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RECOMMENDED QUESTIONS ON THE ROAD TOWARDS
A SCIENTIFIC EXPLANATION OF THE PERIODIC SYSTEM
OF CHEMICAL ELEMENTS WITH THE HELP
OF THE CONCEPTS OF QUANTUM PHYSICS

ABSTRACT. Periodic tables (PTs) are the ‘ultimate paper tools’ of general and inorganic chemistry. There are three fields of open questions concerning the relation between PTs and physics: (i) the relation between the chemical facts and the concept of a periodic system (PS) of chemical elements (CEs) as represented by PTs; (ii) the internal structure of the PS; (iii) The relation between the PS and atomistic quantum chemistry. The main open questions refer to (i). The fuzziness of the concepts of *chemical properties* and of *chemical similarities* of the CE and their compounds guarantees the autonomy of chemistry. We distinguish between CEs, Elemental Stuffs and Elemental Atoms. We comment on the basic properties of the basic elements. Concerning (ii), *two sharp physical numbers* (*nuclear charge* and *number of valence electrons*) and *two coarse fuzzy ranges* (ranges of *energies* and of *spatial extensions* of the atomic orbitals, AOs) characterize the atoms of the CEs and determine the two-dimensional structure of the PS. Concerning (iii), some relevant ‘facts’ about and from quantum chemistry are reviewed and compared with common ‘textbook facts’. What counts in chemistry is the *whole set of nondiffuse orbitals in low-energy average configurations of chemically bonded atoms*. Decisive for the periodicity are the energy gaps between the core and valence shells. Diffuse Rydberg orbitals and minute spin–orbit splittings are important in spectroscopy and for philosophers, but less so in chemical science and for the PS.

1. INTRODUCTION

In recent years several aspects of the “Reduction of Chemistry to Physics” and the “Emergence of Chemistry from Physics” have intensely been discussed in the literature and on the Internet. The problem has two sides. In science, the most advanced theories of chemistry and physics are connected and can be applied to facts,

highlighting the “Unity of Nature”. In philosophy, typically chemical concepts and traditional textbook wisdom are analyzed, stressing their distance from physical concepts, and the “Autonomy of Chemistry”. Physics and chemistry are both very diverse fields. The question of the relation between physics and chemistry is too general to allow for a common compact comment on the emergence of chemistry.

At the present comparatively early stage of philosophical enquiry of chemistry, one specific problem is the repeated citation of a rather *selected* group of more or less well corroborated scientific statements. Sometimes the aim of a philosophical or historical discussion determines this selection. Not all scientific papers were at the state of art at the time of publication, and many of them aren’t a generation later. Theoretical chemistry has developed since our teachers were educated. The interpretation of theory, of computational and of experimental data diffuses only slowly between scientific circles. To overcome general preconceptions, detailed case studies on the relations between specific pieces of chemistry and specific pieces of physics are required, and that on the background of *present* wisdom in *both* scientific subfields.

One must distinguish between the practical successes of theories such as quantum mechanics and statistical thermodynamics, and its defects showing up in sophisticated conceptual analyses. Experts know how to apply first-principles theory without running into discrepancies between prediction and experience, within the well-understood ranges of their accuracy ranges. On the other hand, we have not yet understood the full meaning of all terms in the theories.

We should exploit both the deep physical atomistic roots of matter, and also the flourishing chemical tree of complex matter, at the level of present-day theories, not only stressing the problems of our understanding at levels of previous times. Communication between philosophers, ordinary chemists, computational chemists and physically educated theoreticians will become more fruitful on the basis of modern science.

Besides ‘more physical’ quantitative concepts, such as molecular shape, reaction entropy or reaction rate, there are

also the ‘more chemical’ qualitative concepts, such as reactivity, solvent polarity, aromaticity, functional group, or groups of *chemical elements* (CEs) forming the *periodic system* (PS). So far many chemical concepts are only vaguely defined. Their conceptual analysis is particularly challenging and promising for the cooperation of chemists and philosophers.

