DOI: 10.1002/anie.200800827

Icon of Chemistry: The Periodic System of Chemical Elements in the New Century**

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atoms · electronic structure · elements ·
orbitals · periodic system

1. Introduction

Every science has its basic concepts and principles, and for teaching in schools and universities, they must be expressed distinctly. In research and development, ambiguous definitions may serve as inspiration, although this approach is at variance with the "logician's program" for science.[1a] Particularly in chemistry, fuzzy concepts such as aromaticity, conjugation, electrophilicity, polarity, and so forth are very practical.[1b,c] Another example is the concept of a Periodic System of Elements (PSE), which is graphically rendered iconic by many different periodic tables.[2,28]

Every day, publications appear that integrate the results of various branches of science into the PSE. Since the middle of the last century, historians, didacts, and philosophers have been showing increasing interest in the PSE.[3] The 100th anniversary of the death of Mendeleyev,[4] the most prominent among the creators of periodic tables,[5] triggered a flood of publications. However, only consideration of the most recent theoretical chemical studies on the PSE offers deeper insights, which are outline in the following sections. The most important points are: 1) The origin of the elements' periodicity is the exceptional position of the 1s and np shells ($n=2$–6). 2) The groups before and after the noble gases form the backbone of the PSE. 3) The PSE is complete with Period 7. 4) The electron configurations of the d elements of Group g with charge state $q+$ are $n\mathrm{d}^{g-q}(n+1)\mathrm{s}^0$. 5) There is no nature-given optimal projection of the multifaceted PSE onto a table.

Previous wisdom of the PSE has suffered from the "invention of scientific facts". This scientific phenomenon was uncovered by Ludwik Fleck in a book dating from 1935,[6] which was only recently absorbed by the philosophy of science. In any event, chemical education as well as didactical and philosophical discourses could strongly benefit from advances in the special branches of science. The case of the PSE is an excellent example.

2. Notions of "Element"

In antiquity, the word "element" comprised two different notions. From Thales (ca. 600 B.C.) to Empedokles (ca. 450 B.C.) the concept of an abstract *conserved entity* in the flow of time (e.g. in chemical reactions) emerged. Aristotele (ca. 350 B.C.) added the concept of a direct *carrier of properties* (e.g. "water" as the carrier of the cold and the wet). Around 1660, Boyle introduced the third concept of *elementary simple substances* that cannot be further decomposed in the chemical laboratory. Lavoisier[7] adopted all three notions in the 1780s. But soon the second concept (e.g. oxygen as the carrier of the acidic) had to be abandoned. Around 1870, Mendeleyev stressed the difference between the other two concepts, which saw an element as a conserved entity in a substance and as a simple substance in elementary form.[3q,5,10]

The defining primary property of the "abstract" elements is the nuclear charge Z. It determines, together with the atomic weights, the immense diversity of physical, chemical, and biological properties of the elementary substances and their compounds. Statistical chemometric **factor analyses**[8] extract sets of basic, linearly independent "main factors" as the basic secondary properties of the elements.[9a–c] They reproduce atomic radii, number of electrons in the valence shell, dominant valence numbers, electronegativity, reactivities and thermodynamics of their polar and nonpolar compounds, and so forth, in a simple and approximate manner. An element is not directly visible, though not at all "the substance without qualities" (see also references [3q,9]).

Since the early 19th century (Dalton), at the latest since the early 20th century (Perrin), the elements were atomistically interpreted. A common sentence in contemporary textbooks reads "The electron configuration of a *chemical element* is given by the ground state of the *free atom*." However, the difference between *free atoms* in a physical vacuum and chemically *bound atoms* in an environment of ligands is

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[**] We acknowledge valuable input from our colleagues H. Bent, J. C. A. Boeyens, P. Buck, H. J. Deiseroth, G. Frenking, M. Gröger, M. Kaji, W. Kutzelnigg, M. Reiher, G. Restrepo, E. Scerri, V. Scharf, F. Schmidt, J. Schummer, P. Thyssen, F. Weinhold, A. Wickleder, A. Woyke, and unknown referees. We are grateful for financial support from the DFG (Schw 161), the FCI (160 273) (Germany), and the NSFC (2057 3074) and the SRFDP (2004-024 8017) (China).

unexpectedly large (see Section 4.1).[11,12]

3. One System—Many Tables

Since the creation of the modern concept of the elements (ca. 1785),[7] chemists have strived towards an ordering scheme for the elements in terms of **qualitative chemical** criteria. Scholars as early as L. Gmelin (in his famous handbook, 1843)[13] or Odling (1857)[14] presented some of the "vertical" groups of elements (as they are called today): [Mg–Ba/Cd], [Li–K], [F–I], [O–Te], and [N–Bi]. In the late 19th century the noble gases [He–Rn] were added. Furthermore, "horizontal" similarities as for [Cr–Cu] or [La–Lu], "diagonal" ones as for [Be,Al] or [O,Cl], "knight's move pairs" such as [Ag,Tl], "connected fields" such as the platinum metals [Ru–Pt], and "distant pairs" such as [Al,Fe] and [Ba,Pb] were also found.[15] As a result of all these relationships, the set of elements forms a "**partially ordered system**".[16]

Since 1817[17] Döbereiner's triad rule has highlighted the relevance of the **quantitative chemical-empirical** equivalence weights. However, more "theory-laden"[18] concepts had to be added.[3q,5] Namely, in 1860[19] the atomic weight A, based on **physicochemical laws** (namely for gases, specific heats, and colligative effects) and in 1913[20] the nuclear charge number Z. The atomic cores enabled linear ordering of the elements, while the properties of the valence shells suggest a network according to chemical similarity. The chemical elements could be arranged in a scheme largely determined by nature.

De Chancourtois[21] wound up the "physically" defined row of elements as a **spiral** in 1862. Several of the particularly different similarity groups (alkali, alkaline-earth and earth metals; halogens, chalcogens, and pnicogens/penteles) can then be arranged in adjacent columns. A **rectangular table** of what we now call the main groups was published in 1864 by L. Meyer.[22] And Newlands[23] pointed out a periodicity of eight (or seven), resulting in **the triad rule**. Finally in 1869, Mendeleyev[24] managed the construction of a useful tabulation of all elements.

