On electron counting rules: doublet, octet and 18-electron.

1. Introductory comments

The octet rule is one of the pillars of a chemical education: we learn from a very early stage that main group elements accumulate four pairs of electrons in their valence shell and this simple idea pervades all aspects of our subsequent thinking about structure, stability and mechanism. Lewis' concept of a stable octet was published just over a century ago in 1916, but in fact many of the key ideas can be traced back to Abegg's earlier idea of normal and contravalence and, before that, to Mendeleev's formulation of the period table. In any case, the idea most certainly predates the development of modern wave mechanics, but when the quantum theory of atomic structure did emerge shortly after Schrödinger's work, it immediately provided a conceptually simple rationale for the octet rule. The valence shell contains the *ns* and three *np* orbitals, and if all four are 'used' to accommodate a pair of electrons, we arrive at an octet. The use of inverted commas around 'used' is deliberate here: the sense in which the orbitals are 'used' is a common source of misunderstanding to which I will return later. The central position of the octet rule in foundation chemistry courses owes much to its almost universal success - it works for the vast majority of main group compounds. Indeed, to find genuine exceptions to the octet rule we have to look to the heavier elements of groups 3 and 4, where the inert pair effect stabilises compounds with valence two fewer than the group oxidation: divalent Sn and Pb, for example. The 18-electron rule, first formalised by Langmuir as an extension to Lewis' octets, is, at least in principle, a straight-forward extension, where full 'use' of the nine valence orbitals, $(n+1)s$, $(n+1)p$ and nd, available to a transition metal leads to the accumulation of 18 electrons. However, unlike the octet rule, the 18-electron rule is rigorously obeyed by only a relatively small sub-class of transition metal chemistry, that being organometallic chemistry, and even there, strict adherence to the rule is limited to complexes bearing strong π-acceptor ligands. Beyond this rather narrow subset of compounds, complexes that do not obey the 18-electron rule are in fact the norm rather the exception, and there are countless examples where the electron count is less than 18 along with a smaller, but still substantial, number where it exceeds 18. It is perhaps worth noting that many important biological events are catalysed by one-electron redox processes at transition metal centres, and it goes without saying that the two members of the redox pair cannot both have an 18-electron configuration: if the 18-electron rule were as ubiquitous as the octet rule seems to be, there would be no life!

Given that exceptions to the 18-electron rule are so common and so chemically diverse, it is perhaps inevitable that many different explanations have been put forward to explain them, including π donation from ligands, ionic bonding and steric effects. This diversity of apparently unconnected explanations does, however, tend to obscure the simple differences between the main-group and the transition elements that lead, in a very general sense, to the almost universal adherence to the octet rule but not the 18-electron rule. In the following sections, I will show that all the exceptions to both rules can, ultimately, be traced to the very different radial properties of the valence orbitals involved.

If we accept as a starting point the idea that an octet or 18-electron count implies that the complex is 'using' all of its available valence orbitals, *ns* and *np* or $(n+1)s$, $(n+1)p$ and nd, respectively, the obvious inference then is that complexes with fewer than 8 or fewer than 18-electrons must not be ‘using’ one or more of these orbitals. Why is this failure to make optimum use of the available orbitals apparently so much more common in the transition series than in the main group? In the latter, the valence orbitals share the same principal quantum number (*ns* and *np*), and as a result the average distance of the electron from the nucleus (the expectation value, <*r*>) is similar for both (radial distribution functions for Ge, an exemplary main group element, are shown in Figure 1a). This, in turn, means that the overlap of a bonding partner (the 1*s* orbitals of H in GeH_4, for example) will be approximately equal for both *ns* and *np* orbitals, and so there is no particular reason why some of these orbitals should be used to accommodate electrons (either bonding or lone pairs) while others are left vacant. In fact Kutzelnigg has argued that the emergence of the inert pair effect in the heavier members of groups 3 and 4 (the only genuine departure from the octet rule) can be traced directly to the increasingly contracted nature of the *ns* orbital relative to *np* in these elements which removes the equivalence of these orbitals (so-called ‘hybridisation defects’) to the extent that the former make little contribution to the bonding. Whilst these ‘hybridisation defects’ become important only for the very heavy main-group elements, they are an inescapable feature of transition metal compounds, simply because the principal quantum numbers of the valence orbitals are not all the same; *nd vs* (*n*+1)*s* and (*n*+1)*p*. The positions of the radial maxima therefore also differ, with the *nd* orbital lying much closer to the nucleus than (*n*+1)*s* and (*n*+1)*p* (plots for an exemplary transition metal atom, Fe, are shown in Figure 1b) and the distance that affords optimum overlap with (*n*+1)*s* and (*n*+1)*p* will lead to very small overlap with *nd*, and *vice versa*. The problem is further compounded by that fact that the radial maximum of the *n*d orbitals is very similar to that of the filled ns^2np^6 core, so effective overlap with the former usually comes only at the cost of significant repulsions with the latter. In short, bonding to a transition metal ion inevitably involves a compromise, simply because it is impossible to involve all nine valence orbitals in bonding to an equal extent. This compromise is the root cause of the many exceptions to 18-electron rule.

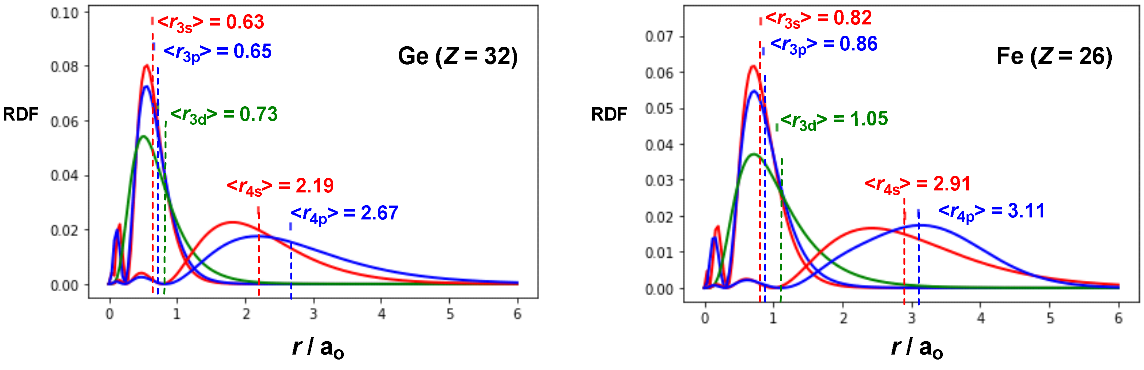

Figure 1. Radial distribution functions for typical main-group (Ge) and transition metal (Fe) elements (calculated at the unrestricted Hartree-Fock level with the universal gaussian basis set (UGBS)).

In the following sections, I will first set out the basic features of bonding in main-group and transition metal compounds to illustrate the origins of the octet and 18-electron rules, before going on to examine the apparent exceptions to the rules. I use the word ‘apparent’ here because in many cases (in fact, the majority of cases!) the failure to adhere to the rules proves to be an illusion created by a naïve approach to electron counting rather than any fundamental breakdown in the assumption that all of the valence orbitals are being used. Nevertheless, many of the exceptions are genuine, and a detailed understanding of their origins serves to highlight many of the important similarities and differences between main-group and transition metal compounds.

2. CH_4 and $[Co(NH_3)_6]^{3+}$: exemplary cases of the octet and 18 electron-electron rules in action.

The two molecules, CH_4 and $[Co(NH_3)_6]^{3+}$, appear in many introductory texts on bonding because they have very high symmetry, which allows for a very transparent treatment of the important features of bonding. The reader should not, however, infer from this that the octet and 18-electron rules are somehow restricted to high-symmetry cases – the key underlying principles extend to molecules of any symmetry. Schematic molecular orbital diagrams for the two molecules are shown side-by-side in Figure 2. In tetrahedral CH_4, the $2s$ and $2p$ orbitals transform as a_1 and t_2, respectively, precisely the symmetries of the four linear combinations of $1s$ orbitals on hydrogen. Each of the four valence orbitals of C therefore forms a bonding/antibonding pair with its counterpart on the H_4 unit, giving four bonding orbitals and hence a stable octet. The sense in which we are 'using' the four valence orbitals on carbon is rather obvious: we are using them to form bonding combinations which then accommodate the 8 electrons. The bonding orbitals, $1a_1$ and $1t_2$, are, of course, delocalised over both carbon and hydrogen, but for electron-counting purposes we attribute them to the central atom. The corresponding diagram for $[Co(NH_3)_6]^{3+}$ shows very similar features. The six linear combinations of lone-pairs on the NH_3 ligands transform as a_{1g}, t_{1u} and e_g, and these linear combinations form bonding/antibonding pairs with the valence $4s$, $4p$ and $3d_{z^2/x^2-y^2}$ orbitals, respectively. Thus these six orbitals are 'used' in precisely the same sense as the *ns* and *np* orbitals are used in a typical main-group compound. A common misunderstanding here is to assume that because most of the metal $3d_{z^2/x^2-y^2}$ character accumulates in the vacant $2e_g$ orbital, these two atomic orbitals are somehow not being 'used' to accommodate electrons. On the contrary, they are being used in the sense that they contribute (albeit to a much lesser extent) to the bonding orbital, $1e_g$, which is occupied. The electrons in the bonding orbital are, therefore, attributed to the metal for electron-counting purposes, despite having a relatively small amplitude on the valence orbital of the metal itself. The three remaining $3d$ orbitals, $3d_{xz/xy/yz}$ are strictly non-bonding in a complex such as $[Co(NH_3)_6]^{3+}$, but are nevertheless fully occupied. They are therefore 'used' in a somewhat different sense, to accommodate lone pairs of electrons in a manner entirely equivalent to the lone pairs in NH_3 or H_2O. There are therefore two quite distinct senses in which a valence orbital is 'used' in electron counting: (i) to form bonding/antibonding pairs, of which the former is occupied and (ii) as a non-bonding orbital, used to accommodate lone pairs.

