1
Chemical Bonding of Main-Group Elements

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1.1
Introduction and Definitions

Prior to any meaningful discussion of bonding in main-group chemistry, we have to provide a reasonably accurate definition of what a main-group element is. In general, we assume that main-group elements are those that essentially use only their valence s- and p-orbitals for chemical bonding. This leads to a number of borderline cases that require closer inspection. Assuming that the *outer* d-orbitals, that is, those with principal quantum number n equal to the period in question, are not true valence orbitals (see discussion of *outer* d-orbital participation in bonding later in the text), we may safely define groups 13–18 as main-group elements. Group 1 is also reasonably assigned to the main groups, albeit under extreme hydrostatic pressures it appears that the elements K, Rb, and Cs turn from ns^1 metals into transition metals and use predominantly their *inner* $(n{-}1)$ d-orbitals for bonding [1]. However, sufficiently high pressures may change fundamental bonding in many elements and compounds [2]. We disregard here such extreme pressure conditions and count group 1 in the main groups.

Matters are less straightforward for group 2: whereas Be and Mg utilize only their s- and p-orbitals, Ca, Sr, Ba, and Ra use their *inner* $(n{-}1)$ d-orbitals predominantly in covalent bonding contributions when sufficiently positively charged, as we discuss in the following text [3]. This leads to a number of peculiar structural features that bring these elements into the realm of ''non-VSEPR d^0 systems'' that encompass early transition elements and even lanthanides, and they have also been termed ''honorary d-elements'' [4]. The heavy group 2 elements are nevertheless usually placed with the main groups, and it seems appropriate to include the discussion of these interesting features in the last section of this chapter.

It thus remains to discuss the inclusion of groups 11 and 12. The group 11 elements Cu, Ag, Au, and Rg clearly have a too pronounced involvement of their $(n\ -1)$ d-orbitals in bonding, even in their lower oxidation states, to be safely considered main-group elements. The group 12 elements Zn, Cd, Hg, and Cn are usually considered to be main-group or ''post-transition'' elements. Yet recently quantum-chemical predictions [5] of oxidation-state Hg(+IV) in the form of the

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molecular tetra-fluoride have been confirmed by low-temperature matrix-isolation IR spectroscopy [6]. This molecule is clearly a low-spin square-planar d^8 complex and thus a transition-metal species. Other, less stable Hg(+IV) compounds have been examined computationally [7], and calculations predict that the tetra-fluoride should be yet more stable for Cn (eka-Hg, element 112) [8]. However, in the largest part of the chemistry of these two elements, and in all of the accessible chemistry of Zn [9] and Cd, d-orbital participation in bonding is minor. We note in passing that Jensen [10] has vehemently opposed assignment of mercury to the transition metals based on the ‘‘extreme conditions’’ of the low-temperature matrix study of HgF_4. The present author disagrees with this argument, as the role of the matrix is only to separate the HgF_4 molecules from each other and to thus prevent aggregation and stabilization of HgF_2. The low temperature is admittedly needed for entropic reasons. It is large relativistic effects that render the borderlines between the later d-elements and the main groups fuzzy in the sixth and seventh period. We nevertheless agree that the oxidation state +IV of Hg or Cn is an exception rather than the rule in group 12 chemistry, and thus discussion of the more ‘‘regular’’ bonding in group 12 belongs to this chapter.

If d-orbital participation in bonding is absent or at least an exception, main-group bonding may be considered simpler than that for transition-metal and f-element species. Although this is true from a general viewpoint, the variety of unusual bonding situations in main-group chemistry is nevertheless fascinating, ranging from the more common localized situations encountered in organic chemistry to delocalized bonding in, for example, electron-poor borane clusters or electron-rich noble-gas compounds to situations with even more complicated bonding-electron counts, for example, for radical-ion species or the bonding situations that may be envisioned for amorphous carbon [11]. We observe that the relative sizes of the valence s- and p-orbitals crucially influence periodic trends, and that hybridization is a more complicated matter than usually considered. In this chapter we focus mostly on general aspects and periodic anomalies, providing a basis for more specific discussions in some of the other chapters of this book.

1.2
The Lack of Radial Nodes of the 2p Shell Accounts for Most of the Peculiarities of the Chemistry of the 2p-Elements

The eigenfunctions of a Hermitean operator form a (complete) orthonormal set. This seemingly abstract mathematical condition is fundamental for the presence of nodes in wave functions. The nodes are needed to ensure orthogonality of the, exact or approximate, solutions of the Schrödinger equation. From the simplest examples like a particle in a box (closely related to the nodal characteristics of valence orbitals of extended π-systems), it is a short way to the radial and angular eigenfunctions of the hydrogen atom, which also define qualitatively the nodal structure of the atomic orbitals (AOs) of many-electron atoms. Orthogonality of AOs may be ensured either via the angular part (determined by the quantum numbers l and m_l) or via the radial part (determined by quantum number n). AOs with different angular momentum are generally orthogonal via their angular part. But valence (and outer core) AOs with increasing principal quantum number n develop nodes in their radial part to stay orthogonal to inner orbitals (with lower n) of the same angular momentum. Although this is exactly true only for the isolated atom, where n, l, and m_l are good quantum numbers, it also carries over approximately to atoms in molecules, with strong consequences for chemistry. The introduction of radial nodes by this "primogenic repulsion" [12] (a term indicating the necessity of staying orthogonal to the inner shells) moves the outer maximum of a radial wave function successively outwards, which makes it more diffuse. At the same time, we have to recall that the radial solutions of the Schrödinger equation for the hydrogen atom may also be written as an effective differential equation of a particle in an l-dependent potential. This effective potential contains a repulsive term due to centrifugal forces for $l \geq 1$ but not for $l = 0$. As a consequence, s-orbitals have finite amplitude at the nucleus, whereas p-, d- or f-orbitals vanish at the nucleus (within a nonrelativistic framework). However, most importantly for the present discussion, the repulsive centrifugal term moves the outer maximum of the p-orbitals to larger radii. Therefore, np-orbitals tend to be larger and more diffuse than the corresponding ns-orbitals, with the major exception of $n = 2$ – because of the lack of a radial node, the 2p-orbital is actually similar in size to the 2s-orbital, which has one radial node to stay orthogonal to the 1s-shell [13]. The approximate relative sizes of the valence s- and p-orbitals in period 2 and 3 many-electron atoms from relativistic Hartree–Fock calculations are shown in Figure 1.1. On average, the 2p-orbitals are less than 10% larger than the 2s-orbitals, whereas the 3p-orbitals

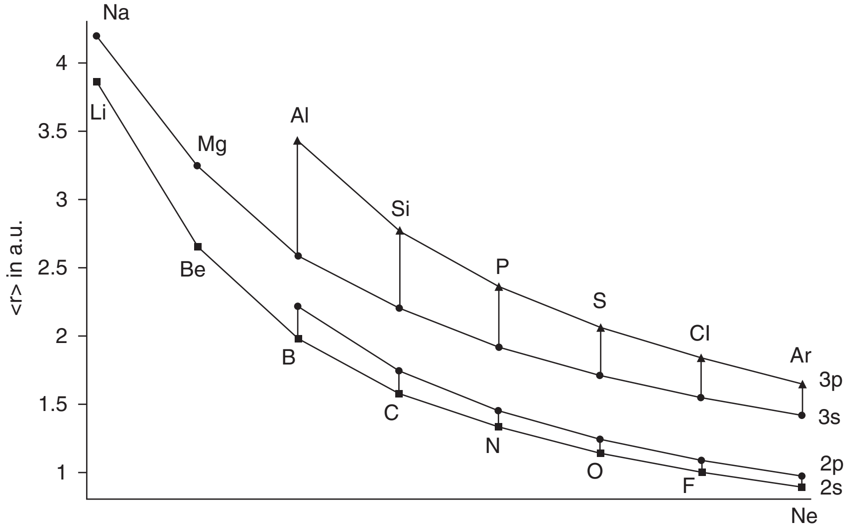

Figure 1.1 Radial expectation values for the valence s- and p-orbitals in periods 2 and 3 of the periodic table (approximate numerical Dirac-Hartree-Fock values from Ref. [14]). Figure adapted from Ref. [13].

exceed the 3s-orbitals by 20–33%. Differences increase further down a given group (modified by spin-orbit coupling for the heavier elements) [13].

