# The Full Story of the Electron Configurations of the Transition Elements

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One of the main topics of chemistry and of the education of chemistry is the ordering, memorizing, and understanding the myriad of facts. The primary tools for this purpose in general and inorganic chemistry are the periodic tables. The structure of the periodic system of elements is determined by the scheme of atomic orbital energies and radii.[1] All textbooks teach, and many chemists believe, the "Madelung order":
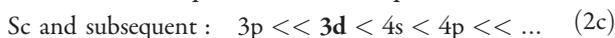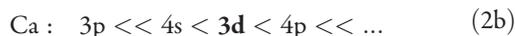
$$1s < 2s < 2p < 3s < 3p < \textbf{4s} < \textbf{3d} < 4p < ... \quad (1)$$

This order explains the electron configurations of the first three periods of the periodic system and of the first two elements of the forth period, K and Ca. The next elements are the light transition metals Sc, Ti, V, and so forth. Transition-metal chemists and ligand-field theoreticians know that transition-metal chemistry is basically $(n - 1)$d-orbital chemistry, not $ns$ or $ns-(n - 1)$d chemistry. Five features must be considered to understand the configurations of the transition elements: d-orbital collapse; d versus s electron repulsions; s Rydberg destabilization; configurations and states in free and bound atoms; and relativistic spin−orbit coupling. Often one or at most two features are mentioned. Chemists should become fully aware of all five features.

## Five Features To Understand the Configurations

### d-Orbital Collapse

The energetic sequence of atomic orbitals varies dramatically from the alkali metals of group 1 to the alkaline-earth metals of group 2, to the earth metals of group 3, and to the heavier transition metals of the subsequent groups (sequences 2):

$$K : \quad 3p << 4s < 4p << \textbf{3d} < ... \quad (2a)$$

$$Ca : \quad 3p << 4s < \textbf{3d} < 4p << ... \quad (2b)$$

$$Sc \text{ and subsequent} : \quad 3p << \textbf{3d} < 4s < 4p << ... \quad (2c)$$

These are known from vacuum atom-spectroscopic data since the early decades of the previous century (see the citations in ref 1). The so-called "d-orbital collapse" (Figure 1) has been reviewed several times *(2−4)*. It is the result of the interplay of nuclear attraction, of imperfect shielding by the inner-core electrons, and of angular-momentum dependent centrifugal forces. It explains why *4s becomes occupied in K and Ca before 3d, but 3d before 4s in the transition elements*. The empirical valence-orbital sequences of some of the free alkaline-earth metal atoms (e.g., sequence 2b) are correctly mapped by the $(n + l, n)$ Madelung rule (sequence 1). It is a mistake, however, to assume
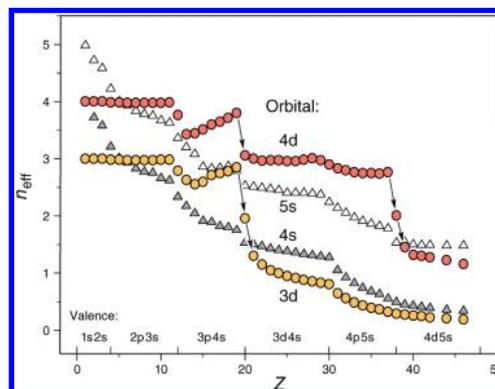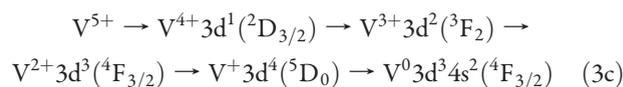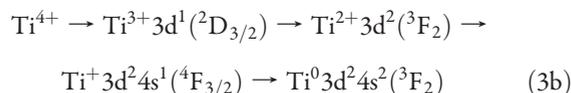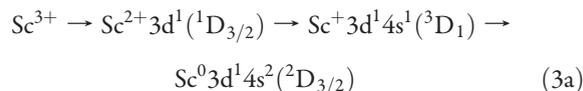


Figure 1. Energetic d-orbital collapse (indicated by arrows) of free neutral atoms at the beginning of the transition rows. $Z$ is the nuclear charge; the orbital symbols above the abscissa indicate shell[2] closing (4s and 5s are filled up twice, before and after the intermediate d filling). The orbital energies $\varepsilon$ are represented by the effective quantum numbers $n_{eff} = 1/(\sqrt{|\varepsilon|}/13.606 \text{ eV})$.[3] The orbital radii vary similarly; for details, see ref 4.

the universal validity of the rule for all elements. It does not hold for the p-, d-, f- (and g-)block elements.