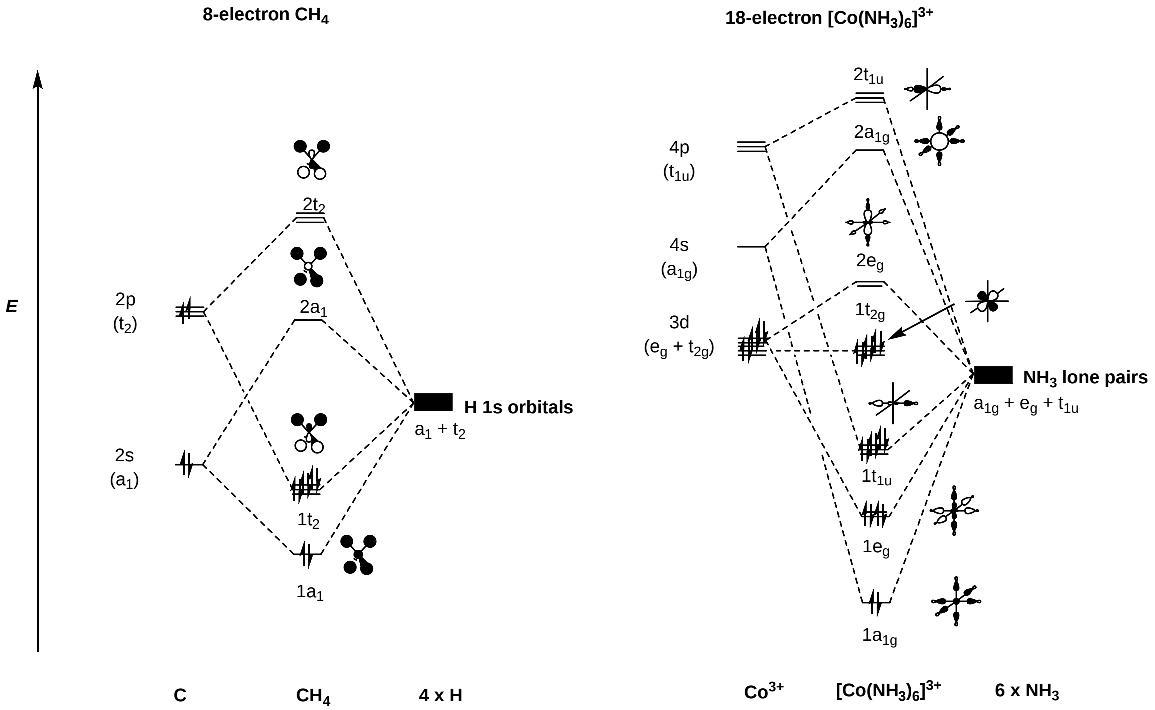

Figure 2. MO diagrams for molecules that confer to the octet and 18-electron rules: ‘8-electron’ CH_4 and 18-electron $[Co(NH_3)_6]^{3+}$.

3. Compounds with too few electrons.

(a) The inert pair effect and the 16-electron rule: two rules, one origin.

The “inert pair effect”, first mentioned by Sommerfeld in 1926, captures the observation that the heavier elements of groups 3 (Al-Tl) and 4 (Si-Pb) show an increasing tendency to adopt an oxidation state two less than the group number. For example, whilst the vast majority of carbon compounds are tetravalent (CCl_4, for example), the heavier congeners $SnCl_4$ and $PbCl_4$ are strongly oxidising while the divalent analogues $SnCl_2$ and $PbCl_2$ are stable compounds despite having only 6 valence electrons. The ‘16-electron rule’ states that square-planar compounds have a stable electron count of 16 rather than the 18 that we expect of transition metal compounds. These square-planar complexes are prominent in the chemistry of groups 9 and 10, particularly amongst the heavier elements (Rh, Ir, Pd, Pt) where they find important applications in catalysis. Notable amongst these are Wilkinson’s hydrogenation catalyst, $RhCl(PPh_3)_3$, and the carbonyl/iodide catalysts in the Monsanto and Cativa processes, $[Rh(CO)_2I_2]^-$ and $[Ir(CO)_2I_2]^-$, respectively. In the biomedicinal field, *cis*-platin, $[PtCl_2(NH_3)_2]^{2+}$ was an important first-generation anti-cancer drug, its therapeutic properties being a direct consequence of its shape. Although the two phenomena, the inert-pair effect and the existence of stable 16-electron compounds, are not usually linked in text-book treatments of electronic structure, there are many striking similarities. Most obviously, 6-electron main-group compounds and 16-electron transition metal compounds are both 2 electrons short of the number expected based on the octet and 18-electron rules, and the fact they are universally diamagnetic suggests that one of the available valence orbitals is not being used in either of the senses defined previously (*i.e.*

not used to form a bond, and not being used to accommodate a lone pair). The similarities extend beyond the ground-state structures into typical reactivity patterns: both classes of compound can react with Lewis bases to form stable compounds with 8 and 18 electrons, respectively. Likewise, both undergo oxidative addition, again generating 8- and 18-electron compounds. All of the above suggests that these two effects share a common origin.

As one of the cornerstones of descriptive main-group chemistry, the inert pair effect is familiar to most undergraduate chemists. The normal tetra-valence of carbon is typically understood in terms of promoting an electron from 2*s* to 2*p*, forming an sp^3 hybrid state which then allows for the formation of four bonds. The earliest explanations for the inert pair effect were then based on the relative stabilisation of the *n*s orbital relative to *np* in the heavier elements, to the extent that the former become chemically inaccessible, in which case the chemical valence is determined by the number of electrons in the *np* sub-shell (np^2 for group 4 giving 6-electron compounds with stoichiometry EX_2). It is important to emphasise that although the *ns* orbital is not involved in bonding to any great extent in these compounds, it is still being 'used' in an electron counting sense in– it hosts a lone pair of electrons, just like the t_{2g} orbitals of $[Co(NH_3)_6]^{3+}$. The orbital that is <u>not</u> being used is the member of the *np* subshell that lies perpendicular to the molecular plane ($1b_2$ in Figure 2, left).

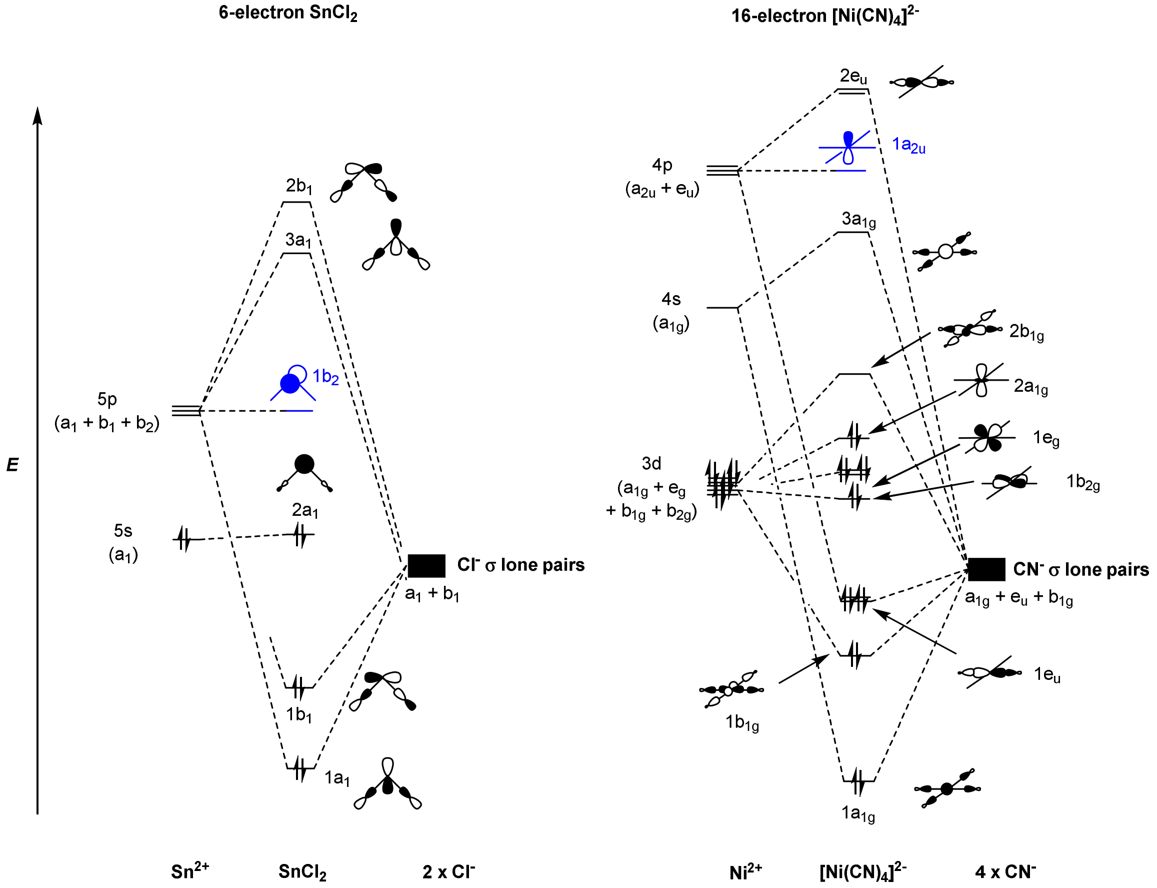

Figure 3. Comparison of the electronic structure in a typical 'inert-pair' 6-electron complex, $SnCl_2$, and a typical 16-electron complex $[Ni(CN)_4]^{2-}$.

