Apparent Octet Rule Violations, Fractionality, and the Interpretation of Localized Molecular Orbital Structures. Polarization and Hybridization Functions in Chemical Bonding

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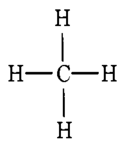
Abstract. Localized molecular orbital (LMO) structures for systems not well represented by single Lewis formulas (e.g., CO_2, CO_3^{2-}, N_2O, O_3, XeF_2, PH_3F_2, SO_2) typically display five or more LMO's to a single center (e.g., "six bonds to carbon" in CO_2). The meaning of such *apparent* violations of the octet rule is examined. For minimum-basis-set wave functions, two or more of the LMO's involved in an apparent violation of the octet rule necessarily employ the same hybrid atomic orbital (AO) on the center in question, resulting in an *overutilization* of the AO function space. Such LMO's are termed *fractional*. As a result of the Pauli exclusion principle, self-cancellations occur when the LCAO expansions for fractional LMO's are inserted into the determinantal wave function and multiplied out. These self-cancellations resolve the apparent rule violations by producing an expansion of the wave function in terms of "simple" molecular-orbital (MO) or valence-bond (VB) structures in which four or fewer pairs of valence electrons are found to the center in question, in transparent compliance with the octet rule. Alternatively, compliance can be shown for a minimum-basis-set MO wave function by transforming the MO's in such a way that the valence AO's on the center in question participate in at most four of the transformed MO's. To be identifiable with normal chemical bonds, the LMO's must employ different orthogonal AO hybrids, as approximately occurs in methane. The analysis presented is compared with views expressed by a number of previous authors, including Wheland, Samuel, Paoloni, Bent, Musher, Coulson, Gillespie, and Harcourt. For systems containing higher row atoms, a distinction is drawn between d orbitals which participate in bonding as (a) *polarization* and (b) *hybridization* functions according to whether these orbitals (a) simply moderate the shape of preexisting orthogonal AO's which participate in normal, nonfractional bonds, or (b) modify nonorthogonal AO's which participate in fractional bonds so as to reduce their mutual overlap, reduce the degree of fractionality, and increase the valency of the parent atom. The d orbitals which contribute to the three-center, four-electron systems discussed by Musher are found to serve as hybridization functions, indicating that the model three-center, four-electron and d-orbital hybridization schemes are not mutually exclusive, but rather represent limiting points along a continuous progression.

I. Introduction

The idea that two-center localized molecular orbitals (LMO's) might be identified with chemical bonds was first suggested by Hund in 1931,[2] soon after the advent of quantum mechanics itself. Though distinct bonds cannot be perceived in exact quantum mechanical solutions, Hund's idea by and large has proven to be quite satisfactory in the context of molecular-orbital theory. For example, structure **1** represents both the localized molecular-orbital structure for methane[3] and the classical Lewis structure, as does **2** for formaldehyde.[3] Following Hund, the similarity of the localized and classical Lewis descriptions would seem to imply that carbon is tetravalent in each case, in conformity with the octet rule.



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$$

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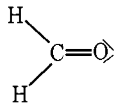

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In contrast, the Boys localized structures for CO_2 and CO_3^{2-} each have six equivalent localized bond orbitals to carbon.[4] Moreover, many localized structures having five or more LMO's to boron,[5] carbon,[5a,b,d,6] nitrogen,[6a,b,e,g,7a,c] or oxygen (in ozone[8]) have been reported, a few of which are depicted in Figure 1 using the notation[4,5i] summarized in Table I. (The same notation is used in structures **1**–**4**.)

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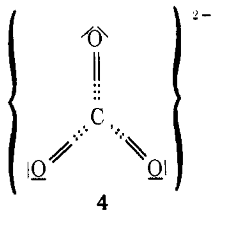

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Clearly, something is amiss. Evidently, either we must accept octet-rule violations and hypervalent bonding as commonplace, even when only first-row atoms are involved, or we must conclude that localized orbitals cannot be related to chemical bonds quite so simply or so directly as Hund had suggested. Several authors, including Bent,[9] Samuel,[10] Paoloni,[7a,b] Muscher,[11] Harcourt,[12] and Gillespie[13] have embraced the first of these alternatives to one degree or another. Nevertheless, our view is that neither an *actual* violation of the octet rule nor a case of hypervalent bonding occurs in any of the instances cited, at least not to the extent that a minimum-basis-set description suffices. Rather, the structures in question simply violate, to an extreme degree, the traditional restriction in discussions of chemical bonding that the bonds to a given center employ mutually orthogonal hybrid atomic orbitals.[14]

Two principal objectives of this paper will be to show how the *apparent* octet-rule violations which occur here can be resolved when the associated overutilization of certain hybrid AO's is taken into account, and to suggest how and why the associated localized bond orbitals differ from "normal" chemical bonds. As we shall see in section III, the first task becomes quite straightforward when proper account is taken of the fact that the minimum-basis-set wave functions in question, like all acceptable wave functions, obey the Pauli exclusion principle. We will be concerned initially with descriptions obtained at the minimum-basis-set level. We recognize, however, that this level of treatment is too confining.

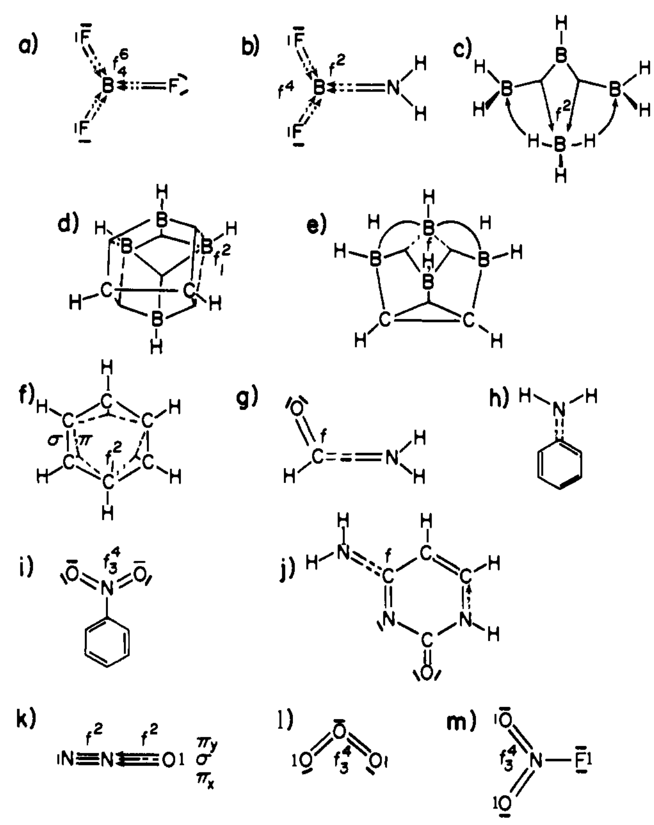


Figure 1. Some Boys localized structures showing apparent octet-rule violations (see Table I for notation). The symbols f, f^n, and $f_m{}^n$ denote fractional bond orbitals (see text). Structures: (a, b) ref 5h; (c) ref 5j; (d, e) ref 5f; (f) a σ-π localized structure for benzene, ref 6f; (g-j) ref 6b; (k) the σ-π localized structure for N_2O, (l, m), ref 8a. The appearance of a, b, and i is changed in the new notation.

Table I. Mulliken Atomic Populations on Center A in Two- and Three-Center LMO's

Symbol[a]	Two-center LMO's	Three-center LMO's
⇢ A	0.15–0.25	0.15–0.25
→ A	0.25–0.50	0.25–0.35
- - - A	0.50–0.75	0.35–0.50
— A	≥0.75	≥0.50

[a] The line symbol is drawn from approximately the LMO centroid to atom A.

Hence, extensions of the argument to larger basis sets, and also to multideterminantal wave functions, will be outlined.

With respect to the second question, we shall find that the essential difference between localized orbitals involved in apparent octet-rule violations and localized orbitals which represent normal chemical bonds can be understood, both mathematically and physically, in terms of the concept of *fractionality*. To be identifiable with normal chemical bonds, the localized orbitals must employ distinct orthogonal hybrid AO's. Fractional bonds do not meet this condition.

Next, some relationships will be traced in section IV between the present findings and other theories and interpretations of molecular structure.[7,9,10,12,13,15] The analysis will also be broadened at this point, particularly on the question of the relationship between hypervalence and the violation of the octet rule.

Finally, the analysis will be extended in section V to systems containing second- and higher row atoms, such as XeF_2, PH_3F_2, and SO_2, for which minimum-basis-set descriptions become much less appropriate. Here, we shall find that the concept of fractionality allows a useful distinction to be made between the participation of d orbitals in chemical bonding as polarization[16] and as "hybridization" functions. In particular, we shall find that d orbitals serve as hybridization functions in the "hypervalent" systems discussed by Musher[11] and will show that the widely discussed alternative three-center, four-electron and d-orbital hybridization schemes are not mutually exclusive, but rather constitute limiting points along a continuous progression.

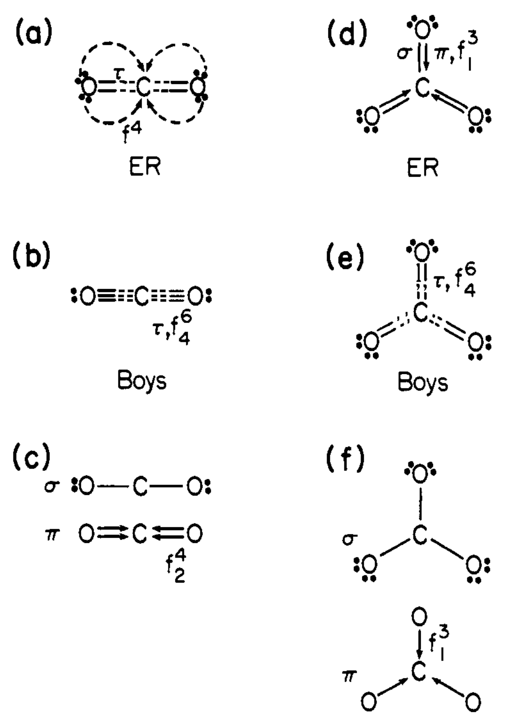


Figure 2. Boys and Edmiston-Ruedenberg localized molecular orbital structures for CO_2 and $CO_3{}^{2-}$ (ref 4): (a, d) ER localizations; (b, e) Boys localizations; (c, f) ER or Boys localizations with imposed σ-π separation.

II. Localized Orbitals for CO_2 and $CO_3{}^{2-}$

We shall begin by summarizing some pertinent localization results[4] for CO_2 and $CO_3{}^{2-}$, which will serve as example systems in the next section. As Figures 2b and 2e show, the Boys localized structures (maximum separation of orbital centroids[17]) each have six equivalent C-O τ-bond, or bent-bond, orbitals. Each of these τ-bond orbitals is distinctly polar, the Mulliken atomic charge[18] on carbon being 0.61 e and 0.66 e in CO_2 and $CO_3{}^{2-}$, respectively. For this reason, each τ-bond orbital is represented by a combined solid-dashed line (Table I).

