orbital energies of $(C^*O)^+$ are remarkably similar to those of NO^+ except for 2σ, which is mostly the C_{1s} and N_{1s} orbitals, respectively. The other MO's are much the same in terms of orbital energy for a carbon core hole as for a nitrogen nucleus. A similar comparison holds for $(CO^*)^+$ with CF^+; in this case, the MO energies are much the same except for 1σ, the O_{1s} and F_{1s} orbitals, respectively.

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SCF-Xα Scattered Wave Studies on Bonding and Ionization Potentials. I. Hexafluorides of Group VI Elements

Notker Rösch,[1a] Vedene H. Smith, Jr.,*[1b] and M. H. Whangbo[1b]

Contribution from the Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Chemistry, Queen's University, Kingston, Ontario, Canada. Received December 10, 1973

Abstract: A SCF-Xα-SW calculation has been carried out for the hexafluorides of the group VI elements S, Se, and Te. The bonding of these molecules is compared by using the charge distribution in different spatial regions in these molecules. The central atom–ligand bond is found to increase in polarity as one moves from S to Te. In contrast to simple overlap arguments, the e_g level is always higher in energy than the t_{2g} level. The calculated ionization spectra agree well with the experimental measurements. Finally, the d orbital participation has been studied for SF_6. The inclusion of d components is necessary in order to reproduce the experimental level ordering. However, its effect on the charge distribution (and possibly also on the bonding) is minor.

M olecules containing elements of the groups VI to VIII in their higher valence states have received considerable attention,[2-8] since they involve atoms which exceed the number of valences permitted on the basis of the Langmuir–Lewis theory of bonding.[9] For this reason they have been called hypervalent molecules.[6] A number of explanations, based either on valence bond [3,7,9] or on molecular orbital theory,[2,3,6-9] have been proposed to elucidate the bonding nature of these molecules. Among the molecules of MX_6 type, sulfur hexafluoride, SF_6, might be the most thoroughly studied system, both experimentally[10-17] and theoretically.[18-28]

Immediate questions arising from the existence of MX_6 molecules are to what extent the d orbitals on the central atom M are important and what the bonding

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structure is. In this paper these questions will be systematically investigated for some hexafluorides of the group VI, namely, SF_6, SeF_6, and TeF_6, using the SCF-Xα scattered wave (Xα-SW) method.[29-31]

The SCF-Xα-SW method provides self-consistent solutions to the Hartree–Fock–Slater (Xα) equations for molecules. The exchange part of the total potential is approximated by a local exchange potential, for spin-up electrons (similar for spin-down)

$$V_{X\alpha}(\mathbf{r}) = -6\alpha\left(\frac{3}{4\pi}\rho^\uparrow(\mathbf{r})\right)^{1/3} \qquad (1)$$

where $\rho^\uparrow(\mathbf{r})$ is the local electronic charge density for spin-up electrons. The total potential (coulomb plus exchange) is further approximated by the muffin-tin model in order to make possible the use of the scattered wave (or multiple scattering) formalism. To this end, the space in and around a molecular cluster is divided into three contiguous regions: (I) atomic spheres around each nucleus, (II) an interatomic region between the atomic spheres and an extramolecular sphere surrounding the molecular cluster, and (III) the region outside the cluster (see Figure 1). The muffin-tin potential is obtained through spherically averaging the potential in regions I and III. In region II the potential is volume averaged. Details of the SCF-Xα-SW method may be found in references.[30,31]

The Xα-SW method is ideally suited for comparative studies like the one presented here, because substitution of elements out of the same group of the periodic systems causes virtually no increase in computing time, though all electrons of the molecule are treated explicitly. Another great advantage is the representation of the molecular orbital wave functions through rapidly converging multicenter expansions whose various radial parts are found by numerical integration. All problems connected with the choice of a proper basis (for example, the optimization of orbital exponents in the LCAO approach) are avoided thereby and the effect of d orbitals on the electronic structure of a molecule may be tested simply by inclusion (or omission) of the corresponding $l = 2$ term in the expansion around the center under consideration.