This appealingly simple model of the energetic inaccessibility of the *ns* electrons was, however, called into question by Drago's careful thermodynamic analysis published in 1958, which showed that the removal of a 6*s* electron of Pb is, in fact, actually less costly than a 4*s* electrons in Ge, but nevertheless the inert-pair effect is much more pronounced in the former. Instead Drago emphasised the balance between the energy required to promote the atomic ground state (ns^2np^2) to the $nsnp^3$ valence state and the energy gained from the formation of two additional bonds to this excited state. His analysis showed that the bond strengths in EX_4 compounds fall off rapidly down the group, leading him to conclude that this, rather than any intrinsic stability of the ns^2 shell, was responsible for the stability of divalent compounds of the heavier elements. More recently, Kutzelnigg has argued that this weakness of the bonds in the high-valent compounds (EX_4) stems from a 'hybridisation defect' which prevents the effective mixing of *ns* and *np* character to form the sp^3 hybrid. A fundamental requirement for effective isovalent hybridisation is that the orbitals involved (*ns* and *np*) have similar radial characteristics because only then can a bonding partner overlap equally with both to promote the necessary mixing. The radial extent of the valence orbitals is most easily quantified by the expectation value $\langle r \rangle$ shown in Figure 1 and also Figure 4. In hydrogenic atoms and ions (*i.e.* those with only a single electron), $\langle r \rangle$ is exactly defined by *n* and *l*: $\langle r \rangle = \frac{a_0}{2Z}\left(3n^2 - l(l+1)\right)$ and so the *np* orbital ($\langle r \rangle = \frac{5}{Z}a_0$) is in fact less radially extended than *ns* ($\langle r \rangle = \frac{6}{Z}a_0$). For poly-electronic atoms, however, the greater electron-electron repulsions in the *np* orbital (which, recall, always has one fewer node than *ns*) cause it to expand, such that $\langle r_{np} \rangle$ is very similar to $\langle r_{ns} \rangle$ for the second period and exceeds it substantially for the heavier elements of the group (compare $n = 2$ and $n = 3$ in Figure 4). In the limit that the radial maxima of *np* and *ns* are very different, the stability of the EX_4 compounds, where all four orbitals must be used for bonding, is necessarily compromised compared to EX_2, where only the two singly occupied *np* orbitals are required for bond formation. Kutzelnigg's hybridisation defect model makes clear that the underlying assumption that the *ns* and *np* orbitals contribute equally to bonding becomes increasingly suspect for the heavier elements of the group where they radial properties diverge, and this is the root cause of the breakdown of the octet rule.

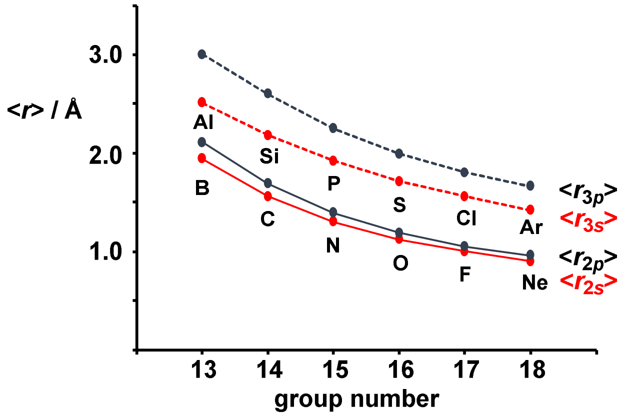

Figure 4. Expectation values, <*r*>, for the ns and np valence orbitals for the first and second row elements. Note the greater radial expansion of 3*p* relative to 3*s* in contrast to the close similarity between 2*s* and 2*p*.

Drago's analysis focussed on the thermodynamic balance between EX_2 and EX_4 (i.e. oxidative addition), but it is instructive to also consider a different aspect of the chemistry of 6-electron EX_2 compounds, their Lewis acidity. $SnCl_2$, for example, is a relatively weak Lewis acid that binds nucleophiles such as Cl^- to form 8-electron $[SnCl_3]^-$ (isoelectronic with PCl_3). The same tendency is apparent in the solid-state structure of $SnCl_2$ itself, where $SnCl_3$ units share bridging Cl^- ions. Given the presence of a vacant *p* orbital in $SnCl_2$ ($1b_2$ in Figure 3) the real surprise is that it is not, in fact, a much stronger the Lewis acid than it is. To understand why the third ligand is only weakly bound, note that both the filled *5s* and empty $5p_z$ orbitals ($2a_1$ and $1b_2$) have significant amplitude along the direction of approach of a Lewis base, perpendicular to the $SnCl_2$ plane. This point is obvious for $5p_z$ but perhaps less so for *5s* but recall that the latter is spherically symmetric, so has significant amplitude in *all* directions. The close approach necessary to overlap with $5p_z$ is therefore opposed by repulsion with *5s* and so bonding is necessarily a compromise. This idea is captured in the the 3-orbital-4-electron model in Figure 5: the bond strength is determined by the balance between the stabilising interaction with vacant 5*p* and the destabilising interaction with filled 5*s*. The fact that the 5*s* orbital is much more contracted than 5*p* is now highly significant: this radial distinction allows significant overlap with the latter to occur before destabilising repulsions with the former become dominant.

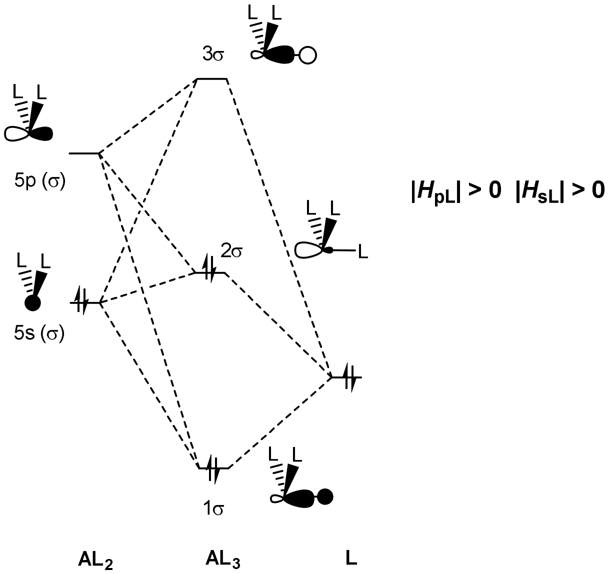

Figure 5. 3-centre-4-electron bond: the overall stabilisation depends on the balance between favourable charge transfer from the ligand donor orbital into the vacant *p* orbital and repulsion with the filled *s*.

As we have noted already, the properties of square-planar 16-electron transition metal complexes bear a striking resemblance to those of 6-electron EX_2 compounds: they are obviously 2 electrons short of the optimal count of 18, but they also undergo oxidative addition and act as weak Lewis acids, in both cases achieving an 18-electron configuration as a result. If, as we have asserted previously, an 18-electron configuration is synonymous with the complete 'use' of the valence (*n*+1)s, (*n*+1)*p* and *nd* orbitals, a stable 16-electron configuration must necessarily leave one of these nine valence orbitals unused. So which orbital is unused, and why is it not used? The molecular orbital array shown in Figure 3 (right) is reproduced, at least in part, in many inorganic texts, where the focus is usually on the *d*-orbital region. The linear combinations of ligand-based orbitals in a square-planar array give strong overlap with only one of the five *d* orbitals, $d_{x^2-y^2}$ ($2b_{1g}$ in D_{4h} point symmetry), which is therefore destabilised and empty. It is, however, being 'used' in an electron-counting sense because the corresponding bonding orbital, $1b_{1g}$, is occupied (it is the precise analogue of the $1e_g$ orbital in the octahedron). The other four *d* orbitals are non-bonding (at least to a first approximation) and filled, so are manifestly 'used' in the sense that they accommodate lone pairs, just as the t_{2g} orbitals in $[Co(NH_3)_6]^{3+}$ are used. There is, in fact, only one of the nine valence orbitals that is not being 'used' in either of the senses set out in the context of $[Co(NH_3)_6]^{3+}$, and that is the $4p_z$ orbital ($1a_{2u}$ in Figure 3) which, just like the $5p_z$ orbital in $SnCl_2$, is neither involved in bonding nor filled by a lone pair. To really understand the origin of the stability of square planar complexes, we need to go one step further and ask <u>why</u> the p_z is left unused: why do 16-electron square-planar complexes bind a 5th ligand using the otherwise redundant p_z orbital, attaining an 18-electron configuration in the process? The answer is that in fact they do precisely this, but usually very weakly – indeed so weakly that the resulting 5-coordinate 18-electron species are usually transition states on a ligand-exchange pathway. Nevertheless, there are a few cases where a 16-electron ML_4 species <u>is</u> in equilibrium with a stable 18-electron ML_5 species the best known example being the nickel tetra-cyanide:

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow [Ni(CN)_5]^{3-} \qquad K = 1.076\ \mathrm{mol^{-1}dm^3}$$

The argument for the rather weak Lewis acidity of $[Ni(CN)_4]^{2-}$ parallels closely the one made previously to rationalise the weak Lewis acidity of $SnCl_2$. If the fifth ligand approaches along the *z* axis in order to overlap with $4p_z$ orbital, it will also incur repulsions, now with the filled $3d_{z^2}$ orbital that is more radially contracted, but is also aligned primarily along the *z* axis. Note the striking parallels between the $5s/5p_z$ pair in $SnCl_2$ and the $3d_{z^2}/4p_z$ pair in $[Ni(CN)_4]^{2-}$: completion of the octet/18-electron configuration requires the second-named orbital to accommodate a lone pair from the ligand, but only at the expense of repulsions with the first, which is more radially contracted but aligned (at least partially) along the same axis. The obvious contrast is that whilst the difference in radial extension of the valence *s* and *p* orbitals only emerges in the heavier main-group elements, the difference between d_{z^2} and p_z is hard-wired into the transition metal because the orbitals have different principal quantum numbers. Nevertheless, the balance between attraction and repulsion that controls binding of a 5th ligand can be tweaked by changes in the identity of the metal. For example, in the 5d congener of Ni, Pt, the radial maxima of the $5d_{z^2}$ and $6p_z$ orbitals are somewhat closer than those of $3d_{z^2}$ and $4p_z$ in Ni, and as a result the repulsions are more dominant and the 5-coordinate $[Pt(CN)_5]^{3-}$ become a transition states on the ligand substitution pathway rather than a stable species in its own right.

(b) π-donor ligands: a case of questionable accounting?