The Edmiston-Ruedenberg (ER) results (maximum intraorbital Coulomb repulsion energy or, equivalently, minimum interorbital exchange energy[19]) are quite different. For CO_2, the LMO structure obtained in the complete (including all occupied MO's) ER localization (Figure 2a) resembles one of the equivalent Lewis double-bond structures.[20a] Thus, C-O double-bond and oxygen lone-pair orbitals are found which define mutually perpendicular planes, much as might be expected by analogy to the isoelectronic allene, $H_2C{=}C{=}CH_2$. However, the ER "lone pair" orbitals on oxygen are quite delocalized and have Mulliken populations on carbon of 0.18 e (this delocalization is required by the cylindrical symmetry of the molecular charge distribution). For $CO_3{}^{2-}$, the ER structure (Figure 2d) corresponds roughly, though not exactly,[4] to the structure obtained from either criterion when the σ and π canonical MO's are localized separately.

Finally, the localizations (Boys or ER) carried out with an imposed σ-π separation (Figures 2c and 2f) display the expected patterns of C–O σ-bond orbitals and oxygen lone pairs, but yield larger numbers of C–O π-bond orbitals (four in CO_2; three in CO_3^{2-}) than are found in any one Lewis structure. As we shall see, the apparent octet-rule violations at carbon can be isolated to these π systems.

III. Apparent Octet-Rule Violations, Fractionality, and the Interpretation of Localized Structures

Let us now inquire into the meaning of the apparent octet-rule violations observed in systems like those shown in Figures 1 and 2. We note that the Lewis-Langmuir octet theory[21,22] envisioned a counting of integral numbers of electrons in valence shells, irrespective of the polarity of the bonds involved. Accordingly, a first inclination is simply to count the LMO's associated with carbon in CO_2 and CO_3^{2-} (by "associated", we mean having a significant Mulliken population of e.g., $\geqslant 0.2$ e on carbon), and to conclude that the bonding to carbon violates the octet rule in each case.

This approach is faulty, however, because the octet rule addresses itself to *electrons*, and not to *orbitals*. Specifically, compliance with the octet rule requires that no more than eight *different* electrons participate simultaneously in the bonding to the center in question (this statement will serve as our working definition of the octet rule). In quantum mechanics, all the electrons make use of all the molecular orbitals as a consequence of the antisymmetry of the wave function and the indistinguishability of the electrons (Pauli principle). Consequently, the association of particular electrons with particular orbitals breaks down,[23] and the fact that more than four valence LMO's are associated with carbon in CO_2 and CO_3^{2-} does not in itself establish that carbon's valence shell contains more than eight different electrons.

It might seem that the objection just raised would preclude any assessment of compliance with the octet rule. This is not the case, however, for one *can* distinguish in quantum mechanics between the *same* and *different* electrons. Just this distinction gives rise to the exchange terms in the SCF energy expression, for example. These terms, it will be remembered, correct for the spurious self-interactions included in the Coulomb term. Ruedenberg[23] describes the physical situation in terms of a *sharing fraction*, $s(x_1,x_2)$, which expresses the conditional probability that two electrons found at the space points x_1 and x_2 will represent the same, rather than different, electrons. For our purposes, it will be sufficient to note that $s(x_1,x_2)$, or better, the related correlation function $f^{\alpha\alpha}(1,2)$ or $f^{\beta\beta}(1,2)$ defined by McWeeny,[24] approaches unity as x_1 approaches x_2 when the two electrons have the same spin. This behavior expresses the well-known fact, embodied in the concept of the Fermi hole[25] and formalized in the statement of the Pauli exclusion principle, that a given electron excludes all others of parallel spin from its immediate vicinity.[23,26]

The futher concept needed at this point is that of an electron loge,[26] which we shall particularize here as a region of physical space which at any moment very probably contains one and only one electron of given spin. Now, the position we take is that localized orbitals can be identified with chemical bonds when the LMO's define regions of space within which such exclusivity holds reasonably well. We note that complete exclusivity is not to be expected, for this would require noninterpenetrating LMO's. Real LMO's fall quite short of this ideal.[27]

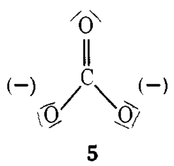
The relationship between localized bond orbitals and exclusivity as manifested by the behavior of the sharing fraction, $s(x_1,x_2)$, is under study by one of us.[28] In this paper, we shall take the simpler but perhaps more illustrative tack of addressing the conditions under which such exclusivity *cannot* hold. Perhaps the clearest case arises when a single atomic orbital or hybrid AO participates equally in two or more LMO's. Now, one statement of the Pauli principle is that two electrons of identical spin cannot occupy the same orbital. It follows, as we shall see, that two or more LMO's which utilize (overutilize) the same AO or hybrid AO cannot employ *different* electrons of the same spin for this purpose.[12a,29] Hence, exclusivity cannot hold, these LMO's cannot be regarded as normal chemical bonds (we shall term them *fractional*), and their number cannot be employed straightforwardly to demonstrate noncompliance with the octet rule.

Indeed, it follows that no antisymmetric wave function constructed from a minimum basis set of atomic orbitals (e.g., 1s, 2s, 2p) can violate the octet rule. Before showing this, however, it will be useful to state here the conclusion to which the above considerations lead. This conclusion is that exclusivity requires, *as a minimal condition*,[30] that the localized orbitals employ distinct partitions of the subspace spanned by the atomic orbitals at each center, i.e., employ distinct orthogonal hybrid AO's. This requirement thus relates the traditional insistence on orthogonal hybrid AO's in discussions of chemical bonding to considerations of exclusivity.

The reader will note that we have purposely tied the discussion of the octet rule to the role played in the expansion of the wave function by the atomic orbitals associated with the center in question. While this approach may not satisfy every reader, it seems to us to be the best available bridge between the pre-quantum-mechanical ideas of Lewis and modern quantum chemical calculations. For completeness, we note that if the wave function employs a single-center expansion or utilizes expansion orbitals centered in the bonding region, it is understood that a *significant expansion*[23] in atom-centered orbitals must first be carried out to express the wave function in the form assumed in the analysis.

Resolution of the Apparent Octet-Rule Violations. At least three approaches can be suggested for demonstrating that a minimum-basis-set wave function necessarily obeys the octet rule. As we shall see, each demonstrates this compliance by rewriting the wave function in terms of one or several *simple* structures, i.e., structures which obey the just-stated minimal condition for exclusivity (distinct orthogonal hybrids) with respect to the center of interest.

To develop the first approach, let us consider the localization results for CO_3^{2-} obtained in the σ–π framework (Figure 2f). Here, an apparent octet-rule violation occurs at carbon because all three localized C–O π-bond orbitals utilize (*overutilize*) the same p_π atomic orbital on carbon. With this in mind, let us replace each of the π LMO's in the determinantal wave function by its LCAO expansion and then multiply out the LCAO expansions in order to express the wave function as a sum of determinants over the π AO's (see the analogous treatment for H_3^- below) and σ LMO's. When this expansion has been carried out, many determinants are found to contain carbon's p_π AO two or more times with the same spin function. Such determinants have two or more identical columns and therefore vanish identically; each would associate two or more electrons of the same spin with the same AO on carbon, in violation of the exclusion principle. When the remaining determinants are regrouped, several simple MO structures arise, each of which is comprised of a single determinant of doubly occupied molecular orbitals. The π MO's in these structures are exclusively localized on one or two centers, while the σ LMO's are unchanged. In this case, the three dominant simple MO structures are related to the leading valence-bond (VB) structures **5**–**7**[20b] essentially by the replacement of each doubly



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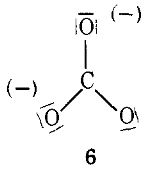

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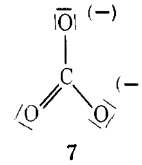

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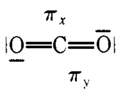
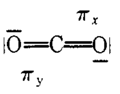
occupied MO by the analogous Heitler–London VB pair function. A variety of long-bond and more highly ionic structures are also produced.

These structures show that just two of the six electrons in the π orbitals are associated with the bonding to carbon in the minimum-basis-set wave function for CO_3^{2-} (though, of course, one cannot say which two). Hence, no more than eight different valence electrons participate simultaneously in the bonding to carbon, and the octet rule is obeyed.

The analysis for CO_2 in the σ–π framework proceeds similarly and produces, among other less important terms, simple MO structures which resemble the key VB structures **8–11**.[20a]


$|\underline{O}\overset{\pi_x}{=}C\underset{\pi_y}{=}\overline{O}|$

8


$|\overline{O}\underset{\pi_y}{=}C\overset{\pi_x}{=}\underline{O}|$

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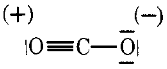
$\overset{(+)}{|O}{\equiv}C{-}\overset{(-)}{\underline{\overline{O}}|}$

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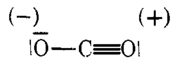
$\overset{(-)}{|\underline{\overline{O}}}{-}C{\equiv}\overset{(+)}{O|}$

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These structures show that just two pairs of π-orbital electrons, not four, are associated with the bonding to carbon. Again, the octet rule is obeyed.

In the second approach, the compliance with the octet rule is demonstrated wholly within the original MO framework by judiciously selecting the set of MO's to be examined. Thus, just four MO's are found to be associated with carbon in both CO_2 and CO_3^{2-} if one localizes only the σ orbitals but retains the delocalized canonical π MO's. For CO_2, two of the σ LMO's and the two π_u canonical MO's contain significant contributions from carbon's valence AO's; in CO_3^{2-}, one finds that three localized C-O σ orbitals plus the A_1'' π canonical MO[4] are associated with carbon.[31] Because the four hybrids on carbon utilized in these MO's are mutually orthogonal, no self-cancellations occur in terms involving the carbon hybrid AO's in either system. Hence, each of the four MO's contributes two electrons to carbon's valence shell, for a total of eight.

It is interesting to note that these MO's significantly associate *six* orbitals with each of the oxygen atoms, and thus produce an apparent octet-rule violation at oxygen. For CO_2, these six MO's are comprised of the four delocalized π canonical MO's plus two of the σ LMO's. As in CO_3^{2-}, further localization *clarifies* the octet rule for oxygen but *obscures* compliance with it for carbon. The inability to find a single set of MO's which simultaneously demonstrates compliance for all centers is symptomatic of an intrinsic (irremovable) delocalization of the electrons. This delocalization is, of course, the molecular-orbital counterpart of the valence-bond concept of resonance.[32]

The relationship between an intrinsic delocalization of the electrons in the MO picture and resonance in the VB picture is further exemplified in the third approach. Here, the determinantal wave function is first fully expanded as a sum of determinants over all the atomic orbitals. The nonvanishing AO determinants are then regrouped in such a way as to express the MO wave function as a linear combination of canonical VB structures.[33] Since, when a minimum-basis-set is used, no canonical VB structure associates more than four pairs of valence electrons with any first-row atom, or more than one pair with hydrogen, this approach demonstrates compliance with the octet rule simultaneously for all atoms. It is of course immaterial whether the starting wave function is written in terms of the canonical MO's, the localized MO's, or some other set, though one such choice may require less manipulative effort than another.

In essence, the particular genius of the molecular orbital approach, it will now be apparent, is that it permits a composite, or hybrid, of several simple structures (such as **8–11**) to be written as a single Slater determinant through the incorporation of self-cancelling terms. This capacity allows the molecular-orbital approach, despite its limitations in other respects, to treat on roughly equal footing both systems for which a single Lewis structure suffices and systems for which several such structures are needed. Hence, we see that resonance in the valence-bond approach and electron-delocalization in the molecular-orbital approach are more than similar in effect; their mathematical formalisms are closely related also.