The Mulliken population analysis[32] provides useful information about the charge distribution of molecules if LCAO-SCF wave functions are available. A corresponding concept may be found for the Xα-SW charge distributions. Namely, the amount of charge inside an atomic region I may be considered equivalent to the gross atomic population. Unlike a population analysis there is no ambiguity in assigning these charges to the various nuclei because it is based on a partitioning of space. The charge in region III may be attributed to the ligands, while there is no obvious assignment for the charge in the interatomic region II (for a detailed discussion see below). Nevertheless, we intend to show here the use of these Xα-SW gross charges for the various regions of the molecule by comparing the observed trends in them with the chemical behavior of the corresponding molecules. To achieve this we make use of the fact that the Xα-SW scheme yields the super-
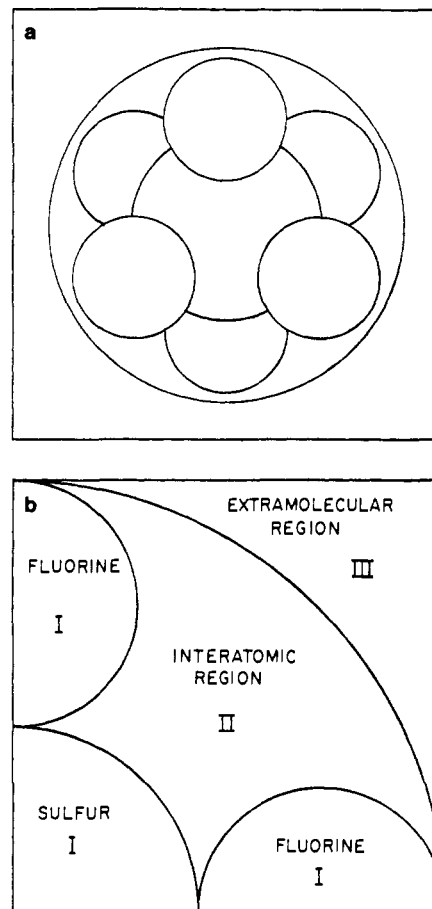

Figure 1. (a) A projected view of the various atomic and the outer spheres used for the partitioning of the MF_6 (O_h symmetry) molecular space. (b) A quadrant of the projection of the spheres of MF_6 on the xy plane.

imposed atomic charge densities of the various molecular regions. Thus the comparison with the gross charge distribution over the corresponding regions after iteration to self-consistency gives useful information on the charge redistribution during molecular formation. We will perform a detailed study of the difference charge density, whose value for the understanding of chemical bonds has been demonstrated for diatomic molecules.[33]

Ground State of MF_6 (M = S, Se, Te)

The ordering of the orbital energies for SF_6 has been of much interest.[17,25,27,28] One way of understanding the level ordering as well as the bonding nature of MF_6 molecules is to study the energy levels of the ligand lattice F_6 and the changes upon introduction of the center atom M. Within the simple Hückel formalism, the qualitative features of the level structure of some symmetric molecules are easily obtained by pure topological arguments. For the X_6 lattice of O_h symmetry, Schmidtke[34] found the following level ordering for the levels generated by ligand p orbitals

$$a_{1g} < t_{1u}(\pi) < t_{2g} < t_{2u} < t_{1g} = e_g < t_{1u}(\sigma) \qquad (2)$$