Many of the most commonly cited instances of the breakdown of the octet and 18-electron rules come when π-donor ligands are present. To clarify, π-donor ligands have one or more additional lone pairs of electrons, over and above the one used to form the σ bond to the metal: the halide ions, F^-, Cl^-, Br^- and I^-, are classic examples, as too are oxides (O^{2-}) and nitrides (N^{3-}), hydroxides (OH^-) and amides (NH_2^-) and even water, H_2O. In contrast, the NH_3 ligands in $[Co(NH_3)_6]^{3+}$ are classic examples of 'σ-only' ligands, in so much as they have only a single lone pair of electrons which is directed along the M-L axes to form the σ bonds to the metal ion. From the main-group, BF_3 is a text-book case of a formally 6-electron complex but we could equally cite boronic acid, $B(OH)_3$, or one of the many stabilised ‘Arduengo’ carbenes, $(R_2N)_2C$, that have emerged over the past decade. BF_3 is typically formulated as a 6-electron compound where the three valence electrons on boron are supplemented by a single electron from each of the F 2*p* orbitals aligned along the B-F bonds (*i.e.* the F ligands are considered to be 1-electron donors). The comparative stability of BF_3 compared to BH_3 is typically rationalised by invoking π-donation from additional lone pairs on the F atoms that lie perpendicular to the B-F bonds and can donate electron density into the B $2p_z$ orbital which is otherwise ‘unused’ in either of the senses defined above (it is both non-bonding and empty). This phenomenon can be captured from a valence-bond perspective through resonance between structures with one B=F double bond or, from a molecular orbital perspective, by the bonding/antibonding interactions between the B $2p_z$ orbital and the in-phase linear combination of F $2p_z$ orbitals, ($1a_2''$ and $2a_2''$ in Figure 6a). These are entirely equivalent, and capture the same physical phenomenon, F→B electron transfer. As an aside, we note that we could, in principle, invoke an entirely parallel argument to rationalise the stabilities of 16-electron complexes with π-donor ligands such as $RhCl(PPh_3)_3$, $[Rh(CO)_2I_2]^-$, $[Ir(CO)_2I_2]^-$ and $[PtCl_2(NH_3)_2]^{2+}$: in all cases the np_z orbital could accept a π-symmetry lone pair from the halide. This has not, to the best of my knowledge, been done, probably because the combination of the very high-energy and diffuse nature of the 5*p* or 6*p* orbitals makes π-donation rather ineffective. Certainly, the fact that there are many stable examples such as $[Ni(CN)_4]^{2-}$ where there are no π donors present suggests that π donation is not a major stabilising factor.

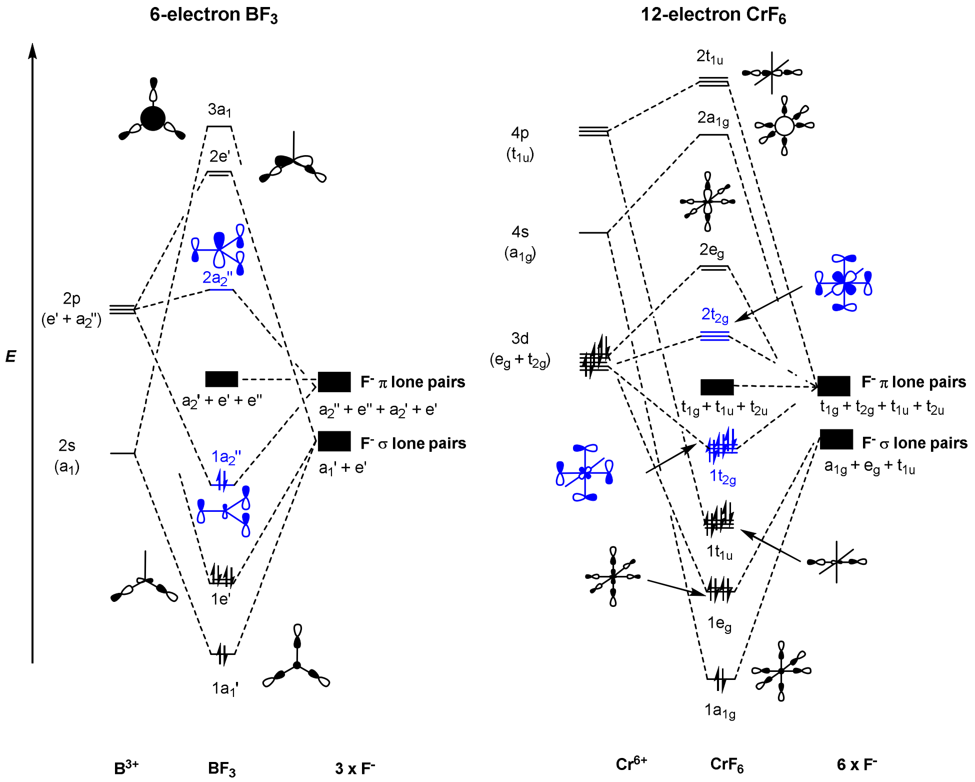

Figure 6. The role of π-donor ligands in BF_3 and CrF_6: in both cases orbitals of π symmetry on the fluorides provide a symmetry match for orbitals on the central atom that would otherwise remain non-bonding.

The discussion of BF_3 highlights the important point that our perspective on electronic structure depends rather critically on how we choose to count electrons on the ligands. Most chemists would agree that the boron is electron deficient, with only 6 valence electrons, and this belief can be traced to the convention that halide ions such as F^- are 2-electron donors (or halogen atoms are 1-electron donors if you prefer a neutral counting scheme). In the context of Figure 6a, the conventional electron count of 2 for the F^- ligand means that we include the σ bonding electrons ($1a_1'$ and $1e'$) in the count at B but we do <u>not</u> count the π bonding electrons in $1a_2''$. The very fact that we then assert π-donation as an additional stabilising mechanism means, however, that each F^- ligand must, on average, donate more than one electron! If we chose to include the electrons in the π-bonding $1a_2''$ orbital towards the formal count on boron we would reach a rather different perspective on the electronic structure: the boron would now have an entirely normal octet while each F^- ligand would donate 7/3 electrons rather than 2. The reactivity (or lack thereof) of BF_3 certainly does not suggest any obvious deficit of electron density at boron.

Contrast the treatment of fluoride ligands situation with the conventional view of imido ligands, $[NR]^{2-}$, which is that they are counted as 6-electron donors. Imido and fluoride ligands are strictly isolobal – they present exactly the same number of electrons and the same number of orbitals, with the same symmetries, to the central atom, but now we <u>do</u> count the π bonding electrons in the count of the central atom. The only objective difference between the two ligands is that the orbitals in $[NR]^{2-}$ are somewhat higher in energy, so whilst it is, without doubt, a stronger π donor than F^-, the stark difference in formal electron counts (2 *vs* 6) presents a very black and white distinction that belies the reality that the amount of electron density donated from the π ligands varies in a more continuous manner. Oxide ligands, O^{2-}, fall somewhere between F- and $[NR]^{2-}$, and indeed they are classified either as 4-, or sometimes 6-, electron donors. Moreover, when halides are placed in bridging positions, they are conventionally considered to be either 4- (μ_2-) or 6-electron (μ_3-) donors. This discussions serves simply to highlight the point that π-donor ligands are intrinsically flexible entities, and the net amount of electron density that they donate to a bonding partner is a sensitive function both of the ability of the ligand to donate and the capacity of the bonding partner to accept. Given that ligands isolobal with F^- are widely accepted to donate anything from 2 to 6 electrons, the assertion that, in the specific case of BF_3 they donate 7/3 of an electron to complete the octet at B does not, perhaps, seem so radical after all.

Amongst the transition elements there are countless examples of apparently electron-deficient compounds with π-donor ligands to choose from but WF_6 will serve to illustrate the key points (Figure 6b). WF_6 is formally a 12-electron compound (6 valence electrons from W supplemented by one from each fluorine), manifestly short of the desired 18-electron configuration. Nevertheless, WF_6, like BF_3, is a perfectly stable entity, which rather suggests that its apparently extreme electron deficiency reflects a certain naivety in our electron-counting scheme rather than any physically real lack of electron density at the B or W centre. In the absence of π-symmetry interactions, the triply degenerate t_{2g} orbital ($d_{xz}/d_{yz}/d_{xy}$) of WF_6 is not used in either of the conventional senses, to form bonds or to accommodate lone pairs: they are the precise analogue of the p_z orbital on B. When we introduce linear combination of the π-symmetry orbitals on fluorine into the picture, however, the W t_{2g} orbitals now find a symmetry match and <u>are</u> used in the sense that they form bonding and antibonding combinations, $1t_{2g}$ and $2t_{2g}$, and the former are filled. Equivalently, from a valence-bond perspective, we can argue that a resonance structure with three double bonds restores the 18-electron configuration at the metal. Note again the fundamental asymmetry in our view of σ and π electrons that stems from the treatment of F^- as a 2-electron donor: bonding combinations of the σ orbitals ($1a_{1g}$, $1e_g$, $1t_{1u}$) are considered to contribute to the total count on the metal while bonding combinations of π orbitals ($1t_{2g}$) are not. If we adopted the alternative view that the π bonding electrons in $1t_{2g}$ should count to the metal, we would again get a rather different perspective on the molecule: WF_6 would be an 18-electron complex while the fluoride ligand would a net 3-electron donor (again, 3 is comfortably in the 2-6 range typically used for ligands isolobal to F^-). The analysis of WF_6, like BF_3, suggests that the fluoride ligand, along with all π donors, is a very flexible electronic buffer, donating as much or as little density from their π-symmetry orbitals as the central atom needs to complete its octet/18-electron count. This buffering capacity of π-donor ligands immediately accounts for the wealth of redox chemistry encountered in their complexes. Take, for example, the redox series $[RuCl_6]^{1-} \rightarrow [RuCl_6]^{2-} \rightarrow [RuCl_6]^{3-} \rightarrow [RuCl_6]^{4-}$, where the number of electrons in the π antibonding $2t_{2g}$ orbital increases from 3 to 6. This series is traditionally viewed as mapping an increase in formal electron count at the metal from 15 to 18 (Ru^{V} to Ru^{II}). We could, alternatively, view the same four ruthenium complexes as a series where the 18-electron count at the metal is conserved by a decrease in net π-donation per Cl^- ligand from 5/2 to 2 in steps of 1/6. The truth is somewhere between these two limiting views, but the relatively small separation of the four redox potentials suggests that the physical electron density at the metal centre fluctuates much less widely than a variation in formal oxidation states from Ru^{V} to Ru^{II} seem to imply.