Cluster analyses of the elements have been performed in recent years.[9,25] Numerical values from the literature of up to 150 different chemical, physical, and material properties of up to 90 elements and their compounds were analyzed. The above-mentioned similarities of elements historically obtained from chemical "sensations" were reproduced numerically, "objectively". On the other hand, the generation of a unique and simply structured periodic table by automatic **self-organizing algorithms** failed, owing to the large number of complex similarity cross-connections.[3c,26]

Numerical **Fourier frequency analysis** of the chemical and physical properties of the first 103 elements[9c] yielded a significant background noise and rather broad periodicity maxima at distances ΔZ of the element numbers around ($\pm 10\,\%$) 32 ($s^2p^6d^{10}f^{14}$), 18 ($s^2p^6d^{10}$), and 8 (s^2p^6), but also at 6, 5, 4, 3, 2, and 1 (i.e. neighboring elements are similar, especially in the d and f blocks). The elements' periodicities are objectively fuzzy. This fuzziness is due to the involvement of the p^6, d^{10}, and f^{14} shells in double steps in Period 2, 4, and 6 and to the many nonvertical similarities. Apparently, the physical nuclear numbers together with a **subset** of the chemical similarity groups (i.e. the noble gases, alkali metals, halogens, etc.) fix the period lengths. One characteristic of the PSE is this "natural backbone" with large property changes between Groups 16, 17, $18\approx 0$, 1, 2. Other characteristics of the PSE are the smooth property variations from element to element of the other groups, and the large number of nonvertical similarities.

The network of furcations is shown in Figure 1.[27] In general, every empirical property yields a different order than the nuclear charge (Figure 2). This situation necessarily results in a **multiply connected topology** for the PSE. The system of elements might be embedded into a multidimensional Euclidean space, for example as a cylinder with ears (see graphic in the Table of Contents).[28]

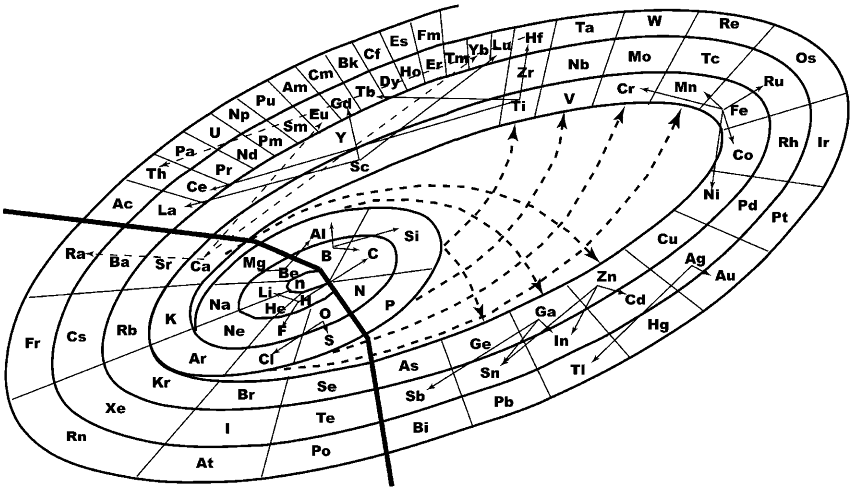

Figure 1. The multiply connected structure of the PSE from neutron (n, $Z=0$) to Fm ($Z=100$). The region under the bold line forms the "backbone" of the PSE. Some of the bi- and multifurcations are also shown. Designed according to Longman and Stewart.[27]

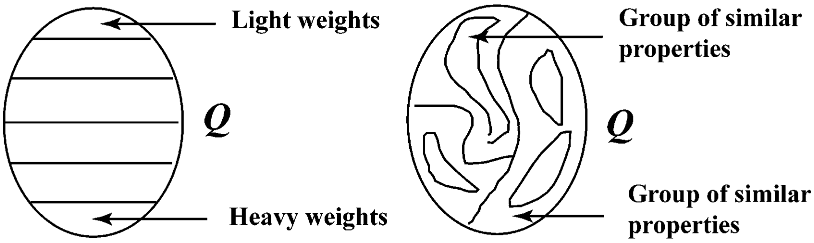

Figure 2. The set Q of chemical elements. Left: ordered by nuclear charge. Right: regions of a similar property. Drawn according to Restrepo.[9a]

The cross-connections indicated in Figure 1 are partly lost if the PSE spiral with its loops is slit somewhere and ironed flat to obtain rectangular, clearly arranged, and **printable tables** for books and classroom walls. For the selection of a specific table, an additional criterion must be favored, for example, the properties viewed as most important or a shape perceived as particularly felicitous.[3d,e,q,29,30] On the other hand, the use of several different tables in a given teaching context may be advocated.[3f,66] About one thousand different table versions can be found in the literature (including more than one hundred spirals), and a slightly reduced "table zoo" is available on the internet.[28]

4. Electron Configurations of the Transition Elements

The backbone of the PSE consists of the element groups usually discussed first in elementary textbooks, that is, those of group numbers g (number of electrons in the valence shell) from 16 to $18 \approx 0$ to 2. These groups should form the starting point of any theoretical rationalization of the PSE. We are currently in a position to reach this goal. A single-electron orbital approach that accounts for electron-pair repulsions forms a sustainable basis for most semi-quantitative explanations in chemistry. Two points must be clarified at first: 1) Which electronic states of the elements are relevant for chemical explanations? 2) Which definitions of orbitals and which atomic orbital (AO) sequences are appropriate?

The electron configuration is the set of (significantly) occupied orbitals in some nearly independent particle approach. The configuration characterizes the more or less inert atomic cores and the valence shells, which are responsible for primary and secondary interactions. Quite "unsystematic" electron configurations are found in chemistry textbooks for the majority of the transition elements. In Group 10, for instance, we find Ni $3d^84s^2$, Pd $4d^{10}5s^0$, and Pt $5d^96s^1$; these descriptions are derived from the spectroscopic details of the free atoms. It is not easy to relate these jumps to the chemical trends of the elements in that group. We will elucidate the common misconceptions.

4.1. Free and Bound Atoms

The empirical chemistry of the transition-metal elements can be interpreted as "pure d AO chemistry", as in the ligand-field model. For example, in Ni^0 compounds such as $Ni(CO)_4$, the dominant electron configuration of the Ni atom is $3d^{10}$ with only a small 4s admixture.[31] A similar situation applies to nickel metal, which has only a small d-hole fraction. Apparently, free atoms and atoms in substances are rather dissimilar.

The $(n+1)$s AO of free transition-metal atoms is a Rydberg orbital.[32] Concerning spatial extension, $nd \ll (n+1)s$. Upon insertion of the atom into a chemical compound, the extended $(n+1)$s AO overlaps with the occupied shells of the adjacent atoms. Because of Pauli repulsion, the AO becomes destabilized, that is, $nd \ll (n+1)s$ is also true energetically. Therefore, the dominant configuration of transition-metal atoms in compounds is $d^{g-q}s^0$ throughout (q = atomic charge; Figure 3, right).[11,12,31]

4.2. Sequences of Orbital Energies and of Orbital Occupation

Among all free atoms M^0, only *one* (Pd) has a d^g ground state with an empty s shell. Among the free transition-metal cations M^+, *half* of them have ground states derived from $d^{g-1}s^0$. And concerning the more highly charged ions M^{q+} ($q > 1$), *all* have ground states with empty s AOs ($d^{g-q}s^0$).[33] The larger the effective nuclear charge in the valence shell (for increasing Z and q), the more pronounced is $nd < (n+1)s$ (spatially and energetically).