The similarity of the radial extent of 2s- and 2p-shells is a decisive factor that determines the special role of the 2p-elements within the p-block, and the main consequences will be discussed further below. We note in passing that the lack of a radial node of the 3d-shell and the resulting small radial extent is crucial for many properties of the 3d-elements, and the nodelessness and small size of the 4f-shell is important for lanthanide chemistry [15]. Finally, the lack of a radial node of the 1s-AO distinguishes H and He from all other elements of the Periodic Table, with far-reaching consequences (different ones for H and He) for their chemistry. These aspects have been discussed elsewhere [16].

1.2.1
High Electronegativity and Small Size of the 2p-Elements

Because of the small r-expectation value of the nodeless 2p-shell, the valence electrons of the 2p-block elements tend to move on average particularly close to the positive nuclear charge. Shielding by the 1s- and 2s-shells is relatively poor, leading to high ionization potentials and electron affinities and, hence, high electronegativity. Indeed, the electronegativities (ENs) of the p-block elements are known to exhibit a particularly large decrease from the second period (first row) to the third period (second row). This holds for all EN scales, with vertical jumps increasing from left to right in the row (from a difference of about 0.4 between B and Al to one of about 0.9–1.0 between F and Cl), consistent with the higher percentage of p-character and the smaller size of the orbitals for the elements further to the right in a given row. The further drop from the third to the lower periods is much less pronounced and nonmonotonous, for reasons discussed later in the text. This makes it already obvious that the nodelessness and small size of the 2p-shell is decisive for rendering the 2p-block elements different from their heavier homologues. The overall small size of the 2p-elements can be appreciated from any tabulation of atomic, ionic, or covalent radii. Again, a jump from the 2p- to the 3p-elements is apparent, with much less pronounced increases (in some cases small decreases from 3p to 4p, see following text) towards the heavier p-block elements. This does of course in turn lead to overall lower coordination-number preferences of the 2p-element, as is well known. The smaller radii *and* the high electronegativities of the 2p-elements are behind their strict obediance of the octet rule, in contrast to the apparent behavior of their heavier homologues, as will be discussed in more detail later in the text.

1.2.1.1 Hybridization Defects

In addition to the *absolutely* small size of the 2p-shell, the *relative* similarity of its radial extent to that of the 2s-orbital (see earlier text) is crucial for understanding the differences between the 2p-elements and their heavier congeners. Covalent bonding is often discussed using the tools of valence-bond (VB) theory (see Chapter 5 in Volume 1), and hybridization is a main requirement of VB models. Kutzelnigg, in his classical article on bonding in higher main-group elements in 1986 [13], has pointed out that the assumptions of isovalent hybridization are only fulfilled for mutually orthogonal hybrids at a given atom. This orthogonality in turn is only achievable to a good approximation when, for example, the valence s- and p-orbitals of a p-block main-group element exhibit comparable overlap with the orbitals of the bonding partner, that is, when they have comparable radial extent. And, as we have seen above, this is the case only in the 2p-series because of the nodelessness of the 2p-shell, whereas for the heavier p-block elements the centrifugal term in the effective potential makes the *n*p-orbitals significantly larger than the *n*s-orbitals (Figure 1.1). Then isovalent hybridization becomes much less favorable. To save the concept of hybridization, it then becomes unavoidable to drop the orthogonality requirement, and Kutzelnigg has introduced the term ''hybridization defects'' and a corresponding mathematical definition for the deviations from ideal, orthogonal, isovalent hybrids [13, 17]. However, the use of non-orthogonal hybrids for the heavier main-group elements in turn wipes out the well-known and still widely used relations between hybridization and bond angles and leads to very different p/s hybridization ratios than one might expect at first glance from structures. It appears that even more than 25 years after Kutzelnigg's milestone paper many chemists are not yet aware of these considerations, and inorganic-chemistry text books tend to ignore these aspects (but see Refs [16, 18]). We thus describe the obvious consequences of large hybridization defects for the heavier p-block elements and their relative smallness for the 2p-series in some detail here. Note that the question of orthogonality of hybrids and thus of hybridization defects arises also when considering bonding in transition-metal complexes from a VB point of view [3, 16]. Here it is mainly the $(n-1)$ d- and *n*s-orbitals that are involved in bonding (see Chapter 7 in this book). It is obvious that their radial extent will not be comparable in all cases, and thus hybridization defects have to be taken into account.

Most practical quantum-chemical calculations use some flavor of molecular-orbital (MO) theory, in recent years in particular within the framework of Kohn–Sham density functional theory. Within MO theory, hybridization is not needed. But to connect to the widely used qualitative hybridization arguments, we can extract local hybridizations a posteriori by using some kind of population analysis. The prerequisite is that we can analyze well-localized MOs. In other words, small ''localization defects'' are required (i.e., Hund's localization condition should be fulfilled reasonably well) [13]. Then we can analyze the hybridization of some kind of localized MOs. The choice of localized MOs and of population analysis does of course to some extent determine the numerical values of the hybridization ratios we get from such analyses, but the qualitative conclusions obtained by different methods are similar. Kutzelnigg in 1986 [13] used Boys' localization [19] and Mulliken populations [20]. The latter have the disadvantage of exhibiting strong basis-set dependencies. A widely used, and nowadays readily available, approach is to consider the natural atomic orbital (NAO) hybridizations of natural localized Molecular Orbitals (NLMOs) within Weinhold's natural bond orbital (NBO) scheme [21]. We note in passing that, although the outcome of the

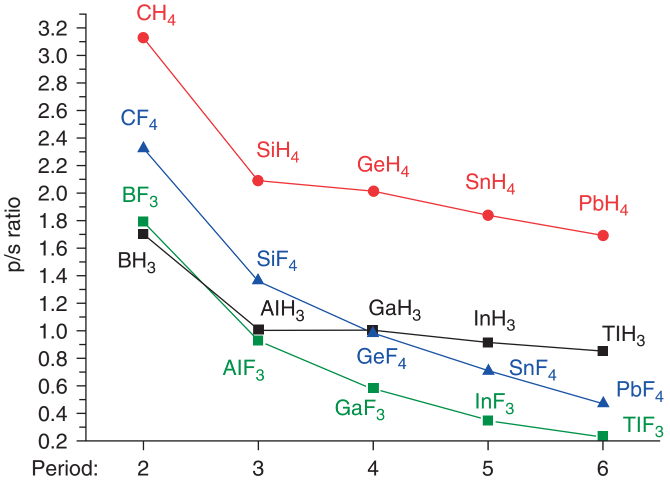

Figure 1.2 NAO/NLMO p/s hybridization ratios for hydrides and fluorides of second and third period elements in their maximum oxidation state (B3LYP/def2-TZVP results).

