

The Role of Radial Nodes of Atomic Orbitals for Chemical Bonding and the Periodic Table

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Abstract: The role of radial nodes, or of their absence, in valence orbitals for chemical bonding and periodic trends is discussed from a unified viewpoint. In particular, we emphasize the special role of the absence of a radial node whenever a shell with angular quantum number l is occupied for the first time (lack of “primogenic repulsion”), as with the 1s, 2p, 3d, and 4f shells. Although the consequences of the very compact 2p shell (e.g. good iso-valent hybridization, multiple bonding, high electronegativity, lone-pair repulsion, octet rule) are relatively well known, it seems that some of the aspects of the very compact 3d shell in transition-metal chemistry are less well appreciated, e.g., the often weakened and stretched bonds at equilibrium structure, the frequently colored complexes, and the importance of nondynamical electron-correlation effects in bonding.

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Introduction

Some of the bonding aspects of the radial nodes of atomic orbitals have been appreciated since the early days of molecular orbital theory. The special role of the 1s, 2p, 3d, or 4f shells has been pointed out already by Jørgensen¹: they lack a core shell of the same angular momentum and thus do not have a radial node. This was re-emphasized by Pyykkö,² who coined the term “primogenic repulsion” for the effect of inner core shells on the shape and energies of valence orbitals and who studied the effects of incomplete shielding of nuclear charge by core shells using the concept of “pseudo atoms”.³ Matters were taken further by Kutzelnigg in his classical work on bonding in higher main-group compounds,^{4,5} in which the concept of “hybridization defects” was used to explain the special role of the p-block elements of the second period (“first row”), in particular of carbon, in contrast to those of the lower rows (see below).

These more or less historical, introductory points already indicate some of the consequences the radial nodes have for chemistry. It is in particular the manifestations of the lack of radial nodes for the indicated first occupation of a given angular momentum subshell that are particularly interesting. Some of the aspects are implicit in discussions by some communities of chemists. However, experience with teaching chemistry students in inorganic chemistry courses, as well as discussions with mainly experimental chemists have suggested to this author, that the importance of radial nodes as a guiding principle to understand periodic trends and chemical behavior is not generally

appreciated. This short review points thus to the consequences of radial nodes and of the associated variations in the radial extents of valence orbitals, from a unified viewpoint. As we aim at a general readership of chemists, the mathematical/physical formalism will be kept to an absolute minimum. We will mainly point to those consequences of the presence or absence of radial nodes, which are directly relevant to chemical behavior and periodic trends.

Some Elementary Theoretical Aspects

Nodes are intrinsic features of atomic and molecular wavefunctions, and they are closely coupled to the orthogonality between wavefunctions for different solutions of the Schrödinger equation. The classical example of a vibrating string (Fig. 1) already indicates how the phase of the different solutions of the underlying differential equation changes at various nodal points, and how this ensures the mutual orthogonality of the solutions. As can be found in any textbook on quantum mechanics, the result may be transferred directly to the particle in a one-dimensional box, and it is obvious that the underlying principles will hold also for more complicated systems. Here, we will restrict considerations to spherical atoms and subsequently transfer the results to atoms in a molecular environment. For hydrogenic atoms, the

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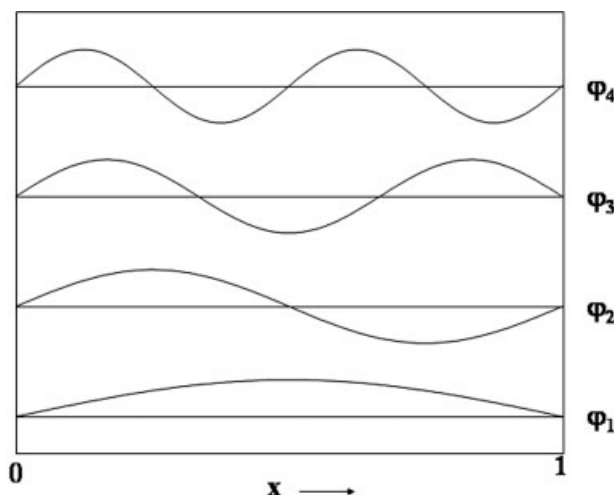


