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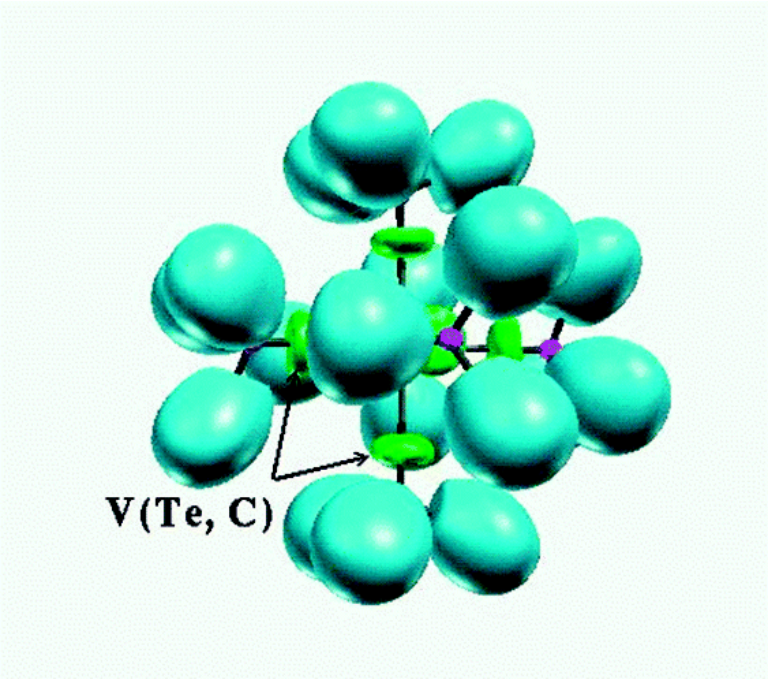

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Chemical Bonding in Hypervalent Molecules: Is the Octet Rule Relevant?

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The bonding in a large number of hypervalent molecules of P, As, S, Se, Te, Cl, and Br with the ligands F, Cl, O, CH_3, and CH_2 has been studied using the topological analysis of the electron localization function *ELF*. This function partitions the electron density of a molecule into core and valence basins and further classifies valence basins according to the number of core basins with which they have a contact. The number and geometry of these basins is generally in accord with the VSEPR model. The population of each basin can be obtained by integration, and so, the total population of the valence shell of an atom can be obtained as the sum of the populations of all the valence basins which share a boundary with its core basin. It was found that the population of the *V*(A, X) disynaptic basin corresponding to the bond, where A is the central atom and X the ligand, varies with the electronegativity of the ligand from approximately 2.0 for a weakly electronegative ligand such as CH_3 to less than 1.0 for a ligand such as F. We find that the total population of the valence shell of a hypervalent atom may vary from close to 10 for a period 15 element and close to 12 for a group 16 element to considerably less than 8 for an electronegative ligand such as F. For example, the phosphorus atom in PF_5 has a population of 5.37 electrons in its valence shell, whereas the arsenic atom in AsMe5 has a population of 9.68 electrons in its valence shell. By definition, hypervalent atoms do not obey the Lewis octet rule. They may or may not obey a modified octet rule that has taken the place of the Lewis octet rule in many recent discussions and according to which an atom in a molecule always has fewer than 8 electrons in its valence shell. We show that the bonds in hypervalent molecules are very similar to those in corresponding nonhypervalent (Lewis octet) molecules. They are all polar bonds ranging from weakly to strongly polar depending on the electronegativity of the ligands. The term hypervalent therefore has little significance except to indicate that an atom in a molecule is forming more than four electron pair bonds.

1. Introduction.

Musher originally defined hypervalent molecules as those formed by the nonmetals of groups 15−18 in any of their stable valence states higher than 3, 2, 1, and 0, respectively.[1] More simply and more comprehensively, a hypervalent molecule may be defined as a molecule in which there are more than four pairs of electrons around the central atom in the conventional Lewis diagram of the molecule. Because the majority of molecules obey the octet rule as formulated by Lewis, it was suggested that the bonding in hypervalent molecules is in some way different from that in "ordinary" molecules that obey the octet rule. The octet rule as proposed by Lewis is an empirical rule based simply on the known formulas of a large number of molecules. There is therefore no fundamental reason there should not be exceptions such as SF_6 and PCl_5, as, indeed, Lewis recognized. Initially, these exceptions were accepted as such, and the bonding was described in terms of sp^3d^n hybrid orbitals,[2,3] as opposed to sp^n orbitals used to describe the bonding in "octet rule"

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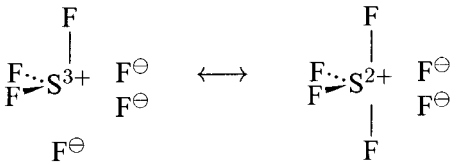
molecules. However, ab initio calculations showed that d orbitals play only a very small role in the bonding in hypervalent molecules.[4−6] Accordingly, other bonding models have been suggested that are in accord with the octet rule, such as the 3-center−4-electron (3c−4e) bond model[7,8] or Pauling's proposal of combinations of resonance structures involving four covalent bonds and additional ionic bonds.[9] These descriptions were formulated to be in accord with the octet rule and also with the polarity of the bonds. They imply that the bonding electrons are not equally shared; that is, they do not contribute equally to the valence shells of both bonded atoms, contrary to the assumption made by Lewis. In formulating the octet rule, he assumed that each bonding pair of electrons contributes fully to the valence shell of both bonded atoms irrespective of the polarity of the bond. The Lewis structure for a diatomic AB molecule is written

and both atoms obey the octet rule irrespective of the polarity of the bond. However, if, for example, we take account of the bond polarity by describing the bond in terms of the two resonance structures

then while the more electronegative atom B has an octet of electrons, A has fewer than 8 electrons in its valence shell, the number depending on the weights assigned to the two structures.[9] The values of the charges on the two atoms may similarly range from 0 to ±1 depending on the weights of the two structures.