H_3^-: An Example System. For clarity, we shall work through a simple example to illustrate the three approaches discussed above. The localized structure for linear H_3^-,

$$\{H_a \rightarrow H_b \leftarrow H_c\}^-$$

displays an apparent violation of the duet rule at the central hydrogen atom. Here, the occupied canonical MO's obtained at the minimum-basis-set level are

$$\phi_1 = N_1(\chi_a + \lambda\chi_b + \chi_c) \qquad \sigma_g \qquad (1)$$

$$\phi_2 = N_2(\chi_a - \chi_c) \qquad \sigma_u \qquad (2)$$

where χ_a, χ_b, and χ_c represent Slater 1s atomic orbitals, λ is a variational parameter, and N_1 and N_2 are normalization constants.

The LMO's, ϕ', are the equivalent orbitals[34] obtained by taking normalized plus and minus combinations of the canonical MO's. Explicitly, one finds

$$\phi_1' = \frac{1}{\sqrt{2}}\{(N_1 + N_2)\chi_a + \lambda N_1\chi_b + (N_1 - N_2)\chi_c\}$$
$$= 0.818\chi_a + 0.346\chi_b - 0.270\chi_c \quad (3)$$

$$\phi_2' = \frac{1}{\sqrt{2}}\{(N_1 - N_2)\chi_a + \lambda N_1\chi_b + (N_1 + N_2)\chi_c\}$$
$$= -0.270\chi_a + 0.346\chi_b + 0.818\chi_c \quad (4)$$

where the numerical coefficients are PRDDO[35] minimum-basis-set values.[36] As might be expected, the π LMO's for CO_2 are found to have similar three-center expansions.[37] Thus, in both cases the LMO's possess sizable delocalized tails of opposite phase as a consequence of their mutual orthogonality.[38]

Now, χ_b plays a significant role in both of the LMO's for H_3^- but appears only in the σ_g orbital in the canonical MO structure, which is simple with respect to H_b. The latter observation illustrates the second approach discussed above and demonstrates compliance with the duet rule at the central hydrogen. As in CO_2 and CO_3^{2-}, localization obscures this compliance and produces an apparent rule violation at H_b. However, χ_a and χ_c participate significantly in both σ_g and σ_u; localization to some degree clarifies compliance for these centers. Thus, the intrinsic delocalization of the electrons again makes it impossible to demonstrate compliance for all centers in a single MO structure.

To illustrate approach 1 in a simple manner, we shall employ the idealized two-center LMO's

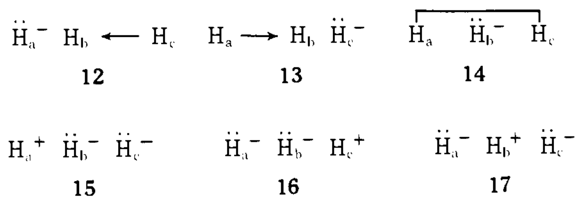
$$\phi_1' = \mu\chi_a + \nu\chi_b$$

$$\phi_2' = \nu\chi_b + \mu\chi_c$$

where $\mu > \nu$. The expansion[39] of $\psi = |\phi_1'\bar{\phi}_1'\phi_2'\bar{\phi}_2'|$ in molecular orbital structures yields

$$\begin{aligned}\psi = {} & |(\mu^2\chi_a\bar{\chi}_a + \mu\nu(\chi_a\bar{\chi}_b + \chi_b\bar{\chi}_a) + \nu^2\chi_b\bar{\chi}_b) \\ & \times (\mu^2\chi_c\bar{\chi}_c + \mu\nu(\chi_c\bar{\chi}_b + \chi_b\bar{\chi}_c) + \nu^2\chi_b\bar{\chi}_b)| \\ = {} & \mu^2\{\underbrace{|\chi_a\bar{\chi}_a\phi_2'\bar{\phi}_2'|}_{12} + \underbrace{|\chi_c\bar{\chi}_c\phi_1'\bar{\phi}_1'|}_{13}\} \\ & - \mu^2\nu^2\underbrace{|(\chi_a + \chi_c)(\bar{\chi}_a + \bar{\chi}_c)\chi_b\bar{\chi}_b|}_{14} \\ & + \mu^2\nu^2\{\underbrace{|\chi_b\bar{\chi}_b\chi_c\bar{\chi}_c|}_{15} + \underbrace{|\chi_a\bar{\chi}_a\chi_b\bar{\chi}_b|}_{16}\} - \mu^4\underbrace{|\chi_a\bar{\chi}_a\chi_c\bar{\chi}_c|}_{17}\end{aligned}$$

after some manipulation. Additional terms such as $\mu\nu^3|(\chi_a\bar{\chi}_b + \chi_b\bar{\chi}_a)\chi_b\bar{\chi}_b|$ and $\nu^4|\chi_b\bar{\chi}_b\chi_b\bar{\chi}_b|$ also arise but vanish identically because the determinants contain two or more identical columns. In the notation of Table I, the (unnormalized) simple MO structures correspond to:

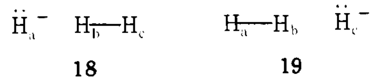


$\ddot{H}_a^-\ H_b \longleftarrow H_c$ **12** $\quad H_a \longrightarrow H_b\ \ddot{H}_c^-$ **13** $\quad H_a\ \ddot{H}_b^-\ H_c$ **14**

$H_a^+\ \ddot{H}_b^-\ \ddot{H}_c^-$ **15** $\quad \ddot{H}_a^-\ \ddot{H}_b^-\ H_c^+$ **16** $\quad \ddot{H}_a^-\ H_b^+\ \ddot{H}_c^-$ **17**

Since $\mu > \nu$, **12, 13,** and also **17** are the principal structures. Compliance with the duet rule is evidenced by the fact that none of the MO structures associates more than two electrons with any hydrogen atom.

The nonvanishing terms produced in the expansion of the determinantal wave function can also be rewritten in terms of the canonical VB structures (approach 3), of which there are six in the present case. Four of these are again represented by structures **14–17** (note, however, that the meaning of the "bond" between H_a and H_c in **14** is changed). The remaining VB structures, **18** and **19,** are analogous to **12** and **13**:



$\ddot{H}_a^-\ H_b\text{—}H_c$ **18** $\quad H_a\text{—}H_b\ \ddot{H}_c^-$ **19**

As no VB structure associates no more than two electrons with any hydrogen atom, compliance with the duet rule is again evidenced.

Generalization and Extension. To summarize and generalize the preceding discussion, we suggest that the question of compliance or noncompliance with the octet rule can be addressed by: (1) expressing the LMO structure as a linear combination of the simple MO structures which result when self-cancelling terms are discarded: (2) transforming the MO's unitarily in such a way as to associate the fewest number of molecular orbitals with the center of interest; and/or (3) expressing the MO wave function as a linear combination of canonical VB structures. Compliance with the octet (or duet) rule is demonstrated if all resultant simple structures associate at most four[40] pairs of valence electrons with the center of interest (or one pair, in the case of a hydrogen atom). When a minimum basis set is used, all three approaches are equivalent and necessarily demonstrate compliance with the octet rule in the special case of a single-determinant wave function of doubly occupied MO's.

To sharpen a previous point, we note that when the hybrid AO's employed are taken to be the orthogonal valence atomic orbital (VAO) hybrids defined by Ruedenberg,[23] the doubly occupied MO's can always be transformed unitarily in such a way as to isolate each VAO on a designated center to a single transformed MO (approach 2). This conclusion follows from the definition of the VAO's as those hybrid AO's which diagonalize the intraatomic part of the one-electron density matrix.[23,41a,b] Here, the exclusion principle exerts its influence by permitting such transformations of the MO's to be made without changing the determinantal wave function itself (apart from a phase factor). Quite different conclusions would follow for structures like those in Figures 1 and 2 if the wave functions were, say, simple Hartree products.

While the third approach is perhaps the most general, the second approach is particularly convenient when extended basis sets are employed. Here, the transformation of the basis set to VAO's establishes at once the extent to which the result given by approach 2 will be in conformity to the octet rule; since each VAO can be isolated to a single transformed MO, it follows that full compliance is shown if just four VAO's have nonzero net atomic populations (diagonal elements of the transformed density matrix).[42]

We note that full compliance with the octet rule is not incompatible with the use of an extended basis set. For example, methane has just four valence MO's, and hence utilizes just four VAO's on carbon, however large the basis set. In contrast, a finding that five or more VAO's participate significantly in the expansion of the wave function would imply that the octet rule is violated to some extent. A parallel treatment over orthogonalized AO's is developed in section IV which provides a means of assessing the degree of noncompliance encountered in such cases (see the discussion following eq 7).

Next, we note that multideterminantal wave functions can be analyzed by applying approach 3 directly. Alternatively, approaches 1 or 2 can be applied by separately transforming or localizing the α-spin and β-spin MO's in each of the individual Slater determinants. If a minimum-basis-set is used, compliance must again be found, since the result will be an expansion of the wave function in structures which are simple for both α- and β-spin electrons.

We emphasize that none of the points addressed above demonstrates that a molecule containing only first-row atoms *necessarily* obeys the octet rule. The analysis establishes only that no minimum-basis-set description can violate this rule. In a sense, therefore, the degree of conformity to the rule by the real chemical system can be judged by the extent to which such a description suffices.[43] Less subjectively, the degree of conformity might be examined by applying the analysis at the extended-basis-set level. We shall not consider such extended-basis descriptions in this paper. We note, however, that many of the points which would arise will be encountered when we turn our attention in section V to systems containing higher row atoms. For now, we caution that conclusions reached on the basis of minimum-basis-set considerations may have to be modified to some extent when more elaborate (extended-basis, and also multideterminantal) wave functions are examined.

Fractionality and the Interpretation of Localized Orbitals. One point which remains to be clarified in this section concerns the manner in which the localized orbitals associated with apparent octet-rule violations are themselves to be regarded. In this connection, the reader will recall that all three approaches discussed above associate just one pair of π electrons with the bonding to carbon in CO_3^{2-}. In essence, all three π LMO's jointly describe this pair of electrons. For this reason, we speak of these LMO's as being *fractional*[44] to carbon (but not fractional to oxygen). In the same way, the four π LMO's in the σ–π description for CO_2 and the six τ-bond orbitals in the Boys descriptions for CO_2 and CO_3^{2-} are all fractional to carbon.

Mathematically, the fractionality arises in each case from the *overutilization*[45] in the localized orbitals of the AO function space for the given atomic center. This overutilization, as we have seen, produces self-cancelling terms when the LMO wave function is expanded. When the nonvanishing terms are regrouped, moreover, the fractional MO's are found to appear individually (as in **12** and **13** for H_3^-), but not jointly, in the resultant simple MO structures.

Physically, then, the concept of fractionality carries a connotation of *nonsimultaneity*, understood in a probabilistic sense. In the earlier terminology, this nonsimultaneity results from the lack of exclusivity on the part of the fractional LMO's and reflects the so-called exclusion principle, or Fermi, correlation between electrons of parallel spin.

There is also a third ramification. Chemically, fractional bonds cannot be expected to be energetically as stabilizing as are normal bonds constructed from distinct orthogonal hybrid AO's.[11b] While in accord with the idea of nonsimultaneity, the reason for this expectation can perhaps best be understood in terms of the effect on the kinetic energy of the sizable anti-

Table II. Some Comparisons for C–O Bonds

System	C-O distance, Å		Diff	Bond energy, kcal/mol[a]
	PRDDO	Expt[a]		
CO	1.16[b]	1.131	0.03	257
CO_2	1.21[c]	1.163	0.05	192
H_2CO	1.24[b]	1.225	0.02	164
CO_3^{2-}	1.33[c]	1.294[d]	0.04	
$(CH_3)_2O$	1.44[b]	1.416[d]	0.02	
CH_3OH	1.43[e]	1.427	0.00	84

[a] Reference 13a. [b] Reference 8a. [c] Reference 4. [d] "Interatomic Distances", *Chem. Soc., Spec. Publ., Suppl.*, **No. 18,** M 70s, 89s (1965). [e] S. Scheiner, D. A. Kleier, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.A.*, **72,** 2606 (1975).