Figure 1. The classical example of a vibrating string, which is related to the solution of the problem of a particle in a one-dimensional box. In both cases, orthogonality between different solutions of the underlying differential equation may be expressed by $\int_{x=0}^1 \varphi_i \varphi_j dx = 0$ for $i \neq j$. Note how the phases of the different solutions, as defined by the nodes, act to fulfill this orthogonality.

solution of the Schrödinger equation in spherical coordinates leads to the well-known separation into radial and angular parts, with their corresponding solutions. The radial solutions $R_{n,l}$ are the well-known products of an exponential (which ensures the correct asymptotic decay and the correct nuclear cusp for s-functions) and of an associated Laguerre polynomial, $L(r)$. They depend indirectly on the angular part, via an l -dependent coupling term. The specific solutions $R_{n,l}$ for some relevant orbitals are (with $\rho = 2Zr/na_0$)⁶

$$\begin{aligned}
 1s : R_{1,0} &= 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho/2}; & 2s : R_{2,0} &= \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \rho) e^{-\rho/4}; \\
 2p : R_{2,1} &= \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/4}; \\
 3s : R_{3,0} &= \frac{1}{9\sqrt{3}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - 6\rho + \rho^2) e^{-\rho/6}; \\
 3p : R_{3,1} &= \frac{1}{9\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} (4 - \rho) e^{-\rho/6}; \\
 3d : R_{3,2} &= \frac{1}{9\sqrt{30}} \left(\frac{Z}{a_0} \right)^{3/2} \rho^2 e^{-\rho/6}. & (1)
 \end{aligned}$$

It is obvious, that the 1s wavefunction is nodeless, whereas the 2s orbital has one radial node at $\rho = 2$, the 3s orbital two radial nodes at $\rho = 3 \pm \sqrt{3}$, and so on. This is due to the necessity of orthogonality of the different solutions, which may be achieved either by angular nodes for orbitals with different l and/or ml , or by radial nodes if l and ml are identical. In analogy, the 2p orbitals have only a “trivial” radial node at $r = 0$. The angular part produces its own node, which cuts through the

same point. The higher p-orbitals obtain further radial nodes at finite r (e.g., 3p at $\rho = 4$). The 3d orbitals have a double node at $r^2 = 0$ but no nodes at finite r . Similarly, the 4f orbitals exhibit only a trivial triple node at $r^3 = 0$ but no further radial nodes at finite r . Obviously, the number of radial nodes increases with principal quantum number n and is thus coupled to higher energies of the corresponding solutions. Although the relative energies are of course important, we wish to emphasize particularly the influence on the radial extent of a given orbital: More radial nodes will move the outermost maximum further away from the nucleus. This will be essential for the discussion in this article.

When turning to multielectron atoms, the energetic degeneracy of different angular momentum for a given n is lifted by electron–electron interactions, but the spherical symmetry remains. While it is now not possible anymore to solve the Schrödinger equation analytically, approximate solutions may still be separated conveniently into an angular part (still consisting of spherical harmonics) and a radial part, which can be solved numerically to any desired accuracy, or approximated as a basis-set expansion. The concept of atomic orbitals is based on a single-determinant approximation to the wavefunction, where the concept of radial nodes is preserved in close analogy to the one-electron atom. The concept may be identified, with somewhat more effort⁷ (e.g., by employing natural orbitals), also in multi-determinantal atomic wavefunctions, and together with the Aufbau and Pauli principles, it serves as fundamental basis for the Periodic Table. Most importantly, the atomic core shells in molecules still resemble their counterparts of the free atoms, in spite of the lower-symmetry environment. We may thus make good use of the concept of radial nodes of atomic orbitals also for understanding chemistry, at least in a qualitative sense.

The 1s Shell

The special role of the 1s-shell is easily appreciated. It tends to be particularly small, and Pyykkö and Zhao have argued⁸ that this may be understood when considering solutions of the atomic Schrödinger equation in different dimensions. However, there is also the case of the H^- ion, which may exhibit very large ionic radii in typical ionic hydrides. We may interpret this as poor buffer capability of the 1s shell for negative charge. It is interesting to note that systems with only a 1s valence shell provide us with the diatomics possessing both the shortest and the longest bond, that is H_2 and He_2 ,⁹ respectively.