So, the introduction of the concept of polarity led to a fundamentally different way of counting electrons, and this led, in turn, to a subtle change in the meaning of the octet rule. The original rule due to Lewis, which took no account of bond polarity, states that the atoms in a Lewis structure of a molecule (except hydrogen) all have 8 electrons in their valence shell. When bond polarity was taken into account, the rule was modified to state that the octet rule is obeyed if the valence shell of an atom contains *no more than* 8 electrons. This rule is obeyed by all atoms in molecules that obey the original Lewis octet rule, but it can only be obeyed by a hypervalent atom if the ligands are sufficiently electronegative.

With the advent of ab initio calculations, it has become possible, at least in principle, to determine the number of electrons in the valence shell of an atom. So, ab initio studies have been carried out with the object of determining if hypervalent molecules obey the modified octet rule and have generated much controversial discussion, as summarized, for example, by Reed and Schleyer.[6] These authors used the natural population analysis (NPA) based on 6-31*G ab initio calculations to obtain natural bond orders in a large number of hypervalent molecules. They found the total bond order to be less than 4.0, with the highest value being 3.96 for H_3PS, while all other molecules which had more electronegative ligands, such as F and O, gave smaller values; in other words, they found fewer than 8 electrons in the valence shell of the hypervalent atom. Cioslowski and Mixon[9] determined bond orders based on the atomic overlap matrix (AOM) and also concluded that the total bond order did not exceed 4.0 for all the hypervalent molecules they studied. For example, in SF_6, the SF bond order was found to be 0.64, so that the total bond order is only 3.84, and there are 7.68 electrons in the valence shell of the sulfur atom. An approximate description of the electron distribution in SF_6 corresponding to the atomic charges and the total bond order is given by an appropriate combination of the following two types of resonance structures in each of which the sulfur atom forms either three or four covalent bonds and either four or three ionic bonds:



In a recent paper, Molina and Dobado[10] studied a large number of hypervalent molecules with fluorine ligands using *ELF*. They found that in every case the valence shell population of the central atom was less then 8.

So, it has become rather generally accepted that the number of electrons in the valence shell of the central atom in a hypervalent molecule is less than 8; in other words, the modified octet rule is obeyed. However, the number of electrons in the valence shell of a hypervalent atom, when they are counted in this way, depends on the electronegativities of the ligands. When the difference between the electronegativities of the ligands is relatively small, this number closely approaches 8 as found, for example, by Reed and Schleyer[6] for H_3PS and Cioslowski and Mixon[9] for ClF_4^+. So, it appears that with even less electronegative ligands this number might exceed 8.

In this paper, we again address the following questions:

(i) How many electrons does the valence shell of the central atom in a hypervalent molecule contain, and is this always less than 8?

(ii) How should the bonding in a hypervalent molecule be described, and is it different from that in a similar nonhypervalent molecule?

We base our discussion on the topological analysis of the electron localization function *ELF* proposed by Becke and Edgecombe.[11,12] This function is particularly suited to answering these questions because it displays separate basins

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corresponding to the core electrons and to the shared and unshared (lone pair) electron density of the valence shell. So, it gives a description of a molecule that corresponds to the Lewis structure and to the electron pair domains of the VSEPR model. Moreover, the electron population of each of the basins can be determined by integration so that we can obtain the total population of the valence shell by finding the sum of the populations of all the basins (both shared and unshared) that have a contact with the core of the atom. Thus, we can get a direct measure of the number of electrons in the valence shell of the central atom in a hypervalent molecule without having to make use of arbitrarily defined bond orders, and so, we can obtain an answer to the first question. Moreover, the populations of the separate basins provide us with important information about the nature of the bonding and, in particular, enable us to compare the bonding in hypervalent molecules with that in nonhypervalent molecules, and so, we can answer the second question.

It is commonly believed that hypervalent molecules are only stable if they have very electronegative ligands such as F, Cl, and O, as has been the case in all the hypervalent molecules studied in previous work. But not all hypervalent molecules have such electronegative ligands as shown, for example, by the known molecules $P(C_6H_5)_5$, $AsMe_5$, and $TeMe_6$.[13] So, we have also included this type of molecule in our study in addition to many of the molecules with more electronegative ligands that have been studied previously.

1.1. *ELF* Function. The *ELF* function was designed by Becke and Edgecombe to provide an orbital independent description of the electron localization.[11] The expression for *ELF* is

$$\eta(\boldsymbol{r}) = \frac{1}{1 + \left(\frac{D_\sigma}{D_\sigma^\circ}\right)^2} \tag{1}$$

in which D_σ and D_σ° represent the curvature of the electron pair density for electrons of identical σ spins (the Fermi hole) for, respectively, the actual system and a homogeneous electron gas with the same density. The analytical form of *ELF* confines its values between 0 and 1. The original derivation of the *ELF* function considers the laplacian of the Hartree−Fock conditional probability of finding a σ-spin electron at position $\boldsymbol{r}_2$ when a first electron is located at $\boldsymbol{r}_1$.

$$D_\sigma = (\nabla_2^2 P_{\mathrm{cond}}^{\sigma\sigma}(1, 2))_{1=2} = \sum_{i=1}^{N} |\nabla\varphi_i|^2 - \frac{1}{4}\frac{|\nabla\rho^\sigma(1)|^2}{\rho^\sigma(1)} \tag{2}$$

As discussed earlier,[14] this expression is formally identical to the difference between the positive definite local kinetic energy of a system of noninteracting fermions $T_s^\sigma[\rho]$ appearing in the Kohn−Sham equation[15] and that appearing in the von Weizsäcker functional.[16]

$$D_\sigma = T_s^\sigma[\rho] - \frac{1}{4}\frac{|\nabla\rho^\sigma(1)|^2}{\rho^\sigma(1)} \tag{3}$$

As pointed out by Tal and Bader,[17] the von Weizsäcker functional[16] is a lower bound to the positive definite local kinetic energy which is locally approached at the Hartree−Fock level when a single orbital makes the dominant contribution to the density in the same region of space. The von Weizsäcker functional is also the positive definite local kinetic energy of a system of noninteracting particles of density ρ^σ for which the Pauli repulsion has been switched off. Therefore, D_σ has the significance of the local excess of kinetic energy due to the Pauli repulsion. In the regions of space dominated by an antiparallel spin pair character, the Pauli repulsion is weak, and therefore, *ELF* is close to 1. Near the boundary between two such regions, where same spin electrons necessarily come close together, they exert a significant Pauli repulsion which decreases the value of the *ELF* function to low values. The kinetic interpretation of *ELF* enables its definition to be generalized to exact wave functions, and it emphasizes the role of the kinetic energy density in the bonding process.[18]

