 (0.016)
SF_4	C_{2v}	S	2.348 (2.809)	S–F_a	0.779 (0.684)
		F_a	−0.590 (−0.708)	S–F_e	0.808 (0.703)
		F_e	−0.585 (−0.697)	F_a–F_e	0.136 (0.157)
				F_a–F_a	0.037 (0.030)
				F_e–F_e	0.096 (0.104)
ClF_4^+	C_{2v}	Cl	1.997 (2.442)	Cl–F_a	1.035 (0.992)
		F_a	−0.291 (−0.422)	Cl–F_e	1.139 (1.100)
		F_e	−0.208 (−0.299)	F_a–F_e	0.132 (0.135)
				F_a–F_a	0.054 (0.039)
				F_e–F_e	0.078 (0.062)
SF_6	O_h	S	3.618 (4.274)	S–F	0.638 (0.522)
		F	−0.603 (−0.712)	F–F	0.132 (0.149)
				F–F′	0.007 (0.008)

[a] MP2 values followed by the HF data in parentheses.

Table IV. HF/6-311++G** GAPT Atomic Charges

molecule	sym	atom	Q_{GAPT}
SO_2	C_{2v}	S	1.540
		O	−0.770
SO_3	D_{3h}	S	2.324
		O	−0.775
SO_4^{2-}	T_d	S	2.931
		O	−1.233
PF_5	D_{3h}	P	3.371
		F_a	−0.700
		F_e	−0.657
	C_{4v}	P	3.374
		F_a	−0.660
		F_e	−0.679
PF_4^-	C_{2v}	P	2.473
		F_a	−0.953
		F_e	−0.784
	C_{4v}	P	2.463
		F	−0.866
SF_4	C_{2v}	S	2.794
		F_a	−0.823
		F_e	−0.574
ClF_4^+	C_{2v}	Cl	2.543
		F_a	−0.563
		F_e	−0.208
SF*6*	O_h	S	3.799
		F	−0.633

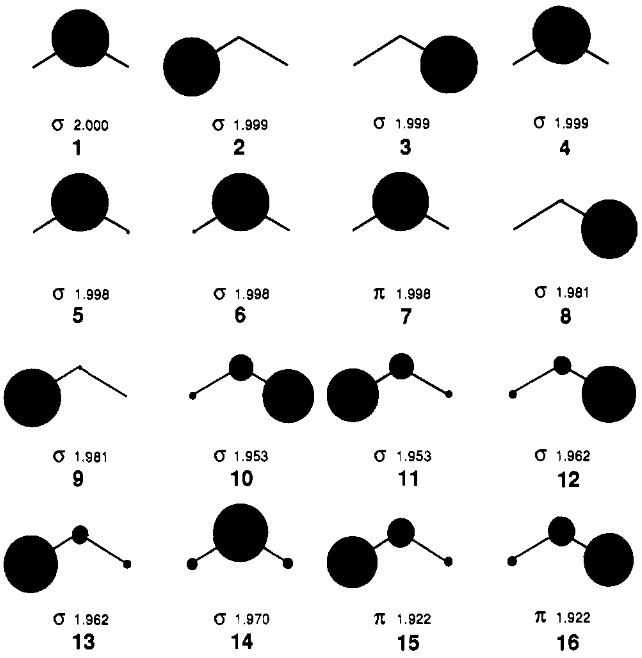

Figure 1. Atomic occupancies (represented by circles) and symmetries (followed by the occupation numbers) of the strongly occupied localized natural orbitals of the SO_2 molecule.