(c) WMe_6: what if there are no π electrons available?

The model set out in the previous section circumvents the apparent electron deficiency in BF_3 and WF_6 by invoking occupied orbitals of π symmetry on the ligands that can push electron density into the otherwise unused orbitals on the central atom. Central to this argument is the fact the σ- and π-symmetry orbitals are orthogonal to each other, such that the additional π donation does not compromise the underlying σ framework. A rather different scenario is found in complexes such as WMe_6, which have a rather unexpected trigonal prismatic geometry rather than the usual octahedron. Trigonal prismatic coordination is preferred by a relatively small subset of high-valent transition metals, all of which have strongly electron-donating ligands – important examples are the 2-dimensional material MoS_2 and NbS_2. The very existence of compounds of this type appears, at first glance, somewhat counterintuitive: the combination of a very high-valent transition metal (W^{VI}, Mo^{IV}) and a ligand that is not very electronegative (CH_3^-, S^{2-}) does not immediately suggest great stability! The CH_3^- ligands in WMe_6 carry only a single lone pair, so how is the electron-deficiency at the metal relieved in the absence of additional lone pairs of π-symmetry? The rather counterintuitive stability is in fact intimately connected to the adoption of the trigonal prismatic rather than octahedral coordination geometry, as illustrated by the Walsh diagram connecting the two shown in Figure 7. In the octahedral limit (Figure 7, left), there is a rather narrow HOMO-LUMO gap between the occupied t_{1u}-symmetric orbitals, localised entirely on the ligands (other than a small contribution from W 6*p*) and the vacant t_{2g}-symmetric orbitals localised entirely on the metal. This situation is clearly sub-optimal in the sense that three t_{1u} orbitals on the CH_3^- ligands are transferring electron density into the high-lying 6*p* orbitals while neglecting three much more stable 3*d* orbitals. The rotation of one triangular face relative to the other to generate a trigonal prism allows two components of the high-lying filled orbital, now with e' symmetry, to overlap with two components of metal 5*d* set, also e'(a so-called second-order or pseudo Jahn-Teller distortion). In effect the rotation opens up a new channel to transfer electron density from the lone pairs on the CH_3^- ligands into the metal 5*d*, rather than 6*p*, orbitals.

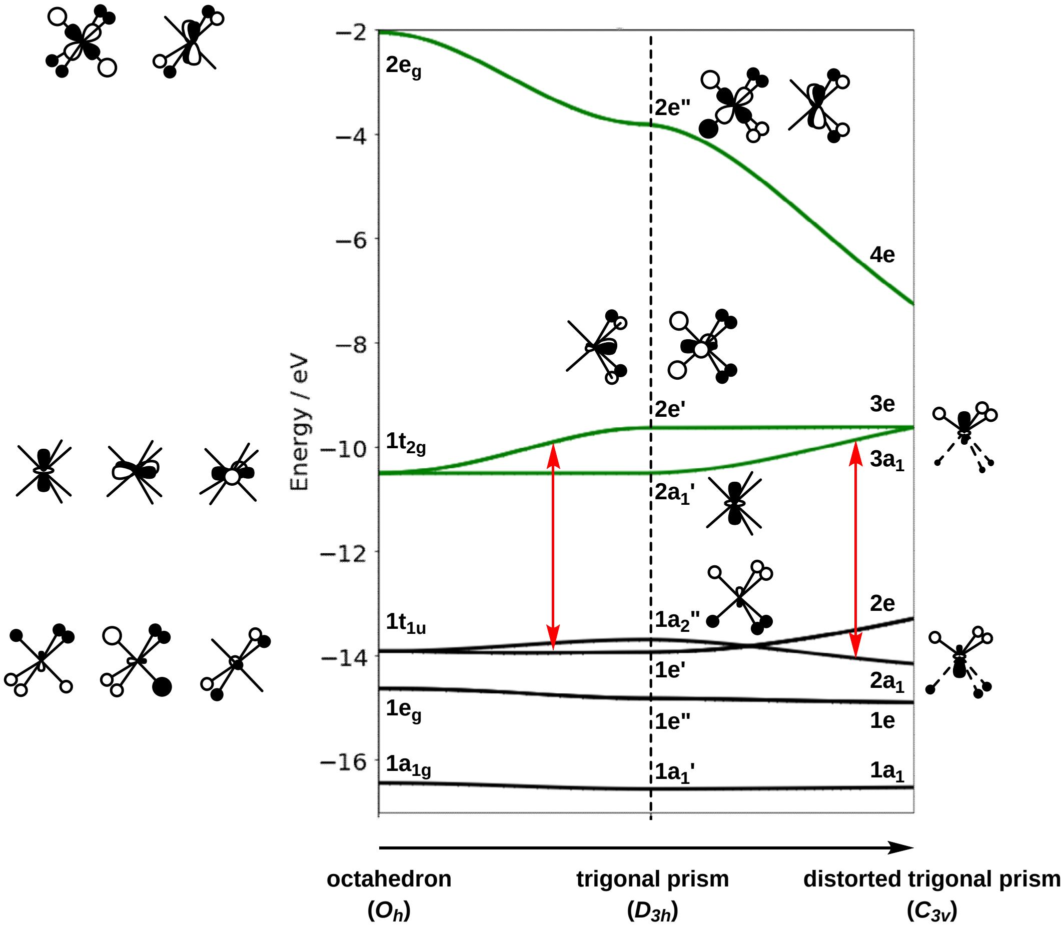

Figure 7. Walsh diagram capturing the increased mixing between W 5*d* and CH_3 σ orbitals afforded in the trigonal prism: note that the orbitals that span the HOMO-LUMO gap are strictly orthogonal in the octahedron. Black and green lines correspond to occupied and virtual orbitals, respectively. The red arrows show the orbitals that are mixed by the second-order Jahn-Teller distortions in the two segments of the potential energy surface.

In terms of electron counting, the transition from octahedral to trigonal prismatic geometry appears, at least superficially, not to have changed anything: the rotation of one triangular face does not alter the fact that there CH_3 is a 1-electron donor, so the total electron count at the W centre cannot exceed 12. What does change is the identity of the orbitals that are 'used' and which are not: in the octahedron, the 12 electrons 'use' the 6*s*, three 6*p* and two 5*d* (e_g) orbitals on W while in the trigonal prism they 'use' the 6*s*, one 6*p* (a_2'') and four 5*d* ($e' + e''$) orbitals. On rearranging from an octahedron to a trigonal prism, two of the linear combinations of ligand lone pairs effectively trade overlap with two of the high-lying 6*p* orbitals for overlap with two of the more energetically appealing 5*d* t_{2g} set. In fact, in WMe_6 the rearrangement goes a step further to allow the third component of the t_{1u} orbital ($1a_2''$ in the trigonal prism) to overlap with the third, as yet unused, component of the t_{2g} orbitals ($2a_1$). Distortion to a C_{3v}-symmetric geometry by moving the W off the centre of the prism allows these two orbitals to interact because they now share a common symmetry, a_1. The $O_h \rightarrow D_{3h} \rightarrow C_{3v}$ coordinate therefore maps the transition from sp^3d^2 hybridisation through spd^4 to sd^5, and in the most stable distorted trigonal prism the 12 electrons occupy, in a formal electron-counting sense, the six most stable orbitals, 5*d* and 6*s*. The important lesson here is that when there is a genuine lack of valence electron density, the geometry will adapt to make optimal use of the lowest-lying orbitals while ignoring the highest-lying ones.

(d) Early transition metals: a case of false expectations?

Complexes of the very early transition metals (Sc, Ti, V) are often cited as exceptions to the 18-electron rule, and indeed there are few if any compounds of titanium that reach such a high formal count. In fact stable titanium complexes appear to be remarkably unfussy about the total number of electrons in their valence shell, which can vary from 8 ($TiMe_4$) to 16 (Cp_2TiMe_2). Steric factors are often cited as the underlying cause – it is simply not possible to pack enough ligands around a single metal centre to make up for the fact that Ti itself has only 4 electrons to start with. We should, however, ask why an early transition metal element such as Ti would ever want to accumulate 18 electrons in the first place? The 3*d* orbitals are at their highest in energy at the start of the transition series, so it seems unlikely that covalent bonding from ligands would be very effective even if the requisite number could be crowded around the metal. Perhaps the best analogy here is to the alkali and alkaline earths, the elements of group 3 and also the lanthanides, where coordination complexes are stabilised primarily by ionic rather than covalent bonding: the metals are trying to shed all their valence electrons to empty the valence shell, not accumulate 8 or 18 to fill it! Coordination numbers and geometries are famously flexible in all these cases because they are dictated by electrostatic and steric factors rather than orbital overlap. A discussion of the stability or structure of $[Na(H_2O)_6]^+$, for example, would not be based on the octet rule, nor should the properties of early transition-metal complexes be shaped by reference to the 18-electron rule. Viewed from this perspective, it seems that any relationship between the stability and coordination geometries of early transition metal complexes and the 18-electron rule is probably coincidental.

4. Compounds with too many electrons (> 8 or > 18)

Turning to the other side of the electron-counting argument, there are very many cases where a molecules exceeds, or at least appears to exceed, formal electron counts of 8 for main-group elements or 18 in the case of transition metal compounds. In the context of what has gone before, there are two possible explanations for this: (1) our electron counting scheme is naïve, just as it was, for example, in the treatment of π-donor ligands discussed previously or (2) some of the valence orbitals has been used more than once (which means that antibonding orbitals are occupied as well as bonding). In the following sections, I discuss examples of both cases, but it is worth noting up front that case (1) (naïve electron counting) is by far the most common!