NBO scheme for d-orbital participation in main-group chemistry (see later text) might to some extent be biased by placing the outer d-orbitals into the ‘‘natural Rydberg set’’ of the NAO scheme [22], no such problem arises regarding the relative role of s- and p-orbitals. Figure 1.2 illustrates the NAO/NLMO p/s hybridization ratios of some simple compounds when moving down a given p-block main group. Starting with simple homoleptic hydrogen compounds in the maximum oxidation state of the central element (Figure 1.2; lone pairs are absent), we see clearly that the 2p-compounds exhibit hybridizations that correspond reasonably well to those expected from the bond angles and the usual formal considerations. This holds notably well for hydrocarbons, in line with the relative success and popularity of using bond angles to discuss hybridization (and vice versa) in organic chemistry. In contrast, the 3p- or 4p-compounds exhibit much larger *n*s- and lower *n*p-character in their bonding hybrids. It is clear, that here the usual simple relations between bond angles and central-atom hybridization cease to function.

Replacing hydrogen by fluorine as bonding partner (Figure 1.2) leads to a drastic reduction of the p/s ratios. Obviously, hybridization defects are enhanced significantly by the more electronegative fluorine substituents [23, 24] (for as yet unclear reasons, BF_3 is an exception to this rule). This goes parallel to strongly positive charges of the central atoms. As the central atom contracts, the sizes of its s- and p-orbitals become even more disparate: the contraction of the valence s-orbitals is more pronounced than that of the p-orbitals. This has further consequences for the bonding and chemistry of such compounds (see below). Note that even for a carbon compound like CF_4, hybridization defects are now already pronounced, and relations between bond angle and hybridization are not straightforward anymore. This also means that the assumptions of Bent’s rule [25] on the relations between bond angles and hybridization for heteroleptically substituted systems have to be modified to account for such hybridization defects.

1.2.2
The Inert-Pair Effect and its Dependence on Partial Charge of the Central Atom

Hybridization defects cause a general weakening of covalent bonds. This is related to the fact that hybridization is effective in stabilizing molecules by (i) improving bonding orbital overlaps and by (ii) minimizing destabilizing antibonding interactions [13]. Hybrids made from s- and p-orbitals with too dissimilar sizes are ineffective for both of these aspects and, thus, make poor covalent bonds (the overall benefits from hybridization may also decrease further down the group [13]). This affects, in particular, compounds of the heavier p-block elements in their maximum oxidation state. Here the valence s-orbital *has to be involved in bonding* and, thus, is required to hybridize to some extent with the p-orbitals. In contrast, in lower oxidation states, the valence s-character of the heavy p-block element tends to accumulate in a non-bonding lone-pair (lp) type orbital, and the bonds tend to be made largely by essentially unhybridized p-orbitals. This is more favorable for making stable bonds. The latter relationships can be extracted easily from the p/s hybridization ratios of ammonia and its heavier homologues in Figure 1.3: whereas isovalent hybridization is still effective for ammonia itself, the segregation into a lone-pair NLMO of predominant s-character and bonds with predominant p-character is apparent for the heavier homologues. Fluorine substitution does again enhance hybridization defects, and thus isovalent hybridization is largely absent now even for NF_3.

These observations provide a modern framework for rationalizing the inert-pair effect, that is, the fact that the highest oxidation state becomes increasingly

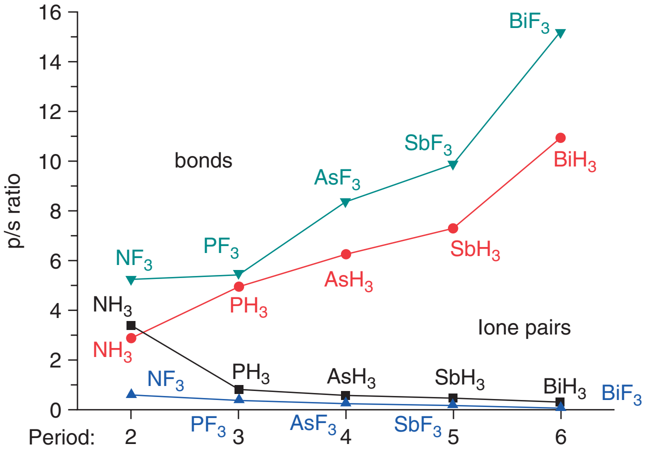

Figure 1.3 NAO/NLMO p/s hybridization ratios for bonds and lone pairs of second- and third-period hydrides and fluorides in lower oxidation state (B3LYP/def2-TZVP results).

unfavorable when moving down a given p-block main group. The first explanations based on an energetic unavailability of the *n*s-orbital were quickly found to be untenable and were replaced in the 1950s by Drago's [26] balance between the necessary energy for promotion to the higher valence state and the additional binding energy provided by the extra bonds in the high-valence compound. Due to a general weakening of bonds down a given group, the balance would then be shifted towards a destabilization of the higher oxidation state. The above considerations on hybridization defects tell us that, for example, an sp^3 valence state will never be reached in a compound like PbX_4 (cf. Figure 1.2) [24]. Instead, the lack of effective isovalent hybridization weakens the covalent bonds in the highest oxidation state. As hybridization is largely absent in the lower oxidation states (see earlier text), essentially pure p-orbitals are then used for bonding, making relatively strong bonds and thus stabilizing the two-electron-reduced oxidation state.

This also provides us with a ready explanation for why the inert-pair effect is much more pronounced for the truly inorganic compounds of a given heavy p-block element than for organoelement compounds or hydrides: [24] electronegative substituents like halogen, alkoxy or amido functionalities enhance hybridization defects dramatically in the highest oxidation state (cf. Figure 1.2), whereas the anyway marginal hybridization in the lower oxidation state is affected much less (cf. Figure 1.3). This explains why, for example, organolead compounds are actually much better known in their oxidation state +IV (e.g., tetraalkyl lead compounds, which for a long time, were used extensively as antiknock additives in gasoline), whereas inorganic lead(IV) compounds are either very unstable or, at least, strongly oxidizing, and lead(II) is the dominant oxidation state [24]. Similar comparisons may be made, for example, for Tl or Bi inorganic versus organoelement compounds. And successive substitution of alkyl groups by electronegative substituents is well known to destabilize the highest oxidation state. We mention here in passing, that for the 6p-elements, the 6p/6s size differences and thus the hybridization defects are aggravated (cf. Figures 1.2, 1.3) by the relativistic contraction of the 6s-orbital (see later text), leading to much more pronounced inert-pair effects compared to the 5p-homologues. The often found designation of the inert-pair effect as a relativistic effect is, however, partly misleading: relativistic effects are comparably unimportant for the hybridization defects of the 4p- and 5p-elements. Indeed, even the term "inert-pair effect" is somewhat unfortunate, given that in the highest oxidation state, the valence s-orbital participates *more* in bonding (relative to the p-orbitals) than assumed from the usual correlations with bond angles (Figure 1.2).