The shielding of nuclear charge by a 1s shell is almost complete, so that effects of incomplete screening that lead to relatively strong binding of valence electrons following 2p, 3d, or 4f shells (see below) are virtually absent. One consequence is a lower electronegativity of Li compared to Na in simple σ -bonded compounds of the alkali metals¹⁰: The 1s core shell shields nuclear charge almost completely for the 2s valence electron in Li, which therefore is removed relatively easily, in spite of its small distance from the nucleus. In contrast, Na and its heavier homologues exhibit only incomplete screening of nuclear charge by the outermost p shell. As a further consequence, the trend of the first ionization potentials exhibits a “kink” between Li and Na when going down the group. Pyykkö showed

that similar trends may be observed in group 2.¹¹ He argued that it is not a special role of Li but a crossing of two trends between the second and third period.¹¹ Consequences of these partial screening effects include nonmonotonous energy trends of certain gas-phase metathesis reactions between group 1 compounds from different rows of the Periodic Table.¹⁰

The 2p Shell

The special role of the p-block elements of the second period (“first row”) is probably the best-documented consequence of radial nodes, or more precisely of their absence for the 2p valence shell. Pyykkö pointed out that the nodeless 2p orbital has a similar radial extent as the 2s orbital (which has one radial node).³ This idea was extended by Kutzelnigg, who introduced the concept of hybridization defects.^{4,5} Because of the similar radial extents of the 2s and 2p shells, these are particularly well suited for hybridization. The resulting hydrides are close to orthogonal at the central atom and are thus able to form good and strong bonds with other bonding partners. This good isovalent hybridization is a typical feature of organic chemistry and therefore deeply rooted in chemistry teaching. In contrast, the 3p orbitals (with one radial node) are already appreciably larger than the 3s orbitals (with two radial nodes), because of an additional centrifugal contribution to the repulsive potential exerted by the 2p core shell.⁴ Therefore, the concept of orthogonal hydrides starts to fail. Hybridization may only be used for the heavier main group elements, when nonorthogonal hydrides are accepted. However, then the famous relations between hybridization and bond angles (e.g., $sp^3 \hat{=} 109.5^\circ$), which are so common in organic chemistry, do not hold anymore.⁴ While hybridization is not necessary in molecular orbital treatments, it is possible to analyze MO wavefunctions *a posteriori* in terms of hybridizations. Depending somewhat on the type of population analysis used (one needs to analyze localized molecular orbitals in terms of their atomic contributions), the average hybridization of, e.g., Si in SiH₄ is computed to be near sp^2 , whereas C in CH₄ is close to ideal sp^3 hybridization. This appears to be a particularly difficult point to grasp for most chemists, as the interrelations between hybridization and bond angle are so deeply rooted in the early education in chemistry (even though the often circular nature of hybridization arguments as structure predictors has been realized early on¹²).

Bonds with the resulting nonorthogonal hydrides tend to be relatively weak.⁴ This is important to realize when one wants to explain the inert-pair effect, that is, the increasing instability of the highest oxidation state of a p-block element when going down the group (compared to the state reduced by two electrons). Drago¹³ explained the trend by the generally weaker bonding with more diffuse orbitals, which are less and less able to compensate the required promotion energy to construct the hybrid orbitals needed. However, closer analysis shows that the “promotion” to the required valence state does not occur, or occurs only incompletely.⁴ The formed nonorthogonal hydrides make relatively weak bonds, and it becomes thus more favorable to remain in the lower oxidation state. Here, the valence s-character is concentrated in a free electron pair at the central atom, and the bonds acquire predominantly p-character.

Electronegative substituents increase the size differences between valence s and p-orbitals at the central atoms. Hybridization defects are thereby enhanced, and the resulting covalent bonds are weakened.¹⁴ This explains for example, why organo-element compounds of the heavier p-block elements in their highest oxidation states are actually often quite stable (sometimes the lower oxidation states are even unknown or postulated only as reactive intermediates), whereas substitution of organic groups by more electronegative elements destabilizes the higher oxidation states. As a good example, we may note the relative stability of organolead(IV) compounds compared with the instability of typical inorganic lead(IV) species.¹⁴ Electronegative substituents increase the positive charge at the central atom. Bonds to it therefore tend to shorten when more electronegative substituents are present.¹⁴ As increasing hybridization defects tend at the same time to weaken the bonds for heavy main-group elements, this may lead to the seemingly paradoxical situation that shorter bonds correspond to lower dissociation energies. A breakdown of the usually assumed correlation between bond length and bond strength results.^{15,16}