### d versus s Electron Repulsions

At great surprise and despite 3d < 4s, energetically and spatially, the ground states of most *unbound, neutral* transition-metal atoms have the 4s occupied by one or two electrons, whereas the energetically lower 3d is not yet completely filled. The *configurations* (orbital occupation schemes) and the lowest-energy *J levels* (in parentheses) of three series of transition-metal cations in vacuum are given by

$$Sc^{3+} \rightarrow Sc^{2+}3d^1(^1D_{3/2}) \rightarrow Sc^+3d^14s^1(^3D_1) \rightarrow$$
$$Sc^03d^14s^2(^2D_{3/2}) \quad (3a)$$

$$Ti^{4+} \rightarrow Ti^{3+}3d^1(^2D_{3/2}) \rightarrow Ti^{2+}3d^2(^3F_2) \rightarrow$$
$$Ti^+3d^24s^1(^4F_{3/2}) \rightarrow Ti^03d^24s^2(^3F_2) \quad (3b)$$

$$V^{5+} \rightarrow V^{4+}3d^1(^2D_{3/2}) \rightarrow V^{3+}3d^2(^3F_2) \rightarrow$$
$$V^{2+}3d^3(^4F_{3/2}) \rightarrow V^+3d^4(^5D_0) \rightarrow V^03d^34s^2(^4F_{3/2}) \quad (3c)$$

where the superscripted number, for example, 3 in $^3F_2$ for $Ti^0$ in sequence 3b, denotes the spin multiplicity $M = 2S + 1$, where $S$ denotes the vector sum of all spins (here $S = 1$). The capital letter

(F) denotes the value of the vector sum of the orbital momenta ($d^2s^2$: two $l = 2$ and two $l = 0$ yield $L = 2$ for the lowest energy state of this configuration). The subscript 2 denotes the value of the vector sum $J$ of $S$ and $L$. These sequences were known from the early decades of the previous century (1) and were mentioned in a few inorganic chemistry textbooks in the 1930s (e.g., ref 5).

The three sequences, 3a−c, show that the lower energy 3d shell[2] is always occupied first. However, because the 3d shell is rather compact, in contrast to the diffuse Rydberg 4s orbital, the electron repulsion in the d shell increases strongly with increasing d occupation. Eventually, it becomes energetically favorable to shift one or even two electrons from the 3d shell into the slightly higher energy 4s, where the electronic Coulomb repulsion is much smaller. A remarkable example is $V^+$ [$3d^4$] + $e^-$ = $V^0$ [$3d^3 4s^2$] in sequence 3c. Similar situations are well-known in ligand-field theory for low-spin versus high-spin transition-metal complexes. This aspect of free neutral (and several singly charged) transition-metal atoms in vacuo has been well explained by Vanquickenborne and others (3, 4, 6−8).

### s Rydberg Destabilization

The situation for chemically bound transition-metal atoms and for free atoms in vacuum is different for two reasons. First, the spatially extended 4s orbital becomes destabilized in chemical substances by the occupied cores of the adjacent atoms (3). This reduces the tendency to occupy the energetically higher s orbital. The dominant electron configurations of the transition elements in chemical substances show quite low s occupations. This holds even in the neutral oxidation state, occurring in metals and alloys, in carbonyls, or in dibenzene sandwich complexes. The dominant configuration of a bound atom of group $G$ with charge $q^+$ is $3d^{G-q} 4s^0$ (9).

### Configurations and States in Free and Bound Atoms

The second reason for differences between chemically bound transition-metal atoms and free atoms in vacuum is that the electronic motions in free atoms are not disturbed by adjacent atoms. Most free atoms have open valence shells, where the electrons can arrange differently. The orbit−orbit and spin−orbit angular-momenta couplings result in a large number of different electronic states with different energies. For instance, the $3d^5 4s^1$ configuration of a free $Cr^0$ or $Mo^0$ atom comprises 504 different states with 74 different degenerate energy levels, scattered over several hundred kJ/mol. The level splittings of the configurations of the second series of transition-metal atoms (Y to Ag) are indicated in Figure 2 by vertical bars.