Related observations pertain to the stability of carbenes and their heavier homologues. It is well known that, for example, CH_2 has a triplet ground state, whereas its heavier homologues feature closed-shell singlet ground states with increasing singlet-triplet gaps down the group. This can be easily rationalized in comparison with the NLMO hybridizations for NH_3 and its heavier homologues (cf. Figure 1.3): isovalent hybridization is still favorable in the second period. Thus, the gain in exchange energy for a triplet state formed by the single occupation of one pure carbon 2p-orbital with π-symmetry and of one carbon-centered approximate $2s2p^2$ hybrid with σ-symmetry is sufficient to render it energetically competitive with the double occupation of the sp^2 hybrid for the closed-shell singlet. In contrast, in SiH_2 hybridization, defects give the σ-type Si-centered orbital largely 3s-character and the Si-H bonds mostly 3p-character. It is clear that double occupation of the σ-type lp is now favored in spite of the loss of exchange energy, giving a singlet ground state. Consequently, we expect that electronegative substituents (i) favor singlet over triplet ground states even for carbenes (and stabilize the singlet further for the heavier homologues) and (ii) stabilize the carbene overall compared to a corresponding tetravalent carbon compound. It is, thus, natural that in N-heterocyclic or ‘‘Arduengo-type’’ carbenes (NHCs), [27] the first stable carbenes found, the carbon atom is bound to two electronegative nitrogen atoms. Although cyclic delocalization and a +M-effect of the nitrogen free electron pairs on the carbene center are often invoked to rationalize the stability of NHCs, it is clear that the electronegativity of the substituents is also important as it favors hybridization defects of the carbon 2s- and 2p-orbitals and thus stabilizes both the lower oxidation state and the singlet ground state.

Mercury is the only metal that is liquid at room temperature; and it is well known that this is caused by the relativistic contraction of the 6s-shell [28, 29], which makes hybridization between 6s- and 6p- orbitals more difficult and thus diminishes the binding strength. That is, relativistically enhanced hybridization defects are responsible for the low cohesion energy and low melting and boiling points of mercury (e.g., compared to cadmium). The nevertheless reasonably inert character of elemental mercury is the consequence of an inert-pair effect also in the possible reaction products: relatively weak bonds in Hg(II) compounds, specifically when bound to very electronegative substituents, are due to strong hybridization defects. NAO/NLMO hybridization ratios for linear HgX_2 molecules (e.g., $6s6p^{0.20}5d^{0.14}$ for HgH_2, $6s6p^{0.06}5d^{0.21}$ for HgF_2) suggest that 6s6p- (or 6s5d-) hybrids may be less suitable qualitative bonding descriptions in such compounds than three-center four-electron bonding involving only the 6s-orbital (cf. discussions about Natural Population Analysis, NPA [22]). Interestingly, relatively weak intra molecular and intermolecular interactions in Hg(II) compounds are also responsible for the widespread occurrence of Hg(I)-species with Hg−Hg bonding [30] and for the existence of $Hg(IV)F_4$ under low-temperature matrix isolation conditions (see earlier text) [5, 6].

As already discussed, electronegative substituents destabilize the heavy p-block elements in their maximum oxidation state. Computationally, this may be seen clearly for calculated energies for 1,1-elimination reactions. For example, along the series PbR_4, PbR_3F, PbR_2F_2, $PbRF_3$, PbF_4 ($R = H$, CH_3), elimination of R_2, RF or F_2 becomes less endothermic or more exothermic [24]. However, at the same time, it is found, that the Pb-R and Pb-F bonds become shorter along the same series. That is, increasing hybridization defects due to electronegative substituents destabilize the Pb(IV) compounds thermochemically; yet they contract the bonds, essentially due to the smaller size of the more positively charged central atom [24]. Indeed, as the 6s-character of the bonds increases on average with increasing fluorine substitution, they become shorter, consistent with the smaller size of 6s- compared to 6p-orbitals. Yet the large difference in the sizes of 6s- and

6p-orbitals is at the same time responsible for the bond weakening. This leads to a breakdown of the frequently and implicitly assumed correlation between bond length and bond strength (in this case binding energy). This has been tested in more detail computationally by constructing the heavy ethane homologue Sn_2H_6 (with staggered structure and direct Sn−Sn bonding) and its successively fluorine-substituted analogues $Sn_2H_xF_{6-x}$ ($x = 0$-5) [31]. It turns out that, indeed, shorter Sn−Sn bond lengths in the fluorine-substituted derivatives do not correspond to larger but, in most cases, to lower Sn−Sn binding energies. That is, contraction of the Sn−Sn bonds due to the increasingly positive central-atom charges goes parallel to weaker bonds due to hybridization defects. Correlations with Sn-Sn stretching frequencies are also in disagreement with, for example, Badger's rule [31]. Further computations on the analogous series with E = C, Si, Ge indicates similar behavior for Ge as found for Sn, a more complicated, different behavior for carbon because of negative hyperconjugation effects, and the most ''normal'' behavior with reasonable correlation between shorter bonds and larger dissociation energies for E = Si [32]. We note that a similar breakdown of the correlation between bond lengths and binding energies has been found experimentally [33] (and was in part analyzed computationally [34]) for transition-metal phosphine complexes, where the more electronegative substituents give shorter but weaker $TM{-}PX_3$ bonds (see also Chapter 7 in this book). Again, hybridization defects are responsible for this breakdown of the usual bond-length/bond-strength correlations.

1.2.3
Stereo-Chemically Active versus Inactive Lone Pairs

A related but separate question concerns the ''stereo-chemical activity'' of the free electron pair in the oxidation state, two units below the maximum one. As we have seen earlier, simple relations between hybridization (and thus of s- or p-character of the lp) and bond angles fail for the heavier p-block compounds, because of hybridization defects. The VSEPR model assumes intrinsically that a lp will exhibit a space requirement in the coordination space of the central atom, in fact, more than a covalent single bond. Something like a ''stereo-chemically inactive lp'' is thus clearly outside the assumptions of the VSEPR model. Indeed, for coordination numbers below 6, the presence of lp is always found to exert a stereo-chemical influence, both in molecules or in extended solid-state structures. For larger coordination numbers than 6, the structural preferences are anyway not very clear-cut and dominated by fluxional situations. It is thus coordination number 6 that gives rise to notable exceptions to the VSEPR model and to a very subtle balance between different influences. Among molecular systems, XeF_6 is the most widely considered case [35–37]. While xenon hexafluoride exhibits partly ionized bonding and a clear stereo-chemical activity of the lone pair in the solid state, gas-phase spectroscopic studies suggest that gas-phase XeF_6 is a fluxional system, consistent with a nonnegligible but weak stereo-chemical activity [35]. Computational studies show that the energy difference between C_{3v} and $C_{2\nu}$ distorted octahedral and regular O_h structures are (i) very small and (ii) very difficult to calculate [36, 37]. Whereas early non-relativistic Hartree-Fock calculations give strongly distorted C_{3v} minima and very high-lying O_h structures, both relativistic effects (because of the contraction of the Xe 5s-orbital) and electron correlation stabilize the O_h structure [36]. The most recent and accurate calculations [37] used explicitly correlated CCSD(T)-F12b methods and showed the C_{3v} minima to be about 4 kJ mol^{-1} below the C_{2v}–symmetrical pseudo-rotation transition states and about 7–8 kJ mol^{-1} below the O_h-symmetrical stationary point on the potential energy surface (without vibrational corrections), consistent with a fluxional situation in the gas phase. XeF_6 is, thus, a remarkable border-line case, just barely on the side of a stereo-chemically active lp. The isoelectronic 5p-anions IF_6^- and TeF_6^{2-} appear to behave very similarly, according to computations [36]. Notably, however, the calculations suggest that, in contrast to these 5p-species, valence-isoelectronic compounds of both lighter and heavier central atoms exhibit regular octahedral structures [36]! For the 3p- or 4p-species (e.g., ClF_6^-, BrF_6^-), this may be attributed to the smaller size of the central atom and thus to steric crowding. In contrast, calculations for 6p-species like PoF_6^{2-}, AtF_6^- or RnF_6 indicate that the large relativistic contraction of the 6s-orbital renders the lp stereo-chemically inactive and thus favors the O_h structures [36].