(a) The octet expansion illusion:

Examples where a main-group element apparently "expands its octet" *i.e.* accumulates *more* than 8 electrons in its valence shell, are very common everywhere except the first long period (C, N, O, F). The classic example of this is octahedral SF_6, which "expands its octet" to 12, but note that this is only true of we demand that each bond in the structural diagram represents a "normal" 2-centre-2-electron bond. The apparent need to accommodate more than four electron pairs in the valence shell appears to demand the availability of more than the four valence orbitals used to construct the octet. The involvement of 3*d* orbitals to provide extra space in the valence shell is, at first glance, an attractive proposition: they share the same principal quantum number as 3*s* and 3*p*, and might therefore be available to supplement the normal valence manifold. The fact that there are no 2*d* orbitals also offers an immediate explanation for the absence of analogous compounds of the first-row elements (OF_6 is not stable, for example). The idea that 3*d* orbitals allow P, S and Cl to 'expand their octet' (PF_5, SF_6, ClF_7, for example) remained popular through to the 1980's, but the advent of accurate quantum chemical calculations around this time effectively quashed the idea: there is little if any evidence to support the idea that *d* orbitals play a major role in the stability of any of these complexes, and in fact the central atoms do not really expand their octet at all. To really understand why SF_6 is stable but OF_6 is not, we have to turn the argument on its head and ask not how sulfur can accommodate more than 8 electrons (because it can not!), but rather how the fluorine atoms can donate <u>less</u> than one electron each.

The use of *nd* orbitals has now largely been discredited and replaced with a multi-centre bonding model associated with the names of Rundle and Pimentel, illustrated in Figure 8 using SF_6 as an example. The valence orbitals of sulphur are the 3*s* (a_{1g} in O_h point symmetry) and 3*p* (t_{1u}), while linear combinations of the radially-directed 2*p* orbitals on the six fluorine atoms (the 'σ symmetry' orbitals in the language used for the transition metals) transform as $a_{1g} + e_g + t_{1u}$. The a_{1g} and t_{1u} orbitals on S and $\{F_6\}$ combine to form four bonding and four antibonding orbitals, and filling the former gives an octet at sulphur, where we have 'used' all four members of the 3*s* and 3*p* manifold in the usual way. Note that there has been no mention (yet) of *d* orbitals, yet this is already a perfectly stable situation – we have 8 bonding electrons and no antibonding electrons and a formal bond order of 2/3 per bond (*i.e.* per line in the structural diagram). So as long as we are prepared to sacrifice the notion that all bonds must indicate electron pairs, the stability of SF_6 makes perfect sense. The remaining four electrons, the ones which apparently caused the sulphur to exceed its octet, are to be found in the non-bonding e_g orbital, which *has zero amplitude on the sulphur*: these electrons remain localised on the fluorine atoms and never enter the valence shell of sulphur. So in fact the octet is not expanded at all, although the coordination sphere is. We can capture this idea in the ionic resonance forms shown in

Figure 4, where the $[SF_4]^{2+}$ component obeys the octet rule and two of the fluorine centres carry a negative charge (and also have a stable octet). It is, therefore, no accident that it is usually O and F that cause the expansion of the coordination sphere, because highly electronegative atoms are needed to stabilise the excess electrons that inevitable cannot enter the valence space of the central atom. We find the same model put to use in the classic example of the 3-centre-4-electron bond, $[HF_2]^-$. Here, the apparent mystery is that the central hydrogen atom is bonded to two fluorine atoms, apparently 'expanding its doublet' to 4 (but note again this is only a mystery if we insist that the lines in the structural diagram correspond to pairs of electrons!). In fact, one linear combination of F 2*p* orbitals (σ_u) has the wrong symmetry to interact with the 1*s* orbital, so 2 of the electrons are, once again, marooned on the external atoms. We could, of course, fix this problem by introducing 2*p* orbitals on H into the mix, but few people would view that as a reasonable proposition.

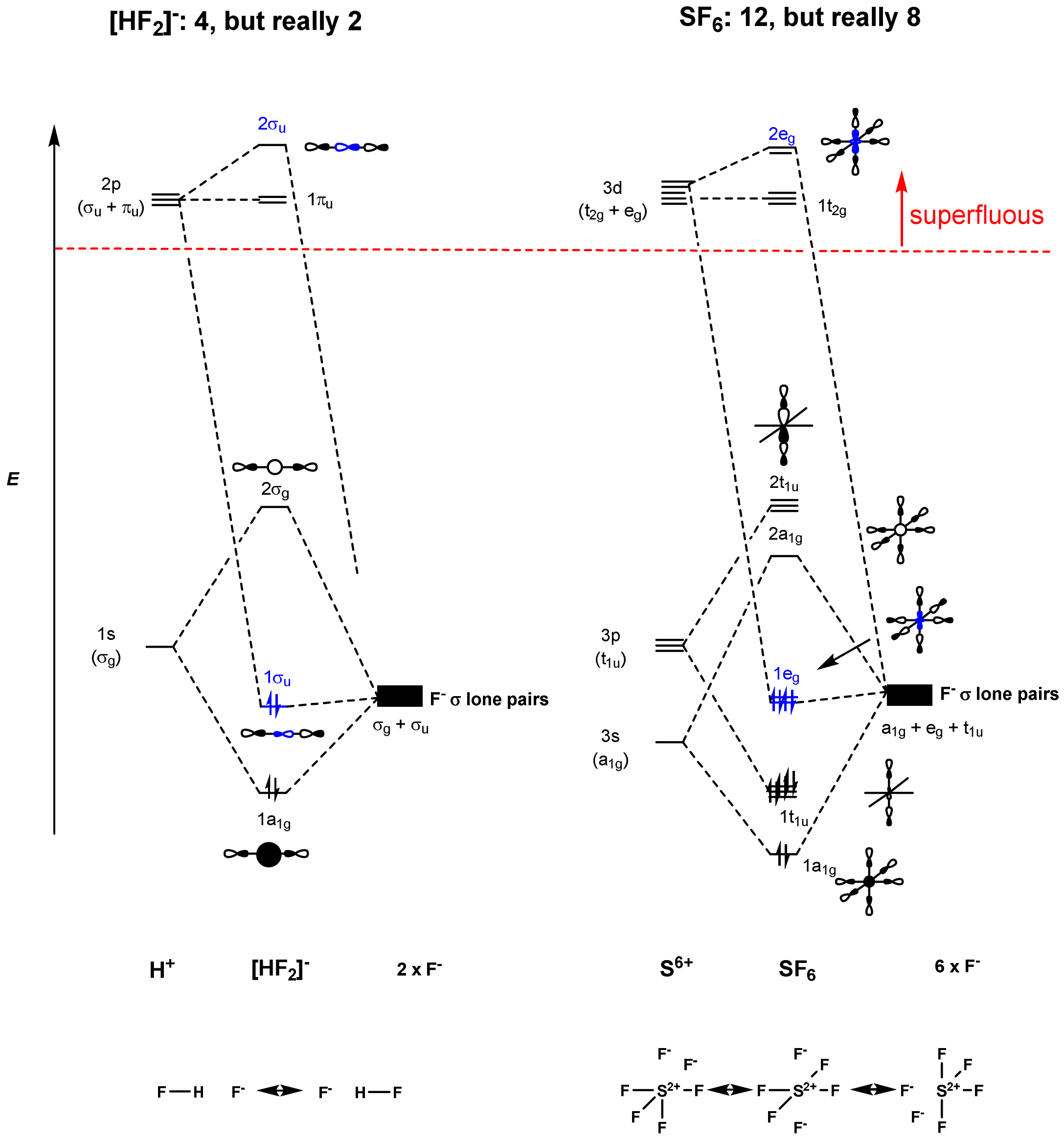

Figure 8. MO diagrams for 'excess electron' species: '4-electron' $[HF_2]^-$ and 12-electron SF_6. In reality, the electron count at the central atom does not exceed the standard 2 or 8 in either case.

What, then, of the *d* orbital argument? The *d* orbitals transform as $e_g + t_{2g}$, and so the previously non-bonding fluorine-based e_g orbital does now find a symmetry match, and so becomes bonding, at least in a formal sense. The net bond order per S-F bond therefore becomes 1, and the electron count at S rises to 12 (in effect we invoke sp^3d^2 hybridisation). How significant really is this contribution from the *d* orbitals though? The 3*d* orbitals are very high energy and so their interaction with the *p* orbitals on fluorine will be weak – quantitative estimates suggest that they are, in fact, so weak as to be insignificant. If we reject the 3*d* orbitals as a plausible explanation of the expansion of the coordination sphere (but not the octet!) in the second row, we are then obliged to offer an alternative explanation for the fact that we do not find analogues amongst the first row elements. In fact, this is not strictly true: trigonal bipyramidal carbon is known, but its stability can easily be rationalised with the Rundle-Pimentel model. Nevertheless, it is certainly fair to say that such cases are very rare. There is certainly a steric argument to made here: the larger sulfur atom can more readily accommodate a higher coordination number. In addition, consider the plausibility of the E^{6+} oxidation state in OF_6 or SF_6. In general, successive ionisation energies increase much more rapidly for 1st row elements than for their 2nd row counterparts (Figure 9), and the sum of the first six ionisation energies for oxygen is 433 eV *vs* only 276 eV for sulfur. This striking difference can be traced, ultimately, to the greater electron-electron repulsions in the nodeless 2*p* orbital, but the bottom line is that S^{6+} is a much more plausible proposition than O^{6+}, and this is probably the dominant factor that prevents the formation of OF_6.

