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Spin-coupled description of the chemical bonding to hypercoordinate chlorine

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Abstract. Modern valence bond theory, in its spin-coupled form, is used to investigate the nature of the bonding in hypercoordinate chlorine fluorides. In each of ClF_2^+, ClF_3, ClF_4^+, ClF_5 and ClF_3O the description that emerges is of very polar two-centre two-electron bonds. The orbital picture is fairly transferable from one system to another: the differences between "normal octet" and hypercoordinate species, or between cations and neutrals, are relatively small.

Key words: Spin-coupled approach – Chlorine fluorides – Hypercoordinate – Valence bond theory

1 Introduction

Chemical species such as ClF_4^+ and ClF_5 may be termed "hypercoordinate", in the sense that the number of F atoms formally covalently bonded to Cl exceeds the maximum predicted by the familiar octet rule. A traditional model of the bonding, deeply rooted in classical valence bond (VB) theory, ascribes this apparent "expansion of the octet" to the supposed utilization of 3*d* orbitals as "valence" orbitals; in the case of chlorine compounds, we are supposed to distinguish between sp^3 (ClF_2^+, ClFO and $ClFO_2$), sp^3d (ClF_3, ClF_4^+, ClF_3O and ClF_3O_2) and sp^3d^2 (ClF_5 and ClF_6^+) hybridization schemes. Of course, a great deal of evidence has now accumulated that the bonding in such molecules has very little to do with the availability of *d* atomic orbitals (see, for example, Refs. [1–11], and references therein). Instead, most of the reliable ab initio investigations published in recent years have placed much greater emphasis on the polarity of the bonds and on the size of the central atom. In terms of the types of basis set typically used in contemporary calculations, the consensus view is that there is no clear-cut demarcation for second-row atoms in the utilization of d functions between hypercoordinate and so-called "normal octet" species, or in the optimum d exponents, or in the energy penalty per bond of excluding such functions. It seems that the role of d functions for second-row atoms is to act mostly as polarization functions, albeit to a greater extent than for first-row atoms.

Modern VB theory, in its spin-coupled form [12], has been used to argue that there are no significant qualitative differences between the hypercoordinate nature of first-row, second-row and noble gas atoms in appropriate chemical environments or between the bonding in "normal octet" and hypercoordinate molecules, except for some differences in bond polarity [10, 13]. The purpose of the present work is to extend those various studies to the fluorides of hypercoordinate chlorine, taking as our examples ClF_2^+, ClF_3, ClF_4^+, ClF_5 and ClF_3O.

2 Computational procedure

The ab initio spin-coupled wavefunctions used in the present work may be written [12]

$$\Psi_{sc} = \mathscr{A}\left[\left(\prod_{i=1}^{n}\psi_i\alpha\psi_i\beta\right)\left(\prod_{\mu=1}^{N}\phi_\mu\right)\Theta_{SM}^{N}\right] \quad , \tag{1}$$

in which the ϕ_μ are singly occupied nonorthogonal spin-coupled orbitals which accommodate the *N* active electrons. The total wavefunction is not invariant to arbitrary unitary transformations of these active orbitals. The total spin function for the active electrons, Θ_{SM}^{N} labelled according to the eigenvalues of $\hat{S}^2$ and $\hat{S}_z$ is expanded in the full spin space [14]. In general, we may also simultaneously optimize the *n* inactive orbitals ψ_i. It is straightforward nowadays also to construct fully variational multiconfiguration modern VB wavefunctions [15]. Typically, a one-configuration *N*-electron spin-coupled wavefunction is very similar to the corresponding many-configuration "*N* electrons in *N* orbitals" complete-active-space self-consistent field function, but it is obviously much more compact and thus much easier to interpret directly.