For low- and high-spin complexes, it is well known that in the case of energetically similar orbital levels the lower one is filled first only if the difference in orbital energies is larger than the difference of energies of repulsion of the two orbitals. Y, Ti, and V present typical examples for the filling of the nd–$(n+1)$s shell:[11,33]

$Y^{3+} \rightarrow Y^{2+}\ 4d^1 \rightarrow Y^{1+}\ 5s^2 \rightarrow Y^0\ 4d^15s^2$

$Ti^{4+} \rightarrow Ti^{3+}\ 3d^1 \rightarrow Ti^{2+}\ 3d^2 \rightarrow Ti^{1+}\ 3d^24s^1$
$\rightarrow Ti^0\ 3d^24s^2$

$V^{5+} \rightarrow V^{4+}\ 3d^1 \rightarrow V^{3+}\ 3d^2 \rightarrow V^{2+}\ 3d^3$
$\rightarrow V^{1+}\ 3d^4 \rightarrow V^0\ 3d^34s^2$

Many students and chemists know the common textbook sentence: "4s is occupied first, but 4s is also ionized first". This seems to violate the principle of microscopic reversibility. A better formulation is this: 1) In the sequence of neutral free atoms K, Ca, Sc, Ti, V … 4s is occupied first in K and Ca. 2) But in the sequence of ions of a given transition metal, for example, V^{5+}, V^{4+}, V^{3+} … 3d is

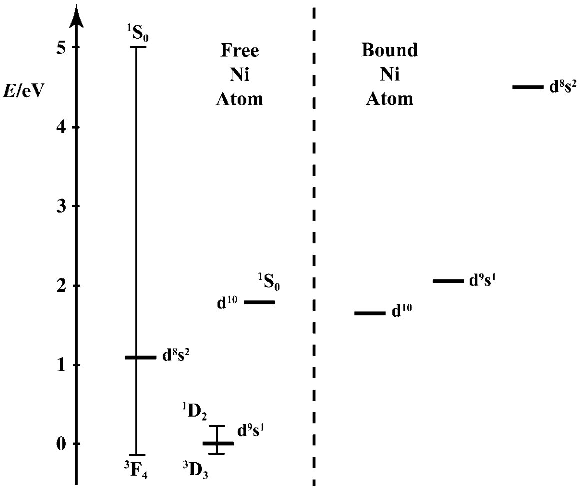

Figure 3. Nickel: Configuration energies of $3d^{10-k}4s^k$, $k = 0, 1, 2$ (——: arithmetic mean of all individual states of the configuration). Left: Single free atom (the vertical lines indicate the highest and lowest energies of the different respective states). Right: Approximate mean of neutral, chemically bound atoms.[12]

occupied first and 4s last. It is then logically consistent that 4s is ionized first in the reverse sequence V^0, V^+, V^{2+}.[34c] This concept was already (or still) clear to some textbook authors around 1930.[34f]

Since the nd AOs are spatially much more compact than the $(n+1)$s AO, in particular for neutral atoms with low effective nuclear charge, the repulsion of two electrons in the nd shell is much bigger than in the $(n+1)$s AO.[34] For instance, the first valence electron of the Y atom goes into the energetically lower 4d shell. But for two electrons, a lower total energy is obtained in the higher and more extended 5s AO, where the repulsion is much smaller. To be sure, concerning the chemically more important transition-metal cations, $n\mathrm{d} \ll (n+1)\mathrm{s}$ is always true. This and the following qualitative statements are fairly independent of the specific definition of the orbital concept.

In contrast to the transition-metal atoms, Groups 1 and 2 ($g=1, 2$) form a special case, with $(n+1)\mathrm{s} < n\mathrm{d}$. Indeed, the ground configurations are $n\mathrm{d}^g$-$(n+1)\mathrm{s}^0$. Quantitative shifts may occur upon inserting such atoms into crystal lattices or molecules. The extended overlapping $(n+1)$s and $(n+1)$p AOs become more destabilized than the nd AOs and can more easily hybridize.[35] For example, the heavier alkaline earth dihalide molecules are bent because of non-negligible $(n+1)$s–nd mixing.[36]

4.3. Configurations, Terms, and States of Open-Shell Systems

A momentous misconception in the case of open shells is that often states and configurations are not distinguished. The nickel atom offers an instructive example (Figure 3). Because of the intricate situation in the field of atomic vacuum spectroscopy, chemistry textbook authors quote the chemically irrelevant d^8s^2 configuration (of the ground state of the free atom) instead of the real $3d^{10}$ main configuration (of the element in chemical substances).[31] The resulting detailed explanation (from the 1930s!)[33b] may be skipped.

The energetically lowest **configuration** average of the free Ni atom is $3d^94s^1$. If the atom has all 10 valence electrons in the lower 3d shell ($3d^{10}$), the energy is about 160 kJ mol^{-1} (1.65 eV) higher because of strong interelectronic d–d repulsion. The $3d^84s^2$ configurational energy is also higher, by about 105 kJ mol^{-1} (1.1 eV), in this case because of the double occupation of the higher 4s AO.[11,34]

The different Coulomb repulsions in the singlet and triplet SL **terms** of the $3d^94s^1$ configuration lead to a slightly stabilized ^{3}D term. (The superscript ^{3} is the spin multiplicity $M=2S+1$, the capital D represents the vector sum L of all orbital angular momenta.) Different populations of the five adjacent components of the 3d shell (d_{xy}, d_{xz},…) by eight electrons yield very different repulsion energies for the $3d^84s^2$ configuration. The ^{3}F term has by far the lowest energy. ^{3}F-$3d^84s^2$ is only 2 kJ mol^{-1} above ^{3}D-$3d^94s^1$, while the highest term ^{1}S of $3d^84s^2$ lies nearly 500 kJ mol^{-1} higher, far above the terms of $3d^94s^1$ or $3d^{10}$.

The relativistic spin–orbit coupling in the Ni atom on the order of 10 kJ mol^{-1} causes a larger splitting for ^{3}F-$3d^84s^2$ with two d holes than for ^{3}D-$3d^94s^1$ with only one d hole. The lowest **state** is $^3F_4$-$3d^84s^2$, just 2 kJ mol^{-1} below $^3D_3$-$3d^94s^1$. (The subscript is J, the vector sum of all orbital and spin momenta.) Another example is Ru with "chemical" configuration $4d^8$; the lowest free atomic configuration is $4d^65s^2$ and lowest free atomic state $^5F_5$-$4d^75s^1$.