while our SCF-Xα-SW calculation of the F_6 lattice

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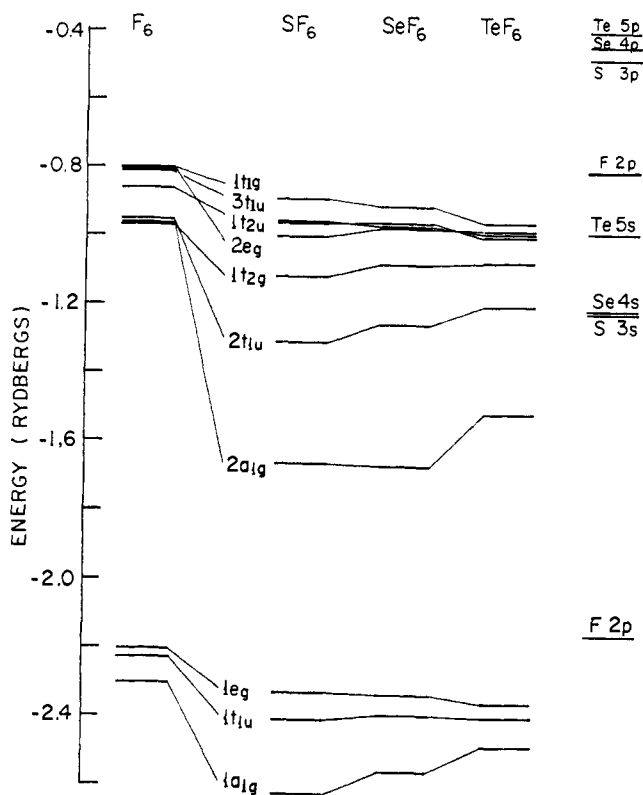(34) H.-H. Schmidtke, *J. Chem. Phys.*, **45**, 3920 (1966).

Figure 2. Comparison of SCF-Xα-SW electronic energies for different molecules of the type MF₆. Also shown are the levels of the F₆ lattice and the SCF-Xα energies of the various free atoms. The levels are labeled according to the irreducible representations of the point group O_h (1 Rydberg = 0.5 au).

(bond distances as in SF_6, touching atomic spheres) gives (cf. Figure 2)

$$t_{2g} \lesssim a_{1g} < t_{1u}(\pi) < t_{2u} < t_{1u}(\sigma) < e_g \lesssim t_{1g} \tag{3}$$

The latter ordering scheme is the result of self-consistent charge distribution of the F_6 lattice, including also a possible effect from the F 2s orbitals; thus it should be more realistic. However, the t_{2g}, a_{1g}, and $t_{1u}(\pi)$ levels are found to be almost degenerate and so are the $t_{1u}(\sigma)$, e_g, and t_{1g} levels. The general agreement is therefore good, the t_{2u} level being in the middle and the e_g level above the t_{2g} level.

Let us now consider the results of the ground state calculation for the MF₆ series (M = S, Se, Te). In our calculation we have used the α_{HF} values determined by Schwarz[35] for the atomic regions and the average of the various atomic α_{HF} values for the regions II and III with the following bond distances:[36] r_{S-F} = 2.9556 au, r_{Se-F} = 3.1559 au, r_{Te-F} = 3.4394 au. The spheres were kept touching and their sizes were chosen such that the potentials were continuous at the point where they are in contact. The resulting radii for the central atomic spheres were: r_S = 1.780 au, r_{Se} = 1.915 au, r_{Te} = 2.188 au. The core electron orbitals, i.e., the orbitals which correspond to the preceding noble gas configuration, were kept frozen at their atomic values. This approximation is known to have virtually no effect on the shape and energy of the valence orbitals.[27,30] The results are shown in Figure 2 together with the

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corresponding atomic Xα orbital energies. Our results for SF_6, using the correct experimental bond length,[36a] are essentially identical with those of a previous Xα-SW calculation.[27] We notice that the energy levels of the F_6 lattice are markedly lowered as compared to those of MF_6, thereby displaying the stabilization of these molecules. The first three energy levels, $1a_{1g}$, $1t_{1u}$, and $1e_g$, are mainly of F 2s orbitals, with a substantial bonding contribution of M to the $1a_{1g}$ level. The next two orbitals, $2a_{1g}$ and $2t_{1u}$, are the ones affected most through the bonding and show strong contributions both from the central atom and the ligands and therefore are strongly bonding orbitals. The remaining orbitals are primarily F 2p orbitals with only small admixtures from the central atom. The orbitals $1t_{2u}$ and $1t_{1g}$ and essentially also $3t_{1u}$ have nonbonding character. The orbitals $1t_{2g}$ and $2e_g$, the latter always being higher in energy, show small contributions from M d orbitals. The first empty level is the $3a_{1g}$ antibonding level, as has been inferred from X-ray absorption spectra.[28] As one moves from S to Te, the "band width" of the top six F 2p levels $(2t_{1u} - 1t_{1g})$ becomes narrower, in good agreement with experimental results.[37]