1.2. Basins of the *ELF* Gradient Field. The topological analysis of the *ELF* gradient field relies on the formal analogy of this field with a velocity field; i.e., $\nabla\,\eta(\mathbf{r}) = d\mathbf{r}/dt$. For each point of the molecular space, the time integration determines a unique trajectory which starts and ends in the neighborhood of points for which $\nabla\,\eta(\mathbf{r}) = 0$, the α- and ω-limits, respectively. Such points are called critical points. They are characterized by their indices $I(m)$ (the number of positive eigenvalues of the second derivative matrix). A point of index 0 is a local maximum or *attractor*, and the set of trajectories ending to this point defines the basin of the attractor. The basins are separated by surfaces (separatrix) which do not belong to any basins.

There are two types of basins. The core basins centered on nuclei (with $Z > 2$) and on the valence basins in the remaining space. The structure provided by the core basins closely matches the inner atomic shell structure. A valence basin is characterized by its synaptic order which is the number of cores to which it is connected[19] provided these core basins are surrounded by the same localization domain. A localization domain is a volume limited by one or more closed isosurfaces $\eta(\mathbf{r}) = f$. If a localization domain surrounds more than one attractor, it is reducible; otherwise, it is irreducible. Upon the increase of the value of $\eta(\mathbf{r})$ defining the bounding isosurface, a reducible domain splits into several domains, each containing fewer attractors than the parent domain. The reduction of localization occurs at turning points which are critical points of index 1 located on the separatrix of two basins involved in the parent domain. Ordering these turning points (localization nodes) by increas-

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ing $\eta(\mathbf{r})$ enables tree diagrams reflecting the hierarchy of the basins to be built. A monosynaptic basin, V(X), corresponds to a lone pair or a group of lone pairs of the atom labeled by X, a disynaptic basin V(X, Y) to a two center bond between X and Y, a trisynaptic basin V(X, Y, Z) to a three-center bond, and so on. This technique of analysis of the bonding has been extensively used.[12,19−30]

1.3. Basin Populations and Related Properties. Quantitatively, basin properties are calculated by integrating the relevant density of property, say $\rho_A(\mathbf{r})$, over the basin volume denoted by Ω_i, i.e.,

$$\langle \hat{A} \rangle_{\Omega_i} = \int_{\Omega_i} \rho_A(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{4}$$

where $\hat{A}$ stands for the 1 electron operator associated with the property. In the case of bielectronic properties, the integration is either performed twice on the same basin volume or over two different basins:

$$\langle G \rangle_{\Omega_i,\Omega_j} = \int_{\Omega_i} \mathrm{d}\mathbf{r} \int_{\Omega_j} \rho_G(\mathbf{r},\mathbf{r}') \mathrm{d}\mathbf{r}' \tag{5}$$

The simplest integrated property is the basin population $\bar{N}(\Omega_i)$, which can be written as the sum of its spin contributions in the case of open shell systems:

$$\bar{N}(\Omega_i) = \int_{\Omega_i} \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = \bar{N}^{\alpha}(\Omega_i) + \bar{N}^{\beta}(\Omega_i) \tag{6}$$

Combining the AIM and *ELF* analysis,[31−33] it is possible to define atomic sub basins as the intersection of a localization basin with an atomic basin. The contribution of atom A to the Ω_i basin population[32] is the integral of the electron density over the sub basin $\Omega_i \cap \Omega_A$:

$$\bar{N}(\Omega_i)|\mathrm{A} = \int_{\Omega_i \cap \Omega_A} \rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \tag{7}$$

The notation $\bar{N}(\Omega_i)|$A has been proposed by Jansen.[32]

The analysis of the *ELF* function fulfills an essential requirement as it distinguishes core and valence basins and unshared and shared basins of the valence shell.

An atomic valence shell V_A is just the union of the valence basins which have a boundary with the core basin of atom A:

$$V_A = V_1(\mathrm{A}) \cup V_2(\mathrm{A}) \cup \ldots V(\mathrm{A, B}) \cup V(\mathrm{A, C}) \cup \ldots \tag{8}$$

Atomic shells defined in this way mutually interpenetrate through the polysynaptic basins V(A, B, ...). Sometimes what is expected to be a monosynaptic (unshared) basin V(B) of a ligand is merged with the expected disynaptic (shared) basin V(A,B) to give a resultant formally disynaptic basin V(A,B). In such situations, the valence shell of atom A encompasses the core of ligand C(B). To compare this latter type of bonding with standard cases, it is convenient to define an effective valence shell population as the difference of the valence shell population of atom A and the number of electrons in the valence shell of the free ligand atom, in other words, the core net charge of B.

$$N_{\mathrm{eff}}(\mathrm{A}) = N_{\mathrm{v}}(\mathrm{A}) - \sum_{B \neq A} Z_{\mathrm{A}} - \bar{N}(\mathrm{C(B)}) \tag{9}$$

The definition of this quantity is purely intuitive because eq 9 relies on an arbitrary choice. Therefore, N_{eff} should be understood as only indicative.