Another important aspect related to the presence of stereochemically active lp are trends in inversion barriers and thus the question of the configurational stability of, for example, amines versus phosphines, carbanions versus silyl anions, and so on. The inversion barriers tend to increase sharply from the 2p- to the homologous 3p-systems. For example, ammonia is fluxional with an inversion barrier of ca. 25 kJ mol^{-1}, in the range of zero-point vibrations [38]. In contrast, PH_3 exhibits a barrier of ca. 130 kJ mol^{-1} and, thus, is a much more rigid molecule [39]. Computations suggest that the barriers further increase moderately to AsH_3 and SbH_3 and, then again, more sharply to BiH_3 (due to the relativistic contraction of the 6s-orbital) [40]. Analogous considerations hold for substituted amines and phosphines. Similarly, carbanions tend to have much smaller inversion barriers than the corresponding silyl anions, which is of fundamental importance for the configurational stability of enantiomers in the case of chiral substitution patterns [41]. These differences between the 2p-species and their heavier homologues (and the relativistically enhanced barriers for the 6p-species) may be rationalized straightforwardly from the above considerations on hybridization defects: pyramidal minimum structures of amines or carbanions are expected to still exhibit to a reasonable approximation isovalent hybridization of both bonding and free electron pairs. In contrast, for phosphines or silyl anions, the lp have largely s-character and the bonds largely p-character (cf. Figure 1.3). At the trigonal transition state for inversion, the lp is required by symmetry to be a pure p-orbital, whereas the bonding orbitals have to hybridize the s- and p-orbitals. Whereas this leads to reasonably sp^2-hybridized bonding at the transition state for the 2p-elements, appreciable hybridization defects apply for the heavier congeners (with large s-character involved in the E–H bonds). As a consequence of the arising poor bonding overlap, the transition state is destabilized in the latter case, leading to substantially increased inversion barriers.

Table 1.1 Central-atom NPA charges Q(E) and NAO/NLMO hybridization ratios of bonds (BD) and lone pairs for minima and inversion transition states of ammonia homologues[a].

		Q (E)	**BD**	**Lone pair**
NH_3	min	−1.04	$sp^{2.87}$	$sp^{3.39}$
	TS	−1.11	$sp^{1.99}$	p
NH_2F	min	−0.38	N-H: $sp^{2.93}$ N-F: $sp^{5.22}$	$sp^{1.58}$
	TS	−0.51	N-H: $sp^{1.38}$ N-F: $sp^{2.80}$	p
NHF_2	min	0.14	N-H: $sp^{3.06}$ N-F: $sp^{5.18}$	$sp^{0.93}$
	TS	0.00	N-H: $sp^{0.92}$ N-F: $sp^{1.98}$	p
NF_3	min	0.58	$sp^{5.24}$	$sp^{0.62}$
	TS	0.44	$sp^{1.30}$	p
PH_3	min	0.02	$sp^{4.95}$	$sp^{0.81}$
	TS	−0.21	$sp^{1.52}$	p

[a] B3LYP/def2-TZVP results.

These considerations are supported by the NAO/NLMO hybridization ratios of NH_3 versus PH_3 at both minimum and transition-state structures (Table 1.1).

Most notably, we may use this framework also to understand the effect of electronegative substituents on inversion barriers. For example, the barrier increases substantially from NH_3 to NH_2F to NHF_2 to NF_3 (cf. also Ref. [42]), consistent with an increase in hybridization defects along this series at the planar transition-state structure (Table 1.1): differences between N−H and N−F bond hybridizations reflect the different H and F electronegativities, consistent with an appropriately modified version (accounting for hybridization defects, see earlier text) of Bent's rule [25]. Interestingly, the N−H bonds at the minimum structure are still close to idealized sp^3 hybridization even in NH_2F and NHF_2, whereas the nitrogen lone pair and the N−F bond(s) feature increasing separation of the nitrogen s-character into the former. At the inversion transition state, the N−H bonds in NH_3 still exhibit the nominal sp^2 hybridization for a trigonal coordination. The substantial and worsening hybridization defects are particularly notable for the N−H bonds in NH_2F and NHF_2; and then they are also significant for the N−F bonds in NHF_2 and especially in NF_3. One might therefore expect to have very large barriers for species like PF_3, AsF_3, SbF_3, or BiF_3. However, in these cases it has been found unexpectedly by computations that inversion proceeds not via a D_{3h}-symmetrical trigonal but via a C_{2v}-symmetrical Y-shaped transition state, leading to lower barriers and, indeed, an inverted trend with the barriers decreasing down the group [43].

1.2.4

The Multiple-Bond Paradigm and the Question of Bond Strengths

Similar arguments may be applied to the relative instabilities and the often ''trans-bent'' structures of multiple bonds between the heavier p-block elements. Very often, these well-studied phenomena are rationalized from the singlet–triplet energy gaps of the carbene-like constituents that make up a given XX'E=E'YY' olefin analogue (or from the doublet–quartet gaps of carbyne analogues for alkyne analogues), using the framework of the Carter–Goddard–Trinquier–Malrieu (CGTM) model [44, 45]. That is, when for example the S-T gap of the carbene, silylene, and so on is large, the bonding is described as a donor–acceptor interaction of singlet closed-shell fragments, thus explaining both the relatively weak bond and the structural distortions from a planar olefin-like arrangement. For small S-T gaps, one combines conceptually triplet open-shell fragments, leading to the standard description of olefin-type double bonding with planar structure. However, just as we have argued above for the stabilities of NHCs and related species, it may actually be more worthwhile to put the relative sizes of s- and p-orbitals, rather than energies, into focus. We then argue via isovalent hybridization to explain the olefin-like case and via increasing hybridization defects for heavier p-block central atoms and for electronegative substituents.

This then also explains the influence of electronegative substituents. For example, enhanced hybridization defects for the positively charged carbon centers explain straightforwardly why the C=C double bond in C_2F_4 is much weaker than that in ethylene: on one hand, the C–C sigma bonding is weakened by the incresased hybridization defects in the fluorine-substituted olefin; on the other hand, the singlet CF_2 fragment is not affected adversely as carbon s- and p-orbitals segregate into lp and C–F bonds, respectively (see above). Similarly, the trans-bent structures of silenes, germenes, or stannenes reflect the lack of efficient isovalent hybridization. In fact, the double bonds are sufficiently weak that the isolated singlet ER_2 fragments become more stable down the group, which is just another manifestation of the inert-pair effect. As we have seen earlier, the latter can be conveniently discussed via hybridization defects for the high-valent compound (in the present case the olefin-homologue) and via segregation of s- and p-orbitals in the low-valent situation (i.e., for the fragments). This closes the circle of arguments and shows that the consideration of the relative sizes of valence s- and p-orbitals does indeed provide a broad framework for discussing periodic trends of main-group structure, stability, and bonding. Similar considerations may be applied to the energetics and bending of formal triple bonds [46].