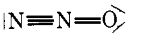
bonding tails possessed by fractional LMO's (cf. eq 3 and 4) as a consequence of their mutual orthogonality.[46] As it happens, fractional bonds experimentally prove to be nearly, but not quite, as short as normal bonds. Thus, CO_2 closely resembles C≡O with respect to its C—O bond length, but more nearly resembles $H_2C{=}O$ in bond energy (Table II). (We shall return to these comparisons in section IV.)

As is shown in Figures 1 and 2, a small f, f^n, or $f_m{}^n$ may be written alongside sets of n fractional LMO's which utilize m orthogonal hybrid AO's to signify, and where possible to quantify,[47] their fractional nature. The symbolism also indicates the polarity of the bond orbitals by means of the line notation of Table I, but we emphasize that *polarity* (which may simply reflect the inclination of the chemical system to attain local electroneutrality[20c]) *is most emphatically not to be equated with fractionality.* For example, the complete Boys localization for C≡O shows a polar triple bond,[8a] but the LMO's are not fractional. In contrast, the complete Boys structure for NO_2F (Figure 1m) shows four equivalent fractional N-O τ-bond orbitals plus an N-F σ-bond orbital,[8a] but none of these LMO's is significantly polar.

IV. Systems Containing First-Row Atoms. Other Approaches

Although the analysis presented in the previous section was developed independently, many of the questions addressed are in fact quite old ones. They date at least to the controversy which arose some 30 years ago between Samuel[10] and Wheland[15] concerning particularly the meaning and appropriateness of Samuel's "classical" pentavalent structures for certain nitrogen compounds. In this section, we shall trace the diverse positions taken by Samuel, Wheland, and a number of later writers, including Paoloni,[7a,b] Bent,[9] Harcourt,[12] and Gillespie,[13] and will examine the relationship of their views to ours. These comparisons will also allow us to extend the analysis in certain ways, particularly on the question of valency and hypervalence. In section V, we shall then apply the analysis to systems containing second- and higher row atoms and will examine its implications for the role of d orbitals in chemical bonding.

Pentavalent Nitrogen and Tetravalent Oxygen. In the controversy with Wheland, Samuel[10] postulated structures **20** for nitrous oxide and **21** for ozone essentially on the basis of experimental evidence concerning molecular volumes and dipole moments. In fact, **21** might represent our Boys LMO structure for ozone[8] (Figure 1l), and the Boys σ-π localized structure for N_2O[8a] (Figure 1k) has an even larger number of bond orbitals to the central nitrogen than would be implied by **20.**



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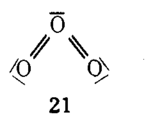
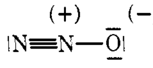


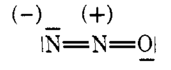
21

Both Samuel and Bent,[9] who subsequently suggested the short N-N, N-O, and O-O bond lengths as a second criterion for favoring structures **20** and **21,** considered N_2O and O_3 to have ten valence electrons around the central atoms, and hence to violate the octet rule.[48] In contrast, Wheland argued that a minimum-basis-set function constructed to represent **20** (he did not discuss ozone) would, after antisymmetrization, be "expressible as a sum of terms, of which a number are identically zero".[15] He noted further that "if these vanishing terms are omitted from further consideration, the function which remains proves to be one corresponding to some modern (i.e., octet) structure, or to resonance among several modern structures (e.g., **22** and **23**; compare our approaches 1 and 3), without any pentacovalent nitrogen atom." Hence, "the octet rule is not an added arbitrary assumption (in a minimum-basis-set treatment), but is a necessary consequence of quantum mechanics and of the exclusion principle. It cannot be violated even if the attempt is made to do so".[15]



$|\mathrm{N}\equiv\overset{(+)}{\mathrm{N}}-\overset{(-)}{\underline{\overline{\mathrm{O}}}}|$

22

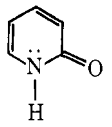


$|\overset{(-)}{\overline{\mathrm{N}}}=\overset{(+)}{\mathrm{N}}=\underline{\mathrm{O}}|$

23

In these respects, Wheland's analysis anticipates our own remarkably closely. However, Wheland further insists that a structure like **20** "from either the pair-bond (VB) or molecular-orbital point of view requires the use of the M-shell (i.e., 3s, 3p, or 3d) orbitals on the nitrogen atom",[15] though this is required only if the five bonds to nitrogen in **20** are to be normal, nonfractional bonds. In adopting this position, Wheland was perhaps motivated by a desire to avoid the misleading implications carried by such structures—a concern which we share and which largely motivates this paper.

Paoloni's position is similar to Samuel's in that he finds support for "classical" pentacovalent structures such as **25** for 3-pyridone.[49] Unlike Samuel, however, he rightly insists that such structures not be given a Lewis pair-bond (VB) interpretation.[7a,b,50] Since he does not consider the two N-C π bonds of the Boys LMO structure for **25** as being in any way distinctive,[7a] however, he apparently considers the octet rule to be violated. We, in contrast, would say that the N-C π bonds in **25** are fractional, since both utilize nitrogen's p_π AO, and would conclude that the octet rule is obeyed. Furthermore, we would expect these bonds, being fractional, not to be as stabilizing as two normal N-C π bonds.[46] In fact, the Pariser-Parr-Pople π-electron energy for **25** (−299.00 kcal/mol) is comparable to that for **24** (−301.91) and **26** (−299.01),[7b] even though **25** has four π bonds while **24** and **26** each have only three.



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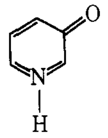
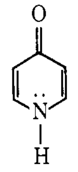


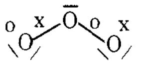
25



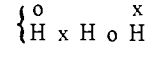
26

Tangent Spheres, Floating Spherical Gaussians, and Exclusivity. Bent's assertion that **21** violates the octet rule is particularly interesting in light of his cogent discussion of the Pauli exclusion principle in drawing motivation for his tangent-spheres model of molecular structure.[51] Thus, Bent's tangent spheres are nonoverlapping regions of space within which, because of the exclusion-principle correlation between electrons of parallel spin, one and only one electron of a given spin is likely to be found. We have suggested that such exclusivity is the essential condition needed for identifying localized orbitals with chemical bonds and have noted that this condition necessarily breaks down when the same hybrid atomic orbital participates significantly in two or more LMO's.

Also related to considerations of exclusivity is Linnett's double-quartet theory.[52] In this approach, the standard tetrahedral arrangement of electron octets around a first-row atom is understood to arise from the exclusion-principle correlation between the four electrons in each spin set. In many cases, the requirements for bonding cause the two spin sets to be oriented similarly, with the result that the most probable configuration would find the electrons near the centroids of charge for the LMO's of the corresponding localized-orbital structure. For fractionally bonded systems, however, Linnett's approach yields non-paired-spatial-orbital (NPSO) formulas like **27** for ozone[52] and, by analogy, **28** for H_3^-. Here, the two



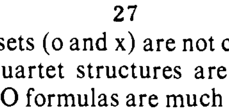
27



28

spin sets (o and x) are not coincident, and the LMO and double-quartet structures are less closely related. Indeed, the NPSO formulas are much more complex than are the single-determinant MO structures that have concerned us here, and a full discussion would be beyond the scope of this paper. It is noteworthy, however, that formulas such as **27** and **28** succeed in accounting for the molecular symmetry in single structures which, unlike the fractional LMO structures, avoid the overutilization of atomic orbitals and thus clearly comply with both the octet rule and the usual rules of valence.

Frost's FSGO (floating spherical gaussian orbital) model of molecular electronic structure[53] has sometimes been compared in form and motivation to Bent's tangent spheres model. Thus, FSGO's do approximate tangent spheres in saturated hydrocarbons,[54] and Frost himself has suggested that the FSGO model is especially close to the "original electron pairing and shared pair concepts of Lewis".[53] These points are of interest here because a "non-Lewis" FSGO structure for O_3 has recently been described.[55] This structure utilizes four "banana-bond" FSGO's positioned between the oxygens and thus nominally possesses two oxygen-oxygen double bonds. As the authors note, however, these four FSGO's optimally position themselves ~75% of the way from the central toward the end oxygen atoms,[55] suggesting **29** as much as **21** to us. In our view,



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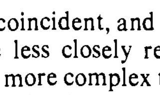
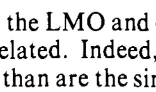


30a



30b

the "non-Lewis" nature of the FSGO structure should be understood to mean that a proper first description in the valence-bond framework would require resonance between the simple Lewis structures **30a** and **30b**, and not to imply that the octet rule is violated.[56] Thus, FSGO's centered in bonding regions, unlike truly nonoverlapping tangent spheres, cannot always be identified with the electron-pair bonds of the Lewis theory.

Valence-Shell Electron-Pair Repulsion Descriptions. The VSEPR model of molecular structure developed by Gillespie and Nyholm[13a,d,57] is similar in many respects to Bent's tangent spheres model. This approach holds that molecular geometry is determined principally by that disposition of localized bond- and unshared-pairs which minimizes the interpair electron repulsions, although the tendency of electron pairs to separate into exclusive domains as a consequence of the exclusion principle is given as a justification for this rule.[13a,d] The VSEPR approach accounts for many aspects of molecular geometry in simple terms and is increasingly employed in introductory chemistry texts.

For CO_2, Gillespie observes that the C-O bonds are shorter and stronger than are normal C=O double bonds (cf. Table II). Accordingly, he suggests that "when the electrons in the valence shell of carbon are confined in two double bonds (as in **8** or **9**) some space is left in the valence shell of the central carbon in the region between the two double bonds".[13b] Consequently, the lone-pair electrons in the crowded oxygen valence shell delocalize into the available space, giving each C-O bond some triple bond character. Clearly, Gillespie's picture closely resembles that obtained in the complete ER localization (Figure 2a),[4] though in our view the delocalization of the oxygen lone pairs is not so much a matter of filling empty space as of preserving the cylindrical symmetry of the charge distribution.

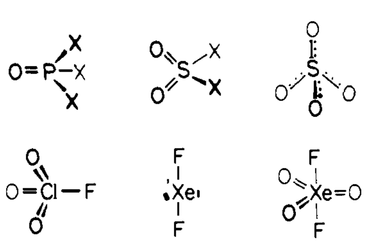


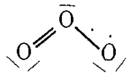
Figure 3. Some valence-shell electron-pair repulsion structures for compounds containing higher row atoms. See ref 13a,b.