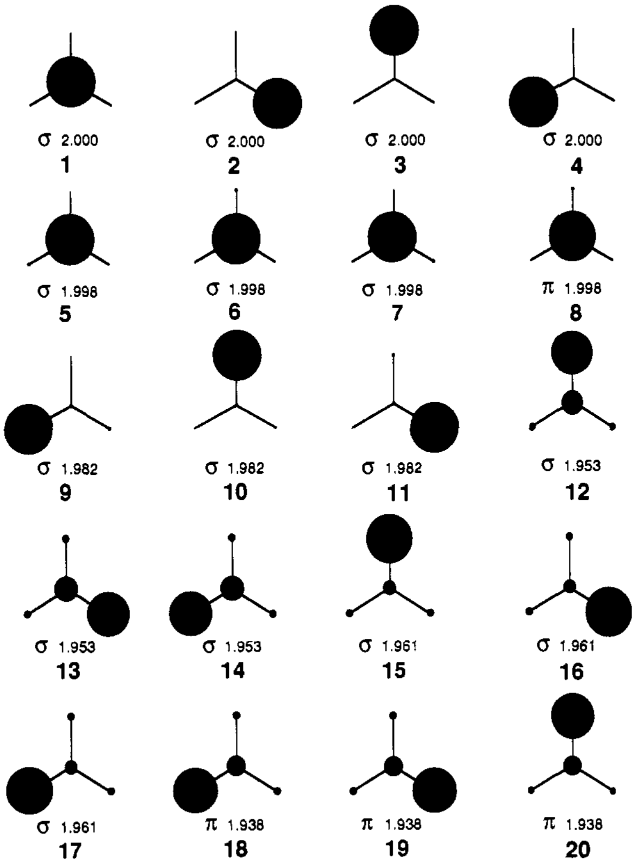

Figure 2. Atomic occupancies (represented by circles) and symmetries (followed by the occupation numbers) of the strongly occupied localized natural orbitals of the SO_3 molecule.

Electronic Structures of SO_2 and SO_3. There are two possible ways of displaying the characteristics of the localized natural orbitals. One of them is provided by tables of atomic occupancies, a mode of presentation that is used in this paper for most of the systems under study. The other possibility is to visualize the LMOs by drawing diagrams that superimpose circles with areas proportional to the atomic occupancies on plots of molecular skeletons. Such diagrams are presented here in Figures 1 and 2 for the SO_2 and SO_3 molecules.

To satisfy the octet rule, bonding in SO_2 has to be represented by a superposition of two Lewis structures, each containing two fully covalent σ S–O bonds and one lone pair on the sulfur atom, in addition to one fully covalent and one fully ionic π S–O bond. This results in the lower limits of 0.0% and 50.0% for the ionicities

Table V. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the SO_4^{2-} Anion

natural orbital	occ no.	atomic occupancies				
		S	O_1	O_2	O_3	O_4
1	2.000	1.000	0.000	0.000	0.000	0.000
2	1.999	0.000	1.000	0.000	0.000	0.000
3	1.999	0.000	0.000	1.000	0.000	0.000
4	1.999	0.000	0.000	0.000	1.000	0.000
5	1.999	0.000	0.000	0.000	0.000	1.000
6	1.998	0.998	0.002	0.000	0.000	0.000
7	1.998	0.998	0.000	0.002	0.000	0.000
8	1.998	0.998	0.000	0.000	0.002	0.000
9	1.998	0.998	0.000	0.000	0.000	0.002
10	1.981	0.001	0.997	0.000	0.000	0.000
11	1.981	0.001	0.000	0.997	0.000	0.000
12	1.981	0.001	0.000	0.000	0.997	0.000
13	1.981	0.001	0.000	0.000	0.000	0.997
14	1.957	0.192	0.779	0.010	0.010	0.010
15	1.957	0.192	0.010	0.779	0.010	0.010
16	1.957	0.192	0.010	0.010	0.779	0.010
17	1.957	0.192	0.010	0.010	0.010	0.779
18	1.962	0.046	0.925	0.008	0.006	0.014
19	1.962	0.046	0.925	0.011	0.013	0.005
20	1.962	0.046	0.012	0.925	0.012	0.005
21	1.962	0.046	0.007	0.925	0.008	0.014
22	1.962	0.046	0.012	0.012	0.925	0.005
23	1.962	0.046	0.007	0.007	0.925	0.014
24	1.962	0.046	0.006	0.009	0.014	0.925
25	1.962	0.046	0.013	0.010	0.005	0.925

of the σ and π bonds, respectively, and requires atomic charges of at least −0.500 for the oxygens and 1.000 for the sulfur atom. For SO_3, the traditional description involves three Lewis structures, each with three fully covalent σ S–O bonds, together with one fully covalent and two fully ionic π S–O bonds. This places the restrictions of at least 66.7% ionic character for the π bonds and of at least −0.667 and 2.000 for the atomic charges of O and S, respectively.