Orbit and spin couplings in free atoms are surely relevant in atomic high-resolution vacuum spectroscopy. In chemical compounds, electronic rotations in atoms are quenched by adjacent atoms. Atomic angular momenta couplings are less relevant to chemical bonding, in particular for qualitative discussions (except for very heavy elements, see Section 7.). In chemistry, the lower atomic **configuration averages** are more relevant. That would mean $3d^94s^1$ for the case of Ni. However, the diffuse 4s Rydberg orbital of a bound Ni atom is severely destabilized by ligands. Hence, the chemistry of neutral Ni is governed by d^{10}, with only slight admixture of d^9s^1 (Figure 3, right).

5. Atomic Orbital Sequences

5.1. On Definitions of Orbitals

Common chemistry uses its own qualitative, fuzzy, semiclassical notion of orbitals.[37] Quantum theory offers various neat definitions for different types of quantum-mechanical orbitals (some of them even measurable) within more or less approximate frameworks.[38] The energy differences of interest can then be soundly represented by orbital energies and elaborate expressions of Coulomb repulsion energies (direct, exchange, and correlation terms).

In general chemistry we need something reliable but more simple, a theoretically and empirically founded rule to predict the relevant valence orbitals for all atoms in chemical compounds. Molecular AO population analyses and determination of energetically favorable atomic configurations without occupied Rydberg orbitals (which are destabilized in molecules) will form the basis. This approach yields a consistent set of AO sequences for chemists, which differ somewhat from those in chemistry textbooks. Theoretically interested readers may find several important "sophistries" in the appendix.

5.2. Different AO Sequences

Most chemistry textbooks teach one single AO sequence, corresponding to the Madelung rule [see sequence (1M) below]. Figure 4 displays AO sequences ε_{nlj} for three different values of Z, derived from ionization energies of average configurations ΔE.[11,33] Figure 4 differs from textbook graphics: 1) The vertical axis carries a defined scale. We plot the effective quantum number $n_\mathrm{eff} \sim 1/\sqrt{-\varepsilon_{nlj}}$ to generate a similar impression as the commonly encountered graphs of AO energies. 2) Different AO sequences are displayed.

We discuss five prototypical cases (to simplify matters, spin–orbit splitting and total angular momentum quantum number j are averaged out):

H atom :

$$1s \ll 2s \approx 2p \ll 3s \approx 3p \approx 3d \ll 4s \approx 4p \approx 4d \approx 4f \ll \ldots \tag{1H}$$

Inner Atomic **C**ore Shells :

$$1s \ll 2s < 2p \ll 3s < 3p < 3d \ll 4s < 4p < 4d < 4f \ll \ldots \tag{1C}$$

Valence Shells :

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < 6d < 7s < 7p < 8s < \ldots \tag{1V}$$

Alkali and Alkaline Earth Valence Shells :

$$np \ll (n+1)s < \{(n+1)p,(n+2)s\} < nd \tag{1A}$$

Madelung Rule in Textbooks :

$$\begin{aligned}&1s \ll 2s \ll 2p < 3s \ll 3p < 4s \ll 3d < 4p\\ &< 5s \ll 4d < 5p < 6s \ll 4f < 5d < 6p\\ &< 7s \ll 5f < 6d < \ldots\end{aligned} \tag{1M}$$

5.2.1. AO Sequence in Hydrogen

The ε_{nlj} sequence of the H atom is $1s < 2p_{1/2} \approx 2s \approx 2p_{3/2} < 3s$ … A simplified model of the H atom[39] can be solved analytically with paper and pencil (i.e., without opaque computer calculations or experimental data processing). For that common model, ε depends only on the principal quantum number $n = n_r + l$: $\varepsilon_{nlj} = -(Z/n)^2$ Ry (n_r and l = radial and angular quantum numbers, $j = l \pm s$, $s = {}^1\!/_2$ = spin quantum number; Ry = 1313 kJ mol^{-1}).

5.2.2. AO Sequence in Atomic Cores

Electrons with angular momentum l are pulled away from the nucleus by centrifugal force. In many-electron atoms with a positive nucleus $+Z$ and n negative screening electrons, any electron with a large l value feels only the fully screened nuclear charge $Z-n$. With a lower square of the angular momentum $\langle \boldsymbol{l}^2 \rangle$, the AO can penetrate deeper into the core, and the energies ε become more stable. For an ε sequence of given n, rule (2) results:

$$ns < np \ll nd(\ll< nf \ll\ll ng) \lesssim \text{hy}''. \tag{2}$$

In this case, 2s lies slightly below 2p, 3s slightly below 3p, and so forth. Furthermore, 3p lies somewhat further below 3d and 4p correspondingly below 4d; 4d lies even further below 4f (provided there are a sufficient number of screening core electrons). All AOs with large l sit completely outside the core and have ε values “hy” analogous to hydrogen. The core orbital levels (from X-ray and XUV spectra or quantum calculations; see lower and left regions of Figure 4) are only screened from the full nuclear attraction by the innermost core shells. The fractional shifts $\Delta\varepsilon/\varepsilon$ according to rule (2) are not that large, and sequence (1C) results.

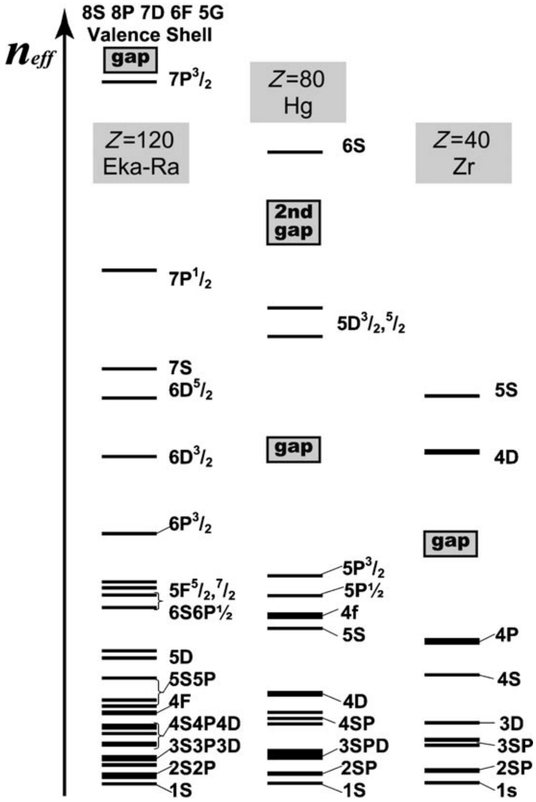

Figure 4. Mean AO energies ε_{nlj}, presented as $n_{\text{eff}} \sim Z/\sqrt{-\varepsilon_{nlj}}$, of the free atoms Zr ($Z=40$), Hg ($Z=80$), and Eka-Ra ($Z=120$). The relativistic j-dependent spin–orbit splittings ($p_{1/2}$–$p_{3/2}$, $d_{3/2}$–$d_{5/2}$, $f_{5/2}$–$f_{7/2}$) must not be neglected for heavy elements. Note the energy gaps between the upper core shells (p^6, $p_{3/2}{}^4$, or $d_{5/2}{}^6$) and the valence shells (Zr 4d, Hg 6s, Eka-Ra 8s).