In cases with different substituents on the central main-group atom, the angles between the less electronegative substituents are normally larger than those between the more electronegative ones. Bent’s rule¹⁷ is often employed to rationalize these observations: s-character concentrates in the bonds to the less electronegative substituents and p-character towards the more electronegative ones. When considering hybridization defects, the relative distribution of s- and p-character towards different substituents still tends to follow Bent’s rule (indeed, the structural deviations from ideal coordination—e.g. in a tetrahedron—tend to be particularly pronounced for heavier main-group central atoms^{14,18}). However, on average the s-character in all bonds taken together tends to be much larger than expected from the angles (except when lone pairs are involved).^{14,18}

There are various further important consequences of the nodelessness of the 2p shell, which were discussed in detail by Kutzelnigg.⁴ As an example, we may mention the well-known bond weakening by lone-pair repulsion (cf. Sanderson¹⁹) for certain types of bonds between main-group atoms (examples for particularly weak single bonds include F₂, H₂O₂, or N₂H₄). Because of the small size of the 2p shell and the resulting relatively short bonds, s- and p-type lone-pairs may weaken the bond by strong Pauli repulsions. For the longer bonds in the heavier homologues, this effect is much less pronounced (and isovalent hybridization is thus needed less⁴). The higher preference of the 2p-elements for multiple bonding is indirectly related to this. The differences between the single- and multi-bonded systems for the lighter and heavier elements derive both from the intrinsically stronger π -bonds for the 2p-elements and (where lone pairs are present) from their relatively weak single bonds.⁴

Kutzelnigg also discussed in detail the state of the art at the time in describing bonding in the so-called hypervalent compounds of the heavier p-block elements.⁴ As is even more clear today, when more refined methods for bond analysis are available than in 1984, the role of the outer d-orbitals in bonding is relatively minor, and the “hypervalency” may be explained better by multicenter delocalization and large bond ionicity. The

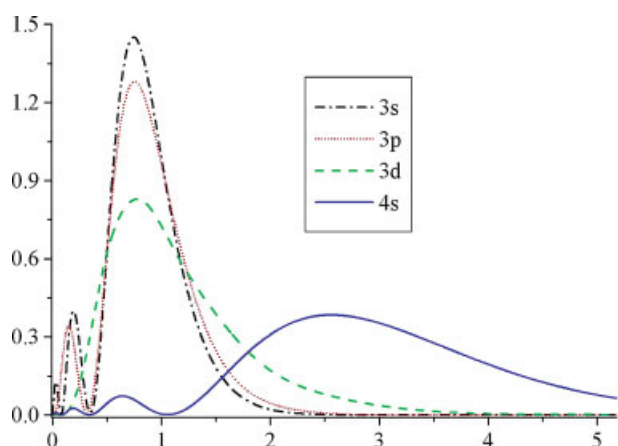


Figure 2. Radial probability densities for various orbitals of the Mn ($S = 5/2$) ground state. The α -AOs derived from B3LYP DFT calculations are shown. Note the similar radial extent of the outermost maxima of 3s, 3p, and 3d shells, and note also the lack of a radial node in the 3d shell. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

latter point brings us to another very general consequence of the lack of “primogenic repulsion” for the 2p-shell. In all groups of the p-block, the by far largest drop in electronegativity down the group is from the 2p- to the 3p-elements. This may also be understood from the small radius of the 2p shell, which leads to large nuclear attraction of the valence p-electrons for the second-period atoms. The very high electronegativities of the 2p elements may actually be the most important result of the nodelessness of the 2p shell for chemistry and the periodic table. They make it very difficult for a first-row atom to act as a central atom in an electron-rich multicenter bond. Of course the high electronegativities of the first-row p-block atoms are of central importance also generally for many other aspects in chemistry.

The 3d Shell

The fact that the nodeless 3d shell is particularly small (in comparison with 4d or 5d) is well known, but in this author’s opinion the consequences are by far not appreciated as much as they should. Although the small 2p shell facilitates sp hybridization and leads to strong bonds for light main-group systems, matters are reversed in the transition metal case. Here the d-orbitals, which dominate the bonding, are “inner” orbitals, belonging to the penultimate ($n-1$) shell. In consequence, weak bonds do not derive from too diffuse and weakly bound valence orbitals as in the heavier main-group elements, but rather from too small ($n-1$)d-orbitals that do not overlap well with the orbitals of the substituents. This problem is most pronounced in the 3d series, because of the very small valence 3d orbitals.