Geometries were taken from experimental data [16], where available, or from appropriate geometry optimizations. The shapes of the various species are shown in Fig. 1, in which the positions of the fluorine atoms are designated as axial, equatorial, apical or basal. On comparing the geometries of ClF_3 and ClF_3O, we notice that the formal addition of an O atom has no significant influence

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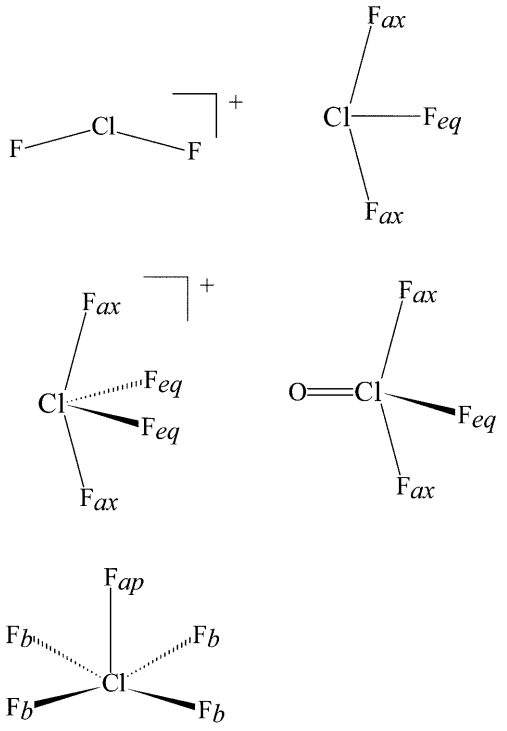

Fig. 1. Schematic representation of the shapes of ClF_2^+, ClF_3, ClF_4^+, ClF_3O and ClF_5. The positions of the fluorine atoms are designated as axial (*ax*), equatorial (*eq*), apical (*ap*) or basal (*b*)

on the axial or equatorial Cl—F bond lengths. The ClO separation in ClF_3O (140.5 pm) is very much shorter than for a typical Cl—O single bond (about 172 pm). In the case of ClF_2^+ the bond length and, particularly, the bond angle depend on the identity of the counterion. We used values of 154.4 pm and 99.7°.

Using basis sets of triple-zeta valence polarization quality [17, 18], as implemented in the GAMESS-UK package [19], we generated sets of localized molecular orbitals (LMOs) from restricted Hartree–Fock valence MOs according to the population localization criterion of Pipek and Mezey [20]. In each case, it proved straightforward to identify LMOs associated with individual Cl—F bonds, Cl=O bonds, chlorine lone pairs and the various nonbonding electrons on the peripheral atoms. The forms of the LMOs indicate fairly high similarity between analogous bonds in the different systems, and they provide no evidence for active *d*-orbital participation in the bonding. We initially performed spin-coupled calculations in which we treated as active only those electrons involved in Cl—F bonds and Cl=O bonds, fixing the inactive orbitals (the ψ_i in Eq. 1) to be the appropriate LMOs. The only restriction on the form of the active orbitals is that we effectively invoked σ–π separation in the ClO unit of ClF_3O. We subsequently relaxed this restriction. In the case of ClF_3 and ClF_4^+, we examined the effect of treating as active also the nonbonding valence electrons on chlorine.

For each system, we found that the optimized spin-coupled orbitals consist of pairs, each clearly associated with a particular two-centre bond (or with a chlorine lone pair) and with predominantly singlet coupling of the electron spins. Although no such constraints were employed in the calculations, the permutational symmetry of the converged spin-coupled orbitals is consistent with the molecular point group.

3 Results and discussion

It is useful to recall at this stage that ClF_2^+ is a "normal octet" species and so we may use it as a benchmark for judging all the other systems. Symmetry-unique spin-coupled orbitals for ClF_2^+ are shown in the top row of Fig. 2. Orbital ϕ_1 consists of a very distorted sp^x-like hybrid on chlorine that incorporates a substantial component on fluorine. A simplistic Mulliken population analysis of this orbital suggests 76% chlorine character. Orbital ϕ_2 takes the form of a distorted 2p function on fluorine and overlaps almost exclusively with ϕ_1: $\langle\phi_1|\phi_2\rangle = 0.77$. Orbitals ϕ_3 and ϕ_4 are the counterparts in the other bond. The total spin function is overwhelmingly dominated by the perfect pairing mode (99.8% in the Serber basis). Thus, the spin-coupled description corresponds to very polar two-centre two-electron bonds.