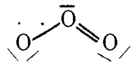
Similarly, Gillespie's VSEPR description for CO_3^{2-}[13c] agrees closely with the complete Boys structure,[4] in which three equivalent sets of τ-bond orbitals are found to carbon (Figure 2e). Because of the short observed C-O bond lengths (Table II), however, Gillespie takes exception to the C-O bond order of $1\frac{1}{3}$ assigned from the octet rule. He argues that "because each double bond in the plane of the molecule is only slightly larger than a single bond, it should be possible to pack the three double electron pairs of the three double bonds around carbon, particularly if they are somewhat polarized towards the oxygens, and there is no reason to assume that when such multiple bonds are formed carbon necessarily obeys the octet rule".[13c] No octet rule violation occurs in our view, however, at least not to the extent that a minimum-basis description suffices (we note that the several C-O bond lengths in Table II are described reasonably well in the PRDDO minimum-basis-set approximation), because the C-O τ-bond orbitals are necessarily fractional. In contrast, the VSEPR approach assumes that the localized electron pairs will occupy exclusive regions of space.[13a] Thus, the concept of fractionality cannot arise, and the VSEPR approach removes the essential discipline of the octet rule, to the possible detriment of the unwary practitioner.

Gillespie also provides VSEPR descriptions for many systems containing higher row atoms,[13a,d,57] a few of which are sketched in Figure 3. Here again, we would expect many of the corresponding localized orbitals to be fractional, though perhaps to a smaller extent than a minimum-basis interpretation would suggest. (See the discussion of d-orbital participation in section V.)

Lastly, we note that Gillespie, like Bent,[9] raises the question of how the short bond lengths in CO_2 and CO_3^{2-} are to be understood. As Gillespie indicates,[13b,c] bond orders defined empirically through the observed bond lengths would sum to considerably more than four in each case. This does not mean, however, that octet-rule violations occur (see the discussion of Coulson bond orders,[58] which are similarly misbehaved, in the next subsection). The Boys structures do indicate similarities in the shapes of the localized orbitals for CO_2 and CO_3^{2-} to the triple- and double-bond orbitals of CO and H_2CO, respectively, and as such successfully anticipate the observed shortening of the C-O bonds. Since the bonds are fractional, however, the LMO's contain significant antibonding regions, and the full shortenings are not realized.[46]

Valency, Bond Orders, and Hypervalence. We note that Harcourt has written extensively on electronic descriptions for electron-rich (or orbitally deficient[11c]) three-orbital, four-electron systems such as H_3^-, O_3, and CO_2.[12] His "increased valence" formulas (e.g., **31** for ozone), like Linnett's NPSO


31a


31b

formulas[52c] (e.g., **27**), represent complicated multideterminantal wave functions and will not be discussed here. We do wish to note, however, that Harcourt considers that his formulas comply with the octet rule[12b] but nevertheless represent an increase in valence at the central atoms, since "more electrons participate in bonding than occurs in Lewis valence-bond (VB) formulas with electron-pair bonds".[12c] We, of course, cannot accept Harcourt's method of counting electrons in terms of orbitals, for the reasons discussed in the initial paragraphs of section III (see Note Added in Proof).

However, the main point we wish to make is that the presence or absence of "increased valence" depends very much on how one choses to define valency. Together with VB "bond numbers", Harcourt employs Coulson bond orders,[58] appropriately generalized,[12a,b] for this purpose.[59] If this approach is taken, even minimum-basis single-determinant MO structures for three-orbital, four-electron systems display increased valence.[12b] For example, the Coulson bond order defined over orthogonalized AO's[60] is 0.703 for each of the adjacent H–H linkages in the PRDDO calculation for H_3^-, making the total valency for the central hydrogen 1.406. If valency is defined as suggested by Armstrong, Perkins, and Stewart (APS),[61] however, the total valency for this hydrogen is found to be $2(0.703)^2 = 0.989$, or essentially unity.

Now, our feeling is that valency ought to be defined in such a way that hypervalence is tied closely to the violation of the octet rule. Manifestly, a definition based on Coulson bond orders would not meet this requirement. In contrast, it can be shown that the APS criterion does. In this approach, the valency for atom A, V_A, is computed from the squares of the elements of the density matrix, **P**, over orthogonalized AO's (OAO's) i on atom A and j on other atoms, B. The B_{AB} are "bond indices".

$$V_A = \sum_{B\neq A} B_{AB} = \sum_{B\neq A}\sum_{i_A}\sum_{j_B}(P_{i_A j_B})^2 \tag{5}$$

By exploiting the duodempotency of the single-determinant MO density matrix, V_A can be rewritten as[61]

$$V_A = \sum_{i_A} 2P_{i_A,i_A} - \sum_{i_A}\sum_{j_A}(P_{i_A j_A})^2 \tag{6}$$

Moreover, by transforming the OAO basis just as is done in obtaining Ruedenberg's VAO's,[23] the one-center off-diagonal elements of **P** vanish, and V_A takes the simpler form

$$V_A = \sum_{i_A} P_{i_A,i_A}(2 - P_{i_A,i_A}) \tag{7}$$

in the new basis. Now, since $0 \leq P_{i_A,i_A} \leq 2$, each transformed OAO contributes at most 1 unit of valency to V_A. Furthermore, both vacant and doubly occupied (inner-shell or lone-pair) OAO's contribute nothing. Hence, $4 - N_{lp}$, where N_{lp} is the number of *rigorously localized* lone pairs, is the maximum APS valency for a first-row atom in a minimum-basis-set MO calculation, and neither hypervalence nor a violation of the octet rule can arise.

This equivalence results because the bond indices, B_{AB}, and consequently the valencies, V_A, directly measure the numbers of pairs of electrons in bonds associated with atoms A. In contrast, Coulson bond orders, in opposition to the chemist's intuitive concept, do not possess this property and do not yield a useful definition of valency.

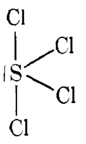
By way of illustration, we note that APS valencies based on PRDDO wave functions[4,8a] for some of the systems considered in this paper are: 3.98 for carbon and 2.46 for oxygen in CO_2; 3.98 for carbon and 1.72 for oxygen in CO_3^{2-}; and 2.77 and 1.87, respectively, for the central and end oxygen atoms in O_3.

When extended basis sets are employed, $4 - N_{lp}$ will still be the maximum APS valency for a first-row atom unless more than four of the valence OAO's which appear in eq 7 have nonzero diagonal density matrix elements. Methane, for example, has only four valence molecular orbitals and can be at most tetravalent. Clearly, therefore, the APS criterion for hypervalence closely parallels the criterion for noncompliance with the octet rule developed over AO's in approach 2 of the previous section. Indeed, eq 7 might well be employed in the OAO basis to assess the degree of noncompliance accompanying a finding that five or more VAO's carry appreciable electron density.

Perhaps the one primary limitation to this approach is that the APS valency is defined in the context of a duodempotent density matrix, for this requires that the wave function be expressible as a single Slater determinant of doubly occupied MO's. One might, to be sure, still employ eq 5 or 7 with wave functions of other types, but the important electron-counting conservation relationship possessed by the bond indices, B_{AB}, in the simpler case would be lost. Whether this theoretical objection will prove a serious impediment in practice remains to be determined.

V. Systems Containing Higher Row Atoms. The Role of d Orbitals in Chemical Bonding

Let us now apply the analysis to systems containing higher row atoms. We shall begin by noting that Musher has pointed out that when higher row atoms " 'expand' their valence by adding ligands, e.g., as in forming SCl_4, BrF_3, and XeF_2 they add them colinearly along the axis of one of the (previously unshared) pairs of p electrons", thereby forming a three-center, four-electron system.[11a] As noted previously, H_3^-, O_3, and CO_2 contain such systems. Musher further observed that when minimum-basis-sets are used, the resultant localized orbitals "differ from the usual bonding orbitals . . . in that the same . . . orbital (on the central atom) is used in two different bonds".[11a] This recognition is also the focus of our argument. Musher, however, apparently considered the octet rule to be violated, since he says that the central atoms "exceed the number of valences allowed them by the traditional theory, and thus utilize more electron-pairs of bonding than provide stability in the Lewis-Langmuir theory".[11a]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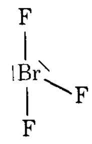
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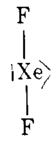
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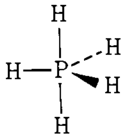
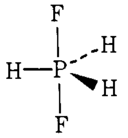
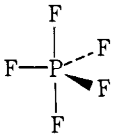
As in Samuel,[10] Bent,[9] and Paoloni,[7a,b] we again find in Musher an inclination to identify the number of electron pairs in an atom's valence shell with the number of localized orbitals found to that atom, even when the LMO's do not employ distinct orthogonal hybrid AO's. Hence, Musher defines the localized orbitals in the three-center, four-electron systems he discusses as *hypervalent*,[11] whereas we would term them fractional. The universally observed lengthening of "axial" over "equatorial" bonds to central non-transition-series atoms in such systems (cf. ref 13a) is explicable on either basis.[46] However, while Musher's term does convey the idea that more bonding attachments occur than might otherwise be expected,[62] we find its application to octet-rule-obeying minimum-basis structures to be somewhat questionable. As discussed previously, we feel that hypervalence ought to be defined so as to imply simultaneously that the octet rule is violated. We certainly would not, however, question the extraordinary impetus Musher's formulation has given to the experimental and theoretical study of "hypervalent" compounds.

Together with Wheland's,[15] Coulson's position comes closest to our own. Like Bent,[9] Musher,[11a] and Harcourt,[12a] Coulson[16a] describes three-orbital, four-electron systems like those represented by the σ bonds of XeF_2 (**34**) in terms analogous to those we have employed for H_3^-. Though the shapes of the two doubly occupied canonical MO's depend on the symmetries of the contributing AO's, in each case the associated equivalent orbitals[34] are largely two-center in character. This analysis, in fact, seems to originate with Rundle,[63] Pimentel,[64] and Jortner et al.[65] Coulson, however, goes on to observe that the XeF_2 determinant, when expanded and regrouped, can be expressed in terms of the canonical valence-bond structures,[16a] each of which obeys the octet rule (cf. our approach 3). Moreover, in discussing the minimum-basis molecular-orbital wave function itself, Coulson notes that "there is a sense in which even the octet rule is preserved", since the doubly occupied nonbonding MO contains no contribution from the central Xe atom.[16a] This recognition, of course, is essentially our second approach for demonstrating compliance with the octet rule.

Clearly, fractional bonds (to use our terminology) allow one to avoid the necessity for postulating energetically expensive d-orbital hybridization schemes, as Musher has emphasized. This is not to say that d orbitals play no role in the expansion of the wave function, but Musher[11] and Coulson[16b,c] argue that in many cases they serve essentially as polarization functions. In part, Coulson's argument is based on the fact that d orbitals in molecular calculations on systems like those under consideration take on much smaller radii than would be appropriate for d electrons in the atoms involved (as judged from calculations on excited atomic states).[16b,c] Additional arguments are that such d orbitals frequently are not needed to obtain molecular stability in quantum chemical calculations and usually are found to have relatively modest populations when they are included.[11c,16b,c]

One of the clearest computational tests of this generally, but not universally,[66,67] accepted point of view has recently been offered by Keil and Kutzelnigg in the form of large-basis-set ab initio calculations on PH_5, PH_3F_2, PF_5, and their nitrogen analogues, carried out both with and without d orbitals on the central atom.[68] Each of these compounds has a three-center, four-electron system of the type discussed by Musher. Keil and Kutzelnigg find that a rather compact d_{z^2} orbital directed along the F-P-F axis increases the binding energy of PH_3F_2 relative to $PH_3 + F_2$ by ~25 kcal/mol but acquires only a modest Mulliken population (0.22 e). Similar results are found for PF_5. Since the idealized sp^3d (sp^2, dp) hybridization model (Figure 4a) would require a d-orbital population of ~1 e, Keil and Kutzelnigg conclude that PH_3F_2 and PF_5 are best viewed as having three-center, four-electron systems in which d orbitals serve as polarization functions.[68]

It has occurred to us, however, that the distinction between d orbitals as polarization functions and d orbitals as "hybridization" functions might be drawn on quite different grounds. Specifically, we suggest that d orbitals serve as polarization functions when they merely moderate the shape of preexisting orthogonal hybrid AO's, but serve as hybridization functions when they increase the number of distinct AO's utilized in the wave function. (In certain cases, d orbitals might serve partly in each capacity.)