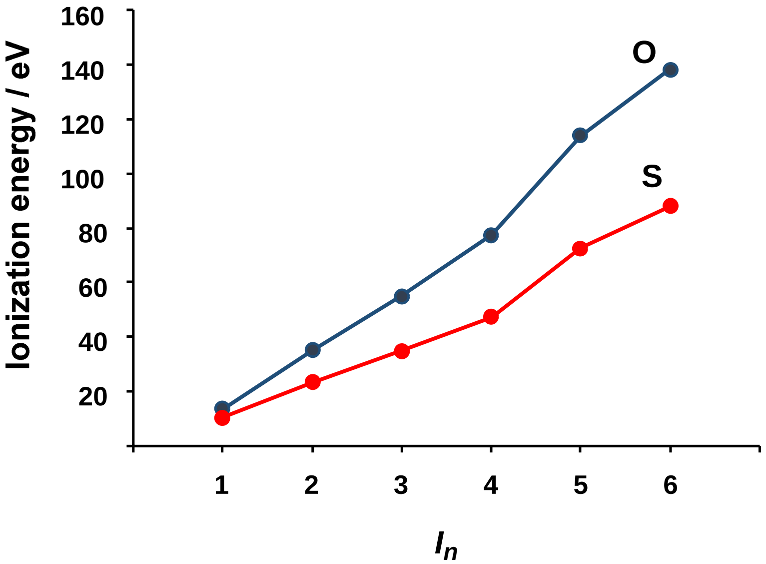

Figure 9. First six ionization energies of O (blue) and S (red). The rise between I_5 and I_6 is due to ionization from the *ns* shell rather than *np*. Note the more rapid rise for the lighter element.

The enduring appeal of the *d*-orbital participation model probably rests, at least in part, in the clear distinction it offers between the first row and the rest of the periodic table: there are, definitively, no 2*d* orbitals, so apparently no possibility of hyper-valency. The ionization energy argument presented above is, in contrast, less black and white in the sense that it leaves open the possibility of hyper-valent compounds of first-row elements, if only the rather large but still finite ionization energy could be compensated by the formation of strong bonds. This enticing possibility has motivated long-standing interest in the synthesis of (still elusive) compounds like NF_5. It certainly suggests that the distinction between the first and subsequent rows is perhaps not quite as sharp as we imagine. Nevertheless, this it is deeply embedded in our chemical thinking, a point that is illustrated by considering the Lewis structures that chemists would typically draw for ozone, O_3 and its second-row congener SO_2 (Figure 9). The vast majority of chemists would draw a zwitterionic resonance form for O_3, thereby avoiding (quite correctly) the accumulation of more than 8 electrons around any one atoms, but will happily offer the alternative structure with two double bonds for SO_2. The number of valence electrons and valence orbitals is identical in the two cases (if we neglect *d* orbitals!), and the molecular orbital pictures are, at first glance, identical. Instinctively, the multiply-bonded structure for SO_2 seems preferable, but probably for no better reason than that we believe that double bonds are better than single ones. Therefore we naturally favour this form when the octet expansion myth appears to grant us permission to do so, despite the fact that we are, perhaps unconsciously, invoking the spurious participation of *d* orbitals as we do so. The zwitterionic form for O_3 is often seen as something of a last resort, to be invoked only when the rules of the game forbid us to expand the octet by using multiple bonds. However, the presence of a positive charge on the central atom in the zwitterionic structure is actually a much more plausible proposition for sulphur than it is for oxygen, and recent studies of the electron density of oxyanions such as $[SO_4]^{2-}$ support an $S^{6+}(O^{2-})_4$ structure with single S-O bonds rather than the traditional one with two double bonds. There seems little reason, therefore, to support the use of neutral multiply-bonded structures in heavier *p*-block compounds, despite the fact that the *d*-orbital participation model apparently grants permission to do so.

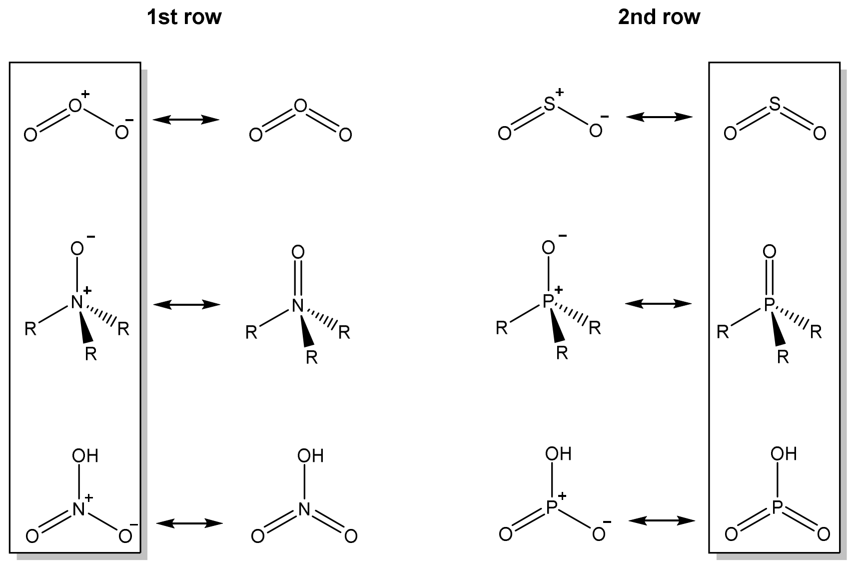

Figure 9. Resonance structures for typical high-valent main group compounds from the first and second periods. The zwitterionic forms are usually presented for the 1st row, while most books favour the multiply-bonded forms, where the octet appears to be expanded, for the heavier analogues.

It is rather hard to find precise analogues to the SF_6 case in the transition metal domain, simply because it requires very high symmetries and therefore very high coordination numbers to generate linear combinations that are strictly orthogonal to all nine valence orbitals, *ns*, *np* and *nd*. Perhaps the best examples are the cubic carbonyl complexes $[M(CO)_8]^-$, M = Sc, Y and La, all of which have a formal electron count of 20 at the metal. In these cases, one of the 8 linear combinations of CO lone pairs, with a_{2u} symmetry, finds no match with any of the valence orbitals on the metal. Precisely like the $1e_g$ orbital in SF_6, the electrons in this orbital never enter the valence shell of the metal, which does not, therefore, exceed the 18-electron count after all. It is also worth noting that we could, if we really objected to the idea of a non-bonding $1a_{2u}$ pair of electrons localised on the CO ligands, introduce a set of valence *f* orbitals into the diagram (albeit at very high energy), one of which (f_{xyz}) would have the required a_{2u} symmetry. This construct again converts a non-bonding orbital into a bonding one, but also meets with precisely the same objections that we made against the introduction of 3*d* orbitals in SF_6 and 2*p* orbitals in $[HF_2]^-$: they are superficially attractive but in fact of minimal energetic significance, and completely unnecessary to rationalise the existence of the molecule.

If we extend the analogy wider to include ligand-based electrons of π symmetry, we can identify a number of less exotic examples, perhaps the best known being the trigonal imido complex $Os(N\text{-}2\text{-}6\text{-}C_6H_3\text{-}{}^iPr_2)_3$ and the tris-alkyne complex $W({}^tBuC{\equiv}C{}^tBu)_3CO$, both of which are described in the literature as 'false' 20-electron complexes. In the imido complex, the electron count of 20 is reached by counting 2 for Os^{6+} and 6 for each of the three NR^{2-}. The *a priori* assumption here is that <u>all</u> of the available electrons on the ligand (σ and 2 x π) are donated to the metal. A symmetry analysis (using idealised D_{3h} point symmetry) quickly shows, however, that one linear combination of the in-plane π orbitals on the $(NR)_3$ unit has a symmetry, a_2', that is incompatible with any of the valence orbitals on Os (6*s*, 6*p* or 5*d*). This a_2' orbital is therefore the exact analogue of the non-bonding e_g orbital in SF_6, the $1\sigma_u$ orbital in $[HF_2]^-$ and the $1a_{2u}$ orbital in $[Sc(CO)_8]^-$. As a final aside, it is worth highlighting the fact that the '20-electron' designation only ever arises because of the convention that imido ligands, $[NR]^{2-}$, should be counted as 6-electron donors *i.e.* that <u>all</u> of the π electrons on the ligands should be awarded to the metal in the electron counting procedure. In reality, $[NR]^{2-}$ donates 16/3 electrons rather than 6: the metal takes what it needs to attain an 18-electron configuration and discards the rest. Note the contrast with the conventional electron counting in CrF_6, where the F^- ligands (isolobal with $[NR]^{2-}$) are counted as 2-electron donors, with the consequence that <u>none</u> of the π-symmetry electrons are assigned to the metal in the first-order treatment. We then identified the π-symmetry orbitals that do overlap with the metal (t_{2g}) and invoked π-donation as an additional stabilising mechanism. In $Os(N\text{-}2\text{-}6\text{-}C_6H_3\text{-}{}^iPr_2)_3$, in contrast, we include <u>all</u> the π-symmetry orbitals to first order, then identify those that do <u>not</u> overlap with the metal ($1a_2'$) and remove them from the count! A more nuanced approach based which does not limit the number of electrons donated to integers would resolve this rather confusing inconsistency.