We turn now to ClF_4^+, for which symmetry-unique spin-coupled orbitals are shown in the second row of Fig. 2. It is relatively difficult to distinguish by eye between the orbitals that make up the equatorial ($\{\phi_1, \phi_2\}$, $\{\phi_3, \phi_4\}$) and axial ($\{\phi_5, \phi_6\}$, $\{\phi_7, \phi_8\}$) bonds. Indeed, the contour plots are remarkably similar to those for ClF_2^+, as are the key overlaps $<\phi_1|\phi_2> = 0.76$ and $<\phi_5|\phi_6> = 0.75$. The full overlap matrix is shown in the upper triangle of Table 1. Simplistic Mulliken analysis suggests 79% chlorine character in ϕ_1 and 72% chlorine character in ϕ_5. The perfect pairing mode again dominates the total spin function (99.6%). Independent of any preconceptions about the importance of counting to 8, it is clear that the spin-coupled descriptions of ClF_2^+ and ClF_4^+ are actually rather similar.

Additional spin-coupled calculations were performed for ClF_4^+, in which we treated as active also the two nonbonding valence electrons on chlorine. At convergence of the spin-coupled procedure, the two additional orbitals (ℓ_1 and ℓ_2) were found to take the form of two angularly split lone-pair-like orbitals at the "empty" position in the equatorial plane of the trigonal bipyramid. These nonbonding orbitals are much more compact that the corresponding bonding hybrids ($<\ell_1|\ell_2> = 0.85$). The full overlap matrix is recorded in the lower triangle of Table 1 and it is clear that although there are some significant overlaps between the nonbonding and bonding hybrids, the overlaps amongst ϕ_1–ϕ_8 show relatively small changes from before. Contour plots of ϕ_1–ϕ_8 were also found to be essentially identical to those from the smaller calculation. The perfect pairing mode remains dominant.

It is interesting to determine to what extent the overall charge on the ClF_2^+ and ClF_4^+ cations influences the polarity of the Cl—F bonds relative to those in the neutral species ClF_3 and ClF_5. Symmetry-unique spin-coupled orbitals for ClF_3 are shown in the third row of Fig. 2. By comparing with the two cations, we see that orbital ϕ_1 (equatorial bond) and, especially, orbital ϕ_3 (one of the axial bonds) show enhanced fluorine character. Simplistic Mulliken analysis suggests chlorine character of 73% and 59%, respectively. The key overlaps ($<\phi_1|\phi_2> = 0.75$ and $<\phi_3|\phi_4> = 0.75$) are much the same as for the cations, and the perfect pairing mode is again dominant (99.6%). All in all, the equatorial and, especially, the axial bonds in ClF_3 appear to be slightly more polar than those in ClF_4^+. We performed addi-