Pessimistic statements about the physical basis of the PS are common in recent literature: The chemical system is underivable from quantum physics; quantum mechanics cannot predict where chemical properties of the elements recur in *periodic tables* (PTs); even the electronic configurations of the elements cannot be derived from quantum theory. In *computational practice*, such statements were correct in some sense before the development of computational quantum chemistry (since the 1960s). In *theoretical principle*, they were correct before the development of conceptual quantum theory (around 1930). The basic problems lie more on the side of qualitative chemistry than of quantitative theory: The ‘natural system’ of CEs is based more on chemical feeling than on clear-cut physical definitions. Some evidence for this situation is the endless discussion about the best shape of PTs in Journals such as *Foundations of Chemistry*, *HYLE*, *Chemical & Engineering News*, or the *Journal of Chemical Education*.

We will here investigate, under which circumstances it may be possible to reduce some pieces of chemistry to physics, how far one has already come in practice, and what are the open questions to be solved in the 21st century. Problems emerging in that process of partial reduction help to clarify, what chemists mean when they use chemical phrases such as CE, Periodic Law, Chemical Property, Electronic Configuration etc. Those terms will be analyzed to some extent in Sections 2–4. Some familiarity both with chemical practice *and* with physical theory is helpful in this game. Some common concepts of quantum chemistry, which are definitely needed in this discourse, are clarified in Sections 5–6 and the appendix. Efforts to relate chemistry and physics epistemologically and ontologically, and then posing tasks to the specialists will lead to insight. Philosophical questions at the level of the *present* state

of art in the natural sciences could be useful in the development of chemical science. Some suggestions and conclusions are presented in Section 7.

2. CHEMICAL ELEMENTS

2.1. *Three meanings of the word*

Chemists and philosophers use the phrase “Chemical Element” in *three* different meanings, which may be designated as chemical, metallurgical and astrophysical (cf. Mendelejeff, 1871b; Paneth, 1931; Van Spronsen, 1969; Restrepo et al., 2004; Hendry, 2004; Scerri, 2001, 2004a, b, 2005).

- (1) *Basic chemical element*: The original and still present meaning of element or principle in chemistry is the basic sub-stance behind chemical stuffs, only implicitly defined through a conservation law in chemical reactions. The properties of the CEs are indirectly ‘reconstructed’ from measurements of reactions. This highlights chemistry as the art of change, as called in Chinese (Schummer, 1996; Schwarz, 2001a; Woyke, 2004). The definition of the most basic chemical concept through a typically physical approach requires deeper interpretation.
- (2) *Metallurgical element or simple material*: The chemical stuff that contains only one CE. It is specified through the stationary physical properties of its different phases and modifications. The properties of the CEs comprise, in addition, relational propensities, such as the reaction propensities of the simple materials *and* of their chemical compounds (Schummer, 1996; Woyke, 2004).
- (3) *Astrophysical spectroscopic element or elemental atom*: Physical atoms in vacuum specified by the nuclear charge. The CEs, however, refer to the properties and reactions of macroscopic materials, made up of chemically deformed atoms. Of course, there exists a strict relation through quantum chemical theory, interactions and statistical physics.

2.2. *Chemical properties*

Early classification schemes in chemistry were based on reactivities and properties of the *chemical materials* (Geoffroy, 1718; Bergman, 1775). There is a nearly unmanageable multitude of different chemical properties, spanning the so-called high-dimensional ‘chemical space’ (Schummer, 1996; Kirkpatrick and Ellis, 2004; Dobson, 2004). It is populated by all the possible chemical compounds, much more than 10^{60} . A thorough exploration of chemical space is impossible. It depends on the scientist, which small subset of properties of which small subset of compounds is selected as relevant.

Since the development of the modern concept of CEs behind the materials (Lavoisier, 1789), the basic nomenclature and classification system refers to the CEs (De Morveau et al., 1787; Fourcroy, 1800). Nature determines only partially, which CEs form similarity groups. This aspect motivated Moore (2003) to suggest the use of different PTs in teaching chemistry. In general, classification schemes work well for ‘typical’, though not for borderline cases.