1.4. Computational Method. The ab initio calculations have been performed at the hybrid Hartree−Fock density functional level B3LYP[34−37] with Gaussian94 software.[38] The geometries have been optimized with the 6-311+G(2df)[39−42] basis set. Though extensive calculations have been carried out at the HF, MP/2 levels or with different DFT schemes and implying an eclectic choice of basis functions,[43] only the B3LYP/6-311+G(2df) results are reported here, as they never significantly differ from the "best" calculation of each system. The analysis of the *ELF* function has been carried out with the ToPMoD program developed in our group at the Laboratoire de Chimie Théorique de l'Université Pierre et Marie Curie,[44,45] and the visualization of the *ELF* isosurfaces has been done with the SciAn software.[46]

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Table 1. Properties of the AX Bonds in Reference Molecules: Disynaptic Basin Population V(A, X), Ligand Monosynaptic Basin Population V(X), Monosynaptic Basin Population V(A), Valence Shell Population N_v(A), Effective Valence Population N_{eff}(A)

	V(A, X)	V(X)	V(A)	N_v(A)	N_{eff}(A)
NF_3	0.84	6.83	2.56	5.08	
NCl_3	1.23	6.50	2.56	6.26	
HNO	1.99	5.16	2.55	6.62	
PF_3	0.84	6.97	2.12	4.64	
PCl_3	1.28	6.59	2.13	5.96	
PMe_3	1.90		2.16	7.86	
HPO	2.02	5.46	2.28	6.35	
PH_2Me (H)	1.97		2.11	7.88	
(Me)	1.83				
AsF_3	7.81		2.35	25.77	5.16
$AsCl_3$	0.99	6.90	2.35	5.32	
$AsMe_3$	1.85		2.48	8.03	
AsH_2Me (H)	2.01		2.35	8.13	
(Me)	1.76				
HAsO	7.47		2.54	12.1	6.21
SF_2	0.60	7.03	2.24	5.68	
SCl_2	0.97	6.62	2.32	6.58	
SeF_2	0.15	7.51	2.34	4.97	
$SeCl_2$	0.90	6.75	2.39	6.58	
ClF	0.49	6.20	6.39	6.88	
BrF	0.15	6.54	6.63	6.78	
BrCl	0.84	6.64	6.68	7.52	

2. Results and Discussion

To provide a basis for comparison with the hypervalent molecules, a group of similar nonhypervalent molecules were studied first. Nonhypervalent molecules are those that obey the Lewis octet rule; so, we will for convenience call them Lewis octet molecules. Not all the molecules of the two groups have been observed experimentally; nevertheless, their structures correspond to minima of the Born−Oppenheimer energy surface.

The core basin populations of the second and third period elements are very slightly larger than the number of core electrons (∼0.1 electrons), and they increase from N to F and from P to Cl. The core populations of the fourth period elements are slightly less than 28: 27.75, 27.76, and 27.82 for As, Se, and Br, respectively. This can be interpreted as a consequence of the radial extension of the 3d subshell into the valence shell. This trend has been previouly evidenced for free atoms by Kohout and Savin.[47,48]

2.1. Group 15 Molecules. 2.1.1. Lewis Octet Molecules. The results of the *ELF* analysis of the electron density for the molecules studied are given in Table 1. Figure 1 shows the localization basins for the PF_3, PCl_3, and PMe_3 molecules. For each atom in the molecule, there is a core basin C(A) containing close to 2 electrons for the period 2 atoms and 10 electrons for the period 3 atoms. Around the phosphorus atom in each of the PX_3 molecules, there are three disynaptic basins V(P, X) corresponding to the three bonds and a monosynaptic basin corresponding to the phosphorus lone pair. The population of the V(P, X) basins decreases with increasing electronegativity of the ligand from 1.90 in PMe_3, which is close to the ideal Lewis value of 2.00, to 1.83 in

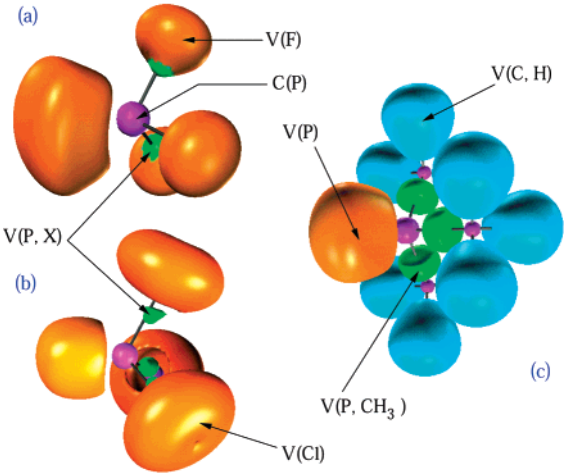


Figure 1. Localization domains of PF_3 (a), PCl_3 (b), and PMe_3 (c). Core domains are represented in magenta, valence monosynaptics in brick red, valence disynaptics in green.

PH_2Me, to 1.28 in PCl_3, and to 0.84 in PF_3. This decreasing bond population reflects the increasing polarity of the PX bond as more density is transferred to the ligand with increasing ligand electronegativity. For the monatomic ligands, we see that the monosynaptic population increases correspondingly from 6.54(Cl) to 6.96 (F). We see only one monosynaptic basin with the form of a torus containing between 6 and 7 electrons for the Cl and F ligands and not three separate lone pair basins as expected from extrapolating the Lewis structure. In fact, as the *ELF* function is totally symmetrical, the shape of the localization basins is mostly driven by the symmetry of the local electron−nucleus electrostatic potential which is determined by the number of nearest neighbors. In the case of a terminal bond, this potential has a cylindrical symmetry, and therefore, off axis attractors are degenerated on a circle yielding a toroidal basin. The population of the monosynaptic basin V(P) remains almost the same in all the molecules (∼2.13), a value only slightly greater than the Lewis expectation of 2.0. The phosphorus valence shell population is the sum of the populations of all the basins that share a common boundary with the phosphorus core, namely, the three disynaptic basins and the monosynaptic basin. This population decreases from 7.86 electrons for PMe_3 to 5.96 electrons for PCl_3 to 5.08 electrons for PF_3 as the ligand electronegativity increases. It is close to 8 for PMe_3 in which the bonds are expected to be nearly purely covalent given the similar electronegativities of C(2.5) and P(2.1) and as shown by the population of the V(P, C) basin of 1.90 electrons. All these molecules obey the modified octet rule, which is to be expected because they also obey the Lewis octet rule.