Let us now turn to an analysis of the electronic charge distribution, as given by the total electronic charges in the various molecular regions Q_M, Q_F, Q_{INT}, and Q_{EXT}. Q_{INT} and Q_{EXT} are the total electronic charges in the interatomic region II and the extramolecular region III, respectively (see the introductory section). The charges are summarized in Table I together with

Table I. Electronic Charges and Charge Differences (Molecular vs. Superimposed Atomic Charges) in Different Molecular Regions for the MF₆ Series

Molecule	Q_M	Q_F	Q_{INT}	Q_{EXT}
F₆	0	8.630	1.830	0.391
SF₆	13.671	7.023	12.303	1.886
SeF₆	31.168	7.300	11.462	1.570
TeF₆	48.647	7.376	11.582	1.416
SF₆ᵃ	13.319	7.051	12.454	1.920

Molecule	ΔQ_M	ΔQ_F	ΔQ_{INT}	ΔQ_{EXT}	$(6\Delta Q_F - \Delta Q_M)$
F₆	0	0.070	−0.381	−0.039	0.420
SF₆	0.702	0.393	−2.066	−0.994	1.650
SeF₆	0.408	0.410	−1.668	−1.200	2.052
TeF₆	0.218	0.456	−1.853	−1.101	2.518
SF₆ᵃ	0.349	0.421	−1.915	−0.960	2.177

ᵃ d orbital components are omitted.

the charge differences

$$\Delta Q_i = Q_i^{molec} - Q_i^{atom} \tag{4}$$

The results of the population analysis quoted in the literature for SF_6[20-26] seem to depend rather strongly on the basis set chosen. The ab initio LCAO–MO calculation with the largest basis set[26] yields the following populations: the total net charges on the sulfur and the fluorine atoms are respectively +2.361 and +0.237, while the total gross charges on the corresponding atoms are +0.389 and −0.065, respectively. This is to be

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compared with the $X\alpha$–SW total net charge q_I and the $X\alpha$–SW total gross charge $\bar{q}_I$ in the atomic sphere I: $\bar{q}_S = +2.329$, $q_F = +1.977$, $\bar{q}_S = +0.571$, and $\bar{q}_F = -0.095$. Here q_I is defined as the atomic number Z_I of the atom I minus the $X\alpha$–SW net atomic population Q_I, while $\bar{q}_I$ is obtained by subtracting off the $X\alpha$–SW gross atomic population Q_I' from Z_I. To obtain Q_I' we followed a procedure suggested by Johnson,[31] which is to distribute the interatomic charge Q_{II} equally among all atoms in the molecule and the extramolecular charge Q_{III} only among the ligands.

These $X\alpha$–SW gross charges compare rather well with those obtained from the population analysis of a LCAO–MO wave function, whereas the $X\alpha$–SW atomic charges (at least for the central atom) are in good agreement with the net atomic charges. On the other hand, a charge of $+2.58$ on sulfur has been inferred from the shift of the ESCA lines for sulfur core electrons.[38] As M goes down from S to Te, both the $X\alpha$–SW net charge q_M and the $X\alpha$–SW gross charge $\bar{q}_M$ increase steadily, 2.33, 2.83, 3.35 and 0.57, 1.20, 1.70, respectively, displaying increasing polarization of the M–F bond. This effect correlates nicely with the increasing differences between the electronegativities for M and F.