Why is overlap with ligand orbitals such a problem in the transition metal series? A definite analysis of this point has been given by Buijse and Baerends.²⁰ They demonstrated the following for the ground state of the MnO_4^- ion, due to the very simi-

lar radial extent of the 3d valence orbitals and the outermost 3p core shell (cf. Fig. 2), strong Pauli repulsions between the metal core shell and the ligand valence orbitals prohibit closer approach of the ligand, which would be required for optimal overlap between metal 3d and ligand orbitals (Fig. 3). This problem is a general one for the transition metals, due to the fact that the outermost core ($n-1$)p and the dominant valence ($n-1$)d orbitals exhibit the same principal quantum number. However, the situation is aggravated for the first transition-metal row by the particularly small size of the nodeless 3d shell. The consequences of this behavior are numerous and apparently not very well known in a wider chemistry community:

- Even at equilibrium structure, most transition-metal complexes, in particular from the 3d series, actually have stretched metal–ligand (or in multinuclear clusters metal–metal) bonds. This explains the generally observed and chemically important relative weakness of metal–ligand bonds in the 3d series compared with the corresponding heavier homologues. It is hard to overestimate the role of this fact in many areas of chemistry. We note in passing that the further expansion from 4d to 5d orbitals and thus better availability of the ($n-1$)d orbitals (as seen relative to the corresponding ns orbitals) is due to indirect relativistic effects.²¹
- As for any stretched bond, the energetic separation between the bonding and antibonding orbitals corresponding to these bonds tends to be smaller than in a “nonstretched” situation. We therefore expect low-lying excited states. Indeed, the fact that transition-metal complexes, again in particular for the 3d series, often tend to be colored (i.e., they absorb light in the visible region of the spectrum) is most probably related to this very fact. More specifically, we have to distinguish different types of excitations, ranging from ligand-field to charge-transfer bands. Considering the former, it is clear that in the example of an octahedral complex, weakened and stretched σ -bonds to the ligands will lead to a relatively low-

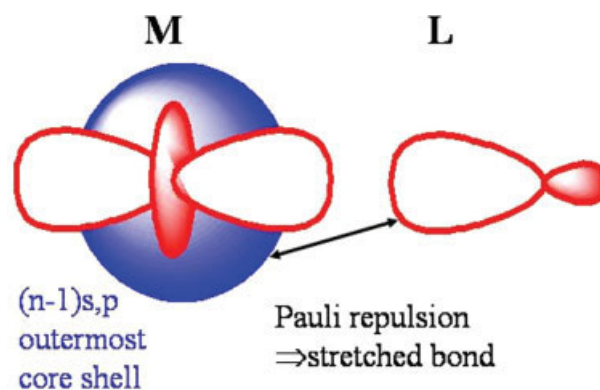


Figure 3. Schematic illustration of the Pauli repulsions between ligand orbitals and the outermost core ($n-1$)s,p shell in a transition metal complex, leading to a stretched bond and poor overlap between ($n-1$)d orbital and ligand orbital even at equilibrium distance. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lying e_g^* ligand-field orbital, with a consequently small ligand-field splitting (similarly, poor π -backbonding will cause a relatively high-lying t_{2g} orbital and thus also contributes to a small ligand-field splitting). Even the brownish color of copper metal might be related to poor overlap of 3d orbitals in the valence band.²²

- c. On the side of the computational treatment of transition-metal complexes, the stretched bonds lead to various problems. First of all, the stretched bonds and the presence of low-lying excited states increase the importance of nondynamical electron-correlation effects, as analyzed in detail for MnO_4^- by Buijse and Baerends.²⁰ A different effect is the difficulty that most quantum chemical methods appear to have with the accurate description of the energy separation between $3d^{m+2}4s^0$, $3d^{m+1}4s^1$, and $3d^m4s^2$ states in 3d transition metal atoms and with the amount of sd-hybridization in bonding.^{23,24} While the former difficulty is not related to stretched bonds (but certainly to the nodelessness and small size of the 3d shell relative to the 4s orbital), the latter may well be. Last but not least, the similar radial extent of the $(n-1)d$ valence orbitals and the outermost core $(n-1)s$ -orbitals and particularly $(n-1)p$ -orbitals requires smaller core-size definitions to be used for transition metals than for main-group atoms when applying the pseudopotential approximation. Usually, at least the $(n-1)p$ -shell should be treated explicitly as valence orbitals.²⁵