The actual ionicities of both the σ bonds (LMOs 10 and 11, Figure 1) and the π bonds (LMOs 15 and 16, Figure 1) in the SO_2 molecule are much higher than the above limits, equaling 62.5 and 56.4%, respectively. This shows that the octet rule is *not* violated in SO_2. The remaining localized natural orbitals describe the core electrons (LMOs 1–7), the σ lone pairs of oxygen atoms (LMOs 8, 9, 12, and 13) and the lone pair of sulfur (LMO 14). It is quite clear that in SO_2 the σ and π contributions to covalent bonding are of comparable magnitudes, the latter being slightly larger.

In the SO_3 molecule, the σ S–O bonds (LMOs 12–15, Figure 2) are less ionic (54.7%) than in SO_2. On the other hand, the ionicity of the π S–O bonds (LMOs 18–20, Figure 2) is significantly higher (70.0%) and large enough to exceed the limiting value of 66.6% that guarantees compliance with the octet rule. The other localized natural orbitals, eight of which (LMOs 1–8) describe core electrons and six of which (LMOs 9–11 and 15–17) correspond to lone pairs on the oxygen atoms contribute only marginally to covalent bonding.

Electronic Structure of SO_4^{2-}. Within the language of traditional inorganic chemistry, the SO_4^{2-} anion is most conveniently described by a single Lewis structure with four fully covalent σ S–O bonds. Such a description, which yields the atomic charges of −1.000 for each of the oxygens and 2.000 for the sulfur atom, does not violate the octet rule.

The computed atomic occupancies, listed in Table V, are in qualitative agreement with the aforementioned picture. The localized orbitals of the atomic cores (LMOs 1–9) are followed by four equivalent lone pairs on the oxygen atoms (LMOs 10–13). These well-localized (99.8%) lone pairs point in the directions parallel to the respective S–O bonds and, therefore, can be regarded as having a local σ symmetry. The next four equivalent LMOs (LMOs 14–17) are those of the σ S–O bonds. These localized natural orbitals describe bonds that are 60.5% ionic. The last eight LMOs (LMOs 18–25) correspond to the π lone pairs of the oxygen atoms. The fact that these lone pairs are not perfectly localized on the oxygen atoms results in a significant π contribution of 0.333 to the covalent S–O bond order. However, the total covalent S–O bond order of 0.945 (Table III) indicates the presence of an almost single bond between the sulfur and oxygen atoms. The calculated atomic charges exceed the limits required by the octet rule, meaning that bonding in SO_4^{2-} has *no* hypervalent character.

Table VI. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the PF_5 Molecule (D_{3h} Symmetry)

natural orbital	occ no.	atomic occupancies					
		P	F_1	F_2	F_3	F_4	F_5
1	2.000	1.000	0.000	0.000	0.000	0.000	0.000
2	2.000	0.000	1.000	0.000	0.000	0.000	0.000
3	2.000	0.000	0.000	1.000	0.000	0.000	0.000
4	2.000	0.000	0.000	0.000	1.000	0.000	0.000
5	2.000	0.000	0.000	0.000	0.000	1.000	0.000
6	2.000	0.000	0.000	0.000	0.000	0.000	1.000
7	1.998	0.997	0.000	0.002	0.000	0.000	0.000
8	1.998	0.997	0.000	0.000	0.002	0.000	0.000
9	1.998	0.997	0.000	0.000	0.000	0.002	0.000
10	1.998	0.997	0.001	0.000	0.000	0.000	0.001
11	1.988	0.000	0.000	0.999	0.000	0.000	0.000
12	1.988	0.000	0.000	0.000	0.999	0.000	0.000
13	1.988	0.000	0.000	0.000	0.000	0.999	0.000
14	1.988	0.000	0.998	0.000	0.000	0.000	0.000
15	1.988	0.000	0.000	0.000	0.000	0.000	0.998
16	1.976	0.008	0.010	0.971	0.000	0.000	0.010
17	1.976	0.008	0.010	0.000	0.971	0.000	0.010
18	1.976	0.008	0.010	0.000	0.000	0.971	0.010
19	1.975	0.010	0.968	0.011	0.005	0.005	0.000
20	1.975	0.011	0.968	0.003	0.009	0.009	0.000
21	1.975	0.010	0.000	0.011	0.005	0.005	0.968
22	1.975	0.011	0.000	0.003	0.009	0.009	0.968
23	1.973	0.022	0.004	0.962	0.004	0.004	0.004
24	1.973	0.022	0.004	0.004	0.962	0.005	0.004
25	1.973	0.022	0.004	0.004	0.005	0.962	0.004
26	1.967	0.097	0.010	0.877	0.003	0.003	0.010
27	1.967	0.097	0.010	0.003	0.877	0.003	0.010
28	1.967	0.097	0.010	0.003	0.003	0.877	0.010
29	1.967	0.089	0.877	0.011	0.011	0.011	0.000
30	1.967	0.089	0.000	0.011	0.011	0.011	0.877