5.2.3. AO Sequence in Valence Shells

The shifts according to rule (2) become comparatively larger for the outer valence shells. The most common AO sequences in the valence shells of most elements (from UV/Vis spectra or computations; see the upper parts of Figure 4) are combined in sequence (1V). Thus, for l values appearing in the valence shell, rule (3) holds. This sequence is the most important for chemistry.

$$np \ll (n-1)f < nd < (n+1)s < (n+1)p \ll \tag{3}$$

5.2.4. The Exceptional Groups 1 and 2

The screening effects in rule (2) are largest for the alkali and alkaline-earth atoms with particularly large ratios of the numbers of screening core electrons to outer valence electrons. For the lighter elements, the $(n+1)$s valence AO moves down below the nd AO, and for the heavier elements $(n+1)$p also moves down. For K, it is even the case that 5s < 3d.[33] This effect is indicated by sequence (1A) for the free atoms of the electropositive elements.

Upon insertion of the atoms into molecules and solids, sequence (1A) may change towards sequence (1V), as mentioned in Section 4.2.[35,41] For Groups 1 and 2, the nd shell is strongly screened and is still of extended Rydberg type. With increasing nuclear charge, the nd AO “collapses” energetically and spatially (Figure 5). From Group 3 onwards it is always the case that $nd < (n+1)s$, in accordance with sequence (1V), in particular for the cations. Transition-metal chemists know it.

5.2.5. The AO Sequence in Textbooks

Even before the invention of quantum mechanics in 1925, the simple UV/Vis spectra of the free alkali- and alkaline-earth-metal atoms had been correctly interpreted with the help of

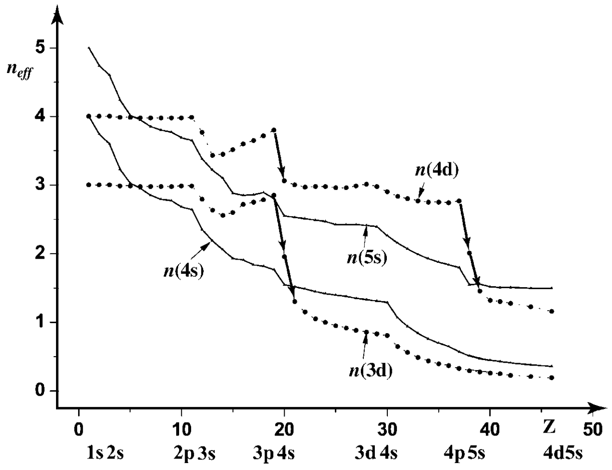

Figure 5. The d orbital "collapse" of free neutral atoms at the beginning of the transition rows. The orbital energies ε are represented by $n_{\mathrm{eff}} \sim 1/\sqrt{-\varepsilon}$. •••••: 3d and 4d, ——: 4s and 5s.

the Bohr model.[33] Ground configurations ns^1 and ns^2 were attached to the atomic ground states. Soon afterwards the complex spectra of the free neutral and charged transition-metal atoms were also correctly assigned, with occupied d AOs. The details of electron–electron interactions appeared in some chemical textbooks around 1930.[34f] However, owing to a simplistic view of a small selection of these results, sequence (1M) was invented.[42] It penetrated into more and more chemistry and even some physics textbooks, although it did not at all reproduce the relevant findings about atoms and ions reflected in sequences (1C), (1V), and (1A). The view of chemists had unconsciously narrowed to spectroscopic details of some free neutral atoms.

As early as 1928, Fermi[43] had obtained different sequences of occupation of s, p, d, and f angular-momentum sates as a function of Z by simple hand calculations of his quantum-statistical atomic model. Tietz[44] found a simple analytical approximation to the screened atomic potential. With its help, Ostrovsky[45] could easily deduce the $(n+l)$ rule for the **special case of vanishing electronegativity**.

5.2.6. AO Sequences in Molecules

The two limiting cases, the simplified H atom (sequence (1H)) without any screening electrons and the textbook atom (sequence (1M)) with a strongly screened nucleus, can both be derived nearly purely analytically. The actual sequences in atomic cores (sequence (1C)), in most valence shells (sequence (1V)), and in the valence shells of strongly electropositive elements (sequence (1A)) can then be qualitatively rationalized as intermediates (Figure 6). This situation had already been suggested in 1964.[46b]

The ε schemes for many atoms reconstructed from spectroscopic data have been reconfirmed since the 1930s by atomic quantum computations.[46a] Since the 1970s, theoretical AO schemes have also become known for the not yet or insufficiently experimentally investigated superheavy elements.[47] These findings of the last 80 years are rather hesitantly penetrating into the chemical and more general literature.

5.2.7. Quite Regular d,s Shells

Experimentally and computationally derived energies of the d^g, $d^{g-1}s^1$, and $d^{g-2}s^2$ *configurations* of the neutral *free* atoms of the second transition row are displayed in Figure 7. They vary rather regularly according to the regular variation of the orbital energies and the two-particle repulsion energies. In contrast, the individual atomic *state* energies vary rather irregularly, owing to the state-specific orbit–orbit and spin–orbit couplings. We note that one-third (nine) of the *SLJ* ground-state configurations of the free atoms of the $3 \times 9 = 27$ d elements differ from the $d^{g-2}s^2$ textbook rule, and an additional two are borderline cases (Ni, Nb). As mentioned earlier, the chemically significant configurations of *bonded* d-element ions Z^{q+} are always $d^{g-q}s^0$.