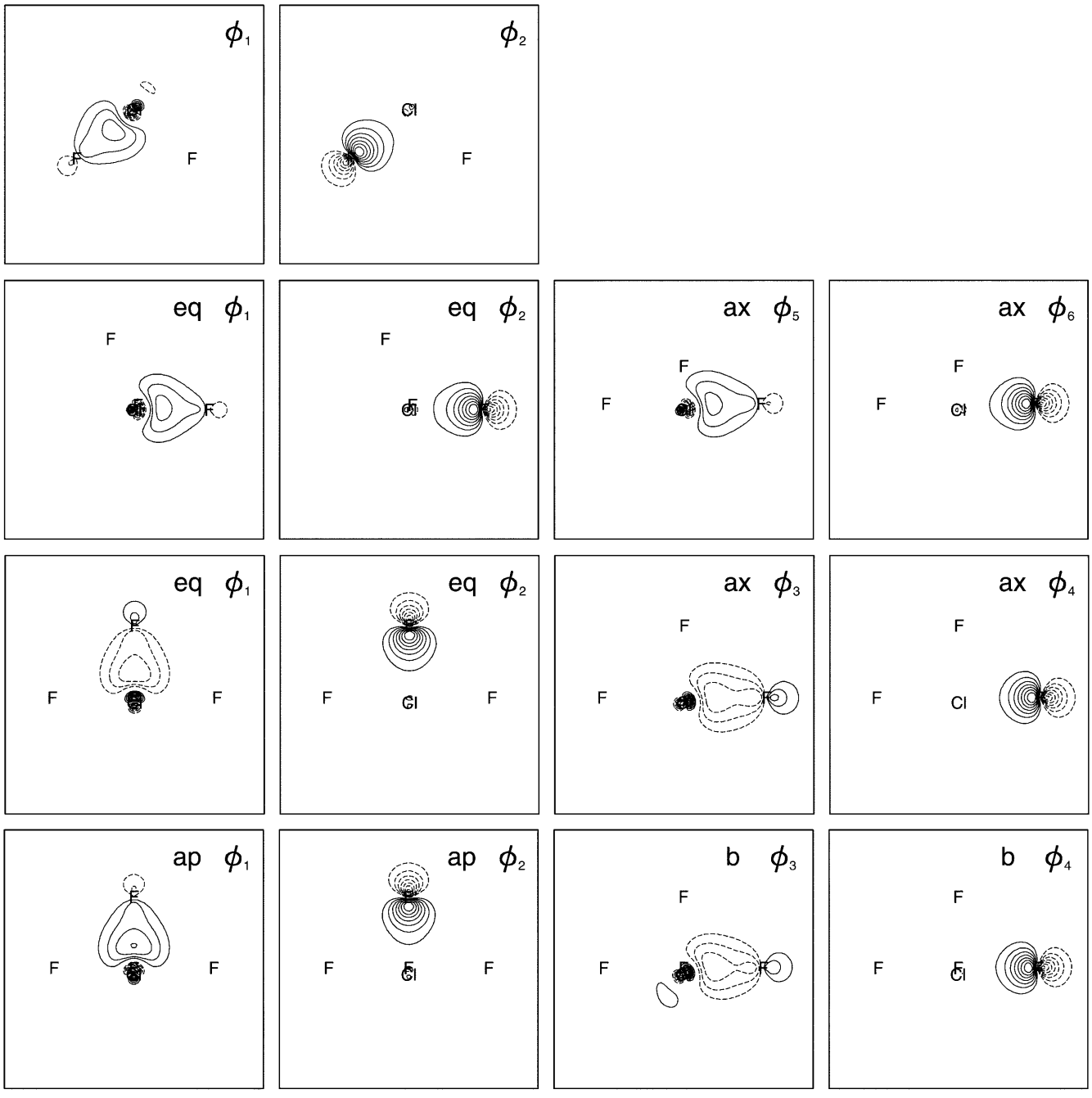

Fig. 2. Symmetry-unique spin-coupled orbitals shown as contour plots in appropriate planes, with (projected) positions of nuclei marked by their chemical symbols. Successive rows relate to ClF_2^+, ClF_4^+, ClF_3 and ClF_5, as described in the text

tional calculations for ClF_3, in which we treated as active also the four nonbonding electrons on chlorine; the differences in the description of the Cl—F bonds were very small. It seems fair to conclude that it is not necessary for the other systems considered in this work to treat as active the chlorine nonbonding electrons.

We find that the symmetry-unique spin-coupled orbitals for ClF_5 (bottom row of Fig. 2) are similar to those for the other systems, in spite of the larger number of bonds. Simplistic analysis suggests chlorine character of 80% and 67%, respectively, for ϕ_1 (apex) and ϕ_3 (base). The key overlaps are $<\phi_1|\phi_2> = 0.74$ and $<\phi_3|\phi_4> = 0.75$, with the perfect pairing mode representing 99.3% of the total spin function. Our description corresponds, again, to highly polar two-centre two-electron bonds, with no evidence for any significant involvement of d functions as valence orbitals.