Electronic Structure of PF_5. Among the 30 strongly occupied localized natural orbitals of PF_5 (Table VI), the first 10 describe the core electrons. These are followed by the LMOs 11–13 and 14 and 15 that correspond to the highly localized (99.8–99.9%) lone pairs located respectively at the equatorial and axial fluorines. These localized natural orbitals possess a local σ symmetry, in contrast to the lone pair LMOs 19–25 that are of a local π character. The bulk of the P–F covalent bonding comes from the σ-like LMOs 26–30, which describe highly polarized bonds.

For the PF_5 molecule, the octet rule imposes the lower limit of 20.0% on the P–F bond ionicity, which corresponds to the atomic charges of −0.200 for the fluorines and 1.000 for the central phosphorus atom. These figures arise from a superposition of five Lewis structures, each with four σ fully covalent and one fully ionic bond. Since the actual atomic charges (Table III) are much larger than these limiting values, one concludes that the octet rule is *not* violated in PF_5.

Electronic Structures of PF_4^-, SF_4, and ClF_4^+. The PF_4^-, SF_4, and ClF_4^+ species share the same bonding situation in which the central atom contributes six valence electrons. To assure compliance with the octet rule, one must consider a superposition of four Lewis structures, each with one lone pair on the central atom, three fully covalent σ bonds, and one fully ionic bond. This

Table VII. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the PF_4^- Anion (C_{2v} Symmetry)

natural orbital	occ no.	atomic occupancies				
		P	F_1	F_2	F_3	F_4
1	2.000	1.000	0.000	0.000	0.000	0.000
2	2.000	0.000	1.000	0.000	0.000	0.000
3	2.000	0.000	0.000	1.000	0.000	0.000
4	2.000	0.000	0.000	0.000	1.000	0.000
5	2.000	0.000	0.000	0.000	0.000	1.000
6	1.998	1.000	0.000	0.000	0.000	0.000
7	1.998	0.998	0.000	0.001	0.000	0.000
8	1.998	0.998	0.000	0.000	0.001	0.000
9	1.998	0.999	0.000	0.000	0.000	0.000
10	1.987	0.001	0.999	0.000	0.000	0.000
11	1.987	0.001	0.000	0.000	0.000	0.999
12	1.987	0.001	0.000	0.999	0.000	0.000
13	1.987	0.001	0.000	0.000	0.999	0.000
14	1.975	0.011	0.008	0.971	0.001	0.008
15	1.975	0.011	0.008	0.001	0.971	0.008
16	1.974	0.020	0.002	0.969	0.007	0.002
17	1.974	0.020	0.002	0.007	0.969	0.002
18	1.974	0.015	0.973	0.010	0.002	0.000
19	1.974	0.015	0.000	0.002	0.010	0.973
20	1.974	0.015	0.973	0.002	0.010	0.000
21	1.974	0.015	0.000	0.010	0.002	0.973
22	1.966	0.101	0.005	0.883	0.005	0.005
23	1.966	0.101	0.005	0.005	0.883	0.005
24	1.965	0.092	0.889	0.008	0.008	0.002
25	1.965	0.092	0.002	0.008	0.008	0.889
26	1.967	0.888	0.033	0.022	0.022	0.033