Evaluation of σ- and π-bond increments reveals that for the 2p-elements of groups 15, 16, and 17, weakening of the corresponding single bonds by the so-called ''lone-pair bond weakening effect'' (LPBW) [47] works in favor of multiple bonding, whereas this aspect does not apply to the heavier homologues. Examples are the weak E-E single bonds of hydrazine, hydrogen peroxide, or difluorine compared to diphosphine, hydrogen disulfide, or dichlorine, respectively. Notably, the LPBW effect is yet another result of the particularly compact, nodeless

2p-shell: the π-type lp exhibit substantial Pauli repulsion with the σ-bonding orbitals [48]. Interestingly, from a VB point of view, such compounds frequently may be classified as charge-shift-bonding cases (See Chapter 5 in Volume 1).

1.2.5
Influence of Hybridization Defects on Magnetic-Resonance Parameters

For the heavier p-block elements, hybridization defects lead to enhanced *n*s-character in bonds, more than one might expect from structural considerations (see earlier). This holds for the highest oxidation state of the central atom, whereas the s-character concentrates into lps for the lower oxidation states, leaving predominantly p-character for the bonding orbitals. One quantity that is known to be particularly strongly connected to the s-character in bonds is indirect NMR spin–spin coupling constants [49]. The Fermi-contact part of such coupling constants depends crucially on the s-character of the valence orbitals involved in bonding as the communication between the nuclear spin moments happens exclusively via the spherically symmetrical part of the spin density around a given nucleus. Larger s-character enhances the communication, leading to larger coupling constants in absolute terms (the sign of the coupling depends also on the relative signs of the two nuclear g-values) for compounds, where the two atoms involved are in their maximum oxidation state. Matters become more complicated when lone pairs are present; then, the bonds have largely p-character. The coupling constants tend to be smaller and are also potentially influenced by involvement of the lp and by other coupling terms.

It has furthermore been demonstrated [50], that a related Fermi-contact mechanism dominates spin-orbit effects on the NMR chemical shifts of nuclei connected to heavy-atom centers (the so-called ‘‘heavy-atom effect on the light-atom shielding,’’ HALA [51], even though the NMR nucleus may also, in fact, be a heavy atom). Here s-character in bonding has also been found to be extremely important in defining the magnitude of such ‘‘spin-orbit shifts’’ (SO shifts). Therefore, the SO shifts are large for p-block elements in their maximum oxidation state (even larger for hydrogen [52, 53]), whereas the SO effects are typically small in lower oxidation states because of the predominant p-character in the bonds [54, 55].

As we have learned earlier, electronegative substituents enhance hybridization defects and, thus, increase the s-character in the bonds. This explains why, for example, substitution of the hydrogen atoms in CH_3I by fluorine atoms in CF_3I does essentially double the spin-orbit effects on the ^{13}C shifts because of the heavy iodine substituent, from about −30 ppm to about −60 ppm, reducing the high-frequency shift in the ^{13}C spectrum from about 145 ppm at the nonrelativistic level to about 115 ppm upon inclusion of spin-orbit coupling [49]. The NPA charge on carbon increases from −0.70 in CH_3I to +0.85 in CF_3I, and consequently, the p/s hybridization ratio of the C-I bond (NAO/NLMO value) decreases from $sp^{4.14}$ to $sp^{1.96}$ (B3LYP/def2-TZVP results). This explains the more efficient Fermi-contact mechanism (direct contributions from fluorine SO coupling are small). Along the same line of argument, the more-than-linear increase of ^{13}C spin-orbit shifts with

n along the series $CH_{4-n}I_n$, compared to the only linear increase along the series $CBr_{4-n}I_n$, has been rationalized; whereas the positive charge on carbon and, thus, the carbon s-character of the C–I bonds increases with n in the former series, it stays relatively constant in the latter series (because of the similar electronegativities of Br and I) [54].

Other properties in magnetic resonance may be mentioned here, for example, hyperfine couplings. As the isotropic hyperfine coupling also depends crucially on the spherical spin-density distribution around the nucleus in question, s-character in bonding and, thus, hybridization defects will be important. Obviously, for open-shell radicals the s-character of the singly occupied MO(s) is the most crucial aspect, but spin polarization of doubly occupied MOs with core or valence s-character may also be relevant (e.g., when the singly occupied molecular orbital is of pure p-character at the given atom).

1.3

The Role of the *Outer* d-Orbitals in Bonding

Whether or not the outer d-orbitals are true valence orbitals for the heavier p-block elements and, thus, allow the octet rule to be violated in ‘‘hypervalent compounds’’ has been one of the most controversial questions in main-group bonding for decades. Whereas, during the past 15 years, the balance has dipped clearly to the side of the d-orbitals acting only as polarization functions rather than having a true valence-orbital character, it is worthwhile to consider here briefly why the controversy has lasted so long. We will then put the hypervalency issue particularly into the context of radial nodes. Other aspects of the topic are discussed in Chapter 3 in this book.

In the early days of discussions of main-group bonding, it was probably Pauling’s electroneutrality principle [56] that favored a picture of the outer d-orbitals as influential valence orbitals: resonance structures with appreciably positive formal charges on the central p-block main-group atom were considered to be unlikely and disfavored. Therefore, for example, a semipolar resonance structure for the sulfate ion with only single S–O bonds, a dipositive formal charge on sulfur, and a negative formal charge on each of the oxygen atoms, consistent with the original suggestion by Lewis [57], was disregarded in the 1960s or 1970s. Hypervalent resonance structures with four S=O double bonds have dominated the inorganic-chemistry textbooks (in fact, they still do so today!). On the other hand, the discovery of noble-gas compounds in the early 1960s gave a boost to three-center four-electron bonding models [58] and MO-based scenarios that avoided ‘‘true’’ hypervalency. In the 1970s, when the first realistic *ab initio* wave functions could be obtained, bonding analyses were inevitably done using Mulliken’s population analysis [20]. As we now know, the Mulliken populations are not only very basis-set dependent (earlier text), but they also tend to provide a much too covalent picture when the electronegativities of the bonding partners differ significantly. This ‘‘cemented’’ the electroneutrality-principle point of view for many more years. More up-to-date methods, either of population-analysis type (e.g., natural population analysis [21]) or of real-space type (e.g., Bader's quantum theory of atoms in molecules, QTAIMs [59]), give a more ionic picture in general and for hypervalent p-block compounds, in particular. This supports multicenter bonding and negative hyperconjugation in MO language or, equivalently, partially ionic resonance structures and no-bond double-bond resonance in VB language. d-Orbital participation, thus, is inevitably computed to be much less pronounced than suggested by Mulliken populations. As partial atomic charges are no true observables (no, not even the QTAIM ones!), none of these schemes alone can provide a definite answer to the true covalency and, thus, to the quantitative involvement of the d-orbitals in bonding. In fact, one can find weaknesses in essentially any of the analysis methods, for example, a bias *against* d-orbital participation in the NBO scheme (because of the classification of the d-functions with the ''natural Rydberg set'' [22]) or a possibly too ionic description by QTAIM charges [60]. Yet the accumulated information provided by a wide range of the most refined models available does, indeed, provide a much less covalent, less electro-neutral picture and, thus, a smaller involvement of the outer d-orbitals in bonding than assumed before.