### Relativistic Spin−Orbit Coupling

Electrons in a heavy atom with large nuclear charge move at velocities of the order of the speed of light, when they come near to the nucleus. The energetic spin−orbit effects in light and heavy transition-metal atoms are in the range of 10 and 100 kJ/mol, respectively (10). A rough rule of thumb is scaling with $Z^2$; that is, the spin−orbit splitting increases by factors of 2 to 4 from period to period. But even if marginal, the effect can determine the transition-metal configuration that is given in the common tables.

## Coulomb-Repulsion Energies in Open d Shells

The qualitative behavior of chemical elements can be rationalized with the help of the dominant electronic valence
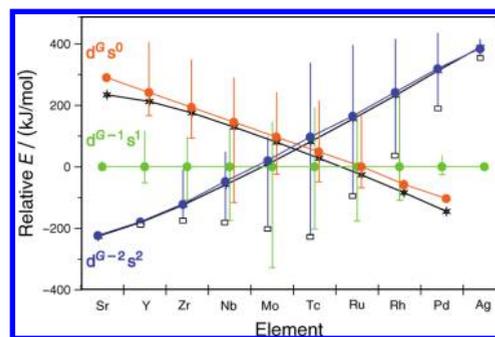


Figure 2. Average configuration energies $E$ of free atoms of period 5 in groups $G = 2−11$ for configurations $d^{G-2}s^2$ and $d^G s^0$ with reference to $E(d^{G-1}s^1) = 0$: the stars are DFT computations(3) and circles are experimentally derived (1, 3). Lines connecting points are used to guide the eye between the discrete points and highlight the trends. The scatter of energies of the individual states of the open d−s configurations is indicated by vertical bars. The squares indicate the lowest states of the Madelung configurations $d^{G-2}s^2$; they are not the overall lowest states for 5 (Mo, Ru, Rh, Pd, Ag) of the 9 D-metal atoms Y−Ag.

configurations of the atoms embedded in a molecular or crystal environment. These may be correctly called the "electronic configurations of the chemical elements". However, what is listed in respective tables of chemical textbooks under this headline is something else, namely, what physicists call "the configurations from which the $J$-level ground states of free unbound atoms in vacuum derive". The latter are easily accessible in the literature (1). However, we must distinguish between bound atoms in chemical substances and isolated atoms in physical vacuum. And we must distinguish between average configuration energies and individual $J$ level energies. (The latter are averages of $2J + 1$ different states.) We must not only consider the different average d−d, d−s, and s−s shell repulsions (6, 7), we must also account for the different individual Coulomb repulsions between the 10 different pairs from the five degenerate d orbitals.

Free as well as bound transition-metal atoms M of charge $q^+$ greater than $1^+$ have, without any exception, the electronic ground configuration $d^{G-q}s^0$ (4, 9). In the free neutral atoms, however, the differential direct and exchange contributions to the Coulomb repulsions between the d and s electrons may be bigger than the comparatively small d−s orbital-energy separations. Then, not all electrons are housed in the lower d shell, but one or two electrons are "squeezed" into the extended s orbital. This holds in particular for the isolated early transition-metal atoms, where the d−s orbital-energy differences are still small. The average configuration energies of the atoms of period 5 (circles in Figure 2) are smooth, without any "exceptions". The free early transition-metal atoms have lowest energy configurations $d^{G-2}s^2$, whereas the free later transition-metal atoms have $d^{G-1}s^1$ or even $d^G s^0$ (Figure 2, Table 1).

But this is only the smaller, commonly discussed part used to explain the configurations of the transition elements. The orbitals of a degenerate open shell can be differently populated by the electrons, leading to different individual term energies; see the vertical bars in Figure 2. The situation in open d and f shells is rather involved (11). Therefore, we discuss, as an example, the "simplest" case of two electrons "1" and "2" in a p shell with orbitals $p_x$, $p_y$, and $p_z$. We may have the two electrons in the same orbital (case a) or in two different orbitals (case b).

In case a, the two-electron orbital-wave function for two electrons in the same orbital is given by eq 4a. Its spatial symmetry is $S^e$ and its energy is given by eq 5a:

$$\Psi_S(1,2) = \{p_x(1)\cdot p_x(2) + p_y(1)\cdot p_y(2) + p_z(1)\cdot p_z(2)\}/\sqrt{3}$$

$$(4a)$$

$$E(p^2\,^1S^e) = (2h_p + J_{x,y} + 4K_{x,y}) \qquad (5a)$$

The two electrons' position wave function is electron-permutation symmetric ($\Psi_S$) and can be combined, according to the Pauli exclusion principle, only with a permutation-antisymmetric antiparallel spin-singlet function. The term symbol is $^1S^e$ *(11)*; $h_p$ is the one-electron energy contribution of a p orbital; and $J_{x,y}$ and $K_{x,y}$ are the direct and exchange contributions to the two-electron $p_x$−$p_y$ Coulomb-repulsion energy, respectively.