Table VIII. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the SF_4 Molecule

natural orbital	occ no.	atomic occupancies				
		S	F_1	F_2	F_3	F_4
1	2.000	1.000	0.000	0.000	0.000	0.000
2	2.000	0.000	1.000	0.000	0.000	0.000
3	2.000	0.000	0.000	1.000	0.000	0.000
4	2.000	0.000	0.000	0.000	1.000	0.000
5	2.000	0.000	0.000	0.000	0.000	1.000
6	1.999	1.000	0.000	0.000	0.000	0.000
7	1.998	0.999	0.000	0.001	0.000	0.000
8	1.998	0.999	0.000	0.000	0.001	0.000
9	1.998	1.000	0.000	0.000	0.000	0.000
10	1.987	0.001	0.000	0.998	0.000	0.000
11	1.987	0.001	0.000	0.000	0.998	0.000
12	1.987	0.001	0.998	0.000	0.000	0.000
13	1.987	0.001	0.000	0.000	0.000	0.998
14	1.976	0.017	0.008	0.966	0.001	0.008
15	1.976	0.017	0.008	0.001	0.966	0.008
16	1.975	0.020	0.970	0.005	0.005	0.001
17	1.975	0.020	0.001	0.005	0.005	0.970
18	1.974	0.032	0.002	0.957	0.007	0.002
19	1.974	0.032	0.002	0.007	0.957	0.002
20	1.974	0.026	0.959	0.007	0.007	0.000
21	1.974	0.026	0.000	0.007	0.007	0.959
22	1.958	0.175	0.006	0.807	0.006	0.006
23	1.958	0.175	0.006	0.006	0.807	0.006
24	1.956	0.162	0.816	0.009	0.009	0.004
25	1.956	0.162	0.004	0.009	0.009	0.816
26	1.970	0.922	0.023	0.016	0.016	0.023

Table IX. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the ClF_4^+ Cation

natural orbital	occ no.	atomic occupancies				
		Cl	F_1	F_2	F_3	F_4
1	2.000	1.000	0.000	0.000	0.000	0.000
2	2.000	0.000	1.000	0.000	0.000	0.000
3	2.000	0.000	0.000	1.000	0.000	0.000
4	2.000	0.000	0.000	0.000	1.000	0.000
5	2.000	0.000	0.000	0.000	0.000	1.000
6	1.999	1.000	0.000	0.000	0.000	0.000
7	1.999	1.000	0.000	0.000	0.000	0.000
8	1.999	1.000	0.000	0.000	0.000	0.000
9	1.999	1.000	0.000	0.000	0.000	0.000
10	1.986	0.004	0.001	0.995	0.000	0.001
11	1.986	0.004	0.001	0.000	0.995	0.001
12	1.987	0.003	0.995	0.001	0.001	0.000
13	1.987	0.003	0.000	0.001	0.001	0.995
14	1.977	0.958	0.013	0.007	0.007	0.013
15	1.977	0.020	0.008	0.965	0.000	0.008
16	1.977	0.020	0.008	0.000	0.965	0.008
17	1.976	0.026	0.964	0.004	0.004	0.001
18	1.976	0.026	0.001	0.004	0.004	0.964
19	1.977	0.044	0.002	0.944	0.008	0.002
20	1.977	0.044	0.002	0.008	0.944	0.002
21	1.976	0.031	0.952	0.008	0.008	0.000
22	1.976	0.031	0.000	0.008	0.008	0.952
23	1.947	0.337	0.007	0.645	0.004	0.007
24	1.947	0.337	0.007	0.004	0.645	0.007
25	1.938	0.281	0.691	0.010	0.010	0.008
26	1.938	0.281	0.008	0.010	0.010	0.691

implies a charge of –0.250 on each of the fluorine atoms and an averaged bond ionicity of 25.0%. Judging by the above criterion, one infers from the large negative charges of their fluorine atoms (Table III) that both PF_4^- and SF_4 satisfy the octet rule. On the other hand, the ClF_4^+ cation appears to be a borderline case with the equatorial fluorines bearing charges of only –0.208.

The above conclusion is confirmed by analysis of the strongly occupied localized natural orbitals displayed in Tables VII–IX. In all three species, the first 9 LMOs describe the core electrons. The lone pairs of the fluorine atoms (LMOs 10–13) come next. These localized orbitals, which are almost parallel to the central atom–fluorine bond and can therefore be called σ lone pairs, are almost perfectly (99.5–99.9%) localized on single fluorine atoms. In the PF_4^- anion and the SF_4 molecule, the σ lone pairs are followed by eight localized natural orbitals (LMOs 14–21) corresponding to the π lone pairs. In the ClF_4^+ cation, the π lone pairs (LMOs 15–22) are preceded by a single lone pair of the chlorine atom.