The charge differences ΔQ_i both on the central atom and the ligands are always positive, indicating a charge contraction in the atomic regions due to bond formation and a decreasing charge in regions II and III. These charge differences not only show the flow of charge to the bond region during the formation of the molecule but they also do not depend as closely on the somewhat arbitrary partitioning of space underlying the scattered wave formalism as do the electronic charges Q_i. ΔQ_M decreases but ΔQ_F increases as one goes from S to Te, as one would expect from the changes of the corresponding electronegativity differences. The difference in charge gain $6\Delta Q_F - \Delta Q_M$ might be considered as a measure of the polarity of the bond. Its trend (see Table I) confirms the above conclusion of an increasing polarity, as one goes from S to Te.

This analysis of the $X\alpha$–SW charge distribution seems to be consistent and in good agreement with the conclusion given by many other workers that a certain amount of electronic charge should be removed from the central atom to the ligands to form hypervalent molecules.[6,39]

Let us compare our findings for the MF_6 ground state with the chemical properties of these molecules. The strong similarity between the level diagrams for SF_6 and SeF_6 (see Figure 2) reminds one of the fact that the chemistry of sulfur and selenium shows many more parallels than that of tellurium.[40,41] This has been rationalized previously through the shielding effect of the 3d orbitals.[8] The general inertness of SF_6 and SeF_6 contrasts with the acceptor properties of TeF_6 which forms adducts of the form TeF_7^- or TeF_8^{2-}.[42,43] TeF_6 also undergoes complete hydrolysis.[42] These differences in chemical behavior may be rationalized

by considering the large polarity of the Te–F bond. If one takes the above mentioned "band width" of the F 2p orbitals as a measure for the interaction between the central atom and the ligands, one would predict a decrease in the M–F bond strength going from SF_6 to TeF_6.

Ionization Potentials of MF_6

Koopmans' theorem enables one to consider the ionization potentials within the frozen orbital approximation as the negative eigenvalues of the Hartree–Fock operator. However, in the SCF–$X\alpha$–SW method one uses the concept of the "transition state" in which half an electron is removed from the ith orbital. Slater has shown[44] that within the $X\alpha$–SW scheme the ionization potential of the ith orbital is given by the one-electron energy of the corresponding transition state. Since the orbital relaxation is taken care of during the transition state calculations, the ionization potentials are in at least as good agreement with experiment as those obtained from LCAO–SCF wave functions using Koopmans' theorem.[45] The level ordering predicted by Koopmans' theorem may not be the same as that from the energy difference method,[46] since this theorem neglects the electron relaxation which is inherent in an ionization process. Even in those cases, the $X\alpha$–SW method gives a consistent and correct level ordering by the very definition of the transition state.[47]

The ionization potentials for the six highest orbitals of the compounds MF_6 were calculated using the transition state concept. The results are shown in Table II together with those of Connolly and Johnson[27]

Table II. Ionization Potentials (eV) of the MF_6 Molecules Calculated by the SCF–$X\alpha$–SW Transition State Procedure[a]

Orbitals	SF_6[b]	SeF_6	TeF_6
t_{1g}	15.88	15.95	16.44
t_{1u}	16.76	16.82	16.90
t_{2u}	16.84	16.73	16.99
e_g	17.52	16.85	16.84
t_{2g}	18.74	18.29	17.98
t_{1u}	21.84	20.89	19.82

[a] The experimental ionization potentials of SF_6 are: 15.69 t_{1u}, 16.96 t_{1g}, 18.40 e_g, 18.71 t_{2u}, 16.98 t_{1u}, 22.5 t_{2g}, and 26.8 a_{1g} (ref 37a); 15.69 t_{1g}, 17.5 t_{1u}, 18.4 t_{2u}, 18.7 t_{2g}, 19.9 e_g, 22.9 t_{1u}, and 27.0 a_{1g} (ref 17). For the experimental ionization potentials of SeF_6 and TeF_6, explicit numbers are not provided in ref 37. [b] Cf. ref 27.

for SF_6. These calculated ionization potentials are in good agreement with the corresponding photoelectron spectra[37a] concerning the structure of the spectrum (i.e., five major peaks for SF_6 and four for SeF_6 and TeF_6). The calculated F 2p "band widths" are 6.0, 4.9, and 3.4 eV for SF_6, SeF_6, and TeF_6, respectively. The corresponding experimental values are approximately 7.0, 6.0, and 4.0 eV. From our calculations the ordering of these levels is as follows.