The *properties of the CEs* can be arranged in different classes, more or less arbitrarily chosen, for instance the following ones:

- (1) Properties of the *free atoms*, such as ionization potential, average atomic weight, nuclear charge Z , number of loosely bound (i.e. valence) electrons g . Here and in the following, g stands also for ‘greatest valence’, or for ‘group number’ in PTs.
- (2) Properties of the different modifications of the *elemental materials*, such as melting points, heats of vaporization, atomic volume of different phases, conductivities. The plot of atomic volumes of the most common phases versus the average atomic weights by Meyer (1870) initiated the general acceptance of the concept of a natural system of CEs (see Figure 2 below).
- (3) Static physical properties of *compounds*, such as melting points, specific heats, solubilities, crystal structures of their different inorganic or organic compounds.

- (4) *Dynamic chemical, relational properties* of the CE, such as reactivity towards oxygen or acids and bases.
- (5) *Chemical properties of the compounds*, such as acidity of their oxides or the reactivity towards different reactants.
- (6) *Derived propensities* of atoms in compounds, such as Pauling electronegativities, effective charges on atoms in homologous molecules, atomic valence state energies, covalent or van der Waals radii.
- (7) *Biochemical and biological properties*, such as positive and negative influences of the elemental stuffs and their compounds on specific life processes. Similarly there are metallurgical, geological etc. properties of the CEs.

All these properties shall be called empirical properties, including those ones that are quite a bit theory- or model-laden and fuzzy, such as those of types 4–6.

2.3. *Principal properties of the elements*

Let V_{pc} be the value of some (observable or derivable) empirical property p of CE c ($p = 1$ to very large P ; $c = 1$ to $C \leq 118$ at present). All the V_{pc} are not independent of each other, but are more or less strongly correlated. For instance, the average atom–atom distances R_{AB} in compounds $\{L_i\}A-B\{L_j\}$ are complicated functions of A, B and the ligands L. But the nearly infinite many R_{AB} can be approximated, in most cases within a few pm, as the sum of two atomic single bond radii R_σ ,

$$(1) \quad R_{AB}(L_i, L_j) \approx R_{\sigma,A} + R_{\sigma,B}.$$

In general, all the P empirical property values V_{pc} of element c can be approximated at some accuracy-level as a sum of a few ‘principle property’ values S_{fc} for main factors $f = 1$ to $F \ll P$. For a review of factor analysis see Appendix A1.

The empirical results of factor analyses seem to indicate that the number of derivable ‘basic principal properties’ of ‘basic elements’ is of the order of $F \sim \sqrt[n]{P}$, $n = 2-3$. To approximate a reasonably wide field of general chemistry, say 100 chemical properties of 100 elements, one needs about 5–10 ‘principal properties’ per CE. If one is interested in biochemical properties, one needs additional ‘biochemical principal properties’,

and so on. However, for basic chemical education and for a first systematization of chemistry by a PT, it is already sufficient to consider only a few properties. So, one aim of research must be how to select a comparatively small set of important empirical properties that can be reduced to a very small number of principal properties that vary systematically over a PT. This small set of principal properties depends on the larger set of empirical properties, which are viewed as important for the intended research program. Somewhat different ordering strategies were developed in material science ('structure maps' of Pettifor (1984, 2003), metallurgical divides by Stone (1979)). Much detailed work in chemical science on 'property compaction' by chemometric methods is still necessary for further advances in the philosophy of the PS.

One open point is the chemical interpretation of the mathematically derived principal properties. If one chooses, say 3, primary principal properties of the CE, the properties still are not yet defined uniquely. Any set of mathematically linearly independent combinations is equivalent. What is the optimal choice of the principal properties for chemical interpretation in a given research program, what does this situation mean?