Although the π lone pairs of fluorines remain well localized on single atoms, they nevertheless contribute to the central atom–fluorine bonding. These contributions increase for both the axial and equatorial fluorines in the order $PF_4^- < SF_4 < ClF_4^+$. In particular, the contributions of the π lone pairs to the covalent bond orders of the axial (equatorial) fluorine atoms are 0.115 (0.119), 0.175 (0.186), and 0.216 (0.241) for PF_4^-, SF_4, and ClF_4^+, respectively.

The major part of the bonding in the tetrafluoride species discussed here comes from the σ-like localized orbitals describing the central atom–fluorine bonds (LMOs 22–25 in PF_4^- and SF_4, LMOs 23–26 in ClF_4^+). Ionicities of these reasonably well-localized (97.2–98.4%) bonds decrease with the increasing electronegativities of the central atoms. The longer axial bonds are less localized and more ionic than their shorter equatorial counterparts. The decrease in ionicities is matched by the increase of the covalent bond orders from the average of 0.556 for the P–F bonds to 1.087 for the Cl–F ones. One should note that the ionicity of the Cl–F_e bond is only 31.3%, which is below the limit imposed by the octet rule.

Finally, lone pairs of the central atoms are described by single localized orbitals (LMO 26 in PF_4^- and SF_4, LMO 14 in ClF_4^+).

Table X. Atomic Occupancies of the Strongly Occupied Localized Natural Orbitals of the SF_6 Molecule

		atomic occupancies						
natural orbital	occ no.	S	F_1	F_2	F_3	F_4	F_5	F_6
1	2.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000
2	2.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000
3	2.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000
4	2.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000
5	2.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000
6	2.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000
7	2.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000
8	1.999	0.999	0.000	0.000	0.000	0.000	0.000	0.000
9	1.998	0.999	0.000	0.000	0.000	0.000	0.000	0.000
10	1.998	0.999	0.000	0.000	0.000	0.000	0.000	0.000
11	1.998	0.999	0.000	0.000	0.000	0.000	0.000	0.000
12	1.988	0.001	0.997	0.000	0.000	0.000	0.000	0.000
13	1.988	0.001	0.000	0.997	0.000	0.000	0.000	0.000
14	1.988	0.001	0.000	0.000	0.997	0.000	0.000	0.000
15	1.988	0.001	0.000	0.000	0.000	0.997	0.000	0.000
16	1.988	0.001	0.000	0.000	0.000	0.000	0.997	0.000
17	1.988	0.001	0.000	0.000	0.000	0.000	0.000	0.997
18	1.976	0.015	0.966	0.008	0.001	0.008	0.001	0.000
19	1.976	0.015	0.966	0.001	0.008	0.001	0.008	0.000
20	1.976	0.015	0.001	0.966	0.008	0.000	0.008	0.001
21	1.976	0.015	0.008	0.966	0.001	0.000	0.001	0.008
22	1.976	0.015	0.001	0.008	0.966	0.008	0.000	0.001
23	1.976	0.015	0.008	0.001	0.966	0.001	0.000	0.008
24	1.976	0.015	0.008	0.000	0.001	0.966	0.001	0.008
25	1.976	0.015	0.001	0.000	0.008	0.966	0.008	0.001
26	1.976	0.015	0.008	0.001	0.000	0.001	0.966	0.008
27	1.976	0.015	0.001	0.009	0.000	0.009	0.966	0.001
28	1.976	0.015	0.000	0.008	0.001	0.008	0.001	0.966
29	1.976	0.015	0.000	0.001	0.008	0.001	0.008	0.966
30	1.958	0.161	0.803	0.009	0.009	0.009	0.009	0.000
31	1.958	0.161	0.009	0.803	0.009	0.000	0.009	0.009
32	1.958	0.161	0.009	0.009	0.803	0.009	0.000	0.009
33	1.958	0.161	0.009	0.000	0.009	0.803	0.009	0.009
34	1.958	0.161	0.009	0.009	0.001	0.009	0.803	0.009
35	1.958	0.161	0.000	0.009	0.009	0.009	0.009	0.803

The lone pair, which lies approximately within the plane of the equatorial bonds, is poorly (88.8%) localized on the phosphorus atom in PF_4^- and therefore contributes as much as ca. 20% to the P–F covalent bond orders. It is localized better (92.2%) on the sulfur atom in SF_4 and reasonably well (95.8%) on the chlorine atom in ClF_4^+.