$$SF_6: \quad t_{1u} < t_{2g} < e_g < t_{2u} \lesssim t_{1u} < t_{1g} \qquad (5)$$

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(47) (a) N. Rosch and K. H. Johnson, *Chem. Phys. Lett.*, 24, 179 (1974); (b) R. P. Messmer, L. V. Interrante, and K. H. Johnson, *J. Amer. Chem. Soc.*, 96, 3847 (1974).
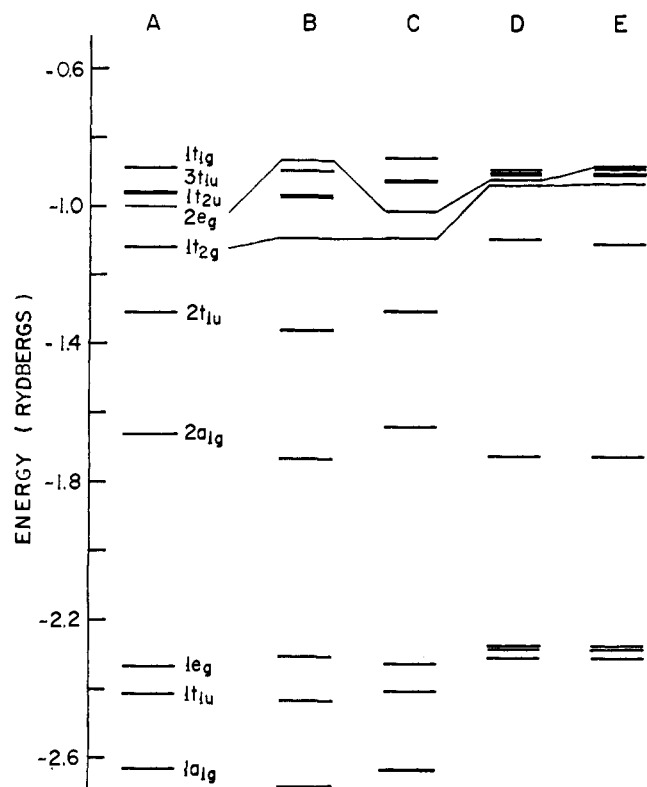
Figure 3. Comparison of different SCF–Xα–SW calculations for SF$_6$: (A) r_{S-F} = 2.9556 au, with d components; (B) r_{S-F} = 2.9556 au, without d components; (C) r_{S-F} = 2.9556 au, R_S = 1.9 au, R_F = 1.2956 au, "overlapping spheres;" (D) r_{S-F} = 4.0 au, with d components; (E) r_{S-F} = 4.0 au, without d components.

$$\text{SeF}_6: \quad t_{1u} < t_{2g} < e_g \lesssim t_{1u} \lesssim t_{2u} < t_{1g} \quad (6)$$

$$\text{TeF}_6: \quad t_{1u} < t_{2g} < t_{2u} \lesssim t_{1u} \lesssim e_g < t_{1g} \quad (7)$$

Except for the positions of the t_{1u} and t_{2u} levels which are close in all cases, the level orderings of the three molecules are the same. As in the ground state of MF$_6$, we notice that the $2e_g$ level is always higher than the $1t_{2g}$ level.

Let us consider the orbital energies and the charge distributions of these two levels in more detail (see Table III). The t_{2g} orbital has more electronic charge

Table III. Orbital Energies and Charge Distributions of the e_g and t_{2g} Levels

Molecule	M	F	INT	EXT	ϵ_i
			(a) e_g		
F$_6$	0.000	0.160	0.023	0.020	0.801
SF$_6$	0.091	0.112	0.166	0.070	1.005
SeF$_6$	0.059	0.120	0.157	0.062	0.972
TeF$_6$	0.057	0.121	0.161	0.052	0.987
SF$_6^a$	0.117	0.121	0.083	0.077	1.017
			(b) t_{2g}		
F$_6$	0.00	0.151	0.151	0.008	0.963
SF$_6$	0.031	0.094	0.365	0.041	1.122
SeF$_6$	0.018	0.102	0.332	0.035	1.083
TeF$_6$	0.017	0.105	0.324	0.031	1.077
SF$_6^a$	0.044	0.103	0.297	0.042	1.094