We see similar trends in the molecules $AsCl_3$ and $AsMe_3$. Although there is a disynaptic basin and a monosynaptic basin around each chlorine atom in $AsCl_3$ and around each fluorine atom in PF_3, this is not the case for AsF_3 where there are only disynaptic basins around each fluorine. The expected monosynaptic (unshared) basins have merged with the disynaptic (shared) basin to produce a disynaptic basin that is primarily located on the fluorine atom. Thus, in this case, the unshared electron density cannot be distinguished

(46) Pepke, E.; Murray, J.; Lyons, J.; Hwu, T.-Z. *Scian*; Supercomputer Computations Research Institute, Florida State University: Tallahassee, FL, 1993.
(47) Kohout, M.; Savin, A. *Int. J. Quantum Chem.* **1996**, *60*, 875−882.
(48) Kohout, M.; Savin, A. *J. Comput. Chem.* **1997**, *18*, 1431−1439.

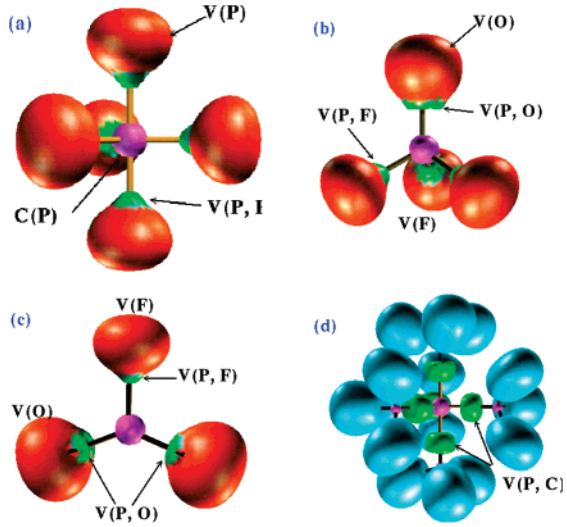


Figure 2. Localization domains of PF_5 (a), PF_3O (b), PFO_2 (c), and PMe_5 (d). Core domains are represented in magenta, valence monosynaptics in brick red, valence disynaptics in green.

from the shared density. This type of topology in *ELF* is observed for large central atoms with very electronegative ligands. It clearly corresponds to a very ionic bond. The sum of the populations of the three disynaptic basins gives the total number of valence shell electrons in the molecule, which is ideally 26 but is found to be 25.77 electrons. In this case, we cannot determine the arsenic valence shell population, but we can obtain an approximate value, which we call N_v^{eff}, by subtracting the number of electrons in the valence shell of each of the free neutral ligand atoms, namely $9 - C(X) = 9 - 2.13 = 6.87$ for X = F.

The unshared "lone pair" basins on arsenic in AsF_3, $AsCl_3$, and AsH_2CH_3 each have a population of 2.35 electrons, and, in $AsMe_3$, a population of 2.48 electrons. These values are larger than those for the corresponding period 3 molecules (2.13 electrons) and significantly larger than the ideal Lewis value of 2.00. Bond lengths increase with increasing size of the central atom, and the extent of sharing of the electron density decreases so that the population of the shared basin decreases and those of the unshared basins of both the ligands and the central atom increase accordingly. In the limit of a very long covalent bond, the population of the shared basin would approach zero, and the population of each monosynaptic basin would increase by 1 electron.

The valence shell population of the central atom $N_v(A)$ increases with decreasing electronegativity of the ligand from 5.32 in $AsCl_3$ to 8.03 in $AsMe_3$ and 8.13 in AsH_2Me, suggesting that the bonds in these two latter molecules are essentially purely covalent, consistent with the approximately equal electronegativities of C(2.5), As(2.2), and H(2.1).

2.1.2. Hypervalent Molecules. All the group 15 hypervalent molecules are formally pentavalent and have five pairs of electrons in the valence shell of the central atom in the Lewis structure. Figure 2 shows the localization basins of four representative molecules: PF_5, PF_3O, PFO_2, and PMe_5. We see a disynaptic basin for each of the bonds in all four molecules and a monosynaptic basin on each F or O ligand.

Table 2 gives the information obtained from the *ELF* analysis for the AX_5, AX_3O, AXO_2, and $AX_3{=}CH_2$ molecules studied.

Table 2. Properties of the AX Bonds in Group 15 Hypervalent Molecules: Disynaptic Basin Population $V(A, X)$, Ligand Monosynaptic Basin Population $V(X)$, Valence Shell Population $N_v(A)$, Effective Valence Population $N_{eff}(A)$

		$V(A, X)$	$V(X)$	$N_v(A)$	$N_{eff}(A)$
NF_5	F_{ap}[a]	0.79	7.20	4.61	
	F_{eq}	1.01	6.75		
PF_5	F_{ap}	1.03	6.82	5.33	
	F_{eq}	1.09	6.78		
PCl_5	Cl_{ap}	1.33	6.56	7.13	
	Cl_{eq}	1.49	6.43		
PMe_5	Me_{ap}	1.86		9.42	
	Me_{eq}	1.90			
PF_3O	F	1.06	6.80	5.13	
	O	1.95	5.88		
PCl_3O	Cl	1.51	6.43	6.33	
	O	1.80	5.93		
PFO_2	F	1.03	6.83	4.51	
	O	1.74	6.13		
$PClO_2$	Cl	1.62	6.36	5.22	
	O	1.80	6.04		
PH_3CH_2	H	2.01		8.52	
	C	2.49	1.20		
PF_3CH_2	F	1.02	6.82	7.07	
	C	4.01			
PMe_3CH_2	Me	1.94		8.41	
	CH_2	2.59	1.21		
AsF_5	F_{ap}	7.88		39.45	5.03
	F_{eq}	7.90			
$AsCl_5$	Cl_{ap}	1.16	6.76	6.10	
	Cl_{eq}	1.26	6.72		
$AsMe_5$	Me_{ap}	1.90		9.68	
	Me_{eq}	1.96			
AsF_3O	F	7.88		31.61	5.07
	O	7.98			
$AsCl_3O$	Cl	1.27	6.71	11.71	5.82
	O	7.89			
$AsFO_2$	F	7.84		23.76	5.12
	O	7.96			
$AsClO_2$	Cl	0.83	7.10	16.73	4.95
	O	7.95			

[a] The abbreviations ap and eq refer to apical and equatorial positions of the substituent.