2.4. *Similarity of elements*

The creation of a natural system of CEs started historically with collating groups of chemically similar *compounds*. This began in the 18th century long before the invention of the concept of CEs. The chemical similarity concepts of early and middle 19th century were based on properties of individual compounds and on some general chemical rules (Cahn, 2002). Similarity groups were found more or less intuitively, using electro-affinity series (Volta, 1794; Berzelius, 1818). Remarkably, those given by Gmelin (1843) corresponded well to the neighborhood regions in the early PTs of the 1860s.

Van Orman-Quine's suggestion (1969) that a mature science should replace vague similarity concepts by mathematically

defined concepts may apply to physics though not necessarily to sciences of complex subjects. Chemical similarity of compounds carrying an infinite number of more or less correlated properties, is something else than the concept of transitive and symmetric mathematical symmetry, referring to simple objects. Chemical similarity also depends on the relevance attached to the properties.

The first vista into the thicket of properties of CE, applying chemometric methods (see Appendix A.1, and Sneath and Sokal, 1973; Pankhurst, 1991; Meister and Schwarz, 1994; Gasteiger, 2003) were published by Zhou et al. (2000) on 50 CE and 7 properties, by Sneath (2000) on 69 CE and 56 properties, by Khramov et al. (2003) on 103 CE and 22 properties, and by Restrepo et al. (2004) on 72 CE and 31 properties. 3–6 principal properties describe over 80% of the variation of all properties. The noble gases turned out as a distinguished group: They, the alkali metals and the halogens form the most pronounced similarity clusters, three subsequent groups in PTs thereby proven as founded by numerical methods. Other elements, however, exhibit diagonal (Be, Al; O, Cl), horizontal (Mn, Fe, Co; Os, Ir, Pt), knight's move (Ag, Tl) or even more distant relations (Mg, Zn; Sr, Pb), as symbolized in Figure 1 (Rayner-Canham, 2004; Restrepo et al., 2004; Sneath et al., 2006).

Five points are important: (1) The chemical similarity of compounds was historically of great help for the invention of PTs. (2) The intuitively found similarity groups of CE of the 19th century, and the chemometric clusters of CE of the early 21st century are similar. (3) Groups of CEs in the PS are not given by nature alone. (4) Similarity information on CE is

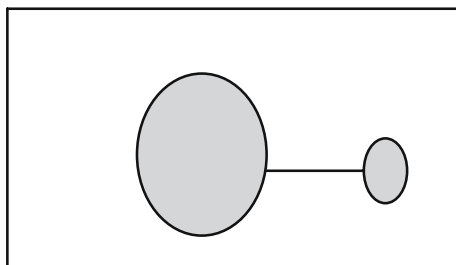


Figure 1. Typical region of similar elements in a PT.

HOW TO EXPLAIN THE PERIODIC SYSTEM

definitely not sufficient to create a PT. (5) The situation is just the other way around: if we have a PT, it helps us to memorize those chemical similarities of the CEs that are important for that PT.

This leaves us with three open questions: (1) How can one derive the principal chemical properties and the chemical similarities of the CEs? (2) What is needed to derive a chemically useful PT? (3) How can one understand and explain the vertical, horizontal, diagonal and more distant relations in a PT?

3. THE BASIC INDICES OF THE CEs

3.1. *Properties of the CEs and the characteristic atomic numbers*

As soon as reliable equivalent weights became available (Richter, 1792; Berzelius, 1818), relations between the numbers of similar elements were investigated, (i) within what are now called vertical groups (Döbereiner, 1817, 1829; Lenßen, 1857; Odling, 1857; Pettenkofer, 1858; Tschermak, 1859–60) and then (ii) also horizontally between groups (Béguyer de Chancourtois, 1862; Meyer, 1864; Odling, 1864; Newlands, 1864, 1865; Hinrichs, 1866). Thereby the strategy towards a two-dimensional arrangement of qualitative similarity fields (Gmelin, 1843; Gladstone, 1853) was put on a sound numerical basis. The last steps of popularization were then undertaken by Mendelejev (1869a, b, c, 1871a, b) and in particular by Meyer (1870).