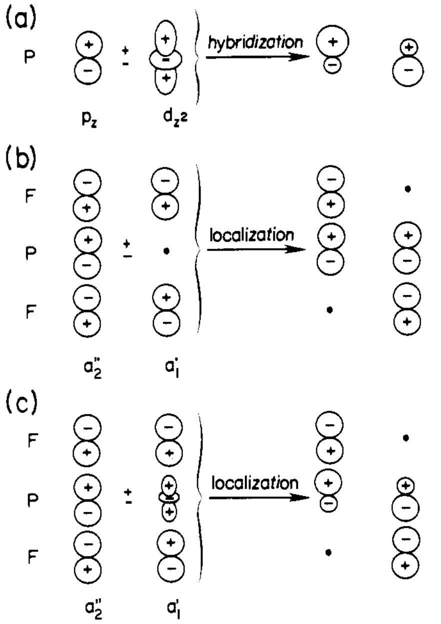


Figure 4. Atomic and molecular orbitals for the axial F-P-F system in PH_3F_2 or PF_5. (a) Idealized pd hybrids. (b) Bonding (a_2'') and nonbonding (a_1') symmetry orbitals. In the absence of d-orbital participation, the localized equivalent orbitals (which here are idealized by deleting small antibonding contributions on the second F) employ the same hybrid AO on P. (c) When a d function participates in the a_1' MO, the localized orbitals now employ nonequivalent hybrids on P which qualitatively resemble the idealized pd hybrids.

To trace the implications of this suggestion, let us first recall that the transformation of the AO basis to VAO's[23] simultaneously determines the number of MO's to which an atom's valence AO's can be confined. In CH_4, which has just four valence MO's, d orbitals would necessarily serve as polarization functions. In PH_3F_2 and PF_5, however, a different situation arises. Here, three VAO's on phosphorus will be utilized in the equatorial P-H or P-F σ bonding, and a fourth of p_z type will take part in the bonding F-P-F MO of the three-center, four-electron system (Figure 4b). By symmetry, an added d_{z^2} orbital on phosphorus could contribute to the higher, nonbonding orbital of a_1' symmetry, as shown in Figure 4c, but not to the bonding orbital of a_2'' symmetry.[69] While s orbitals on P can also contribute to the a_1' orbital, essentially,[71] an added d_{z^2} function will populate an additional VAO on phosphorus.[41b] In "polarizing" a molecular orbital to which AO's on phosphorus previously *had not* (appreciably) contributed, the d_{z^2} AO increases the dimensionality of the AO function space on P utilized in the wave function, and thus serves in the manner expected for a hybridization function. We note that Ratner and Sabin[66] have previously suggested that d orbitals play a particularly important role in the bonding when, as here, occupied MO's are present for which the usual s and p functions on the atom in question do not provide a basis. Similarly, d_{xz} and d_{yz} functions on P also stabilize the axial F-P-F systems in PH_3F_2 and PF_5, evidently via p_π-d_π back-bonding.[68] As the only functions on P of proper symmetry, these functions would also serve as hybridization functions in the present classification and would be singled out for special consideration by Ratner and Sabin.

Next, let us consider the four-electron F-P-F systems in the localized-orbital framework. From this point of view, the axial

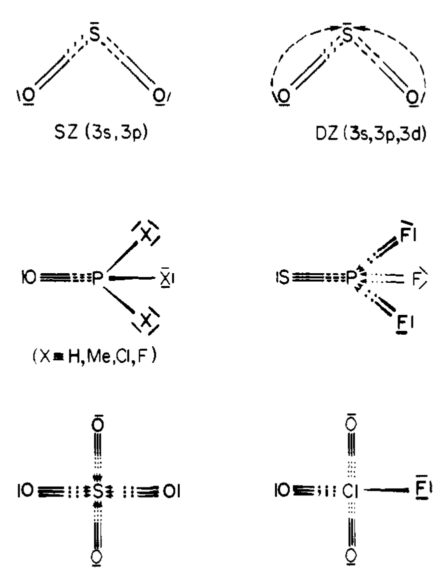


Figure 5. Some Boys localized structures for systems containing second-row atoms (ref 74). The notation of Table I is used. For SO_2, SZ and DZ denote single- and double-ζ basis sets for valence atomic orbitals. The P–F bonds for PF_3O are more polar than shown.

P–F σ-bond orbitals are fractional because each utilizes the same p_z function on P when an s,p basis set is employed (Figure 4b). As is shown schematically in Figure 4c, however, the two phosphorus hybrids are no longer identical when a d_{z^2} function is included, but now have the form $(1 - a^2)^{1/2}p_z \pm ad_{z^2}$. Hence, the d-orbital participation reduces the overlap between the hybrid AO's, and consequently reduces the fractionality of the axial P–F σ bonds. This, too, we suggest, is the mark of a hybridization function. The reader will note particularly the similarity of the "hybridization" combination of the p and d AO's in Figure 4a to the "localization" combination of MO's shown in Figure 4c. A rough calculation based on the d_{z^2} and inferred valence-shell p_z populations[68] suggests that the overlap between these hybrid AO's is reduced from unity to approximately 0.3 in PH_3F_2 and in PF_5.

Finally, let us consider the matter in the light of the APS[61] definition for valency discussed in section IV. Here, the transformation which diagnonalizes the phosphorus intraatomic part of the one-electron density matrix over orthogonalized AO's can be expected to produce hybrid OAO's which correspond closely to the four hybrid VAO's discussed two paragraphs earlier. When a d_{z^2} orbital is included on P, the fifth such hybrid OAO will correspond essentially to this orbital. Moreover, the associated diagonal element of the density matrix should approximately equal the Mulliken population (0.22 e for PH_3F_2[68]) found in the AO basis. From eq 7, then, this orbital can be expected to contribute a valency of $\sim 0.22 \cdot (2 - 0.22) \simeq 0.4$ to the valency of phosphorus, thereby raising the valency of phosphorus substantially above the value obtained in the absence of d orbitals.[72] In our view, this behavior is also in accord with that expected for a hybridization function and is, moreover, inconsistent with that expected for a polarization function. In contrast, $d_{x^2-y^2}$ and d_{xy} functions on P in PH_3F_2 and PH_5 contribute mainly to the equatorial P–H bonding[68] and evidently serve primarily as polarization functions.

Corresponding statements hold concerning the utilization of d functions by first-row atoms and of p functions by hydrogen atoms. Here, we anticipate that such functions will generally be found to serve as polarization functions except in fractionally bonded systems.

In summary, our assessment for the axial F–P–F systems in PH_3F_2 and PF_5 is that an added d_{z^2} orbital on phosphorus serves as a hybridization function. It increases the number of VAO's utilized in the wave function, it reduces the fractionality of the axial P–F σ bonds, and it increases the valency of phosphorus. Moreover, it is clear that the extent of the decrease in fractionality and of the increase in valency must be a continuous function of the population of the added d_{z^2} orbital. Hence, we see that the three-orbital, four-electron and d-orbital hybridization models are not in fact mutually exclusive, but rather constitute *limiting points along a continuous progression.* Musher's systems containing higher row atoms occupy intermediate points along this progression, and therefore are indeed to some extent hypervalent.

Additional results which bear on the role of d orbitals in chemical binding have been reported by Guest, Hillier, and Saunders in a series of ab initio SCF[73,74] and localized orbital[74] calculations using basis sets with, and sometimes without, d functions. The Boys localized structures for some of their systems are shown in Figure 5 using the notation of Table I. We note that all of these structures display apparent octet-rule violations. Moreover, some show remarkably large numbers of localized bond orbitals associated with the central atoms, e.g., *nine* to phosphorus in PF_3S, *ten* to sulfur in SO_2Cl_2, and *twelve* to sulfur in SO_4^{2-}. Evidently, many of these localized orbitals are highly fractional.

Guest and Hillier note that d orbitals seem to be particularly important under just such circumstances, i.e., "where the second-row atom is exerting a valency greater than its natural value".[74b] To test this conclusion, which follows from our analysis, we summarize some pertinent ab initio results in Table III.[75] A first look at the data indicates that a word of caution is in order, for several comparisons suggest that small basis sets seriously overestimate the importance of d-orbital participation.[67,76,77] Nevertheless, one cannot help but take notice of the very large stabilization energies, ΔE_d, of 226–589 kcal/mol and d-orbital populations of 1.13–2.87 e obtained in the small-basis calculations on the "hypervalent" systems SO_2, PO_2^-, PF_5, and SO_4^{2-}. Moreover, the comparison of nonfractional P≡N (d population, 0.29 e) to fractional PO_2^- (1.45 e),[76] isoelectronic to SO_2, is instructive, as is the comparison of H_2S (ΔE_d, 34 kcal/mol; d population, 0.15 e)[78] to SO_2 (226 kcal/mol; 1.17e).[73b] Collins, Schleyer, Binkley, and Pople in recent work with STO-3G + d basis sets have also noted the enhanced importance of d orbitals in "hypervalent" systems.[79]

Among the larger basis results, we note that Keil and Kutzelnigg[68] find that ΔE_d increases by four- to sixfold and that the d-orbital population increases by ca. tenfold on going from tricoordinate PH_3 (D_{3h}) to pentacoordinate PH_5 or PH_3F_2. Similarly, Rauk, Allen, and Mislow[70] find that ΔE_d increases from 22 kcal/mol for PH_3 (D_{3h}) to 64 kcal/mol for PH_5. Furthermore, ΔE_d roughly doubles on going from SiH_4 (19 kcal/mol)[77] to SiH_5^- (36 kcal/mol)[80] using similar basis sets on silicon. Schwenzer and Schaefer's series H_2S (28 kcal/mol), SH_4 (59 kcal/mol), SH_6 (123 kcal/mol)[81] is also of interest, although the reported valence-shell d-orbital populations seem anomalous. Lastly, we note that even the larger basis sets yield quite large stabilization energies for SO_2[82,83] and PF_5.[68,84] Indeed, Rothenberg and Schaefer[82] have commented that d functions are much more important in SO_2 than in H_2S and have suggested that such functions are "required to describe the severely distorted S atom in SO_2". Our analysis suggests that the special factor is the fractional nature of the SO_2 π system.