The population of the disynaptic $V(P, X)$ basins increases with decreasing electronegativity of the ligand from 1.01 (ax) and 1.03 (eq) in PF_5 through 1.33 (ax) and 1.49 (eq) for PCl_5 to 1.86 (ax) to 1.89 (eq) for PMe_5. These increasing values reflect the decreasing polarity of the bond, and they approach the ideal Lewis value of 2.00 for a pure covalent bond as observed previously for the same bonds in the Lewis octet molecules. The similar values for the population of the disynaptic basin $V(A, X)$ for the same bond in the Lewis octet molecules and the hypervalent molecules shows that the bonds in both types of molecules are very similar, ranging from very polar bonds in the fluorides to nearly pure covalent bonds in PMe_5 and $AsMe_5$. There is nothing unusual about the bonds in hypervalent molecules.

The population of the valence shell of the phosphorus atom $N_v(A)$ varies from 4.51 in PFO_2 to 9.44 in PMe_5, that is, from values less than 8 to values greater than 8, depending on the electronegativity of the ligand. The effect of electronegativity of the ligand is seen clearly in the series PF_5, PCl_5, and PMe_5, for which the phosphorus valence shell is 5.37, 7.15, and 9.44 electrons, respectively. The molecules PMe_5, PH_3CH_2, and PMe_3CH_2, of which the last is a known

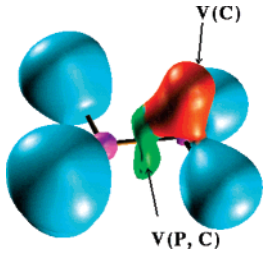
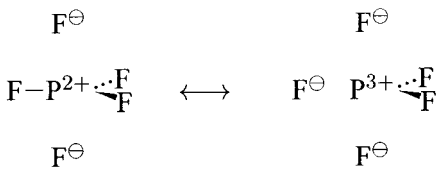


Figure 3. Localization domains of H_3PCH_2. Core domains are represented in magenta, valence monosynaptics in brick red, valence disynaptics in green.

molecule, all have a phosphorus valence shell population which exceeds 8 as a consequence of the weak electronegativity of the H, Me, and $=CH_2$ ligands. These molecules are therefore exceptions to the modified octet rule.

The bonding in the PMe_5 molecule is rather well represented by the structure where the bonds represent equally shared electron pairs, that is, essentially pure covalent bonds with 10 electrons or 5 pairs in the valence shell of the phosphorus atom. The more ionic molecule PF_5 may be represented by an approximately equal mixture of the following two types of resonance structures with either two or three covalent bonds:



This description implies an average of 2.5 covalent bonds consistent with a population of 1 electron or half a pair for each bond, as observed.

The population of the V(P, C) basin in F_3PCH_2 of 4.01 electrons is larger than that for a corresponding P—C bond (e.g., 1.90 in PMe_3) and is equal to the ideal Lewis value for a double bond consistent with the customary formulation of the model with a P═C double bond. The population of the V(P, C) basin in PH_3CH_2 is, however, only 2.46 electrons. The geometry around the C atom in PH_3CH_2 is nonplanar (the angle of the PC direction with the CH_2 plane is 145°), and there is a monosynaptic basin on the carbon atom which has a population of 1.2 electrons (Figure 3). The population of the V(P, C) basin and the presence of the monosynaptic basin on phosphorus is consistent with a description of the molecule by means of the two resonance structures.

$$H_3P{=}CH_2 \quad H_3P^{+}{-}CH_2^{-}$$

In contrast, the molecule $F_3P{=}CH_2$ is planar with a P—C basin population of 4.0 electrons, and there is no monosynaptic basin on carbon. It appears that the electronegative fluorine atoms hold two pairs of electrons in the P—C bonding region and thus prevent them from delocalizing into the nonbonding region of the carbon atom.

The P—O disynaptic basins have populations ranging from 1.74 in PFO_2 to 1.95 in PF_3O which are much smaller than the Lewis population of 4.00, reflecting the considerable polarity of these bonds. However, because the disynaptic basin populations are roughly twice the value of the corresponding V(P, F) basin assigned to a single bond in these molecules, the P—O bond can reasonably be considered to be polar double bonds. They can be described by appropriate weight of two resonance structures, a covalent structure and an ionic structure:

$$P{=}O \quad P^{2+}O^{2-}$$

The common representation $P^{+}{-}O^{-}$ corresponds to an equal mixing of the two former structures which does not allow for the fact that the charges may be less than or greater than ±1.

The population of the valence shell of phosphorus in these molecules ranges from 4.51 electrons in PO_2F to 9.42 electrons in PMe_5, and the three molecules PMe_5, PH_3CH_2, and PMe_3CH_2 all have more than 8 electrons in the valence shell of phosphorus. These molecules therefore do not obey the modified octet rule.

Of the molecules of arsenic in Table 2, there are only two that have V(As, X) disynaptic basins that are separate from the ligand monosynaptic basins. These are $AsCl_5$, which has an arsenic valence shell electron population of 6.10, and $AsMe_5$, which has an arsenic valence shell electron population of 9.68, which exceeds the value of 8. In the other molecules, the disynaptic basin is merged with the monosynaptic basin so that the number of electrons in the arsenic valence shell cannot be determined. The calculated N_v^{eff} values range from 4.95 to 5.82 which are consistent with the large electronegativities of the ligands.

2.2. Group 16 Molecules. 2.2.1. Lewis Octet Molecules. In the AX_2 molecules, there are two monosynaptic basins and two disynaptic basins as expected from the Lewis structure. The monosynaptic V(A) basins have rather similar populations ranging from 2.24 in SF_2 to 2.39 in $SeCl_2$, which are larger than the Lewis population of 2.0 electrons (Table 1). The shared V(A, X) populations are small, ranging from 0.15 in SeF_2 to 0.97 in SCl_2, consistent with the expected polarities of these bonds, while the populations of the ligand monosynaptic basin is correspondingly large, up to 7.51 electrons in the very polar SeF_2 molecule.