While historically the PTs evolved from a combination of 1st the *similarity concept* of CEs, 2nd the *atomic masses* and 3rd the *valence numbers* (Cahn, 2002), the scientific view has changed its direction in the meantime. The PS is now based on *nuclear charge numbers and numbers and types of valence electrons*. The question to be solved now is: How can one qualitatively, and how can one quantitatively explain the different vertical, diagonal and horizontal similarities of CEs on the basis of only two integer numbers, a nuclear (Z) and an electronic (g) one?

3.2. *Ordinal number of the elements: Z*

There is a human tendency in atomism since antiquity to attach natural numbers to the atoms. After Dalton (1805, 1808), Prout (1815) propagated this idea against reliable empirical noninteger average atomic weight ratios (Thomson, 1813; Wollaston, 1814; Döbereiner, 1816; Berzelius, 1818). Still the idea of ordinal numbers behind the atomic weights survived (e.g. Newlands, 1865). However, it lasted until 1913 (Van den Broek; Moseley; Bohr) that ordinal numbers of the CEs were safely measured and then identified as the *nuclear* charge numbers Z , equal to the numbers of *electrons* of the neutral atoms.

Quantum chemistry derives static and dynamic properties of atoms, molecules, crystals and macroscopic materials by first principles from nothing else than the atomic Z numbers (and the atomic weights). At first, this was possible only in principle, though not in practice, as stressed by Dirac (1929), although seldom recognized in citations. A strong current of reliable *ab initio* results emerged only against the end of the 20th century (Kutzelnigg, 1993, pp. 1–6; Löwdin, 1964; Lipkowitz and Boyd, 1990; Von Ragué Schleyer, 1998).

3.3. *Cardinal numbers of the elements: g*

If the *linear* Z order of the CEs is known, and in addition chemical similarity groups, the topological structure of two-dimensional arrangements of the CEs is probably determined within small limits. Respective arrangements of cylindrical, screw-like, cone-like, spiral or fan-like shapes were proposed by Béguyer de Chancourtois (1862), Hinrichs (1867) and Meyer (1872). They can be easily transformed into the more common rectangular shapes. In addition to the qualitative and continuous-quantitative chemical properties, the integer highest valence number g began to play the dominant role.

It took more than half a century to clearly distinguish the atomic weight A from the different equivalent weights Q_v , which are accessible to direct measurement, and to define different valence numbers v for a CE:

$$(2) \quad A = v \cdot Q_v.$$

The development of the inorganic concept of variable proportions ([Dalton, 1808](#); [Frankland, 1852](#)) and of the organic topological type and geometric structure theories ([Dumas, 1839](#); [Couper, 1857–59](#); [Kekulé, 1857](#); [Butlerov, 1861](#)) contributed to this development. Odling (1857) first recognized the connection between the valence numbers and the natural system of elements. Meyer's first PT (1864) explicitly carries the maximum valence numbers g in the headline above the groups. Miller (1865) reported:

“Owing to the labours of many distinguished men, a classification of the elements into families has been made; and this classification rests upon what is known as the atomicity [viz. valency] of the elements.”

Chemistry had shifted the foundation of its basic classification scheme of CEs from chemical properties to two theory-laden numbers, the successive ordinal number Z and the quasi-periodic valence number g . This ‘physicalization’ happened long before any tight connections between chemistry and (mechanical, statistical and quantum) physics. The theory-phobia of some leading chemists since the time like Liebig, Kolbe or Ostwald did not prevent chemistry from basing herself in more abstract concepts. The first steps from explaining the PS within chemistry towards explaining the PS by abstract theory and then explaining chemistry with the help of that PS were initiated.