^{a} Overlapping spheres.

in the interatomic region than the e_g orbital, while the latter contains a larger amount of electronic charge in

the extramolecular region. Thus we may say that the e_g level is more diffuse than the t_{2g} level and therefore higher in energy. The charge of the levels under consideration is mainly distributed over the interatomic and the ligand regions, as can be seen from Table III. Therefore these levels are related to the ligand–ligand interaction rather than the central atom–ligand bonding. However, if we limit ourselves to the consideration of only the central atom–ligand bonding following the traditional concept, we may attribute a stronger bonding character to the e_g level than the t_{2g} level, since the e_g level has more charge on the central atom. In that sense, the notion that an orbital of more bonding character is lower in energy may not necessarily be true. This difficulty arises because we are dealing with delocalized orbitals with which it is not always easy to define chemical bonds in the case of a highly symmetric molecule. In view of this observation, the assignment of the e_g level based upon bonding arguments seems to be worth reconsideration.[17] If we transpose the experimental assignments for the e_g and the t_{2g} levels of the SF$_6$ photoelectron spectra,[28] the level ordering obtained from the Xα–SW method is in perfect agreement with that of the above experiment. We will discuss this subject once again in the next section.

d Orbital Participation

There has been much controversy about whether d orbital participation is necessary for molecules containing second-row atoms.[2,3,6–9,18–20] Early consideration advocated the d orbital contributions to bonding,[48] while many people nowadays seem to consider d orbitals as polarization functions. Since d, f, g, ... functions are all members of a complete set, their inclusion in the basis set will certainly improve the wave function of a system. However, if their contributions to the wave function are small, no chemical significance can be attached to them.

Recently Ratner and Sabin[49] have proposed a symmetry criterion for assessing the importance of such basis functions; it is crucial to include orbitals of higher angular momentum quantum number, if the usual s and p functions do not provide a basis for the irreducible representation to which an occupied molecular orbital belongs. This is the case for the MF$_6$ molecules, since there are occupied orbitals of e_g and t_{2g} symmetries for which s and p functions do not provide a basis. Thus they concluded that d functions are qualitatively necessary for the bonding in SF$_6$. To elucidate this rather involved problem we carried out several calculations of the SF$_6$ molecule with and without d orbitals at two different bond lengths (experimental[36a] and r_{S-F} = 4.0 au). One more calculation was done with overlapping atomic spheres;[50] that is, the sulfur and fluorine atomic spheres were arbitrarily enlarged by 0.12 au to make them overlap. The results are shown in Figure 3.

In agreement with other types of calculations,[20,24–26]

(48) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc., London*, 332 (1954).

(49) M. A. Ratner and J. R. Sabin, *J. Amer. Chem. Soc.*, **93**, 3542 (1971).

(50) N. Rösch, W. G. Klemperer, and K. H. Johnson, *Chem. Phys. Lett.*, **23**, 149 (1973). This paper has shown that non-muffin-tin corrections can be obtained by the use of overlapping atomic spheres when an outer sphere is poorly filled by atomic spheres. In our case we enlarged the atomic spheres arbitrarily in order to explore the tendency of possible changes in the level ordering.

the e_g level increases in energy from the fourth to the outermost position, if the d orbital component is omitted, while the t_{2g} level remains relatively stable. The changes in the other levels are not significant. (However, it should be pointed out that the e_g and t_{2g} levels, which belong to the same representations as the added basis, are lowered but all the other levels raised by including a d component on the central atom.[51]) From their charge distributions the t_{1g}, t_{1u}, and t_{2u} levels have been characterized as nonbonding levels. Therefore, it seems natural that they are not sensitive to whether or not the d orbital component is included on the sulfur atom. The assignment of these levels as the nonbonding orbitals is therefore reasonable. Then the e_g level should be assigned as the one below these orbitals.