The final system considered in the present work is the chlorine fluoride oxide ClF_3O. Symmetry-unique spin-coupled orbitals involved in the Cl—F bonds are shown in the top row of Fig. 3. The key overlaps are $<\phi_1|\phi_2> = 0.76$ and $<\phi_3|\phi_4> = 0.75$. Simplistic analysis of ϕ_1 (equatorial) suggests 72% chlorine character, whereas the corresponding value for ϕ_3 is 60%.

Table 1. Orbital overlaps for ClF_4^+ with chlorine nonbonding electrons treated as active (*lower triangle*) or as inactive (*upper triangle*)

	ℓ_1	ℓ_2	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8
ℓ_1	1									
ℓ_2	0.80	1								
ϕ_1	0.42	0.17	1	0.76	0.18	0.04	0.31	0.09	0.31	0.09
ϕ_2	0.16	0.01	0.74	1	0.04	−0.01	0.12	0.00	0.12	0.00
ϕ_3	0.17	0.42	0.28	0.06	1	0.76	0.31	0.09	0.31	0.09
ϕ_4	0.01	0.16	0.06	−0.02	0.74	1	0.12	0.00	0.12	0.00
ϕ_5	0.38	0.38	0.39	0.13	0.39	0.13	1	0.75	−0.22	−0.09
ϕ_6	0.15	0.15	0.13	−0.01	0.13	−0.01	0.74	1	−0.09	−0.02
ϕ_7	0.38	0.38	0.39	0.13	0.39	0.13	−0.06	−0.05	1	0.75
ϕ_8	0.15	0.15	0.13	−0.01	0.13	−0.01	−0.05	−0.01	0.74	1

The similarities to ClF_3 are rather obvious, but it is also useful to notice that the $\{\phi_1,\phi_2\}$ pair in ClF_3O is actually little changed from that in the "normal octet" species ClF_2^+.

The second row of Fig. 3 shows the spin-coupled orbitals involved in the ClO σ and π bonds. Orbital σ_1 is based on an sp^x-like hybrid on Cl, but it exhibits some delocalization onto the O atom. Its "partner", σ_2, with $<\sigma_1|\sigma_2> = 0.84$, is a somewhat deformed O(2p) function. The corresponding π bond is very much more polar. Simplistic analysis suggests 88% chlorine character for σ_1, whereas the corresponding value for π_1 is only 49%. The second π electron is accommodated in an $O(2p_\pi)$ orbital ($<\pi_1|\pi_2> = 0.79$). The slight asymmetry in the contour plot of π_1 is linked to a nonnegligible overlap with the equatorial bonding hybrid ($<\phi_1|\pi_1> = 0.41$). As might now be expected, the total spin function for ClF_3O is dominated by the perfect pairing mode, with a weight of 96.5%.

We carried out additional calculations for ClF_3O in which we lifted the restriction of σ–π separation. The availability of additional degrees of freedom leads to a modest lowering of the total energy. The description of the Cl—F bonds is essentially unchanged, but the ClO unit is now described instead in terms of two Cl-based and two O-based bent-bond orbitals, which are fairly similar to linear combinations of the previous σ–π separated orbitals.

4 Conclusions

Using only 3*s* and 3*p* atomic orbitals, we can of course generate no more than four linearly-independent sp^x hybrid orbitals localized on chlorine. However, we may easily form a greater number of (formally) Cl-based orbitals if we allow each sp^x-like hybrid to delocalize onto the peripheral atoms, as in the spin-coupled