There are many further aspects of the small 3d shell that might be mentioned. When one considers, for example, valence-bond concepts in transition-metal chemistry, the relative size of the $(n-1)d$ and of the ns orbitals (possibly even of the np orbitals) becomes important for the construction of suitable hydrides. Interestingly, for simple hydrides, Landis found that sd^n hydrides may be constructed that are surprisingly close to orthogonal.²⁶ However, it remains to be seen whether this observation may be transferred to different types of ligands.²⁷

The small size of the $(n-1)d$ orbitals, and again in particular of the 3d orbitals, leads to substantially larger electronic repulsions inside the $(n-1)d$ shell than in the comparably more diffuse ns orbital. This has consequences for the relative stability of the above-mentioned $3d^{m+2}4s^0$, $3d^{m+1}4s^1$, and $3d^m4s^{2+}$ configurations.^{7,24} Furthermore, the largely core-like character of the 3d-shell for the group 12 element Zn makes it particularly unlikely to activate the d-shell for chemical bonding to achieve higher oxidation states than +II (higher oxidation states are more likely for Hg²⁸). Last but not least, the “scandide contraction,”³ that is the incomplete screening of nuclear charge by the 3d electrons, has various consequences for the chemistry of the main-group elements following the 3d-series. This aspect seems to be related at least partially to the nodelessness and small radial extent of the 3d shell (incomplete-screening effects appear to be less pronounced for the 4d and 5d shell).

The 4f and 5g Shells

The mostly core-like character of the 4f shell for the lanthanide elements is well known. The fact that the 5f-shell may partici-

pate in bonding for the earlier elements of the actinide series (for the later elements it also starts to become core-like) is partly due to expansion caused by indirect relativistic effects.²⁹ But in part, the more valence-like character of the 5f-shell is also due to its radial node. On the other side, the core-like character of the 4f-shell is of course in part due to the lack of a radial node. Again, incomplete screening effects (the lanthanide contraction) are important for the chemistry of elements following the lanthanide series.

There are no experimentally realized examples of chemical compounds in regions of the Periodic Table (beyond $Z = 125$), where the 5g shell might play a role, and calculations are also rare.³⁰ There is thus not much we may say at this point about the importance of the lack of a radial node. Most probably, there will be partial compensation between the resulting reduced radial extent and a probably very pronounced indirect relativistic expansion.

Conclusions

Radial nodes of the relevant valence orbitals throughout the Periodic Table contribute significantly to the most important periodic trends and to what is often called “secondary periodicity”. In particular, the lack of radial nodes (and thus of “primogenic repulsion”) for the 1s, 2p, 3d, and 4f shells makes each of the series, in which these shells are initially occupied, special in their own way: The elements H and He are very different from all other elements, because of the special properties of the 1s shell. In case of the 2p shell, its small size improves hybridization with 2s and thus allows rather strong bonds. Essentially all of the well-known and important differences between the first-row (second-period) p-block elements and their heavier homologues derive from the nodelessness of the 2p-orbitals.⁴ One consequence that often seems to be overlooked is the particularly large electronegativity of the first-row elements. For example, by facilitating partially ionic bonding, the lower electronegativities of the heavier p-block elements are a more important reason for the occurrence of “hypervalent” compounds than any d-orbital involvement.

When turning to the 3d shell, its nodelessness now weakens bonding between metal and ligand, mainly because of the similar size of 3d and 3p shells and the resulting Pauli repulsions²⁰ between valence and outermost core electrons. Beyond the generally weaker bonding of the 3d compared with that of the 4d or 5d complexes, the often strong colors of many 3d complexes may be explained directly as a consequence of “stretched bonds”. Nondynamical correlation effects are particularly pronounced in the 3d series. Finally, the 4f shell is already too compact to participate efficiently in chemical bonding and is thus usually considered as core-like.

It is the opinion of this author that by appreciation of the role of radial nodes (and of their absence in the mentioned cases), many important observations throughout the periodic table may be understood from a unified viewpoint. These aspects should be taught in general and in inorganic chemistry courses, and their consideration as a basis in research is recommended.

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