The only way of having the e_g level not in the topmost position is to include the d orbital component. Thus we have to conclude that the d orbital participation is important as far as the assignment of the SF_6 photoelectron spectrum is concerned.

Let us consider this problem from another viewpoint. The charge distributions and ΔQ value are not very much affected through an omission of the d orbital component (see Table I). Without the d component electronic charge is slightly more drained from the central atom to the ligands. Considering the unchanged general level structure and charge distribution, one

might be able to explain the formation of the MF_6 molecules even without invoking the d orbital participation.[53]

Another point we can make from Figure 3 is that the e_g level is higher than the t_{2g} level regardless of the S–F bond length and of the overlapping sulfur and fluorine atomic spheres. One of many reasons given by La-Villa[17] in assigning the 19.69-eV peak as e_g is that the overlap of the sulfur d orbital with the fluorine 2p orbitals is greater in the e_g than in the t_{2g} orbital. Our calculation with overlapping spheres may be considered as a test for this question as it should increase the interaction of the sulfur d orbital and the t_{2g} and e_g levels of the F_6 lattice. However, there is hardly a change in the character of these levels and their relative positions is unaltered.

The bonding of other hypervalent sulfur fluorine compounds shall be examined in a forthcoming paper.[54]

(51) This behavior seems to be general. It has been shown[52] that the inclusion of the polarization functions raises most of the molecular orbital energies except for a few which strongly mix with the added functions. We note that a strong mixing should come from those levels which belong to the same representations as the added basis.[49]

(52) (a) J. I. Musher, *J. Amer. Chem. Soc.*, **94**, 1370 (1972); (b) H. Nakatsuji and J. I. Musher, *Chem. Phys. Lett.*, **24**, 77 (1974).

(53) The importance of d orbital participation is usually judged by considering the magnitude of a d orbital population, which depends significantly on the number of s and p basis orbitals used. For a systematic study on this topic, see R. S. Mulliken and B. Liu, *J. Amer. Chem. Soc.*, **93**, 6738 (1971). They also expressed an interesting opinion that d orbital participation in molecules, small or large, may be called a chemical effect when absent in free atoms.

(54) M. H. Whangbo, V. H. Smith, Jr., and N. Rösch, to be submitted for publication.

Ab Initio Calculations on Large Molecules Using Molecular Fragments. Characterization of Unsaturated Sulfur-Containing Molecules

L. E. Nitzsche and Ralph E. Christoffersen*

Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66045. Received March 15, 1974

Abstract: An *ab initio* procedure for the investigation of large molecules is applied to a series of unsaturated sulfur-containing molecules. Prototype molecules used to characterize the procedure include thioformaldehyde, carbon disulfide, and carbonyl sulfide. For each molecule studied, the equilibrium geometry, molecular orbital ordering, various one-electron properties, and population analyses were determined and compared to experimental findings and other theoretical calculations where possible. In general, accuracies for geometric properties were found to be comparable to that observed in molecules containing first-row atoms only. Also, molecular orbital ordering for valence orbitals was found to be in excellent agreement with more extensive basis set calculations. Other one-electron properties were also calculated, and the adequacy of the basis was assessed.

This study is the second of a series done on sulfur-containing molecules using the molecular fragment procedure. The first study[1] was concerned with mole-

(1) R. E. Christoffersen and L. E. Nitzsche, "*Ab Initio* Calculations on Large Molecules Using Molecular Fragments. Development of an Analytical Tool and Extension to Molecules Containing Second Row Atoms," Proceedings of the 1973 International Conference on Com-

cules in which the sulfur could be considered to be either in an "sp³" or "sp²" hybridized state. This study concerns sulfur-containing molecules in which the sulfur can be considered to be in an "sp" hybridized state.

Since the details of the molecular fragment procedure

puters in Chemical Research and Education, Ljubljana, Yugoslavia, 1973, in press.