Electronic Structure of SF_6. The 35 strongly occupied localized natural orbitals of SF_6 are displayed in Table X. The first 11 orbitals belong to the cores of sulfur and fluorine. They are followed by six equivalent lone pairs (LMOs 12–17) of the fluorine atoms. Each of these lone pairs is more than 99.7% localized on a single atom and points in the direction of the respective S–F bond. In contrast to these orbitals that have a local σ character, the lone pairs represented by the LMOs 18–29 are perpendicular to the S–F bonds. Each of these 12 equivalent LMOs of a local π character is 96.6% localized on a fluorine atom. This means that the S–F covalent π bonding is only of marginal importance in SF_6. The local component of the covalent σ bonding is provided by the remaining six localized orbitals (LMOs 30–35). Each of these orbitals is 96.4% localized on a S–F bond that is 66.6% ionic.

Overall, bonding in the SF_6 molecule is characterized by the S–F covalent bond order of 0.638 and the atomic charges of 3.618 for sulfur and –0.603 for each of the fluorine atoms (Table III). These values should be contrasted with the picture implied by application of the octet rule in which 15 Lewis structures, each involving 4 fully covalent σ bonds and 2 fully ionic bonds between sulfur and fluorine, are superimposed. The resulting S–F bonds with an average 33.3% ionicity correspond to the atomic charges of 2.000 for sulfur and –0.667 for each of the fluorines. Since the actual ionicities are higher, one safely concludes that bonding in SF_6 *does not* violate the octet rule.

Conclusions

All of the systems under study are characterized by natural orbitals with occupancies close to either zero or two. This means that the MP2 method is the appropriate level of approximation for these systems and therefore it can be stated with confidence that the computed electronic wave functions are of a sufficient accuracy to be of use in a definitive study of bonding. The analysis of the computed wave functions reveals that in most of the systems studied the bonds between the central and the peripheral atoms are highly polarized. The degree of ionicity of these bonds varies with the electronegativity differences, being the largest for the phosphorus molecules and the smallest for the ClF_4^+ ion. Only the latter species is a candidate for hypervalency, with the computed bond ionicities and atomic charges bordering those required for the satisfaction of the octet rule.

The tables of strongly occupied localized natural orbitals make it possible to discuss detailed aspects of bonding, providing all the necessary information in a quantitative, yet compact and concise manner. Because of these advantages, we believe that they will find widespread use as the means for a uniform and unbiased description of electronic structures of molecules. In particular, the local symmetries of the LMOs let us deduce the relative magnitudes of the σ- and π-type contributions to the overall bonding. The π-type contributions are found to be as important as their σ-type counterparts in the SO_2 and SO_3 molecules. On the other hand, in the SO_4^{2-} anion, the π-type interactions are responsible for only ca. 35% of the covalent bond order. The π-type contributions to bonding in the fluorides are of even less importance.

The present study not only affords a clear-cut analysis of bonding in molecules involving the second-row elements (P, S, and Cl) but also provides clues to why the first-row elements (such as C, N, or O) fail to form stable hypervalent compounds. The most probable reasons for this failure are 2-fold: First of all, the electronegativities of these elements are too high to make the differences between the electronegativities of the central atom and the ligands (presumably F atoms) large enough to result in ionic bonds that are usually quite strong. In other words, should such compounds exist, they would be expected to be of a truly hypervalent character. Second, the first-row atoms tend to form relatively short bonds that would result in overcrowding of ligands, implying strong steric repulsions. Since both the concepts of steric repulsions and electronegativity can be defined in a rigorous manner (see refs 14 and 15, respectively), this explanation warrants further study.

Acknowledgment. The idea of analyzing electronic structures of "hypervalent" molecules with rigorous interpretive tools has arisen from the suggestions made to the senior author by Professor Paul von Ragué Schleyer. This work was partially supported by the National Science Foundation under the contract CHE-9015566, the Camille and Henry Dreyfus Foundation New Faculty Award Program, the Florida State University through time granted on its Cray Y-MP digital computer, and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF 25076-G6).

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