2.2.2. Hypervalent Molecules. The data from the *ELF* analysis of these molecules are given in Table 3. The localization domains of SF_6, $TeMe_6$, SCl_4, and SO_2F_2 are shown in Figure 4. In each case, the number and geometry of the disynaptic and monosynaptic basins in the valence shell of the central atom is the same as the number and geometry of the domains of VSEPR model, except for very polar bonds where the disynaptic basin is merged with the monosynaptic basin, as, for example, in SeF_4. In the AX_6 molecules, the populations of the V(A, X) disynaptic basins increase from 0.36 in SeF_6 to 1.15 in $SeCl_6$ to 1.83 in $SeMe_6$ and from 1.03 in SF_6 to 1.21 in SCl_6, with decreasing electronegativity of the ligand. The disynaptic basins in the sulfur molecules have larger populations than those in the corresponding selenium molecules, consistent with the

Table 3. Properties of the AX Bonds in Group 16 Hypervalent Molecules: Disynaptic Basin Population V(A, X), Ligand Monosynaptic Basin Population V(X), Monosynaptic Basin Population V(A), Valence Shell Population N_v(A), Effective Valence Population N_{Eff}(A)

		V(A, X)	V(X)	V(A)	N_v(A)	N_{eff}(A)
SF_6		1.03	6.80		6.18	
SeF_6		0.36	7.54		2.18	
SCl_6		1.21	6.68		7.26	
$SeCl_6$		1.15	6.80		6.9	
$SeMe_6$		1.83			10.98	
$TeMe_6$		1.85			11.10	
SF_4	F_{eq}	0.87	6.92	2.30	19.56	5.80
	F_{ap}	7.76				
SeF_4	F_{eq}	7.77		2.47	33.58	6.06
	F_{ap}	7.82				
SCl_4	Cl_{eq}	1.36	6.54	3.22	20.42	6.56
	Cl_{ap}		7.24			
$SeCl_4$	Cl_{eq}	1.20	6.72	2.49	20.38	6.50
	Cl_{ap}	7.79				
SF_2O	F	7.76		2.39	19.80	6.02
SeF_2O	F	7.73		2.62	25.75	6.13
SCl_2O	Cl	1.01	6.86	2.40	6.09	
$SeCl_2O$	Cl	0.85	7.00	2.64	11.93	6.04
SF_2O_2	F	0.88	6.94		5.64	
SeF_2O_2	F	7.86			31.70	6.14
SCl_2O_2	Cl	1.48	6.67		6.60	
$SeCl_2O_2$	Cl	1.24	6.81		18.18	6.38
SF_2O	O	1.89	5.77	2.39	19.80	6.02
SeF_2O	O	7.67		2.62	25.75	6.13
SCl_2O	O	1.67	5.85	2.40	6.09	
$SeCl_2O$	O	7.59		2.64	11.93	6.04
SO_2		1.82	5.58	2.90	6.54	
SeO_2		7.34		3.25	17.93	6.15
SF_2O_2	O	1.94	5.95		5.64	
SeF_2O_2	O	7.97			31.70	6.14
SCl_2O_2	O	1.82	6.0		6.60	
$SeCl_2O_2$	O	7.85			18.18	6.38

[a] The abbreviations ap and eq refer to apical and equatorial AX bonds.

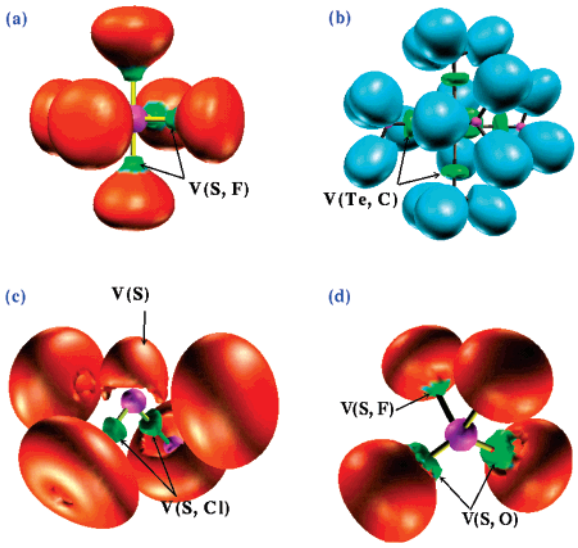


Figure 4. Localization domains of SF_6 (a), $TeMe_6$ (b), SCl_4 (c), and SF_2O_2 (d). Core domains are represented in magenta, valence monosynaptics in brick red, valence disynaptics in green.

greater electronegativity of sulfur than selenium. In the molecules for which the group 16 element valence shell population N_v(A) can be obtained, the values range from 2.18 for SeF_6 through 7.26 for SCl_6 to 11.0 for $SeMe_6$ and 11.1 for $TeMe_6$, consistent with the electronegativities of the central atom and the ligand. The values for $TeMe_6$ and $SeMe_6$ approach the ideal Lewis value of 12, suggesting that the Te−C and Se−C bonds in these molecules are close to pure covalent single bonds, consistent with the similar electronegativities of carbon and the central atom (C, 2.5; Se, 2.5; Te, 2.0).

Table 4. Properties of the AX Bonds in Group 17 Hypervalent Molecules: Disynaptic Basin Population V(A, X), Ligand Monosynaptic Basin Population V(X), Monosynaptic Basin Population V(A), Valence Shell Population N_v(A), Effective Valence Population N_{Eff}(A)

		V(A, X)	V(X)	V(A)	N_v(A)	N_{eff}(A)
ClF_3	F_{eq}	0.52	7.30	5.12	5.98	
	F_{ap}	0.17	6.98			
BrF_3	F_{eq}	0.38	7.18	5.12	20.62	6.86
	F_{ap}	7.56				
ClF_5	F_{ap}	0.91	6.93	2.54	5.38	
	F_{eq}	0.49	7.24			
BrF_5	F_{ap}	0.79	7.08	2.55	34.50	6.90
	F_{eq}	7.79				

[a] The abbreviations ap and eq refer to apical and equatorial AX bonds.

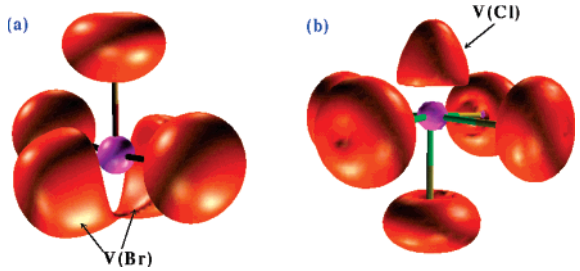


Figure 5. Localization domains of BrF_3 and ClF_5. Core domains are represented in magenta, valence monosynaptics in brick red, valence disynaptics in green.