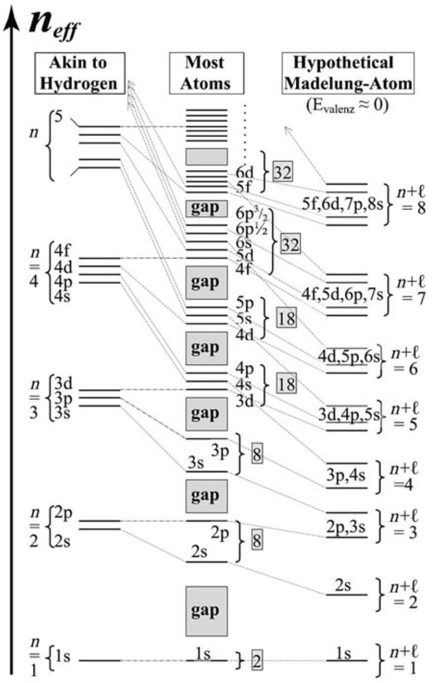

Figure 6. Qualitative order of AO energy levels, $n_{\mathrm{eff}}-1/\sqrt{|\varepsilon_{nl}|}$. Left: Hydrogen-derived order of core orbitals (sequence (1C)), $n_{\mathrm{eff}} \approx n$. Right: Madelung order (sequence (1M)) of hypothetical "strongly electropositive" atoms, $n_{\mathrm{eff}} \approx n+l$. Middle: Most common order in atomic valence shells (sequence (1V)), $n_{\mathrm{eff}} \approx n-\delta_l$, δ = quantum defect, displaying the basic energy gaps between core and valence shells.

6. The Cause of Quasi-Periodicity and the Period Lengths

Chemistry textbooks lack a convincing rationalization for why just the noble gases and the neighboring p groups (g = 15–17) and s groups (g = 1, 2) form the PSE's backbone, and why the vertical d groups are empirically less evident.

6.1. The Basic Gaps Between Core and Valence Energy Levels

The most prominent feature of the actual valence schemes is the clustering of $(n+1)$p, $(n+1)$s, nd (and possibly $(n-1)$f) levels, and a comparatively large energy separation ("gap" in Fig-

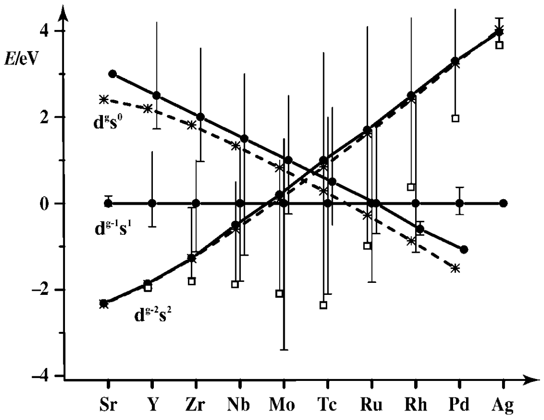

Figure 7. Configurational energies ΔE (in eV = 96.6 kJ mol^{-1}) of the free atoms Sr–Ag of Row 5 for $d^{g-2}s^2$ and d^gs^0 relative to $d^{g-1}s^1$. ——: DFT computation, -----: experimentally derived.[11] The energies of the individual states of the open ds configurations are indicated by vertical lines. □: lowest states of the textbook configurations $d^{g-2}s^2$.

ures 4 and 6) above the upper core levels 1s and np (n = 2–6), respectively. The closed $1s^2$ and np^6 shells of the noble gas atoms of group 18 ≈ 0 and of the isoelectronic ions of the elements in the adjacent groups (O^{2-}, F^-, Ne, Na^+, Mg^{2+})[48] not only have comparatively low energies, but they are also comparatively poorly polarizable, as there are no virtual AOs nearby. Just the closed $1s^2$ and np^6 upper core shells are chemically inactive and "hard". This rule will end around $n = 6$, since there is no longer a large gap above $7p_{3/2}$. It is questionable whether Eka-Rn still has a "stable noble gas shell".[49]

However, since a little above an ns valence shell ($n \geq 2$) there is the np (main-group elements), or since a little above an nd valence shell ($n \geq 3$) there is the ($n+1$)s (transition-metal elements), the closed s^2 shells (Na^-, Mg, Al^+) and the closed d^{10} shells (Co^-, Ni, Cu^+) are not particularly inactive. These closed shells become inert only at higher Z values. The $2s^2$ shell behaves like an inactive shell for O and F, and nd^{10} becomes inactive for Zn, Cd, and Tl (the nd–(n+1)s separation is not yet large enough to prevent the existence of Hg^{IV} under special conditions).[50] Half-filled shells are also not automatically stable, but they give rise to particularly large splittings into stable and unstable *SLJ states* (see the vertical bars for Nb-d^5, Mo-d^5s, Tc-d^5s^2 in Figure 7). In compounds however, half-filled shells occur at different electron numbers, for example, in octaheadral coordination they occur for d^3 and d^8.

6.2. Horizontal Structure of the PSE

The stable noble gas shells with gaps above them give rise to two important consequences. The antecessor elements have valence-active p holes and are electronegative; the successor elements have loosely bound valence-active electrons and are electropositive. The p shells of Groups 14–18 give rise to covalent electron-pair bonds and lone pairs, with valence and oxidation numbers v in steps of 2 (e.g. for sulfur from group $g = 16$, $v = 6, 4, 2, 0, -2$). In the case of loosely bound electrons from Groups 1 and following, the oxidation numbers vary in steps of 1 (e.g. for manganese from group $g = 7$, $v = 7, 6 \ldots 1, 0, -1$). Historically, the highest and lowest valence numbers were a decisive criterion for the group assignment of an element.[5,22]

Groups 3–11 are mainly defined through their distance from the noble gases, that is, the number of valence electrons in the d shell above a p^6 core. The total ionization energy expense of atoms increases with the third power of the ionic charge; the ionic lattice-energy gain increases with the second power. This situation leads to a stability optimum for medium oxidation numbers around $+3 \pm 2$, depending on the ionic radii and polarizabilities of the respective elements. The specific chemical properties of the d elements are not different enough to devise a distinct group assignment as is the case for the main-group elements.

The chemical periodicity of the elements became established by the recurrences of strong property variations of the main-group elements before and after the noble gases. We note the peaks in the plot of atomic volumes, which were decisive for the acceptance of the PSE concept.[22b] Chemists were also looking for smooth variations. While the halogens and alkali metals still sat together in the center of Meyer's first "main groups" table,[22a] the "PSE spiral" was cut early on between just these groups, so that now the most different groups occur at opposite edges of the common tables.

6.3. Vertical Periodicity

The lanthanoid contraction[51,52] upon the first population of an f shell in Period 6 and the somewhat different behavior of the early actinoids in the next row are well known. A related variation upon the first population of a d shell in Period 4 and the somewhat different behavior of the heavier d- and p-block elements are called d-block, transition-metal, or scandid contraction. Particularly special is the first p shell in Period 2. Below we explain and stress the anomaly of the hypothetical Period 8.

This "secondary" two-step periodicity has been discussed in empirical chemistry since 1915.[53] Quantum-chemical rationalizations have been developed in the meantime.[54] Atomic l (or lj) valence shells are subject to the attractive potential V_a of the screened nucleus. The kinetics of the electrons is determined by the Heisenberg uncertainty and Pauli exclusion principles. If there is an occupied shell of the same l in the core, the Pauli exclusion principle acts as a repulsive "pseudopotential" V_p on that one valence shell. The first l shells (1s, 2p, 3d, 4f) "feel" only the attractive V_a; they are comparatively compact. The next l shells (ns with $n \geq 2$, np with $n \geq 3$, etc.) feel $V_a + V_p$. They are more expanded, and the respective canonical orbitals have additional spherical nodes. Consequently, concerning spatial extension, $2\mathrm{p} \geq 2\mathrm{s}$, while $n\mathrm{p} > n\mathrm{s}$ for $n > 2$. The elements in the middle of the carbon row show strong s–p hybridization, while this tendency is much less pronounced among the heavier main-group elements. Similarly $3\mathrm{d} \geq 3\mathrm{p}$, while $n\mathrm{d} > n\mathrm{p}$ for $n > 3$. Many complexes from the first transition row have weak covalent bond contributions and high-spin ground states, while the heavier transition-metal complexes form stronger d covalences with low-spin character.

7. The Superheavy Elements: The End of the Periodic System?

To date, atoms of nearly all elements up to $Z = 118$ (Eka-Rn, "Moscowium") have been synthesized.[55] Reliable chemical knowledge up to $Z = 108$ (Eka-Os, Hassium, $g = 8$) is essentially based on theoretical–experimental cooperation.[3i,47a,56] Chemical information about the even heavier elements comes from relativistic ab initio calculations.[47,49]

The details of chemical trends in **Period 7** sometimes deviate from the previous rows.[3i] The fractional relativistic changes $\Delta_{\mathrm{rel}}X/X$ increase in the valence shells roughly with Z^2, that is, by factors of 2 to 4 from period to period. The energetic and spatial spin–orbit splittings ($7\mathrm{p}_{1/2}$–$7\mathrm{p}_{3/2}$, $6\mathrm{d}_{3/2}$–$6\mathrm{d}_{5/2}$, $5\mathrm{f}_{5/2}$–$5\mathrm{f}_{7/2}$) become dominant (Figure 4). Also, the angular behavior of AOs and hybrids changes. For example, the $\mathrm{p}_{1/2}$ AO has a spherically symmetric electron density. The s and $\mathrm{p}_{1/2}$ AOs are relativistically stabilized, the d and f AOs become destabilized. The closed configurations $6\mathrm{d}^{10}7\mathrm{s}^2$ for Eka-Hg and $6\mathrm{d}^{10}7\mathrm{s}^27\mathrm{p}_{1/2}{}^2$ for Eka-Pb are predicted to be more "noble" than might be chemically expected. In contrast, Eka-Rn ($7\mathrm{s}^27\mathrm{p}_{1/2}{}^27\mathrm{p}_{3/2}{}^4$) will be more active than Xe and Rn, no longer a noble gas but a reactive condensed phase.[47,49,56–58]

Quantum mechanically, the complete breakdown of chemical systematics is expected to occur from **Period 8** onwards. The AO energy separations decrease with increasing principal quantum number, the density of states in the valence shell increases significantly, and there is no longer a pronounced gap above the closed 7p shell. The order of each of the spin–orbit-split $8\mathrm{p}_{1/2}$, $8\mathrm{p}_{3/2}$, $7\mathrm{d}_{3/2}$, $7\mathrm{d}_{5/2}$, $6\mathrm{f}_{5/2}$, and $6\mathrm{f}_{7/2}$ levels varies in a complex manner with Z, ionic charge, and the distribution of the valence electrons over the various orbital levels.[60] In addition to the 7d and 6f shells, the 5g shell, too, collapses through the valence shell into the core. However, this does not occur near $Z = 121$ (Eka-Ac) as "predicted" by the Madelung rule,[60] but around $Z = 125$. A "new chemistry" should be expected on the basis of relativistic quantum-theoretical insight.[47,59] The advances in heavy-nucleus synthesis have triggered the publication of periodic tables for Z up to 200 or even 1000, yet with complete neglect of quantum-chemical experience and on the basis of the questionable, empirical, inaccurate, nonrelativistic Madelung rule.[61]

8. Conclusions

The successful systematization of chemical elements started nearly 150 years ago on a largely empirical, chemical basis. As stated by Dirac more than 75 years ago,[62] the theoretical principles of the mathematical part of chemistry are definitively codified in quantum theory. It was only in recent years that a big step forward has been made towards a deeper reductionistic understanding of the PSE, on a combined atomistic–quantum-chemical and macroscopic–statistical basis. The basic aspects of the PSE could be extracted and rationalized. Like chemistry as a whole, the PSE in particular consists of quantitative concepts and relations of physical theory *and* of fuzzy qualitative notions of typical chemists. Chemistry is more than a purely autonomous empirical art, and it is also more than an insufficiently developed part of physics.

The word "element" comprises several different notions: at the macroscopic level the (simple) elementary substance and the (basic) conserved element in changing substances,[10] at the microscopic level bound atoms in chemical substances and free atoms in physical vacuum. Historically, the periodic tables were designed as a useful ordering scheme for the basic abstract elements. Nowadays the notions of periodic tables of chemical elements (for chemists), of simple substances (for material scientists), and of free atoms (for atomic spectroscopists) are often insufficiently distinguished (for an exception, see reference [28]).

There are dozens of definitions of "atoms in molecules". The corresponding atomic properties are somewhat different, for example, the charges[8] or the radii. Bound atoms of the same element are also different because of different bonding situations. However, the difference from free atoms in vacuum is usually bigger[63] and is particularly striking in the case of the transition elements.

Chemical elements and their atoms are defined by *one* physical primary property, the nuclear charge Z_i. Z_i determines *one* chemical primary property, the electronic valence configuration VK_i of the bound atoms. The linear arrangement according to Z_i reveals more or less sharp quasi-periodicities of a multitude of empirical chemical properties. In general chemistry, these trends can be rationalized by means of VK. In quantum chemistry, the properties can be determined numerically from Z (in complex cases, however, this is impracticable). Furthermore, the isotopic atomic weights A_{ij} and their frequencies are needed for kinetics, thermodynamics, stoichiometry, and rotation–vibration spectroscopy. The chemical properties of the elements depend not only on Z, but also on our cosmological and geochemical history.

The host of basic chemical properties can be roughly represented by a good handful of linearly independent basic properties of the chemical elements. These are the secondary properties of the elements, in addition to Z, VK, and A. Homologous VKs turn the vertical groups of elements into "natural kinds".[3q]

Element lists and periodic tables often display "electron configurations of the elements" which, however, refer to the ground states of free atoms. In the case of the transition elements, those differ from the dominant VK of bound atoms. Four points are important. 1) In the case of open shells, the state-averaged ground configuration and the configuration of the atomic ground state may be different. 2) The extended ($n +$

1)s Rydberg orbitals of d elements are generally destabilized in chemical compounds and are less relevant in chemistry. 3) Although the $(n+1)$s AO may be singly or doubly occupied in some free atoms Z or Z^+, the nd AOs are generally energetically lower and overlap better than the $(n+1)$s to form coordinative bonds. 4) The order of electronic orbital occupation of the series of neutral atoms $(Z, Z+1, \ldots)$ may differ from that of the series of ions $(Z^{q+}, Z^{(q-1)+}, \ldots)$ of the same atom. Independent of which configurations are given in the tables, the dominant *VK*s in substances are $\mathrm{d}^{g-q}\mathrm{s}^0$ for elements from groups $g \in [3,10]$ with atomic charges $q+$.

The properties of the elements support a complex network of similarities. Three criteria define a periodic table. The choice of the nuclear charge for the definition of elements and as the first ordering principle is undisputed, despite the large differences between H, D, and T and the similarities of some rare-earth elements. The very different elements before and after the noble gases impress a periodicity on the whole system, which is without alternative. However, the selection of properties as particularly important and the individually favored shape determines the projection of the multiply connected PSE onto orthogonal tables in a manner swayed by interests and aesthetics. For example, whether He should be above Be or Ne,[3o] Al above Sc or Ga, Y above La or Lu, Hf above Th or Rf, and so forth. Selected vertical similarities come to the fore. IUPAC orients our view by the recommendation of the present standard table.[51]

The energetic sequence of AOs is not universal. Realistic sequences lie between the limiting hydrogen and Madelung cases with sequence (1H) and sequence (1M). In the deep cores of heavy atoms (X-ray spectra), we find sequence (1C), which is somewhat similar to sequence (1H). The sequence in the valence shell of the electropositive elements, sequence (1A), is not that different from sequence (1M). The sequence (1V) in the valence shells of all other atoms, however, is intermediate. A realistic chemistry lecturer would first teach sequence (1V) as the empirical rule between the two textbook models. Concerning Groups 1 and 2, $(n+1)\mathrm{s} < n\mathrm{d}$ would be mentioned as an “exception”.

Available electrons fill energetically low-lying shells. But filled shells are chemically inactive only if separated from higher shells by a large energy gap.[64] According to sequence (1V), this situation is only found for $1\mathrm{s}^2$ (He shell) and for $n\mathrm{p}^6$ ($n=2$ to ca. 6, Ne to Rn). From the experimental as well as quantum chemical and spectroscopic points of view, helium is not akin to Groups 2 and 12 with semiopen $(\mathrm{sp})^2$ configurations.[3o] The $n\mathrm{s}^2$ and $n\mathrm{d}^{10}$ shells become inactive only at correspondingly higher Z.

The periodicity of the valence shells, arising from the particular stability of the $n\mathrm{p}^6$ shells ($n=2$–6), comes to an end for nuclear charges somewhat above 100. Eka-Rn is no longer a noble gas. While Mendeleyev could reliably predict Sc, Ga, und Ge by purely empirical interpolation, the extrapolation into the region of superheavy elements requires validation by relativistic quantum chemistry. Incidentally, the chemically meaningful stability of the nuclei also comes to an end in this Z range. Only fleeting single molecules and no condensed phases are viable. The PSE seems complete with Row 7.

Indeed, the $n+l$ rule has little meaning in chemistry. However, since the rule occurs in all textbooks and is absorbed by all students and teachers, it will die out only very slowly. Only a few chemists need correct details about the electronic structure of the chemical transition elements; their re-education in graduate courses is not too difficult. Most other undergraduate students will not need the $n+l$ blunder in their future career. So it does no harm, as some scientists argue. Since the inherited wisdom of the chemical community forms the basis of discourses in the philosophy of chemistry, biased conclusions are unavoidable.[1c,3b,i,j,l,p,q,t,u,v] The example of the PSE shows two things. “Facts” and “truth” are not that clear, even in the hard sciences. And the discussion between chemists, didacts, and philosophers can help chemistry to recognize its own scientific problems and then elucidate and clarify them. The new book by Scerri on the PSE was instrumental in this respect.[65,3q]

Appendix: Notes on Orbitals and Ionization Potentials

It is convenient to communicate data as given in easily accessible compilations, such as those from atomic vacuum spectroscopy.[33] The first ionization potentials (*IP*s) are the energy differences of the ground states of the free neutral atoms and the free cations, for example, for vanadium $IP[\mathrm{V}^0(^4\mathrm{F}_{3/2}{-}3\mathrm{d}^3 4\mathrm{s}^2) \rightarrow \mathrm{V}^{1+}(^5\mathrm{D}_0{-}3\mathrm{d}^4)]$. This spectroscopic quantity is quite complicated and depends on d–d, d–s, and spin–orbit couplings. For chemistry, the energy differences of chemically relevant configuration averages are more interesting, such as $\Delta E[\mathrm{V}^0\,(3\mathrm{d}^5) \rightarrow \mathrm{V}^{1+}\,(3\mathrm{d}^4)]$ and $\Delta E[\mathrm{V}^{1+}\,(3\mathrm{d}^4) \rightarrow \mathrm{V}^{2+}\,(3\mathrm{d}^3)]$.

According to the Koopmans theorem, the energies ε of “canonical” Hartree–Fock orbitals often offer reasonable estimates of ionization processes, $-\varepsilon \approx IP$ or ΔE. In this simple form, the Koopmans theorem holds true for closed or evenly populated systems, provided no configurational reorganization occurs upon ionization. But most atoms have open shells, and transition-metal configurations often reorganize drastically (see Section 4.1 for Y and V). In any case, the representation of several states by one mean orbital set requires sophisticated two-electron energy corrections.[11,34]

The atomic *IP* versus *Z* curves typically presented in the textbooks exhibit irregularities for precisely those elements that have a different type of reference configuration. For example, in the row Ca–Zn with common $\mathrm{d}^{g-2}\mathrm{s}^2$ reference, chemically less relevant peaks appear for Cr and Cu, for which a $\mathrm{d}^{g-1}\mathrm{s}^1$ reference was chosen.[40] The lanthanoids form an exception in this respect, as their f shells sit deep in the atomic cores. Their atomic states are chemically relevant, as they are only weakly perturbed by the ligands.

An adequately averaged set of (experimentally or computationally derived) ΔE values is suitable for the construction of an atomic orbital energy scheme that reproduces the chemically relevant configurations of the elements in compounds with the help of the simplified Aufbau rule. The atomic configuration energies vary rather smoothly with Z; no “exceptions” occur

(Figure 7). For chemical purposes, the Rydberg s levels of the free atoms must be appropriately “corrected”.

Received: February 20, 2008
Revised: August 24, 2008

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