In case b, two electrons in two different p orbitals, there are two different possibilities for the two-electron orbital-wave function. For the case of $p_x$ and $p_y$, the position wave functions of $D^e$ and $P^e$ symmetry are given by eqs 4b,c and yield the energies in eqs 5b,c

$$\Psi_{D,P}(1,2) = \{p_x(1)\cdot p_y(2) \pm p_y(1)\cdot p_x(2)\}/\sqrt{2} \quad (4b,c)$$

$$E(p^2\,^1D^e, \,^3P^e) = (2h_p + J_{x,y} \pm K_{x,y}) \qquad (5b,c)$$

The position functions (eqs 4b,c) are electron-permutation symmetric and antisymmetric, respectively, and can be combined

with either a permutation-anti−symmetric antiparallel spin-singlet function ($^1D^e$) or with a permutation-symmetric pseudoparallel spin-triplet function ($^3P^e$).

The three individual *term energies* (eqs 5a,5b,c) are lower or higher than the average *configuration energy* $E(p^2) = (2h_p + J_{x,y})$. Such configuration energies had been discussed in the literature *(6, 7)*. Different position wave functions yield different energies, and they also determine the "Pauli allowed" spin multiplicities. The common argument, spin determines the energy, inverts causal logic.

The term energy splittings within the d−s configurations are of a similar order of magnitude as the energy differences between the configuration energies of $d^{G-2}s^2$, $d^{G-1}s^1$, and $d^Gs^0$ (Figure 2). Therefore, the already somewhat complicated discussion of the comparatively simple smooth trends of the average ground *configurations (6, 7)* is not yet advanced enough to understand which configuration yields the ground *term*.

As an example, we discuss the free neutral Mo and Tc atoms on the basis of quantitative empirical data. According to the smooth trends mentioned above, the lowest configurations in the middle of transition row 5 are $d^{G-1}s^1$, that is, $d^5s^1$ for Mo and $d^6s^1$ for Tc with $d^5s^2$ highest (Figure 2, Table 1). Now, the "half-filled shell rule" comes into play; it says that the term splitting of a half-filled shell is particularly large; the $^6S$ term of $d^5$ is particularly low. Figure 2 shows it for Nb $d^5s^0$, Mo $d^5s^1$, and Tc $d^5s^2$. Nb $d^5s^0$ ($^6S$) is comparatively low, but still not the lowest term. Mo $d^5s^1$ ($^7S$) is the by far lowest term of the $d^5s^1$ configuration. And the $^6S$ term of Tc $d^5s^2$ is so strongly stabilized that it becomes the lowest term. The textbooks qualitatively rationalize these facts by assuming incorrect ground configurations ($d^4s^2$ for Mo and $d^5s^2$ for Tc) and then applying the half-filled shell rule to Mo instead of Tc. Further on in row 5, Rh and Pd have lowest configuration averages $d^9s^0$ and $d^{10}s^0$, respectively. But because $d^8s^1$ shows a significant term splitting, the ground term of Rh is $d^8s^1$ ($^3D$). Similar examples can be found in rows 4 and 6 (Table 2).

## Minor Spin−Orbit Splittings Can Determine the Free Atomic Ground State

The relativistic spin−orbit coupling (of the order of 10 kJ/mol in the first transition series of period 4) splits the term into several J levels. Eventually, the J levels are weakly split by nuclear
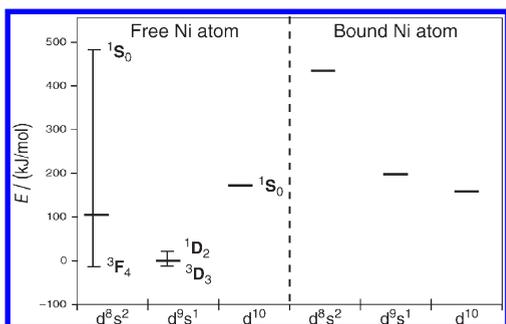
**Table 1. Ground Configurations (Configuration State-Averages) of Free Neutral Transition-Metal Atoms from Group G**

| Period | $d^{G-2}s^2$ | $d^{G-1}s^1$ | $d^Gs^0$ |
|---|---|---|---|
| $4^a$ | Ca−Mn ($G = 2$−$7$) | Fe−Cu ($G = 8$−$11$) | |
| $5^a$ | Sr−Nb ($G = 2$−$5$) | Mo−Ru, Ag ($G = 6$−$8$, $11$) | Rh, Pd ($G = 9$, $10$) |
| $6^{a,b}$ | Yb−Os ($G = 2$−$8$) | Os−Au ($G = 8$−$11$) | |

$^a$ Data derived from UV−vis vacuum atomic spectra *(1, 3)*. $^b$ The experimentally derived configuration energies for Os were not accurate enough to decide whether $d^{G-2}s^2$ or $d^{G-1}s^1$ is lower.

**Table 2. Atoms from Transition Periods 4−6 with Different Lowest Configuration, Configuration with Lowest $^{2S+1}L$ Term or $jj$ term, or Configuration with Lowest J Level**

| Free Atom | Group | Period | Ground Configuration | Configuration of $^{2S+1}L$ Ground Term$^a$ | Configuration of J Ground Level |
|---|---|---|---|---|---|
| Nb | 5 | 5 | $d^3s^1$ | $d^4s^1$ ($^6D$) | $d^4s^1$ ($^6D_{1/2}$) |
| Cr | 6 | 4 | $d^4s^2$ | $d^5s^1$ ($^7S$) | $d^5s^1$ ($^7S_3$) |
| W | 6 | 6 | $d^4s^2$ | $d^5s^1$ ($^7S$); $d_{3/2}^4s^2$ | $d^4s^2$ ($^5D_0$)$^b$ |
| Tc | 7 | 5 | $d^6s^1$ | $d^5s^2$ ($^6S$) | $d^5s^2$ ($^6S_{5/2}$) |
| Fe | 8 | 4 | $d^7s^1$ | $d^6s^2$ ($^5D$) | $d^6s^2$ ($^5D_4$) |
| Os | 8 | 6 | $d^7s^1$ or $d^6s^2$ | $d^6s^2$ ($^5D$); $d_{3/2}^4d_{5/2}^2s^2$ | $d^6s^2$ ($^5D_4$) |
| Co | 9 | 4 | $d^8s^1$ | $d^7s^2$ ($^4F$) | $d^7s^2$ ($^4F_{9/2}$) |
| Rh | 9 | 5 | $d^9s^0$ | $d^8s^1$ ($^4F$) | $d^8s^1$ ($^4F_{9/2}$) |
| Ir | 9 | 6 | $d^8s^1$ | $d^7s^2$ ($^4F$); $d_{3/2}^4d_{5/2}^3s^2$ | $d^7s^2$ ($^4F_{9/2}$) |
| Ni | 10 | 4 | $d^9s^1$ | $d^9s^1$ ($^3D$) | $d^8s^2$ ($^3F_4$)$^b$ |

$^a$ In the case of the heavy atoms from period 6, it may be recommended to replace the nonrelativistic approximation of $^{2S+1}L$ terms by the relativistic approximation of $jj$ terms. The latter ones are given after the semicolon. $^b$ Owing to relativistic spin−orbit stabilization, the lowest J level of the slightly higher term becomes slightly lower than the lowest J level of the lowest term (given in the preceding column).

Figure 3. Configuration energies of Ni: (right) average values of chemically bound $Ni^0$ and (left) free $Ni^0$ atoms in vacuum. The energy levels are indicated by the horizontal lines and the lowest and highest $J$ levels are indicated by vertical bars.

multipole interactions that are usually irrelevant for chemical stability and reactivity. There are cases (e.g., Ni in Table 2) where two $S$-$L$ terms from two different configurations are energetically adjacent, and a small spin−orbit coupling inverts the order of the lowest configurations. For example, the ground configuration of neutral Ni in chemical substances is $d^{10}$ (Figure 3) *(4, 9)*. The lowest configuration of free $Ni^0$ atoms is $d^9s^1$ (Figure 3, Table 1); $d^8s^2$ is about 100 kJ/mol higher (Figure 3) *(1, 3, 4)*! The term splitting of $d^8s^2$ is large, the lowest $d^8s^2$ ($^3F$) term is just 2 kJ/mol above the $d^9s^1$ ($^3D$). However, the small spin−orbit splitting of $d^8s^2$ ($^3F$) with two d vacancies ($\pm13$ kJ/mol) is slightly larger than that of $d^9s^1$ ($^3D$) ($\pm10$ kJ/mol). The lowest $J$ level $^3F_4$ of $d^8s^2$ is finally just 2 kJ/mol *below* the $^3D_3$ of $d^9s^1$ *(3, 4)*. These comparatively small and complicated angular-momentum couplings in free atoms are damped in chemical compounds by the ligands; they hardly play any role for the closed $d^{10}$ shell of chemically bound $Ni^0$. Nevertheless, most chemistry textbooks define $d^8s^2$ (and not the lower $d^9s^1$) configuration as the basic valence configuration of Ni, whereas the dominant valence configuration of $Ni^{q+}$ in chemical compounds is $d^{10-q}$.

## Concluding Remarks

The empirically correct energetic sequence of *bound atomic valence orbitals* above the $(n-1)p^6$ rare-gas core shells in the p and d blocks is

$$(n-1)\text{p} \ll (n-1)\text{d} < n\text{s} < n\text{p} \qquad (6)$$

(For rows $n \leq 3$, there are no d shells; for $n \geq 6$, there is the $(n-2)$f shell below $(n-1)$d.) The electron configurations of the transition metals of group $G$ in charge state $q+$ vary regularly as $(n-1)\text{d}^{G-q}\,n\text{s}^0$. Sequence 6 explains the structure of the periodic system and the period lengths of 2, 8, 8, 18, 18, 32, and 32 *(3)*. There are three exceptions from sequence 6. First, all *inner atomic shells*, which determine the X-ray phenomena (where spin−orbit splittings cannot be neglected), exhibit the more hydrogen-like energetic sequence 7:

$$\text{Cores}: 1\text{s} \ll 2\text{s} < 2\text{p}_{1/2} < 2\text{p}_{3/2} \ll 3\text{s} < 3\text{p}_{1/2}$$

$$< 3\text{p}_{3/2} < 3\text{d}_{3/2} < 3\text{d}_{5/2} \ll 4\text{s}... \qquad (7)$$

The second exception concerns the valence shells of *groups 1 and 2*, the alkali and alkaline-earth metals. In the series of elements, $(n-1)$d collapses below $n$s only after group 2, and $(n-2)$f only after group 3. The elements of groups 1 and 2 have

an exceptional s occupation according to sequence 8, though only in the less common neutral and negative binding states (metals, alloys, metal-organic compounds, alkalides $R^+A^-$). Usually their valence shell is empty, forming cations $A^+$ or $AE^{2+}$.

$$\text{s block}: (n-1)\text{p} \ll n\text{s} < (n-2)\text{f}, (n-1)\text{d}, n\text{p} \qquad (8)$$

The third exception concerns the *free neutral transition-metal atoms in vacuum*, including the f block. Their ground-state configurations depend in an involved manner on the often-discussed *averaged* d−d and d−s Coulomb-repulsion energies and also on the *individual* orbit−orbit (term) and spin−orbit splittings, even if the latter are small. The correct quantitative explanation is vital for the interpretation of atomic vacuum spectra, but exceeds the scope of general chemical education. There are only a few special topics in chemistry that require the correct understanding of free atoms in vacuum (e.g., atom-molecular gas-phase reactions) or of orbit−orbit and spin−orbit couplings of bonded open-shell atoms (e.g., the chemistry of the transition, lanthanoid, and actinoid metals; spin-flip enhanced reaction mechanisms; so-called spin-forbidden processes).

Finally, it is misleading to present free atoms as prototypes for the microscopic description of chemical elements in compounds. The common qualitative textbook explanations of the atomic ground states (correctly: $J$ levels) are incorrect. Therefore, we plead for teaching the correct atomic-orbital order (sequence 6) together with the regular exception, sequence 8, for the s block. One need no longer apologize for irregularities.

## Acknowledgment

## Notes

1. We distinguish dissimilar concepts: the natural periodic system of elements versus its different graphic representations by periodic tables; elements in chemical substances versus allotropic elemental substances; unperturbed single atoms in vacuum versus chemically bonded atoms.
2. We favor "$n$ shell", "$nl$ shell", "$nlj$ shell" over "$n$ shell", "$nl$ subshell", "$nlj$ subsubshell".
3. The graphic in Figure 3 is quantitatively correct, in contrast to qualitatively incorrect artwork in many chemical and physico-chemical textbooks.

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