In summary, while only a few suitable comparisons are available, we conclude that an increased sensitivity to d-orbital participation in "hypervalent" systems is indicated and that a meaningful distinction can be drawn between the participation of d orbitals as hybridization functions and as polarization functions. The systems of the type discussed by Musher

Table III. Participation of d Orbitals in Chemical Bonding

System	E_d[a]	ΔE_d[b]	d pop.[c]	Basis set[d]	Ref
SiH_4	−290.520	59	0.45	Min STO + 3d	BL[e]
	−291.236	19	0.11	$6s^{12}4p^{9}1d^{1}$	RYS[f]
SiH_5^-	−291.725	36		$6s^{12}4p^{9}1d^{1}$	WS[g]
PH_3 (C_{3v})	−338.796	48	0.26	STO-3G + split d	HS[h]
	−341.309	47	0.29	Min STO + 3d	BL[i]
	−342.450	32		$6s^{12}4p^{9}1d^{1}$	RAM[j]
	−342.452	21		6s3p1d GTO lobe	PW[k]
	−342.460		0.08	$6s^{12}4p^{9}1d^{1}$	RYS[f]
PH_3 (D_{3h})	−342.332	8	0.03	$7s^{10}4p^{6}1d^{1}$	KK[l]
	−342.385	22		$6s^{12}4p^{9}1d^{1}$	RAM[j]
PH_5 (D_{3h})	−343.457	35	0.29	$7s^{10}4p^{6}1d^{1}$	KK[l]
	−343.493	64		$6s^{12}4p^{9}1d^{1}$	RAM[j]
PH_3F_2 (D_{3h})	−541.102	51	0.34	$7s^{10}4p^{6}1d^{1}$	KK[l]
PF_3 (C_{3v})	−632.567	139	0.71	STO-3G + split d	HS[h]
PF_5 (D_{3h})	−832.94	276	1.13	$9s^{9}5p^{5}2d^{2}$	HVR[m]
	−837.837	129	0.64	$6s^{12}4p^{9}1d^{1}$	SV[n]
			0.74	$7s^{10}4p^{6}1d^{1}$	KK[l]
PN	−398.821		0.28	Min STO + 3d	BL[o]
PO ($^2\pi$)	−414.137		0.50	Min STO + 3d	BL[i]
	−415.630	23	0.29	Ext STO + 3d,4f	ML[p]
PO^- ($^3\Sigma^-$)	−414.117		0.74	Min STO + 3d	BL[i]
PO_2^-	−488.77		1.45	Min STO + 3d	BL[o]
P_2	−679.116	43	0.17	Min STO + 3d	BL[i]
	−681.500	29	0.17	Ext STO + 3d,4f	ML[p]
H_2S	−397.842	34	0.15	Min STO + 3d	BL[e]
	−398.682	32[q]	0.08	$6s^{12}4p^{9}2d^{2}$	RS[r]
	−398.686		0.06	$6s^{12}4p^{9}1d^{1}$	RYS[f]
	−398.693	28[q]	−0.07	$7s^{12}5p^{9}1d^{1}$	SS[s]
SH_4	−399.669	59[q]	0.05	$7s^{12}5p^{9}1d^{1}$	SS[s]
SH_6	−400.730	123	0.11	$7s^{12}5p^{9}1d^{1}$	SS[s]
SF_6	−992.931	185		"Very large GTO"	R[t]
SO_2	−541.008	226	1.17	STO-3G + d	HS[h]
	−541.050	252	1.27	STO-3G + split d	HS[h]
	−541.758		0.79	STO-3G, double ζ	GHS[u]
	−546.788	100	0.59	$6s^{10}4p^{6}1d^{1}$	RS[r]
	−547.209	162	0.43	$6s^{12}4p^{9}1d^{1}$	RS[v]
SO_4^{2-}	−688.428	589	2.87	STO-3G + split d	HS[w]
Cl_2	−919.006	19	0.08	Ext STO + 3d,4f	ML[p]

[a] Total energy with d orbitals, hartrees. [b] Energy lowering per second-row atom upon inclusion of d orbitals, kcal/mol. [c] Mulliken d-orbital population per second-row atom, electrons. [d] basis set on second-row atom: STO, Slater-type orbtial; GTO, Gaussian-type orbital; xa^y denotes x linear variation functions of symmetry a contracted from y primative GTO's. [e] Reference 78. [f] Reference 77. [g] Reference 80. [h] Reference 73b. [i] D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967). [j] Reference 70. [k] J. D. Petke and J. L. Whitten, *ibid.*, **59**, 4855 (1973). [l] Reference 68. [m] J. M. Howell, J. R. Van Wazer, and A. R. Rossi, *Inorg. Chem.*, **13**, 1747 (1974). [n] A. Strich and A. Veillard, *J. Am. Chem. Soc.*, **95**, 5574 (1973). [o] Reference 76; see also D. B. Boyd, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967. [p] Reference 67. [q] Includes effect of addition of p orbitals on H. [r] Reference 83. [s] Reference 81. [t] B. Roos, cited in F. A. Gianturco, C. Guidotti, U. Lamanna, and R. Moccia, *Chem. Phys. Lett.*, **10**, 269 (1971). [u] Reference 74. [v] Reference 82. [w] Reference 73a.

are indeed hypervalent, to some extent, but remain fractional to some extent also.

Finally, we note again that the analysis presented in this paper is subject to whatever limitations may be attached to the approach of addressing the octet rule in terms of the role played in the expansion of the wave function by the atomic orbitals assigned to the respective nuclear centers. It is clear that the difficulties encountered in this connection are especially severe for d orbitals, whose radial maxima may lie well into the bonding regions, if not actually closer to the attached atoms. However, the same uncertainties would seem to apply to the proposition that one can discuss molecules in terms of the atoms they contain. If, for example, one believes that valencies of atoms can be meaningfully discussed, as most chemists do, our analysis would seem to provide a reasonable vehicle for doing so.

VI. Summary

Many chemical systems yield localized-orbital structures fully in conformity with chemical intuition. For other systems, such as CO_2, CO_3^{2-}, O_3, XeF_2, PH_3F_2, and SO_2, however, five or more localized orbitals are found to be associated with a central atom. Given the unquestioned practical utility of the octet rule and of the usual rules of valence, these structures precipitate a crisis of sorts on the question of their interpretation in the context of the classical valence theory.

In the analysis developed here, localized molecular orbitals are termed *fractional* when two or more LMO's significantly utilize (overutilize) the same hybrid atomic orbital basis function on a given center. As a consequence of the Pauli exclusion principle, self-cancellations then occur in the expansion of the wave function. For a molecular-orbital wave function constructed from a minimum basis set of atomic orbitals, these self-cancellations resolve the apparent octet-rule violations by producing an expansion of the wave function in molecular-orbital or valence-bond structures which associate four or fewer pairs of valence electrons with the center in question. Compliance can also be shown by transforming the molecular orbitals unitarily in such a way that the valence AO's on the center in question participate in at most four of the transformed MO's. To be identifiable with normal chemical bonds, the localized orbitals must employ distinct orthogonal hybrid AO's at each center. At bottom, the exclusion principle prevents the occurrence of a "real" violation of the octet rule when a minimum basis set is used. An extended-basis-set wave function, in contrast, may, but need not, violate the octet rule.

An examination of the literature shows that Wheland,[15] Coulson,[16] and, in part, Musher[11] previously have expressed views compatible with those presented here. In contrast, other authors, including Samuel,[10] Bent,[9] Harcourt,[12] Gillespie,[13] and, in part, Musher[11] have taken positions substantially at odds with certain of those taken here. For example, Gillespie's VSEPR approach yields descriptions for CO_2 and $CO_3{}^{2-}$ similar to those obtained by localizing the molecular orbitals[4] but improperly implies that the octet rule is violated, because it proceeds from an assumption (i.e., that localized electron pairs necessarily occupy regions of space which contain one and only one electron of given spin) which is incompatible with the concept of fractionality. In addition, Harcourt's use of the term "increased valence" and Musher's use of the term "hypervalent" in contexts in which the octet rule is obeyed are questioned. It is shown, in contrast, that the Armstrong-Perkins-Stewart definition of valency[61] provides a criterion for hypervalence which requires that the octet rule simultaneously be violated when a single-determinant wave function is used.

Finally, systems containing second- and higher row atoms, where minimum basis sets become much less appropriate, are examined. Here, the concept of fractionality is found to provide a basis for distinguishing between the participation of d orbitals in chemical bonding as polarization functions and as "hybridization" functions. In the latter case, d orbitals characteristically serve to reduce the overlap between the hybrid AO's utilized in fractional bonds, though not necessarily to the point at which the overlap vanishes, consequently reducing the degree of fractionality and increasing the valency of the fractionally bonded atom. Moreover, this view shows that the much discussed alternative three-center, four-electron and d-orbital hybridization schemes are not mutually exclusive, but rather constitute limiting points along a continuous progression, the "progress variable" being the d-orbital population. Ab initio calculations are surveyed and are found to confirm that d orbitals are particularly important under the expected circumstances, i.e., when fractional bonding is present.

Note Added in Proof. As a result of recent communications with Professor R. D. Harcourt, we wish to elaborate on a point raised in the first paragraph of "Valency, Bond Orders, and Hypervalence" in section IV. Our stated objection to Harcourt's "method of counting electrons in terms of orbitals" is appropriate when Harcourt employs doubly-occupied bond orbitals for the two-electron bonds of his "increased-valence" formulas.[12] As Harcourt points out,[12a] spin-correlation effects then arise, and certain of the bond orbitals are fractional (our term). In this approach, the (unnormalized) "increased-valence, bond-orbital" wave function for the π system of structure **31a** for ozone would be written as

$$\Psi(\mathrm{IVBO}) = |\pi_\ell \bar{\pi}_\ell \pi_r \bar{r}| + |\pi_\ell \bar{\pi}_\ell r \bar{\pi}_r|$$

where ℓ, c, and r denote $2p_\pi$ AO's on the left, center, and right oxygens, $\pi_\ell = (c + k\ell)/(1 + k^2)^{1/2}$, $\pi_r = (c + kr)/(1 + k^2)^{1/2}$, and k is a variational parameter. Bars denote β spin functions. No comparable spin correlation occurs in Harcourt's alternative "increased-valence, Heitler-London" formulation,[12a,c,d] in which the wave function for **31a** becomes

$$\Psi(\mathrm{IVHL}) = |\ell \bar{c} \pi_r \bar{r}| + |c \ell r \bar{\pi}_r|$$

since no AO appears more than once with the same spin function in the expansion of either determinant of $\Psi(\mathrm{IVHL})$. Harcourt concludes that three π electrons (those occupying spin orbitals ℓ, $\bar{c}$, and π_r or c, ℓ, and $\bar{\pi}_r$) participate in the bonding to the central oxygen, O_c, and that the $\Psi(\mathrm{IVHL})$ wave function therefore may represent an increase in valence at the central atom depending upon the value of the parameter k.[12b] In our view, however, just two π electrons (those occupying $\bar{c}$ and π_r or c and $\bar{\pi}_r$) are involved in the bonding to O_c in $\Psi(\mathrm{IVHL})$, and the normal rules of valence are preserved. To count ℓ or ℓ as participants in the bonding to O_c, and to implement the intended descriptions of the O_ℓ–O_c two-electron bonds of the IVBO and IVHL structures as, respectively, molecular-orbital and valence-bond pair functions,[12a,c,d] the "IVHL" wave function for **31a** should be written as

$$\begin{aligned}\Psi'(\mathrm{IVHL}) &= |(\ell \bar{c} + c\ell)\pi_r \bar{r}| + |(\ell \bar{c} + c\ell) r \bar{\pi}_r| \\ &= \Psi(\mathrm{IVHL}) + |c\ell \pi_r \bar{r}| + |\ell \bar{c} r \bar{\pi}_r|\end{aligned}$$

in accordance with the accepted form for a wave function containing two singlet-coupled Heitler-London pair functions.[85] Three of the four electrons now apparently are associated with the bonding to O_c, but spin-correlation effects produce self-cancelling terms in the two additional determinants of $\Psi'(\mathrm{IVHL})$, and our original objection to counting electrons in terms of orbitals again applies. Thus, whether $\Psi(\mathrm{IVHL})$ or $\Psi'(\mathrm{IVHL})$ is used, we take exception to Harcourt's use of the term "increased valence". (Interestingly, we note that the summed bond numbers plus bond orders computed by Harcourt are somewhat smaller for "increased-valence" structures than for the simple molecular-orbital structures.[12a]) Finally, we note that Harcourt does clearly recognize (and signifies by employing light, rather than heavy, bond lines) that certain "two-electron" bonds in "increased valence" structures have special character. For example, the resolution of $\Psi(\mathrm{IVHL})$ into canonical valence-bond structures produces a linear combination of one structure which has a conventional Heitler-London O_ℓ–O_c pair bond plus an unshared pair on O_r and a second structure which has an O_ℓ–O_r long bond. The O_ℓ–O_c bond in $\Psi(\mathrm{IVHL})$ thus is a partial bond, though it is not fractional in the sense that we have defined the term.