3.4. *Quasi-periodicity*

The transition metals (TMs), the few known lanthanids and hydrogen underlined problems of periodicity already at the birthtime of the PTs. Since several similarity groups of elements have horizontal extension, an empirically defined recurrence of properties along the Z series of CEs is fuzzy. The vagueness of the chemical similarity concept anyhow forbids exact periodicity of chemical properties. Meyer (1864), who had based his PT on atomic weight, maximum valence and chemical

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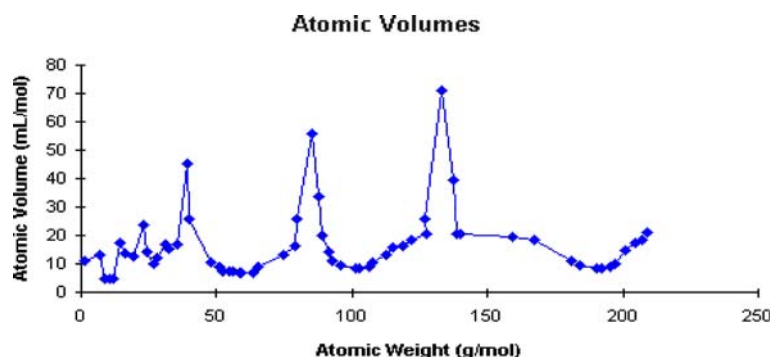


Figure 2. Atomic volumes (in mL/mol) of the most common condensed phase of CEs 'at ordinary conditions' versus atomic weight (in AMU in g/mol), modern curve from the Internet.

similarity, was instrumental for the final acceptance of Mendelejev's similar ideas (1869a, b, c, 1871a, b): Meyer published his atomic volume curve in 1870. It looked like Figure 2, which documents the nonperiodicity of the PS.

Two questions emerge. (1) The scientific one is: Which amount of periodicity can be safely traced back by chemometric methods? (2) The historical-philosophical one is: What is or was more decisive for shaping the PTs, the vague quasi-periodicity of chemical properties, the appeal of curves of physical parameters, or the hypothetical concept of highest valence g ?

Khramov et al. (2003) applied numerical Fourier (so-called spectral) analysis to 22 properties of the first 103 elements. Depending on the property, different period lengths were found. Periodicities of 8, 18 and 32 were evident for some properties, corresponding to the filling of sp, dsp and fdsp shells. For some properties, also periodicities of 6, 4, 3 and 2 showed up. At present one can only speculate about the origin of these frequencies: noise in the experimental data; 6 – filling a p-shell or an upper $d_{5/2}$ spin-orbit component of a d-shell of heavier elements; 4 – filling $p_{3/2}$ or $d_{3/2}$. No periods corresponding to half-filling were found, not even the chemically relevant periodicity of 7 from half-filling the 4f-shell of the lanthanids (Holleman and Wiberg, 1951; Remy, 1952). Further numerical analyses are still necessary to obtain a rough

idea of what the different periodicities of the properties of the CEs really are and mean.

4. THE 2-DIMENSIONAL STRUCTURE OF THE PT

4.1. *Nuclear charge and atomic weight*

From the scientific point of view, atoms in molecules are characterized by two things: (1) The *forces between the atoms*: they originate in the electronic shells. The electron number is determined by the nuclear charge number Z , which is sufficient to characterize a CE in *ab initio* quantum chemistry. (2) The *motions of the atoms* under the valence forces, i.e. chemical reactions and physical vibrations: they depend on the nuclear masses A . On the one hand, the possible masses of stable nuclei are determined by Z in the theory of nuclear physics (references given by Karol (2004) and Kibler (2004)). On the other hand, the actual ratios of isotopes in the elements occurring on earth resulted from cosmological history. That is chaotic, i.e. deterministic but unpredictable from the physical laws alone.

The historically arisen atomic mass distribution determines static and dynamic phenomena, (1) the stoichiometry of chemical reactions and the values of molar properties, and (2) the reaction and diffusion rates, tunneling effects, molecular vibrations and librations. Atomic dynamics and reactions are at the heart of chemistry. Classical and quantum dynamical theories have progressed towards predicting reaction steps, reaction mechanisms and reaction rates at qualitative, semi-quantitative and quantitative levels, on the basis of internuclear forces and nuclear masses (Löwdin, 1964; