

# Theoretical Basis and Correct Explanation of the Periodic System: Review and Update

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The periodic system of chemical elements (PSE) is one of the most ingenious inventions of human culture; it is one of the most essential ordering concepts of chemistry (1). Since its creation nearly one and a half centuries ago, its principles remain a hot topic of scientific, educational, historic, and philosophic discussions. In this century alone, about 50–100 articles related to the periodic system have already been published just in this *Journal*. These discussions, and parallel ones in other journals and in about 20 books and brochures of the past decade, are in general quite illuminating concerning chemical and cultural aspects.<sup>1</sup> Theoretical and physical aspects, however, are often afflicted with serious misconceptions. Scientific achievements sometimes diffuse rather slowly among different scientific communities. To promote this process, we ask a series of modest questions and give short answers without detailed explanations (Table 1). Then, a coherent theoretical background is explicated. Novel, logically consistent views on old empirical and theoretical facts (2) supply the foundation of a deeper understanding of the structure of the PSE, as represented by different periodic tables. A representative periodic table is shown in Figure 1.

## The Backbone of the Periodic System

The atomic weight (mass),  $A_{\text{ave}}$ , was clarified at the Karlsruhe congress in 1860 (1). In 1862, de Chancourtois was the first to arrange the chemical elements linearly according to  $A_{\text{ave}}$ . He wound up the array of elements to a spiral so that elements with characteristic chemical properties periodically appeared one below the other. Since then, a significant fraction of all graphical representations of the periodic system has been cyclic (7). The horizontally and vertically “doubly connected” arrangements display a comparatively large fraction of the relations between the elements (1, 2, 8). According to recent empirical chemometric investigations, the groups of most similar elements are the main groups just before and after the *noble gases* (group  $G = 18$  or 0 in Figure 1) (9). These groups are the *nonmetallic halogens*, *chalcogens*, and *pnictogens* ( $G = 17, 16, 15$ ) and the *alkali*, *alkaline-earth*, and *earth metals* ( $G = 1, 2, 3$ ). The strong variation of properties of just these groups, 15 to 18 and 0 to 3, strongly contributes to the appearance of periodicities of 8, 18, and 32 elements. This has recently been re-examined by mathematical Fourier analysis (10). The periodicity of the transition-element groups is empirically less well pronounced than that of the main-group elements (9).

Meyer's (11) first, simple, rectangular periodic table of 1862 explicitly contained groups 14 (C, Si, [<sup>73</sup>E], Sn, Pb), 15 (N, P, As, Sb, Bi), 16 (O, S, Se, Te), 17 (F, Cl, Br, I), 1 (Li, Na, K, Rb, Cs, Tl?), and 2 (Be?, Mg, Ca, Sr, Ba). The yet unknown noble gases were still missing in the center, and the unknown earth metals were missing at the right edge.<sup>7</sup> Meyer had labeled the groups by their typical valence numbers, which now can be explained by the dominant electronic configurations of the *bonded* atoms. Soon, rectangular tables with the valence (electron) numbers running from 1 to 8 (or 18) became the prevailing type of graphical representations. Thereby, the backbone of the periodic system was split up. Since then, the noble gases form the left or right edges of nonspiral, flat, easily printable tables.

## Core–Valence Gaps

The empirical chemical center of the periodic system, the noble-gas family, is microscopically characterized by very stable  $1s^2$  or  $np^6$  ( $n \leq 6$ ) closed “valence” shells with high ionization potentials. The three preceding elements of the noble gases have 1, 2, or 3 strongly electronegative (i.e., energetically low lying)  $np$  vacancies in period  $n$ , giving rise to oxidation states  $1-$ ,  $2-$ , or  $3-$ . Each electron pair can then form a polar double bond, for example, to an O atom, or two polar single bonds, for example, to two halogen atoms. Therefore, the oxidation or valence numbers are changed in *steps of two* (e.g., for S from  $2-$  to 0,  $2+$ ,  $4+$ , or  $6+$ ).

The successor elements in period  $(n+1)$  have 1, 2, 3, and so forth weakly bound electrons in the  $(n+1)s$  or  $nd$  valence shells above the  $np^6$  closed-core shell. This gives rise to common oxidation states  $1+$ ,  $2+$ ,  $3+$ , and so forth. For the next groups, the number of electrons in the d shell can vary in *steps of one*. The most stable oxidation state  $q+$  depends on the balance between the total ionization energy,  $\infty + (q^3)$ , and the lattice or solvation energy,  $\infty - (q^2)$ . The decisive point for the successor elements is the energy sequence  $np \ll nd, (n+1)s$ . The comparatively stable outer shells,  $1s^2$  of He,  $2p^6$  of Ne,  $3p^6$  of Ar, and so forth, with large energy gaps above and the energetic distances between the different  $nl$  shells, determine the successive lengths of the periods from one to the next noble gas, namely, 2, 8, 8, 18, 18, and 32 (2).

## Energetic Sequences of the $nl$ Shells

The next question is now, why does a large energy gap appear above the outer  $np$  shells? In the hydrogen atom, levels

Table 1. Questions and Short Answers To Introduce the Periodic System of Elements

| Question  | Answer   |
|---|--|
| Why are the halogens and the alkali metals among the first groups treated in chemistry courses?   | A few groups before and after the noble gases <sup>2</sup> form the empirical <i>and</i> theoretical <i>backbone</i> of the PSE.   |
| What is the physical origin of the periods' lengths?  | There is a large <i>energy gap</i> among the atomic outer-core shells 1s and 2p through 6p and the following valence shells. <sup>3</sup> This causes the exceptional position of the noble gases and of the adjacent groups just before and after them. The sequence of orbital-energy distances forms the quantum-chemical origin of the periodicity, of the "periodic law" of 2, 8, 8, 18, 18, and 32.  |
| Why are the closed p <sup>6</sup> shells of the <i>noble</i> gases more stable than other closed shells, viz. s <sup>2</sup> and d <sup>10</sup> of chemically <i>active</i> metals (of groups 2, 12, and 10)?  | A little above ns <sup>2</sup> there is the np shell, and a little above (n - 1)d <sup>10</sup> there is the ns shell; there are <i>no</i> pronounced energy gaps. The near-degenerate (s-p) <sup>2</sup> and (d-s) <sup>10</sup> shells are not really closed.  |
| All textbooks give the electron configurations of the transition elements as ns <sup>2</sup> (n - 1)d <sup>G-2</sup> , admitting a few exceptions. Why then is transition-metal chemistry practically pure d-AO chemistry? (G is the number of valence electrons or the group number in the PSE, and n is the principal quantum number or the period number.) | For all chemically <i>bonded</i> transition-metal atoms, (n - 1)d < ns, energetically and spatially. (n - 1)d is <i>always</i> occupied first in transition-metal cations. The leading configuration of cations M <sup>q+</sup> of charges q from G through 0 is (n - 1)d <sup>G-q</sup> ns <sup>0</sup> . Only the chemically less important <i>free</i> neutral atoms in vacuum have an exceptional ns occupation.   |
| He, Be–Ra, and Zn–Hg all have an outer ns <sup>2</sup> configuration. Should one count them all as s block elements? Should the first and last elements of the lanthanoid and actinoid series, <sup>4</sup> La, Ac and Lu, Lr, be counted as d or as f elements?  | More important than nomenclature are the facts of chemical behavior depending on the outer-core shells and the frontier orbitals. <sup>5</sup> The metals of groups 2 versus 12 differ in their outer-core and frontier valence shells. For instance, the alkaline-earth elements Mg through Ra have outer (n - 1)p <sup>6</sup> cores, while the group 12 elements Zn, Cd, and Hg have outer (n - 1)d <sup>10</sup> cores. Helium differs more, because it has an inactive 1s <sup>2</sup> shell without frontier valence orbitals nearby. In period n, bonded Y, La, and Ac atoms from group 3.0 versus the last elements of the f series, Lu and Lr from group 3.14, have (n - 2)d <sup>10</sup> (n - 1)p <sup>6</sup> versus (n - 2)f <sup>14</sup> (n - 1)p <sup>6</sup> core shells, with somewhat different atomic and ionic radii (lanthanoid and actinoid contraction). |
| Are the (n + l, n) Madelung rule and the triad rule basic chemical principles?  | The Madelung rule <sup>6</sup> was constructed for neutral, free, chemically unbound atoms. Its statement that ns is occupied before (n - 1)d applies <i>only to the first two groups</i> of the PSE. The sequence of atomic nl shells changes from the core to the valence region and also changes in the valence shell from the first two to the later groups. The triad concept is a <i>corollary</i> of the "periodic law", which follows quantum-chemically from the above-mentioned core–valence gaps above 1s and np, n ≤ 6.  |
| Can one extrapolate the trends of the chemical properties of the elements in the periodic table with the help of the Madelung rule up to nuclear charges of Z = 120 or 200 or 1000?   | Of course <i>not</i> . The common vertical and horizontal trends begin to change significantly already below period 6. Furthermore, owing to the short nuclear lifetimes, there will be only very little condensed-phase chemistry and only little gas-phase spectroscopy from the end of period 7 onward.   |

with the same n value are very similar (12), for example,<sup>8</sup>

$$2s, p \ll 3p_{1/2} \lesssim 3s_{1/2} \lesssim 3d_{3/2} \lesssim 3p_{3/2} \lesssim 3d_{5/2} \ll 4s, p, d, f$$

The *inner-core* X-ray spectra of heavy atoms such as Xe or W show that 3s and spin–orbit split 3p and 3d are still energetically nearby

$$2p \ll 3s_{1/2} \lesssim 3p_{1/2} < 3p_{3/2} \lesssim 3d_{3/2} < 3d_{5/2} \ll 4s$$

Neglecting spin–orbit coupling, the inner atomic orbital energies can be described by:

Inner-core shells:

$$1s \ll 2s < 2p \ll 3s < 3p < 3d \ll 4s \quad (1)$$

The relative s–p–d energy separations become more and more pronounced for the outer shells. Electrons in the outer shells "feel" the attracting nuclear charge being strongly shielded by the inner, repelling, core electrons. The shielding becomes more effective if a larger centrifugal pseudoforce "pushes" the electron away from the nucleus. The effect is roughly proportional to  $\langle l^2 \rangle$ .<sup>9</sup> Therefore, the energetic sequence for the outer shells is:

Result of core shielding:

$$ns < np \ll nd \ll nf < n(H) \quad (2)$$

where n(H) refers to the hydrogenic energy. The resulting sequence for the outer shells of most atoms of, for example, the fourth period with a 3p<sup>6</sup> core, is

$$3p \ll 3d < 4s < 4p \ll \dots$$

This differs from sequence (1) for the inner-core shells. For about 80 years, it has been known (in principle, see the references in ref 8) that the following relations hold:

Outer shells (general):

$$(n-1)p \ll (n-2)f < (n-1)d < ns < np \ll \dots \quad (3)$$

Outer shells (group 1):

$$(n-1)p \ll ns < np < (n-1)d < (n-2)f \dots \quad (3a)$$

Note that in the alkali-metal atoms (group 1), (n-1)d is above ns and np. A shell is stable and chemically inactive if it has a low energy, *and* if it is not easily polarized. The latter is the case if the low-energy shell has no vacancies (i.e., is filled with electrons, which occurs rather automatically for a low energy) and if,

| Group G | Period n |       |       |       |        |       |       | Common Valence Config.            | Charact. Valence Orbital | Group Name           |
|---------|----------|-------|-------|-------|--------|-------|-------|-----------------------------------|--------------------------|----------------------|
|         | 7        | 6     | 5     | 4     | 3      | 2     | 1     |                                   |                          |                      |
| 0       | Rn 86    | Xe 54 | Kr 36 | Ar 18 | Ne 10  | He 2  | (n 0) | s <sup>0</sup>                    | (p)                      | noble gas (aerogen)  |
| 1       | Fr 87    | Cs 55 | Rb 37 | K 19  | Na 11  | Li 3  | (H 1) | s <sup>1</sup>                    | s                        | alkali metal         |
| 2       | Ra 88    | Ba 56 | Sr 38 | Ca 20 | Mg 12  | Be 4  |       | s <sup>2</sup>                    | d                        | alkaline-earth metal |
| 3.0     | Ac 89    | La 57 | Y 39  | Sc 21 |        |       |       | (ds) <sup>3</sup>                 |                          |                      |
| 3.1     | Th 90    | Ce 58 |       |       |        |       |       | f <sup>1</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.2     | Pa 91    | Pr 59 |       |       |        |       |       | f <sup>2</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.3     | U 92     | Nd 60 |       |       |        |       |       | f <sup>3</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.4     | Np 93    | Pm 61 |       |       |        |       |       | f <sup>4</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.5     | Pu 94    | Sm 62 |       |       |        |       |       | f <sup>5</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.6     | Am 95    | Eu 63 |       |       |        |       |       | f <sup>6</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.7     | Cm 96    | Gd 64 |       |       |        |       |       | f <sup>7</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.8     | Bk 97    | Tb 65 |       |       |        |       |       | f <sup>8</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.9     | Cf 98    | Dy 66 |       |       |        |       |       | f <sup>9</sup> (ds) <sup>3</sup>  |                          |                      |
| 3.10    | Es 99    | Ho 67 |       |       |        |       |       | f <sup>10</sup> (ds) <sup>3</sup> |                          |                      |
| 3.11    | Fm 100   | Er 68 |       |       |        |       |       | f <sup>11</sup> (ds) <sup>3</sup> |                          |                      |
| 3.12    | Md 101   | Tm 69 |       |       |        |       |       | f <sup>12</sup> (ds) <sup>3</sup> |                          |                      |
| 3.13    | No 102   | Yb 70 |       |       |        |       |       | f <sup>13</sup> (ds) <sup>3</sup> |                          |                      |
| 3.14    | Lr 103   | Lu 71 | Y 39  | Sc 21 |        |       |       | [f <sup>14</sup> ]d <sup>3</sup>  |                          |                      |
| 4       | Rf 104   | Hf 72 | Zr 40 | Ti 22 |        |       |       | d <sup>4</sup>                    |                          |                      |
| 5       | Db 105   | Ta 73 | Nb 41 | V 23  |        |       |       | d <sup>5</sup>                    |                          |                      |
| 6       | Sg 106   | W 74  | Mo 42 | Cr 24 |        |       |       | d <sup>6</sup>                    |                          |                      |
| 7       | Bh 107   | Re 75 | Tc 43 | Mn 25 |        |       |       | d <sup>7</sup>                    |                          |                      |
| 8       | Hs 108   | Os 76 | Ru 44 | Fe 26 |        |       |       | d <sup>8</sup>                    |                          |                      |
| 9       | Mt 109   | Ir 77 | Rh 45 | Co 27 |        |       |       | d <sup>9</sup>                    |                          |                      |
| 10      | Ds 110   | Pt 78 | Pd 46 | Ni 28 |        |       |       | d <sup>10</sup>                   |                          |                      |
| 11      | Rg 111   | Au 79 | Ag 47 | Cu 29 |        |       |       | d <sup>10</sup> s <sup>1</sup>    | ds                       |                      |
| 12      | Cn 112   | Hg 80 | Cd 48 | Zn 30 | (Mg12) | (Be4) |       | s <sup>2</sup>                    | s                        |                      |
| 13      | Uut 113  | Tl 81 | In 49 | Ga 31 | Al 13  | B 5   |       | s <sup>2</sup> p <sup>1</sup>     |                          | triell               |
| 14      | Uuq 114  | Pb 82 | Sn 50 | Ge 32 | Si 14  | C 6   |       | s <sup>2</sup> p <sup>2</sup>     |                          | tetrel               |
| 15      | Uup 115  | Bi 83 | Sb 51 | As 33 | P 15   | N 7   |       | s <sup>2</sup> p <sup>3</sup>     |                          | pentel, pnictogen    |
| 16      | Uuh 116  | Po 84 | Te 52 | Se 34 | S 16   | O 8   |       | s <sup>2</sup> p <sup>4</sup>     |                          | chalcogen            |
| 17      | Uus 117  | At 85 | I 53  | Br 35 | Cl 17  | F 9   | (H 1) | s <sup>2</sup> p <sup>5</sup>     |                          | halogen              |
| 18      | (Uuo118) | Rn 86 | Xe 54 | Kr 36 | Ar 18  | Ne10  | He 2  | s <sup>2</sup> p <sup>6</sup>     |                          | noble gas            |

Figure 1. Periodic table, representing some aspects of the periodic system of chemical elements (mainly to support the discussions in this article, perhaps not for the classroom): element symbol and element number  $Z = 0-118$ ; period number  $n$ ; group number  $G$ , related to the number of valence electrons; typical electronic valence configuration of the bound atoms ("neighbor configurations" such as  $s^1p^3$  instead of  $s^2p^2$  may be more important for some atoms in the group); characteristic valence orbitals of highest angular momentum; and chemical group name. (Elements that do not belong to the group are put in parentheses. The dashed lines indicate alternative or controversial group assignments; they are not meant to represent the authors' views. Note that the richness of chemistry sometimes prevents clear-cut classifications and assignments. See the collection of PTs by Leach (43).)

in addition, there are *no hybridizing orbitals energetically nearby* (2, 5, 6). This holds for  $1s^2$  of He and for the  $np^6$  shells of the other noble gasses.

## Do Valence Configurations Alone Determine the Chemistry?

The occupied-orbitals valence configuration of an element (e.g.,  $ns^2$  in groups 2 or 12) is an important determinant of the chemical behavior of that element. In particular, the angular behavior and the node structure of the s, p, d, and f valence orbitals are decisive for the overlap possibilities, for covalent-bond formations, and for the bond angles (2, 13–15). However, it is often not sufficiently realized that the chemical properties of an element also depend on the *lowest virtual* orbitals, on the *energies and spatial extensions* of all frontier<sup>5</sup> orbitals, and in the case of heavy elements also on the *spin-orbit splittings* (e.g., for the later elements of period 6, there is a dramatic splitting of 6p into  $6p_{1/2}$  and  $6p_{3/2}$ ). In addition, the extension and softness of the *outer-core shells* is important, too.

Several parameters for four light and heavy elements of groups 2 and 12 are presented in Table 2: (i) the calculated  $(n-1)p$  or  $(n-1)d$  outer-core orbital energies and radii (related to core polarizabilities and bond lengths, respectively); (ii) the  $ns$  valence-orbital energies and radii (related to electronegativities and covalent overlap bonding); (iii) the experimental excitation energies from  $ns$  to the next higher  $(n-1)d$  or  $np$

virtual orbitals (related to hybridization); and (iv) the common ionic radii and electronegativity values. The pronounced differences of the numerical values, and the different orbital types involved, explain why there are chemical differences of the elements within one group and even bigger differences of the elements of groups 2 and 12 (5a), despite having the same valence configuration  $ns^2$  (44b).

## Electron Configurations of the Transition Elements

Much has been published about the problem of  $(n-1)d$  versus  $ns$  population of transition-metal atoms (e.g., refs 5 and 17). However, only a fraction of the relevant points are usually discussed. "The Full Story of the Electron Configurations of the Transition Elements" will be told in a separate contribution (18). Here, we briefly mention two points. The first point is that the order of orbitals in the valence shell changes from group 1 to the higher groups (see relations 3 and 3a). As a concrete example, we present the sequences of orbital levels, as derived from the spectroscopic data of period 6 elements (2, 8, 12):

group 1 (Cs)

$$5p \ll 6s < 6p \ll \underline{5d} \ll \dots \underline{4f} \quad (4a)$$

group 2 (Ba)

$$5p \ll 6s < \underline{5d} < 6p \ll \dots \underline{4f} \quad (4b)$$

Table 2. Core and Valence-Shell Parameters of Atoms with  $ns^2$  Valence Configuration

| Atom | Outer-Core |           |           | Valence |           |           | Lowest $ns$ Singlet Excitation to: |           |                 |                 |
|------|------------|-----------|-----------|---------|-----------|-----------|------------------------------------|-----------|-----------------|-----------------|
|      | Orbital    | $E^a$ /eV | $R^a$ /pm | Orbital | $E^a$ /eV | $R^a$ /pm | Orbital                            | $E^b$ /eV | $R_{ion}^c$ /pm | EN <sup>d</sup> |
| Ca   | 3p         | -36.5     | 67        | 4s      | -5.34     | 222       | 3d                                 | 2.71      | 100             | 1.0             |
| Ba   | 5p         | -24.7     | 102       | 6s      | -4.44     | 269       | 5d                                 | 1.41      | 135             | 1.0             |
| Zn   | 3d         | -20.8     | 47        | 4s      | -8.13     | 151       | 4p                                 | 5.80      | 73              | 1.7             |
| Hg   | 5d         | -16.5     | 78        | 6s      | -8.93     | 150       | 6p                                 | 6.07      | 117             | 1.5             |

<sup>a</sup>Orbital energies and radii from relativistic atomic-orbital calculations (16). <sup>b</sup>Optical excitation energies from UV-vis spectra (12). <sup>c</sup>Standard ionic radii,  $R_{ion}$ , for coordination number of 6. <sup>d</sup>Allred-Rochow electronegativities, EN.

group 3 (La)

$$5p \ll 5d < 6s < \underline{4f} < 6p \ll \dots \quad (4c)$$

groups 4 seq. (Ce, Pr, ..., La, Hf, ...)

$$5p \ll \underline{4f} < 5d < 6s < 6p \ll \dots \quad (4d)$$

The virtual  $(n-1)d$  levels of the *alkali-metal* atoms (group 1) lie high above the valence  $ns$  and  $np$  levels; the  $(n-2)f$  levels are even more weakly bound. The  $(n-1)d$  of the *alkaline-earth* elements (group 2) lie between the  $ns$  and  $np$  valence levels;  $d$  admixture (hybridization) influences the bonding of alkaline-earth-metal compounds. The  $d$  shell becomes the lowest, dominant valence shell of the *transition metals* from group 3 onward; the so-called  $d$ -orbital collapse is complete in group 3 (19). The corresponding  $f$ -orbital collapse in the lower periods 6 and 7 occurs even more suddenly at group 4; from that group onward, that is, from the second members of the lanthanoid and actinoid series (Ce, Th),  $f$  orbitals participate in bonding. The  $g$ -orbital collapse occurs around group 5 (2).

The second point is the behavior of the  $ns$  orbital. In free neutral atoms in vacuum, the diffuse Rydberg  $ns$  level is usually occupied by one or two electrons. In chemical compounds, the metal  $ns$  orbital overlaps with the occupied core shells of adjacent atoms (ligands). Owing to the Pauli exclusion principle (Pauli closed-shell repulsion), the  $ns$  orbital energy is raised, and the electronic  $ns$  population is reduced in transition-metal compounds. These two points explain the low relevance of  $ns$  in comparison to  $(n-1)d$  in transition-metal chemistry (20). It is an interesting science-philosophical problem to explain why most chemists (including a reviewer) insist on the validity of the Madelung rule of the late 1930s (21) for all transition elements. The Madelung rule:

$$5p < 6s < 4f < 5d < 6p < 7s \dots \quad (5)$$

is conventionally interpreted by most chemists as concerning the orbital energy sequence, in contrast to the experimental findings of the 1920s (relationships 3 and 4), which were quantum-chemically reproduced since the 1960s. Not a single element of periods 4 seq. (sequences 4) follows the hypothetical rule, relationship 5, which applies to Ca and Sr only.

### s-, p-, d-, and f-Block Elements

There are discrepancies between the common definition and the actual usage of "*l*-block elements". One author (W.H.E.S.) defines an *l*-block element as one having dominant valence-active *l*-type orbitals (but no important ones of higher *l* value). We stress that, in chemical journals, actual chemical behavior is most important and this involves the highest occupied (core and

valence) orbitals and the lowest unoccupied orbitals, as well as the impossibility of a complete characterization of atoms by a simple main configuration. Thus, we distinguish between theoretical s-, p-, d-, and f-block elements, and chemical-empirical main-group, transition-metal, and lanthanoid and actinoid (sometimes called "inner-transition") elements.

For the other author (R.L.R.), valence active orbitals may include the highest ones in the core (if used in back bonding). It is also often convenient to include the exceptional He (even without low-lying p orbitals) with the other aerogens (noble gasses) in the "p block" as usual.

Finally, we support the common classification of Sc and Y (albeit without low-lying f orbitals) with the lanthanoids, and possibly even the early actinoids, as "rare earths". All of these elements, except for Th, have 3+ as an important oxidation state, and this may further excuse a writer even in assigning them all to the "f block" when labeling columns in tables. A term such as "rare earths/lanthanoids and actinoids" is accurate but at times too clumsy. Our nomenclature should also not ignore further points. First, the names "lanthanoid" and "actinoid" mean "like lanthanum" and "like actinium" and may well include La and Ac themselves. Second, having to say "lanthanum and/or lutetium and the lanthanoids" instead of "the lanthanoids", for example, is clumsy, too. And third, one author (R.L.R.) holds that zero may be taken as a legitimate integer for the number of, e.g., f electrons in a shell of interest.

Questions of esthetics and symmetry of the PSE will be discussed at the end of this section.

According to the one suggested definition, hydrogen and the elements of groups 1, 2, and 12, with one or two electrons in an s valence shell, would belong to the *s block* (44b). The  $1s^2$  shell of He is better called a core shell. The s elements differ among each other with respect to their core and valence shells, as mentioned above. The formation of complexes of weak and strong ligands  $NH_3$ ,  $CN^-$ , and so forth with  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  support the inclusion of group 12 in the transition or d block, not the main or p block.

There is little controversy counting the six groups 13 through 18 as the *p block*. The p-block elements from period 2 have a very small  $1s^2$  core and an  $(sp)^{6-10}$  valence shell with four valence orbitals of similar radial extension ( $s, p_x, p_y, p_z$ ). For the heavier elements, the tendency toward  $ns-np$  hybridization is reduced, since the  $np$  shell is radially more extended than the  $ns$  shell. There is also little verifiable tendency toward  $np-nd$  hybridization, since the  $nd$  is too diffuse (13). The  $p^6$  shells of Ne and Ar in group 18 are chemically rather inactive (like the  $1s^2$  shell of He). It is difficult to classify He, Ne, and Ar according to the chosen definition. The  $np^6$  shells of the heavier noble gasses Kr, Xe, and Rn become more and more active. Eka-Rn ( $_{118}Uuo$ )



is predicted not to be noble or a gas. It has neither a low-lying p shell (the  $7p_{3/2}$  level is destabilized by spin-orbit coupling) nor is there a large gap to the relativistically stabilized 8s (20).

Groups 3 to 11 have active  $(n-1)d$  valence orbitals. By one definition, these nine groups would be counted in the *d* block. Again, another definition includes group 12. The dominant configurations of ions of charge  $q+$ , and of neutral bonded atoms in chemical compounds, are  $(n-1)d^{G-q}$  and  $(n-1)d^G$ , respectively, in groups  $G = 3-10$  (21). Bonded coinage metals ( $G = 11$ ) also have valence-active *ns* orbitals. Concerning the *ns* occupation of single, unbound, transition-metal atoms, see ref 18.

Correspondingly, one might count only the elements with “active” *f* valence electrons as the *f*-block elements. In periods 6 and 7, this would be the case for the 13 lanthanoid elements after d element La (22), namely, for Ce ( $Ce^{3+}4f^1$ ) through Yb ( $Yb^{3+}4f^{13}$ ) and for the 13 actinoid elements after d element Ac, namely, for Th through No. When the *f* shell is filled up at the end of the series,  $f^{14}$  becomes the closed-core shell for Lu, Hf, and so forth and for Lr, Rf, and so forth. They have  $4f^{14}5p^6$  and  $5f^{14}6p^6$  cores, respectively. The dominant valence shell of Lu, Hf, and so forth in period 6 is 5d; we might then count ten d elements, La and Lu through Au. The chemical properties in period 7 deviate already from the trends in the upper periods (23). The  $6p^6$  core is no longer that inert (core participation in bonding), the 5f is not that compact (f contribution to covalence), and in addition, the 5f and 6d are strongly spin-orbit split. Therefore, the early actinoids (e.g., Th, U, or Pu) prove to be less similar to the early lanthanoids (Ce, Nd, or Sm, respectively); it happens, however, that they show many similarities with the heavy d elements Hf, W, Os. And while Lu is a typical 5d element, bonded Lr has more 7sp than 6d orbital contribution. On the other hand, according to their similar chemical behavior, the elements with barely empty  $f^0$  and barely full  $f^{14}$  shells are legitimately counted in the series of 15 lanthanoid elements.

Any chemical substance, any molecule, or any element has its characteristic individual properties, both of empirical and of quantum-theoretical kinds. Cluster and factor analyses of the properties of the chemical substances have uncovered about half a dozen important independent basic properties of the chemical elements (see the reviews in section 3 of ref 2a or in sections 2 and 3 of ref 8). The chemical elements form more or less pronounced similarity clusters in the multidimensional space of basic properties. One must choose somewhat arbitrary borderlines on the continuous property scales (e.g., see ref 24) to classify the chemical compounds and elements. The empirical classification of the elements as metals and nonmetals, and as semimetals and metalloids in between, is not fully unique. The *horizontal* array of the 10 elements from Sc to Zn is usually called the “light transition-metals”. Sometimes the zinc family ( $G = 12$ ) is excluded from the transition elements. The 17 trivalent elements, Sc, Y, and La through Lu, are often counted as the rare-earth elements (25). Sometimes the 15 actinoids Ac through Lr are included, too. The heaviest of the noble gasses are no longer chemically noble. There are continuing discussions about the best positions of H, He, Zn, La, or Lu, and so forth in the PSE, see for example (1, 22, 26). The decision on how to classify the elements depends somewhat on the specific scientific interests of the author; one can then argue if one's own taste is different.

The interpretations of empirical definitions are more “flexible” than those of theoretically based definitions. The unique theoretical definition of *l*-block elements as given here

overlaps well with the different possible choices of main-group, transition, and lanthanoid elements, but it is not fully equivalent to them. Many authors adopt, at least implicitly, another theoretical definition of *l*-block elements, namely, as the ones with the highest-occupied orbitals of *l*-type of the chemically unbound, free atoms. According to the empirically (or theoretically) derived sequences of orbital energies of the free atoms, many transition elements and lanthanoids would then belong to the *s* block. Thus, the often-implied *l*-block definition is not meaningful. Indeed, the present authors do not apply it. In reality, many periodic tables are divided in an “esthetic” manner into 2 *s*, 6 *p*, 10 *d*, and 14 *f* groups. Under this unscrutinized presupposition, e.g. (22), group 12 is included among the *d* groups, although Zn and Cd do not have any *d* valence orbitals (as one of us interprets them); and one and only one of the fringe elements of the lanthanoids is included in the *f* block, although *f* orbitals are less important for the bonding of both La and Lu. For additional mitigation, however, we also note that the outer *d* orbitals of group 12 are indeed useful for back bonding, for example, in cyanide complexes. This type of “core-shell binding” also plays a role for the early seventh period elements at least up to U, namely, by the  $[Rn]6p^6$  shell.

### Limits of the “Periodic Law” and Its Corollary, the Triad Rule

Döbereiner's triad rule of 1817 concerning the (atomic or) equivalence weights of the elements was instrumental for the introduction of physical numbers into the arrangement of chemical elements (1, 8, 27). From time to time, connections between the proton (*Z*), neutron (*N*), or mass numbers (*A*,  $Z + N = A$ ) and the chemistry of the elements were investigated. It has been argued, for instance, that the identity of the elements resides in the chemically invariable nuclei (correct), but “not at the ever-changing level of [the valence] electrons” (28). However, the typical behavior of the chemical elements is determined by their dominant valence configurations. The orbital occupation numbers of differently bonded atoms vary only a little, and they change systematically from element to element, corresponding to orbital energy sequences (4). It is a logical slip to miss the fact that the average valence configurations of the elements determine the double-step periodicity of 8, 8, 18, 18, 32, and 32. A consequence of this quantum-chemically based “periodic law” is the Triad rule:

$$2A_{\text{ave}}(n) \approx A_{\text{ave}}(n-1) + A_{\text{ave}}(n+1), \text{ and}$$

$$\text{nowadays } 2Z(n) = Z(n-1) + Z(n+1) \quad (6)$$

which holds for one-half of the elements of periods  $n$ ,  $n-1$ , and  $n+1$  in a given vertical group. The number of triads can be changed by changing the most common arrangement of elements in the periodic tables (e.g., see 27). Shifting H from group 1 to 17, one obtains the triad  ${}^1_1\text{H}-{}^9_{17}\text{F}-{}^{17}_{17}\text{Cl}$ . Shifting He from group 18 to 2, one loses the triad  ${}^2_2\text{He}-{}^{10}_{18}\text{Ne}-{}^{18}_{18}\text{Ar}$ . Shifting B and Al from group 13 to 3, one gains the triad  ${}^5_3\text{B}-{}^{13}_{13}\text{Al}-{}^{21}_{21}\text{Sc}$ , but loses  ${}^{13}_{13}\text{Al}-{}^{31}_{31}\text{Ga}-{}^{49}_{49}\text{In}$ , and so forth. This has no deep chemical meaning, it simply shifts the focus from these to those relations among the elements. Or one may maximize the number of triads by placing some elements more than once in the chart (25 p. 3, 44a)

Meyer (11), and later Mendeleyev, were quite successful with the triad rule to predict atomic weights by *interpolation*, for

**Table 3. Dominant Valence Shells (Upper Line) and Outer-Core Shells (Lower Line) of the Traditional s-, p-, d-, and f-Block Elements in Periods 1–7**

| Row <i>n</i> | s Block  | f Block   | d Block  | p Block  |
|--------------|--|---|--|--|
| 1            | 1s <sup>a</sup>  |   |  |  |
| 2            | 2s(2p) <sup>b</sup><br>[He] = 1s <sup>2</sup>  |   |  | 2s2p <sup>a,b,c</sup><br>[He] = 1s <sup>2</sup>  |
| 3            | 3s(3p)<br>[Ne] = ...2s <sup>2</sup> 2p <sup>6</sup>                                  |   |  | 3s3p <sup>a</sup><br>[Ne] = ...2s <sup>2</sup> 2p <sup>6</sup>   |
| 4            | 4s(4p,3d) <sup>d</sup><br>[Ar] = ...3s <sup>2</sup> 3p <sup>6</sup>                  |   | 3d(4s) <sup>d,e</sup><br>[Ar] = ...3s <sup>2</sup> 3p <sup>6</sup>   | 4s4p <sup>a</sup><br>[Zn <sup>2+</sup> ] = ...3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup>                                     |
| 5            | 5s(5p,4d)<br>[Kr] = ...3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>              |   | 4d(5s) <sup>e</sup><br>[Kr] = ...3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>  | 5s5p<br>[Cd <sup>2+</sup> ] = ...4s <sup>2</sup> 4p <sup>6</sup> 4d <sup>10</sup>  |
| 6            | 6s(6p,5d)<br>[Xe] = ...4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>              | 4f5d(6s) <sup>f,g,h</sup><br>[Xe] = ...4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>   | 5d <sub>3/2</sub> 5d <sub>5/2</sub> (6s) <sup>e,i</sup><br>[Lu <sup>3+</sup> ] = ...4f <sup>14</sup> 5s <sup>2</sup> 5p <sup>6</sup> | 6s6p <sub>1/2</sub> 6p <sub>3/2</sub> <sup>i</sup><br>[Hg <sup>2+</sup> ] = ...5s <sup>2</sup> 5p <sup>6</sup> 5d <sup>10</sup>    |
| 7            | 7s(7p,6d) <sup>i</sup><br>[Rn] = ...5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup> | 5f <sub>5/2,7/2</sub> 6d <sub>3/2,5/2</sub> (7s) <sup>g,h,i,i</sup><br>[Rn] = ...5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>6</sup> | 6d <sub>3/2,5/2</sub> 7s7p <sup>i</sup><br>[Lr <sup>3+</sup> ] = ...5f <sup>14</sup> 6s <sup>2</sup> 6p <sup>6</sup>                 | 7s7p <sub>1/2</sub> 7p <sub>3/2</sub> <sup>i,k</sup><br>[Uub <sup>2+</sup> ] = ...6s <sup>2</sup> 6p <sup>6</sup> 6d <sup>10</sup> |

<sup>a</sup> The 1s<sup>2</sup> of He and the ns<sup>2</sup>np<sup>6</sup> of Ne and Ar behave as inert-core shells. <sup>b</sup> No Pauli repulsion on the 2p shell; therefore, it is small (i.e. radially nearly as compact as the 2s shell, not like the higher np > ns). <sup>c</sup> The 1s<sup>2</sup>2s<sup>2</sup> of O and F behave as core, with only a 2p valence shell. <sup>d</sup> No Pauli repulsion on the 3d shell, which is small (i.e. radially nearly as compact as the 3p core shell). <sup>e</sup> Zn, Cd, and Hg have s<sup>2</sup>p<sup>6</sup>d<sup>10</sup> cores and primarily s(p) valence shells, with polarizable d<sup>10</sup> core. <sup>f</sup> No Pauli repulsion on the 4f shell, which is small (i.e. radially inside the 5p core shell). <sup>g</sup> But for La and Ac, the f is still diffuse; they have primarily d(s) valence shells. <sup>h</sup> Lu and Lr have f<sup>14</sup>s<sup>2</sup>p<sup>6</sup>d<sup>10</sup> cores and primarily d(sp) valence shells, with polarizable f<sup>14</sup> core. <sup>i</sup> The spin–orbit splitting can no longer be neglected even at the qualitative level. <sup>j</sup> The early row-7 elements have chemically active, polarizable 6p<sup>6</sup> cores. <sup>k</sup> The 7s<sup>2</sup>7p<sup>6</sup> shell is no longer an inert, noble-gas shell.

example,  $A_{\text{ave}} \approx 73$  for the element between Si and Sn ( $A_{\text{ave}}(\text{Ge}) = 72.64$ ). However, the prediction of the atomic masses of the super heavy elements by *extrapolation* (29) is an order of magnitude less reliable, with errors up to 15 u, since the factor  $f(Z)$  in the relation  $A_{\text{ave}} = f(Z)Z$  is not at all constant. In any case, the approximate validity of the triad rule ends where the periodic law ends.

The quantum-theoretical structure of the PSE is as complex as the empirical trends of properties of the elements. Each period and each *l* block has different outer-core shells and different (occupied and virtual) valence shells. In addition, there are quantitative differences of the orbitals, for example, in spatial extension (2s ~ 2p, but  $ns < np$  for  $n > 2$ , and other “primogenic” orbital effects) (13, 14). These cause the “secondary” vertical periodicity, that is, the second period’s specific character, the fourth-period scandoid and sixth-period lanthanoid contractions, and so forth (13, 14, 30). Some details are summarized in Table 3.

In addition to these complex shell effects, which can be understood at the nonrelativistic level of approximation, corrections toward relativistic reality become more and more important in the lower parts of the periodic system. The relativistic effects increase with some power  $\geq 2$  of  $Z$ . Therefore, it is hardly possible to *extrapolate* from the lighter elements into the hypothetical eighth or even the seventh period. Already the properties of the elements of the sixth period deviate from simple extrapolation (23, 31, 32). In general, going down in a group, the atomic and ionic radii increase and the electronegativities decrease. These trends are attenuated or even inverted for the elements following the first d elements Sc–Cu (i.e., Zn, Ga, etc.) and the first f elements La–Lu (i.e., Hf, Ta etc.) (33). As one example we mention the ionic radii of the monovalent coinage elements:  $R[\text{Cu(I)}_{\text{CN}=2}] = 46$  pm,  $R[\text{Ag(I)}_{\text{CN}=2}] = 67$  pm, and  $R[\text{Au(I)}_{\text{CN}=2}] = 58$  pm.<sup>10</sup> For many years, most tables displayed a large ionic radius for Au(I) comparable to the metallic radius of about 135 pm, although experimental structure determinations repeatedly gave indications of the order  $\text{Cu(I)} < \text{Au(I)} < \text{Ag(I)}$ .

Only after theoretical clarification (34) did correct entries  $R[\text{Au(I)}_{\text{CN}=2}]$  around 58 pm appear. The periodic system can be extended into the region of super-heavy elements only on the basis of modern quantum-chemical calculations.

Hypothetical extensions of the periodic table (35) based on the Madelung rule let the 5g shell begin misleadingly in group 3, while 5g really becomes relevant only from group 5 or 6 onward (2, 31). In addition, in some regions of the eighth period, there are *small* energy separations between the upper 7p<sub>3/2</sub> “core shell” and a whole “band” of valence shells 8s, 8p<sub>1/2</sub>, 7d<sub>3/2</sub>, 7d<sub>5/2</sub>, 6f<sub>5/2</sub>, 6f<sub>7/2</sub>, 5g<sub>7/2</sub>, 5g<sub>9/2</sub>, 9s, and 9p<sub>1/2</sub>. This suggests a “new chemistry”. From the present scientific point of view, the “construction of a table of elements with the 8th and 9th periods (100 super heavy elements) is not meaningful”, because little is known about the stability and existence of the nuclei and about the electronic configurations in superheavy compounds (36).

From bismuth onward ( $Z = 83$ ,  $A = 209$ ),<sup>11</sup> the lifetimes are finite for all isotopes and decrease roughly as  $e^{-1.3Z}$ , with large deviations in both directions. If the lifetime of the most stable isotope is less than a year (i.e., for <sup>85</sup>At, <sup>86</sup>Rn, <sup>87</sup>Fr, and from <sup>100</sup>Fm onward), the radiation damage will quickly destroy solid compounds. For elements Eka-Tl (<sup>113</sup>Uut) and Eka-Pb (<sup>114</sup>Uuq) the lifetime reaches 1 s; these and the heavier elements seem unamenable to chemical investigation. The single, fleeting molecules of elements with lifetimes in the ms to  $\mu$ s range such as Eka-Rn (<sup>118</sup>Uuo) and following will be hard even to investigate spectroscopically. Ordinary chemistry seems to end with the seventh period, unless the hoped-for heavier “island of stability” is found.

### The Original Meaning of the Madelung Rule

The quantum-theoretical understanding of the complex spin–orbit coupled *J*-states of many-electron atoms was developed in the late 1920s and early 1930s and reviewed by Condon

and Shortley (38). A simple approximate mnemonic was sought in the 1930s (39) for the configurations of the  $J$  ground states of *neutral free* atoms. Madelung's empirically based construct reproduces a selection of four facts on the periodic system, namely, (i) that  $np$  is occupied after  $ns$  in the later main groups; (ii) that  $ns$  is occupied after  $(n-1)p$  in the first two main groups; (iii) that the spin-orbit-coupled ground states of more than half of the transition-metal atoms in vacuum derive from  $(n-1)d^{G-2}ns^2$  configurations; and (iv) the period lengths of 2, 8, 18, and 32 that result from (i) through (iii). However, several other facts do not fit, namely, (i) that the energetic sequence of orbitals changes from group 1 to group 2 to the subsequent groups (see relationships 4), (ii) that for all atoms of groups 3 through 18, the  $(n-1)d$  orbital is below the  $ns$ , (iii) that the lower states of all bound transition-metal atoms have (nearly) empty  $ns$  orbitals, that is, that transition-metal chemistry is mainly  $d$  chemistry, (iv) that the  $(n-2)f$  orbital is still unoccupied in group 3, (v) that all cations  $M^{2+}$ ,  $M^{3+}$ , and so forth have unoccupied  $s$  orbitals in chemical substances and in vacuum, and (vi) that 10 of the 27  $d$  elements (according to one definition) do not have free neutral atoms  $M^0$  with a filled  $ns^2$  shell. In any case, free atoms are not so interesting in chemistry.

It has been deplored from time to time that the Madelung rule has not yet been derived quantum-theoretically. Of course, this is impossible since this approximate rule of thumb is at variance with too many facts. A more general and correct rule had already been derived in the 1960s, corresponding to relations 4 (40).

## Concluding Remarks

The conceptual difference of macroscopic elementary substances (e.g., diamond or fullerenes) versus elements in substances (such as in methane or diamond) being conserved during chemical reactions is now generally accepted. An important microscopic difference should also be recognized, namely, that between free atoms in vacuum versus modified, partially charged atoms in compounds plus the neutral ones in the elemental substances, in particular that between their various atomic orbital-level schemes. For instance, the  $C$  atoms both in organic molecules and in the allotropes of carbon are affected by their surroundings. Atoms in vacuum are the limiting case of zero influence from such surroundings. 0.00 is here just a real number like any other. As in all cases of classification, the often-noted distinctions are indeed useful at times, but can therefore also be exaggerated. Thus, honest and broad views of the fundamental nature of concepts may differ. The PSE should be viewed as a chemically useful arrangement of chemical elements at the macroscopic level and of chemically bonded atoms at the microscopic level.

The "periodic law" was obtained at the level of qualitative chemistry by combination with several numerical data (atomic weights, valence numbers, atomic volumes, some thermodynamic parameters) and under the desire to construct a systematic table of elements (1, 2, 41, 44). More than a century later, the quantitative analysis of a large quantity of numerical data of chemical substances has substantiated that the PSE focuses the view on a specific selection of similarity relations among the elements. The periodicity of elements along the  $Z$  series is empirically anchored in the groups of strongly electronegative nonmetals immediately to the left of the noble gasses and in the strongly electropositive metals to their right.

Since quantum chemistry can reproduce and rationalize many of the empirical chemical findings, the "periodic law" can now also be rationalized theoretically, though not in such a simple and straightforward manner as, for instance, in the case of Hückel's  $4n + 2$  rule. The quantum-chemical origin of the "periodic law" is the sequence of upper occupied and lower virtual orbitals, and the energetic gaps occurring between  $1s$  and  $2s$ ;  $2p$  and  $3s$ ;  $3p$  and  $3d/4s$ ;  $4p$  and  $4d/5s$ ;  $5p$  and  $4f/5d/6s$ ;  $6p$  and  $5f/6d/7s$ . There no longer appears to be a pronounced gap above  $7p_{3/2}$ . The orbital energy sequence systematically changes from hydrogen, to the inner shells of many-electron atoms, to the outer shells of most atoms, to the weakly bound outer shells of the electropositive metal atoms of groups 2 and 1. The actual orbital sequences come out as a compromise between the nuclear–electron Coulomb attraction, approximately  $-Z/R^2$ , all the electron–electron Coulomb repulsions, approximately  $+1/r^2$ ,<sup>12</sup> and the "centrifugal force", approximately  $+l(l+1)/R^3$  ( $R$  is the electron–nuclear distance,  $r$  is the electron–electron distance). The most common valence-orbital sequence is relationship 3. Only for the electropositive elements, the higher angular momentum  $d$  and  $f$  orbitals suffer from the "centrifugal force". With increasing nuclear charge, the  $(n-1)d$  and  $(n-2)f$  valence orbitals collapse to their ordinary positions above  $(n-1)p$  in groups 3 and 4, respectively. The Madelung rule is of limited value in chemistry and may even be misleading. The chemical properties of the elements are governed by the electron configurations (core type, number, and angular momenta of valence electrons) and by the energetic and radial details of the atomic core and valence shells. All elements are qualitatively different in at least one of these respects, leading from a complex quantum-chemical picture to the richness of chemistry.

In many, though not all cases, approximate, simple rationales can be developed to explain complex reality. Border cases are unavoidable, where yes-or-no classifications are inappropriate. The main two yardsticks for good models and ordering schemes are (i) sufficient empirical accuracy and (ii) compatibility with quantum-chemical principles. In addition, beauty is regarded as one of the criteria for a good physical theory. Classification schemes depend on the chosen criteria. Empirical and theoretical classifications are at best highly similar, though seldom identical. Ordering schemes may be slightly deformed to achieve more esthetic symmetry. The artificial borders introduced in empirical, in theoretical, and in esthetical schemes may be slightly different. This is the case, for instance, for main, transition, and rare-earth elements, for the above-defined  $sp$ ,  $d$ , and  $f$  block elements, and for the 2 + 6, 10, and 14 block elements. This is not fatal at all, since one should never argue heatedly in science about the correct classification of border cases.

In 1935, Fleck (42) observed that some "scientific facts are invented by scientific communities" and, deplorably, need not always have a realistic basis. The Madelung rule, created in the community of chemists and atomic physicists, is a typical example. This "man-made fact" is perpetually passed on by teachers to students. The tendency to follow some story simply because all textbooks tell it is sometimes backed by the argument that one should not confuse undergraduate students by telling them too many correct, important facts. However, in contrast to the humanities, the subjects of science are simple enough to confront the assertions with both logic and the reproducible empirical data. If some structure of nature looks too involved for the moment, leave it open



instead of preaching a clear-cut, though incorrect, doctrine. Then there would be no more need to reeducate the students, for instance, against the Madelung rule, when they meet transition-element chemistry. So, the final lesson from the present discussion is the appeal to guard chemistry against nonscientific tendencies.

## Notes

1. See the collection of references in ref 2a, in particular to recent books, ref 3 therein. A good example is the reflection on periodic tables in *Nature Chemistry* (3) that focuses on empirical data arrangement, on cognitive reproducibility, and on graphical outlay, colors, and typeface. This is characteristic for the purely empirically interested members of a scientific community being less interested in embedding their field of knowledge into a broader scientific context.
2. Chemists and dictionaries differ about the spelling “gasses”. We retain the double “s” to mark the previous vowel as short and accented when another vowel follows.
3. We use the common terms *n* shell, *nl* shell, and *nlj* shell, although some chemists and educators prefer the term *nl* subshell, while never mentioning *nlj* (subsub)shells.
4. The IUPAC recommends “lanthanoids” and “actinoids” instead of “lanthanides” and “actinides”, since -ides are usually anionic compounds such as halides, sulfides, etc. See <http://en.wikipedia.org/wiki/Lanthanoid> (accessed Jan 2010).
5. Frontier orbitals are the orbitals energetically near the borderline between the highest occupied and lowest unoccupied (virtual) orbitals. They dominate bond formation and chemical reactions. The (partially) occupied valence orbitals alone are not sufficient to explain chemistry (4–6).
6. Madelung (39c) said that the tabulation of “idealized” (i.e., artificially made more regular) orbital occupations in the *SLJ* coupled ground states of the free uncharged atoms empirically follows the  $(n+l), n$  sequence. He did not mention orbital energies nor charged atoms.
7. The transition elements, being characterized by more nonvertical similarities, compare ref 9, were still tentatively and separately grouped by Meyer in the early 1860s (11).
8. The subscripts are the “total angular-momentum quantum numbers”  $j = l \pm 1/2$ , describing the spin–orbit splitting. The spin-energy contributions are spectroscopically relevant, but usually less important in the chemistry of the light elements. However, spin–orbit coupling is important for all so-called spin-forbidden processes, for the valence shells in the lower periods, and for all inner core shells.
9.  $\langle l^2 \rangle$  means the square of the orbital angular momentum:  $0 \hbar^2$  for *s* ( $l = 0$ );  $2 \hbar^2$  for *p* ( $l = 1$ );  $6 \hbar^2$  for *d* ( $l = 2$ ); and  $12 \hbar^2$  for *f* ( $l = 3$ ).
10. CN is the coordination number. The effective ionic radii increase strongly with the number of adjacent atoms.
11. The (meta)stable  $^{209}\text{Bi}$  isotope has the longest lifetime ever determined ( $2 \times 10^{19}$  years), orders of magnitude longer than the lifetime of the world (37). Every second, more than  $10^{16}$  Bi atoms decay on our earth.
12. The electron–electron Coulomb repulsion is often theoretically split up into three contributions, direct Coulomb (so-called Coulomb), exchange Coulomb (so-called exchange), and Coulomb correlation (so-called correlation). There is no exchange force in addition to the Coulomb force.

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