We may place the issue of hypervalent bonding into the more general context of the discussion throughout this chapter: hypervalent p-block compounds are stabilized by semipolar or partially ionic resonance structures in VB language or by multicenter bonding in MO language. Either way, a partial positive charge on the central atom is desirable. This is favored by (i) a high electronegativity of the substituents and by (ii) a low electronegativity of the central atom. This is why fluorine substitution is most favorable in stabilizing hypervalent compounds, followed by oxygen substitution. At the same time, it is clear that the high electronegativity and small size of the 2p-elements makes them rather unfavorable as central atoms, consistent with observation. The nodelessness of the 2p-shell renders the 2p-elements electronegative and small and, thereby, helps to fulfill the octet rule in the 2p-series. In contrast, the heavier p-block elements are larger and less electronegative and, thus, favored as central atoms. In other words, the nodal structure of the valence *n*p-orbitals, rather than the availability of the outer *n*d-orbitals, is decisive for the apparent violation of the octet rule for the heavier elements.

Of course, the octet is usually not actually violated. Multicenter bonding models require some MOs that are essentially nonbonding and concentrated only on the substituents, and thus, the number of electrons in the valence shell of the central atom rarely exceeds the octet. However, here we should distinguish, between what Musher [61] more than 40 years ago termed hypervalent compounds of first and second kind, respectively. In the first class, the central atom is not in its maximum oxidation state, and thus, the central-atom *n*s-character concentrates in a lp. Then, as we have discussed in detail above, the bonds are made mainly from *n*p-orbitals of the central atom, and thus, the assumptions of the usual three-center-four-electron bonding models are nicely fulfilled. In contrast, hypervalent compounds of the second kind exhibit the maximum oxidation state and, thus, necessarily involve the *n*s-orbitals fully in bonding. One thus sees (i) extensive hybridization defects (see earlier text), (ii) a more complicated bonding pattern in which the *n*s-orbitals are also involved in multicenter delocalization [62], and c) often a subtle "true" hypervalency. The latter point has been demonstrated most convincingly by Häser [63] in his unique analysis scheme: Häser's method is based on projecting the one-particle density matrix onto spheres around the atom. Expansion of the radius of the sphere around the central atom in, for example, PF_5 or SF_6 followed by integration of the AO contributions to the sphere populations up to a certain radius around the central atom indicated that the octet was violated, albeit very slightly, in contrast to hypervalent compounds of the first kind (e.g. XeF_2), where no octet violation could be registered by this approach. Closer analysis indicated populations with d-symmetry around the central atom in hypervalent compounds of the second kind [61]. However, these populations did not possess true valence-orbital character but essentially described the outermost rim of the attractive potential trough of the atom, already close to the substituents. Interesting further insights were obtained regarding the multicenter delocalization in, for example, PF_5 [61]. Indeed, analyses of such species by natural resonance theory (NRT [64], based on a superposition of Lewis structures from strictly localized NBOs) also indicate slight violations of the octet in contrast to compounds of the first kind. An aspect that deserves further scrutiny is to what extent the octet may also be violated when multicenter delocalization involves predominantly π-type orbitals on the substituents (in the sulfate ion or iso-electronic ions little octet violation mentioned earlier seems to be apparent from NRT, but more systems need to be analyzed). Unfortunately Häser's approach has not been pursued further, because of his early demise. The method appears to be very powerful in the context of hypervalency discussions or for monitoring hybridization.

1.4
Secondary Periodicities: Incomplete-Screening and Relativistic Effects

So far the nodal structure of the valence s- and p-orbitals themselves has been in our focus, allowing us to explain the special role of the 2p-elements compared to their heavier homologues. The further modulations of chemical and physical properties as we descend to a given group from period 3 on are often summarized under the term "secondary periodicity" [65, 66]. The main influences here are incomplete screening of nuclear charge by filled core or semi-core shells and the effects of special relativity. The former reflect shell structure of the atom as a whole and are already important for differences and similarities of the homologous third and fourth period elements, whereas the latter become crucial mainly for the chemistry of the sixth period elements. These aspects have been discussed in detail in various review articles (see, e.g., Refs [16, 28, 67]), and we, thus, touch them only briefly.

The most well-known incomplete-screening effect in the periodic table, the lanthanide contraction, is due to the successive filling of the 4f-shell by 14 electrons, leading to a contraction of the size of the later lanthanides and of the elements following them in the sixth period. This lanthanide contraction is most notable for the early 5d transition metals (e.g., regarding the similarity of the properties of Zr and Hf). It is still effective for the late 5d- and early 6p-elements, but in this case it is overshadowed by the relativistic contraction of the 6s-shell (see below) [65]. The combined action of lanthanide contraction and relativity is responsible for a somewhat higher electronegativity of, for example, Pb versus Sn. As discussed above, the relativistic contraction of the 6s-shell is responsible for an enhancement of the inert-pair effect for the 6p-elements.

Somewhat less well known but nevertheless important is the incomplete screening of nuclear charge by filling of the 3d-shell (sometimes called the ''scandide contraction'' [28, 65]). It is responsible for a contraction of the valence orbitals of the 4p-elements, in particular of those following directly on the 3d-series. This leads to a pronounced similarity of the electronegativities (in fact a slightly larger one for the 4p-element in the modern scales) and covalent radii of Al versus Ga, Si versus Ge, P versus As, and so on. For example, in covalent bonds to carbon or hydrogen, Ga is slightly smaller than Al (even more so for element-element bonds). In contrast, the slightly higher electronegativity of Ga reduces electrostatic interactions in more ionic compounds, and thus, a more ''normal'' behavior with larger bond lengths for Ga is found, for example, for halides. Whereas this has not been studied in detail so far, the scandide contraction probably enhances hybridization defects for the early 4p-elements as it likely affects the 4s-orbitals more than the 4p-orbitals and, thus, may overall increase the relevant differences in their radial extent. This may explain certain irregularities in the chemical properties for 3p- versus 4p- homologues, even further to the right in the p-block, that is, for S versus Se or Cl versus Br.

It is interesting that incomplete screening of nuclear charge appears to be most pronouncedly caused by those shells that have no radial node such as the 3d- and 4f-shells. It is so far unclear why, for example, the 4d-contraction should be less effective than the 3d-contraction (the actinide contraction would be smaller than the lanthanide contraction without relativistic effects but is significantly enhanced by the latter, thus becoming overall larger [68]). We may even consider a ''2p-contraction'' in the comparison of ionization energies and electronegativities for Li versus Na or Be versus Mg. It has been shown computationally [69, 70], that the question whether Li or Na is more electronegative depends on the bonding situation: while σ-bonded ligands with some covalency (e.g., hydride or alkyl) give rise to a somewhat higher electronegativity of Na compared to Li, more electronegative ligands with some π-donor character (e.g., NH_2, OH, halogen, Cp) give more positive Na than Li charges. Closer analysis indicates that the Li 2s-orbital is very well shielded by the 1s core shell, whereas the 3s-orbital of Na experiences more incomplete shielding by the 2p-shell [65]. Together with the opposing effect of the larger radius of Na compared to Li, this leads to these somewhat unusual and subtle trends. Pyykkö has analyzed them further using ''pseudo atoms'' in which core shells have been deleted and the nuclear charge has been reduced, in analogy to earlier related studies for the lanthanide and scandide contractions

[65, 69, 71]. Notably, the observation of ''inverted lithium-sodium electronegativities'' by computations had been motivated by peculiar anomalies in the gas-phase thermochemistry of the group 1 elements [65].