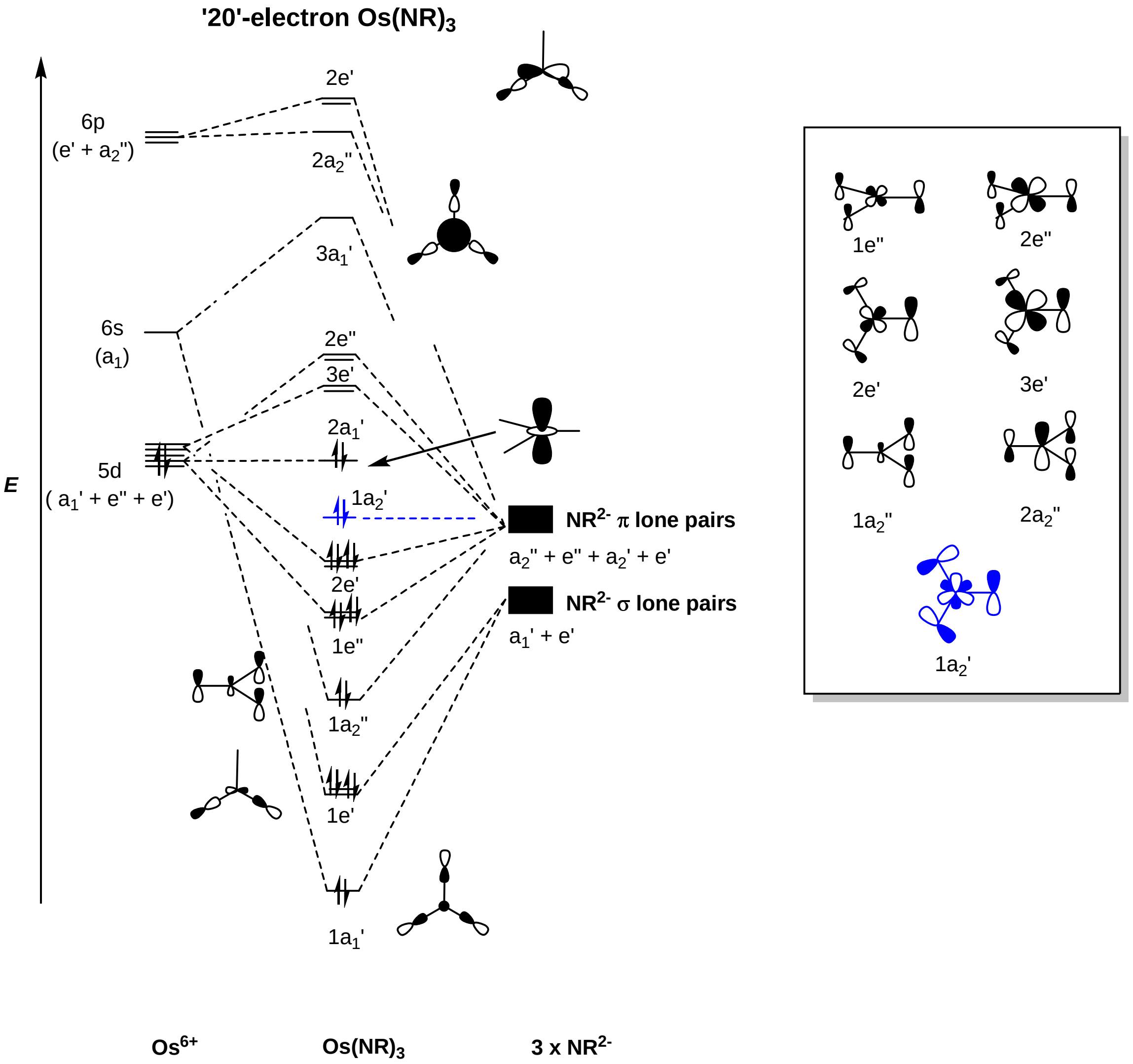

Figure 10. MO diagram for 'fake 20-electron' Os(NR)$_3$. The π-symmetry orbitals in the box show that one linear combination, with a_2' symmetry (picked out in blue), finds no symmetry match with any of the *s*, *p* or *d* orbitals on Os, and so one pair of electrons does not enter the valence shell of the metal. The f_{xyz} orbital with a_2' symmetry is shown, but in reality is too high to make a meaningful contribution to bonding, just as in [Sc(CO)$_8$]$^-$.

In summary, expansion of the octet in main-group compounds is largely a myth, caused by an unjustified assumption that lines on a structural diagram must correspond to conventional 2-centre-2-electron bonds. If we accept that the presence of non-bonding orbitals may divert electron density away from the central metal, at the conceptual cost of the 2-centre-2-electron bond as the fundamental component of bonding, then we have no need to invoke any such expansion and the *d* orbitals invoked by Pauling and others become superfluous.

Late transition metal complexes with > 18 electrons.

Within the transition series, there are very many compounds that appear to exceed the 18-electron count. In fact these are so numerous, and often so mundane, that they escape notice - 20-electron $Ni(\eta^5\text{-}C_5H_5)_2$ is an oft-quoted example, but even very simple hexa-aqua species such as $[M(H_2O)_6]^{2+}$ with M = Co (19-electron) , Ni (20-electron) or Cu (21-electron), fall into this category. There are no symmetry-related tricks that allow the ligands to hide pairs of electrons here – all linear combinations of the ligand orbitals find a symmetry match amongst the standard *nd*, $(n+1)s$, $(n+1)p$ manifold – so the inescapable conclusion is that one or more of the orbitals must be being ‘used’ twice! To understand what this means, recall the discussion of the classic octet and 18-electron systems, CH_4 and $[Co(NH_3)_6]^{3+}$, where we argued that valence orbitals are ‘used’ in the sense that their bonding combination with the ligand orbital is occupied while its antibonding counterpart remains empty. If we then also use the M-L antibonding orbitals to accommodate electrons then we have, in a sense, ‘used’ the orbital twice. The most obvious chemical consequence of the occupation of the antibonding orbitals is that the complexes become increasing prone to losing a ligand, thereby reducing the formal electron count by two. The substitutional lability of the hexa-aquo complexes of Co, Ni and Cu is a simple example, but the 2+2 cycloaddition of alkenes to 20-electron $Ni(\eta^5\text{-}C_5H_5)_2$ is driven by the formation of 18-electron $Ni(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_7H_9)$.

The occupation of antibonding orbitals is, of course, only possible when the orbital is in fact not very strongly antibonding at all – otherwise the energetic penalty is too high. Electron counts of more than 18 are therefore very much the preserve of the late first-row transition metals with weak-field ligands, where bonding is primarily ionic in nature. A corollary of this ionic bonding is that the antibonding $2e_g$ orbital becomes increasingly localised on the metal and, conversely, the amount of metal character in the bonding $1e_g$ orbital becomes vanishingly small. This lays bare the underlying cause of the apparent excess of electrons on the metal: we are including four electrons in the count that, to a very good approximation, never enter the valence sphere of the metal. The situation is in fact very reminiscent of SF_6, the only real difference being that the failure of the four electrons in $1e_g$ to enter the valence shell of sulphur was imposed by symmetry rather than by the contracted nature of the orbitals. Nevertheless it becomes increasingly hard to justify including the electrons in σ bonding orbitals in the valence count on the metal, and if we accept that the $1e_g$ orbital is now ligand-based then the valence count at the metal drops back to 18. If the *d* shell is completely filled, as it is for example in $[Zn(H_2O)_6]^{2+}$, it is only a small further step to argue that the 3*d* orbitals are no longer part of the valence manifold, and indeed it is a matter of some debate whether Zn should really be considered as a transition metal given that it does not have a partially-filled *d* shell in any of its common oxidation states (Zn^{3+} is known but certainly not common). If we remove the 3*d* orbitals from the valence space, we are left with 12 valence electrons (2 from each H_2O ligand) and only four valence orbitals (4*s* and 4*p*), leaving the four electrons in the $1e_g$ orbital marooned entirely on the ligands, precisely the situation in SF_6.

The very ionic nature of the bonding in complexes of the first row transition metals, along with the large repulsions between electrons in the node-less 3*d* orbitals, presents one further challenge to conventional electron counting schemes. Consider $[Fe(H_2O)_6]^{2+}$: does it obey the 18-electron rule or not? It is beyond dispute that it has 18 valence electrons, but to conform to the spirit as well as the letter of the 18-electron rule, these electrons should occupy all the bonding and non-bonding orbitals leaving all anti-bonding orbitals empty (*i.e.* all 9 valence orbitals should be used once and only once, as is the case in $[Co(NH_3)_6]^{3+}$). $[Fe(H_2O)_6]^{2+}$ is, however, a 'high-spin' complex with a $t_{2g}^4e_g^2$ configuration, and so the 18-electron count is not associated with the orbital filling pattern set out in Figure 2. Perhaps the descriptor 'accidentally 18-electron' would be appropriate for complexes of this type.

Throughout this article I have tried to establish parallels between main-group and transition metal complexes, but in this final section it is impossible to identify direct main-group analogues of the complexes with more than 18 electrons. The simple reason for this is that valence orbitals of the main-group elements extend well beyond the core, and so overlap with bonding partners is typically large. The energetic penalty for populating an antibonding orbital is therefore high, and the result of doing so is typically bond fission rather than formation of a stable molecular species. There have been a few reported studies of 2-orbital-3-electron 'half-bonds' such as $[HF]^-$, but these remain very much the domain of gas-phase spectroscopists rather than synthetic chemists. Stable radical anions are therefore largely confined to aromatic π systems, where the weaker π overlap renders population of the antibonding orbital feasible. The ability of transition metal complexes to tolerate electrons in the antibonding orbitals can therefore be traced all the way back to the very radially contracted nature of the *nd* orbitals (Figure 1), and in particular to their proximity to the filled *ns*, *np* core. Overlap of the *nd* orbital with a ligand is compromised by repulsions from the core, and as a result bonds involving the *d* orbitals are intrinsically weak.

Concluding remarks

In this article I have tried to analyse the basis for the electron-counting rules that we rely on in all areas of chemistry, and to highlight the assumptions that underpin them. This then forms a basis for understanding the exceptions to the rules, which are numerous for the 18-electron rule but remarkably rare for octet rule. In the vast majority of cases, exceptions to the rules prove to be a result of a naïve approach to electron counting that does not fully acknowledge the subtle features of the bonding. Where the central atom is electron-deficient, it usually turns out that we have neglected electron pairs on the ligands that really do interact with valence orbitals on the central atom (BF_3, for example) while in cases that appear to exceed 8 or 18, it turns out that we have included electrons in the count that, in fact, never really interact with the valence orbitals of the central atom at all. In some case these electrons are excluded by symmetry (as in SF_6) while in others it is because the contracted nature of the *d* orbitals precludes effective overlap even when symmetry considerations permit it. To find genuine exceptions to the octet and 18-electron rules, we have to look to the divalent 6-electron compounds, EX_2, of the heavier elements of group 14 (the inert pair effect) and square-planar 16-electron complexes, respectively. The link between these two families are perhaps not obvious, but in fact they share many common features: in both cases, a single *p* orbital is left unused because donation of a pair of electrons into it would introduce strong repulsions with a more radially contracted, filled, orbital. The tendency to maximise overlap with *d* orbitals at the expense of *p* orbitals in conditions where electrons are in short supply is a natural consequence of the fact that the latter are always the highest energy orbitals of the valence manifold.