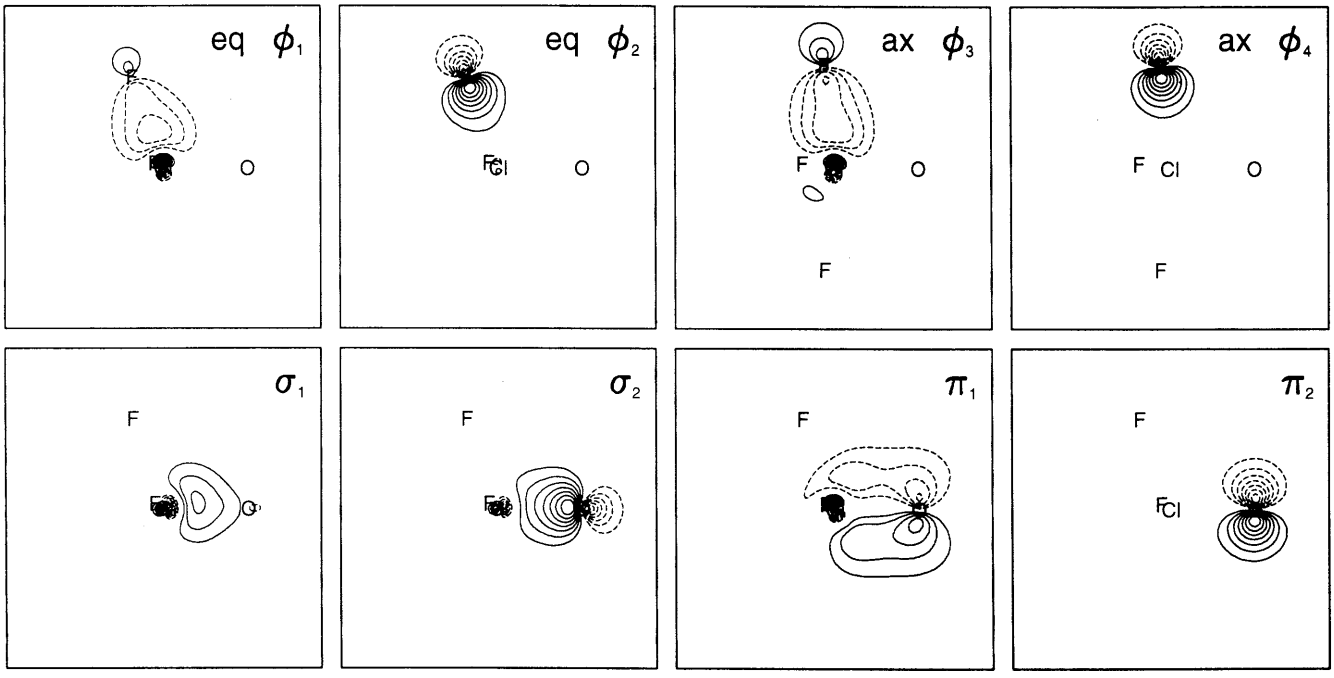

Fig. 3. Symmetry-unique spin-coupled orbitals for ClF_3O, shown as contour plots in appropriate planes, with (projected) positions of nuclei marked by their chemical symbols

calculations. In this model, the bonding in ClF_2^+, ClF_3, ClF_4^+, ClF_5 and ClF_3O is described in terms of very polar two-centre two-electron bonds. The orbital description is fairly transferable from one system to another, with no significant differences between "normal octet" and hypercoordinate species, or between cations and neutrals. One consequence of the high polarity of the bonds is that the total electron population around the chlorine atom is much lower than might be expected from naïve counting based only on the number of bonds to peripheral atoms.

The very compact spin-coupled descriptions presented here could, of course, be expanded in terms of classical VB structures based on strictly localized orbitals. In this way, the wavefunctions could be re-expressed in terms of resonance between a plethora of ionic structures, each of which is consistent with the octet rule. Thus, whether or not one wishes to ascribe aspects of the bonding to so-called "expansion of the octet" is largely a matter of taste.

As in our previous work, we have found it useful to employ an aide-memoire which we call the "democracy principle": almost all valence electrons can participate in chemical bonding if provided with sufficient energetic incentives. Simple concepts of atomic size and of bond polarity (often linked to electronegativity differences) have proven to be of particular utility in qualitative descriptions of the bonding. High formal oxidation states are more likely to occur in molecules with (some) highly polar $X=O$ double bonds than in systems with larger numbers of X–F bonds.

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