1.5
''Honorary d-Elements'': the Peculiarities of Structure and Bonding of the Heavy Group 2 Elements

We have already concluded that the *outer* d-orbitals of the p-block elements are polarization functions but no true valence orbitals. This is well-known to be different for the *inner* d-orbitals of the transition metals, which dominate covalent bonding in the transition series. The heavier group 2 elements (Ca, Sr, Ba, Ra) also exhibit such *inner* (*n*-1)d-orbitals. Whereas these play essentially no role in bonding for the bulk metals or for neutral metal clusters, which are clearly dominated by the valence s-orbitals of the elements, matters become different with increasing positive charge on a given heavy group 2 element. Indeed, as we proceed to the most electronegative bonding partners (e.g., fluorine or oxygen), the *absolute* role of covalent bonding decreases, but the *relative* role of the (*n*-1)d-orbitals in the diminishing covalent bonding contributions increases to the extent that, for a molecule like BaF_2, covalent bonding is almost entirely due to the Ba 5d-orbitals. This places these elements at the border line with the early transition metals and the lanthanides, and Pyykkö has coined the term ''honorary d-elements'' to indicate this [4]. The importance of d-orbital involvement in bonding for the heavy alkaline earth elements is not a purely theoretical matter but manifests itself in structural peculiarities. The oldest example are observations in the 1960s that the molecular dihalides of the heavier group 2 elements in the gas phase may actually exhibit bent rather than linear structures whereas the Be or Mg dihalides are all clearly linear (see Ref. [3] for further literature). Different spectroscopic or electron diffraction techniques gave partly conflicting results, and the bent nature of molecules like BaF_2 was later established beyond doubt by up-to-date computational methods [72]. Such calculations provided evidence that even smaller bending angles and larger linearization energies could be obtained when replacing halogen or other π-donor ligands by pure σ-donors like hydride [73] or alkyl [74] ligands. Indeed, experimental evidence for bent group 2 or lanthanide(II) dialkyl complexes is now available [75]. Bending of the group 2 metallocenes had been discussed even earlier. However, from today's perspective, these metallocenes are at best quasi-linear with very shallow bending potential curves, as π-bonding actually favors linear arrangements [76].

Detailed bonding analyses gave a rather interesting picture of those factors that favor the bent or linear structures: [3] linearity is obviously enhanced by Pauli or electrostatic repulsion between the M–X bonds or between X^- anions, respectively, in agreement with the assumptions of the VSEPR model. Two apparently very different factors favoring bending had been discussed controversially for decades, (i) involvement of (*n*-1)d-orbitals in σ-bonds to the ligands (see earlier text) and

(ii) ''inverse'' polarization of the M^{2+} cations, leading to an electrostatic stabilization of the bent structure. Computations [67, 68] indicated that (i) both factors contribute to the bending and (ii) they are not strictly separable. The latter point may be appreciated from the fact that the polarizability of the cation is dominated by its outermost ($n-1$)p-shell. The ($n-1$)d-orbitals, thus, act as the primary polarization functions of the semi-core orbitals. At the same time, bending due to involvement of the valence ($n-1$)d-orbitals in covalent bonding will clearly lead to Pauli repulsion with the core and thus deformation of the penultimate p-shell. Therefore the covalent and core-polarization aspects of bending are closely interrelated as could be shown by a number of analysis procedures [67, 68]. The complications are due to the fact that outermost core ($n-1$)p- and valence ($n-1$)d-orbitals share the same principal quantum number.

The role of π-bonding is also subtle: for the given group 2 examples with ''weak π-donor'' halide or related ligands, π-bonding clearly favors the linear structures [77]. For more covalent transition-metal examples with strong donor ligands like ZrO_2, overlap of the π-type oxygen lp with an in-plane Zr d-orbital actually favors even more pronounced bending [72]. These aspects show up also for more complex heteroleptic complexes. Indeed, the ''non-VSEPR'' structures are not restricted to exotic dicoordinate species but extend also to higher coordination numbers. For example, both computations and experiments indicate that rather peculiar structures may be favored for dimeric M_2X_4 systems [78, 79] for exactly the same reasons that also account for the bending of the monomers. This author has argued that many peculiar bulk solid-state structures of heavy alkaline-earth dihalides or dihydrides (and of many early transition-metal compounds) also reflect the involvement of the ($n-1$)d-orbitals in σ-bonding [3].

To complete the link to the transition metals, we note in passing that the peculiar distorted trigonal prismatic structures of species like WH_6 or $W(CH_3)_6$ or the preferences for square pyramidal rather than trigonal bipyramidal structures of TaH_5 or $Ta(CH_3)_5$ may be rationalized along similar lines (again π-bonding for analogous halide complexes gives the ''classical'' VSEPR structures in those cases). Importantly, however, covalency is much more important for such d^0 species further to the right in the periodic table, and at the same time, core polarizability is expected to be much less pronounced than for group 2 species. Therefore, a covalent interpretation of such structures by d-orbital participation in σ- (and partly π-) bonding is much more reasonable than arguing via core polarization as has been done within the framework of a proposed ''extended VSEPR model'' [80] based on the Laplacian of the charge density. More detailed arguments may be found in Ref. [3]. We note that a decomposition of the Laplacian into strictly localized NBOs for complexes like Me_3NbCl_2 and Me_2NbCl_3 confirms the ''covalent'' rationalization; [81] it turns out that maxima in the negative Laplacian, previously tagged ''core shell charge concentrations'' within extended VSEPR studies, in fact, reflect the backside lobes of the ($n-1$)d-orbitals involved in covalent σ-bonding. This is consistent with the fact that the ''charge concentrations'' are even present when a frozen core is used [82].

1.6
Concluding Remarks

In this chapter, we have tried to emphasize general aspects of main-group chemical bonding, with particular emphasis on periodic trends. The periodic table remains the most important classification tool in chemistry, and it is crucial to understand even subtle secondary periodicities if one is to make efficient use of the various elements for different chemical applications. The radial nodal structure of the valence orbitals has been pointed out to account for more of the known trends than most practitioners of chemistry are aware of. For example, the inversion barriers of phosphines or silyl anions, the dependence of the inert-pair effect on the electronegativity of the substituents, the stability of carbene- or carbyne-type species or of multiple bonds between heavy main-group elements are all intricately linked to hybridization defects of s- and p-valence orbitals of disparate sizes. Even the question of hypervalency is closely connected to the effects of ''primogenic repulsion''.

Further important influences on the periodic trends arise from partial screening of nuclear charge (including lanthanide/actinide contraction, scandide contraction, and even a 2p-contraction) and from the effects of special relativity. Various aspects of main-group bonding are covered in more detail elsewhere in this book.

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