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References and Notes

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(30) That the condition stated is a minimal condition is shown by the results of a study of electron-pair bond loges and exclusivity by R. F. W. Bader and M. E. Stephens [*J. Am. Chem. Soc.*, **97**, 7391 (1975)] which appeared shortly before this paper was submitted. These authors find that while nonoverlapping bond loges possess appreciable exclusivity ("localizability") in LiH, BeH_2, BH_3, and BH_4^-, such a description holds much less well for CH_4 and not well at all for H_2O, HF, and other systems. See also ref 27.

(31) Strictly speaking, carbon's atomic orbitals participate in more than three σ LMO's as a consequence of a slight delocalization of the σ lone pairs on the oxygen atoms. However, we show later that it is always possible to transform the MO's in such a way that a first-row atom's valence AO's participate in just four MO's when a minimum basis set is used. In the present case, three of these MO's will be σ orbitals, and the fourth will be the π CMO of A_1'' symmetry.

(32) G. G. Hall and J. Lennard-Jones [*Proc. R. Soc. London, Ser. A*, **205**, 357 (1951)] recognized at an early date that a departure from strict localization is a characteristic feature of conjugated (resonance stabilized) systems. See also ref. 6c.

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(37) For CO_2, the expansion for one of the π_x LMO's is $0.819\chi_O + 0.412\chi_C - 0.183\chi_{O'}$ in an obvious notation. The remaining π LMO's are related by symmetry.

(38) This result follows from the fact that the same AO on the central atom participates in both LMO's, necessitating an offsetting negative contribution to the overlap. Note, however, that the third center need not carry a large Mulliken population, since the contributing overlap and net atomic populations will have opposite signs.

(39) Note that $|f + g| = |f| + |g|$, where f and g are orbital product functions. Structure **17** arises because of a double counting in the sum **12** + **13**.

(40) In approaches 1 and 3, certain of the simple structures typically will associate fewer than four pairs of electrons with some centers, in part as a consequence of the incorporation of ionic character in the MO wave function.

(41) (a) Suppose that χ_{1a}, the first hybrid VAO on center A, has been isolated to the first of the N molecular orbitals via the obvious series of $N - 1$ successive two-orbital transformations. Since the one-center matrix element $P(\chi_{1a},\chi_{ja})$ for $j \neq 1$ is zero in the VAO basis and χ_{1a} does not appear in any transformed MO beyond the first, it follows that the remaining VAO's cannot appear in the first transformed MO. The second VAO on A can then be isolated to the second transformed MO, etc. Note that if A has n VAO's, the last $N - n$ transformed MO's produced by this procedure will be indeterminate to within a unitary transformation. (b) Ordinarily, VAO's do not correspond to the hybrid AO's which appear in localized molecular orbitals, but rather are symmetry functions, when such exist (cf. ref 23).

(42) Net atomic populations are invariant to a unitary transformation of the doubly occupied MO's. Thus, the net atomic population of a VAO is simply twice the square of the VAO coefficient in the MO to which it can be isolated. Hence, appreciable net atomic populations for more than four VAO's imply an octet-rule violation.

(43) To demonstrate rigorous compliance, it would seem necessary to show that the exact wave function can be expanded as a sum of Slater determinants, each constructed from a (possibly different) minimum basis set of atomic orbitals. We do not believe that such a proof can be given, though it would be of interest to test the accuracy of optimal wave functions of this type.

(44) The term fractionality was first used (by us) in ref 5a,b. The present definition (cf. ref 45) is more precise.

(45) Note that the appearance of the four hybrid valence AO's of center A in five or more LMO's associated with center A is a sufficient, but not a necessary, condition for an "overutilization of the function space". The necessary and sufficient condition is that orthogonal components of the AO function space cannot be matched on a one-to-one basis with the MO's associated with center A. Thus, an overutilization arises, to a degree, whenever the associated LMO's employ nonorthogonal hybrid AO's on the center in question, as usually occurs (see ref 14).

(46) The process of formation of chemical bonds can be viewed as arising from the lowering of the kinetic energy associated with the smoothing of the wave function which results when the amplitudes of the contributing atomic orbitals are superimposed [ref 23; see also C. W. Wilson, Jr., and W. A. Goddard III, *Theor. Chim. Acta*, **26**, 195 (1972); W. A Goddard III and C. W. Wilson, Jr., *ibid.*, **26**, 211 (1972); and K. Ruedenberg in "Localization and Delocalization in Quantum Chemistry", Vol. I, O. Chalvet et al., Ed., D. Reidel, Dordrecht, Holland, 1975, pp 223–245]. For fractional LMO's, the presence of the appreciable tails of opposite phase (cf. ref 38) limits the lowering of the kinetic energy and therefore diminishes the ultimate binding energy obtained upon readjustment of the wave function pursuant to the dictates of the virial theorem.

(47) When n equivalent bond orbitals utilize an m-dimensional atomic-orbital function space (e.g., the four equivalent fractional C–O π-bond orbitals in CO_2 utilize two π AO's on carbon), the degree of fractionality can be defined as m/n. Less restrictive definitions for use with nonequivalent fractional bond orbitals are presently under study by one of us (T.A.H.).

(48) Bent also suggests in ref 9, without elaboration, that compliance with the octet rule might alternatively be taken to mean that four valence AO's per atom are sufficient to approximate the wave function, as is the case in the systems in question.

(49) U. Vogeli and W. von Philipsborn [*Org. Magn. Reson.*, **5**, 551 (1973)] have recently shown that **25** exists in solution in the tautomeric form 3-hydroxypyridine. However, the questions of interpretation which arise for structures such as **25** are still valid, and indeed appear to apply unchanged for the analogous *N*-methyl systems studied by Paoloni (ref 7a,b).

(50) Paoloni incorrectly implies in ref 7a,b that the VB wave function for **25** vanishes identically, i.e., contains only self-cancelling terms. In fact, a long-bond structure is produced which has a lone pair on nitrogen and a π bond between the flanking carbons. Nevertheless, the objection raised by Paoloni and co-workers to the uncritical interpretation of structural formulas in valence-bond terms was both well placed and timely.

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(72) Note that the contributions from other valence OAO's should not be greatly diminished, since a change in population for a hybrid OAO strongly involved in bonding (hence having a population of ~1 electron) changes its contribution to the valency only to second order; cf. eq 7.

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Structure and Formation of Gaseous $C_2H_5S^+$ Ions[1]

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Abstract: Characterization of $C_2H_5S^+$ ions in the gas phase using their collisional activation (CA) spectra shows that only $CH_3SCH_2^+$ (**a**), CH_3CHSH^+ (**b**), and $\overline{CH_2CH_2S}H^+$ (**d**) are stable. Contrary to previous evidence, $CH_3CH_2S^+$ (**c**) is less stable, isomerizing to **b** in $<10^{-5}$ s, and no evidence for the formation of $HSCH_2CH_2^+$ (**e**) or $CH_2{=}CHSH_2^+$ (**f**) could be found. The cyclic ion **d** is relatively more stable than its $C_2H_5O^+$ analogue, this isomer accounting for most of the $C_2H_5S^+$ ions formed in the mass spectra of *n*-alkyl thiols. For decompositions of $C_2H_5SR^{+\cdot}$ ions, C-S bond cleavage is facile in comparison to C-O scission in ethyl ethers, despite the relatively low stability of the initial product **c**; apparently the looseness of the activated complex is an important factor in making this reaction competitive. A variety of mechanisms for the formation of such ions (eq 1-6) were tested, and the isomeric products in general agree with the predicted structures.

Of the possible isomeric ions of the formula $C_2H_5S^+$, **a**–**f** (Table I), several have been postulated as products of unimolecular ion decompositions in the mass spectra of thiols and thioethers[3-6] and of ion-molecule reactions.[7,8] In an effort to obtain more conclusive data, we have examined $C_2H_5S^+$ isomers from a variety of sources using collisional activation (CA) mass spectra; such data have proven to be uniquely useful for structural characterization of gaseous organic ions of lifetimes $\geq 10^{-5}$ s, as CA spectra are insensitive to ion internal energy.[9] This report constitutes an extension of previous CA studies of analogous even-electron $C_2H_5O^+$ and $C_2H_6N^+$ isomers,[10] probing the effect of replacing a first-row heteroatom by a second-row analog.

The major fragmentation pathways proposed previously for the mass spectra of thiols and thioethers are shown in Scheme I; formation of isomers **a**–**c**, and **d** or **e**, is consistent with isotopic labeling and correlative evidence.[3-6] No studies postulating the formation of isomer **f** were found.

Isomers **c** and **d** have attracted particular interest; the abundances of peaks corresponding to the formation of these ions by reactions 4 and 5 are remarkable in comparison to the mass spectra of the corresponding oxygen-containing compounds.[3-5] The mass spectrum of CH_3CD_2SH shows $[(M - D)^+]/[(M - H)^+] = 45{:}55$, which was interpreted to indicate that **c** formation (eq 4) is equivalent to that of **b** (eq 1),[6] in sharp contrast to the behavior of oxygenated compounds.[11] Appearance potential studies find the heat of formation (ΔH_f) of $C_2H_5S^+$ ions thought to have structures **a, b,** and **c** to be experimentally indistinguishable,[5,6] and higher than the estimated value of **d**;[7] in contrast, the values for the oxygenated analogs show substanital differences (Table I). The ΔH_f value of $(C_2H_5S)^+$ derived from C_2H_5SH of 203 kcal/mol[6] (210 for $C_2HD_4S^+$ from C_2D_5SH)[5] presents a special dilemma, as this should represent a minimum value for ions **b, c,** and **d** (eq 1, 4, and 5, respectively) if these are formed without reverse activation energy. The apparent equivalence in stability of **c** to that of **a** and **b**, in contrast to their oxygen analogs, has been attributed by Keyes and Harrison[5] to the much *less* effective resonance stabilization of **a** and **b**, lowering their stabilities to be comparable to that of **c**. However, SCF molecular orbital calculations[12] for $HOCH_2^+$ and $HSCH_2^+$ indicate that sulfur forms a *stronger* π bond to the adjacent cationic center than does oxygen. It has also been suggested that the formation of **c** is more competitive relative to that of its oxygen analog owing to the greater ability of sulfur to stabilize the positive charge on itself in ion **c**. [3c]It should be noted that no direct experimental evidence for the existence of the $CH_3CH_2S^+$ isomer **c** appears to have been reported.

The cyclic ion **d** has also eluded direct experimental characterization.[13] Formation of **d** by eq 5 has been proposed to account for the much larger relative abundance of $(C_2H_5S)^+$ ions in the spectra of *n*-alkyl thiols than that of $(C_2H_5O)^+$ in