The expected lone pair basin is observed in the AX_4E and AX_2OE molecules and has a population in the range 2.30−2.39 for the sulfur molecules and from 2.47 to 2.69 for the Se molecules, except for the unexpectedly high value of 3.22 electrons for the S atom in SCl_4.

In the AX_4E molecules, the monosynaptic basin on the ligand is merged with the disynaptic V(A, X) basin so the true valence shell population of A cannot be determined. The N_v^{eff} values range from 5.80 to 6.56, consistent with the large electronegativities of the F and Cl ligands.

2.3. Group 17 Hypervalent Molecules. The only known hypervalent molecules of the group 17 elements are interhalogen molecules with a more electronegative halogen as the ligand. We have studied the ClF_3, BrF_3, ClF_5, and BrF_5 molecules. The data from the *ELF* analysis of these molecules are given in Table 4. The localization domains for the BrF_3 and ClF_5 molecules are shown in Figure 5. For BrF_3, we see two monosynaptic basins in the equatorial positions, and in ClF_5, we see one monosynaptic basin, in agreement with the VSEPR model. In BrF_3, separate shared domains are not observed, as they are merged with the fluorine unshared domains. In ClF_5, a shared basin is observed in both the apical and equatorial positions. Each of these unshared basins has a population of approximately 2.5 electrons. As in all the other molecules studied, the population of each "lone pair" basin is significantly greater than 2. The BrF and ClF disynaptic basins have a population of less than 1 electron, with the axial bond in ClF_3 having a

lower population than the equatorial bond in agreement with the VSEPR model which predicts that the axial bonds are longer and weaker than the equatorial bonds, as has been observed experimentally.[49] In ClF_5, the $V(Cl, F_{ax})$ basin has a larger population than the equatorial $V(Cl, F_{eq})$ basins, again in agreement with the VSEPR model which predicts that the equatorial bonds will be longer and weaker than the axial bonds, as has been observed experimentally.[49] In the two cases where the valence shell population can be obtained, it is considerably less than 8; the value for ClF_3 is 6.98, that of ClF_5 is 6.90, and no examples of molecules with $N_v(A)$ greater than 8 are expected.

3. Summary and Conclusions

The octet rule as defined by Lewis in 1916 states that the valence shell of each atom in a molecule contains 8 electrons when each shared pair is counted as contributing fully to the valence shell of both bonded atoms; in other words, each bond is treated as a fully covalent bond. Lewis knew that there were exceptions to his rule, and since that time, many more exceptions have been found. These exceptions have been described as hypervalent when an atom has more than 8 electrons in its valence shell, commonly 10 or 12 as in PCl_5 and SF_6, and as hypovalent when there are less than 8 electrons, commonly 6 as in BCl_3 in its valence shell. Over the years, many attempts have been made to formulate the electronic structures of hypovalent and hypervalent molecules so that they obey the octet rule. For example, in the case of hypervalent molecules, the polarity of the bonds has been allowed for by using descriptions based on resonance structures involving no more than four covalent and the proper number of ionic bonds, so that the octet rule is obeyed.

With the advent of ab initio calculations, it became possible, at least in principle, to determine the electron population of the valence shell of an atom. For formally single bonds, the bond order as determined from the population of the molecular orbitals was found to be equal to, or less than 1, depending on the electronegativity of the ligands. For hypervalent molecules in which the ligands were all strongly electronegative, the total bond order was found to be almost equal to, or less than, 4, depending on the electronegativity of the ligands. Hypervalent molecules have, therefore, been said to obey the octet rule, although in fact they obey a modified octet rule according to which an atom may have *no more* than 8 electrons in its valence shell. Whereas Lewis assumed 2 electrons per single bond in formulating its octet rule, the modified octet rule was introduced as a consequence of allowing for bond polarity which decreases the number of bonding electrons to less than 2 per bond.

In our topological analysis of the electron localization function *ELF* for a number of hypervalent molecules with ligands of varying electronegativity, we found that the total valence shell population of the central atom in a hypervalent molecule, that is, the sum of the populations of the disynaptic or shared and monosynaptic or unshared basins, may be less than or more than 8. With relatively weakly electronegative ligands, this number may approach 10 in a group 15 molecule and 12 in a group 16 molecule. Clearly, these molecules do not obey the Lewis octet rule in either its original or modified form.

We found the population of the disynaptic basin corresponding to a given A−X bond to be very similar in both hypervalent and nonhypervalent (Lewis octet rule) molecules. Thus, the bonds in hypervalent molecules are not significantly different from the bonds in the corresponding nonhypervalent molecules, and for both classes of molecule, they range from essentially nonpolar to very polar bonds. There is, therefore, no real reason to consider hypervalent molecules as a special case that is different from nonhypervalent (Lewis octet) molecules. It is worth noting that recent spin-coupled calculations of hypercoordinated chlorine species lead to the same conclusion.[50] They are simply molecules in which one atom, generally the central atom, forms more than four bonds in the Lewis sense. Such molecules are relatively common for the elements of groups 14−18 of period 3 and beyond. This is because the atoms of these elements are larger than those of period 2 elements and can accommodate more than four pairs of shared electrons in their larger valence shells and because there is sufficient space to pack more than four ligand atoms around the central atom.[51,49] The octet rule remains a useful rule for beginning students as an aid for writing Lewis structures provided it is recognized that there are many exceptions. However, there is no need to replace the octet rule by the modified rule, according to which an atom may contain no more than 8 electrons in its valence shell, because there are also exceptions to this rule and it is not a useful aid for writing Lewis structures. In conclusion, it is worth noting that, although great prominence has been given to the octet rule over many years, Lewis himself recognized the limitations of the octet rule, which he originally called the rule of 8, when he stated that in his opinion the rule of 2, (electrons in stable molecules are nearly always found in pairs) is more important, although he was unable to give an explanation for this observation.

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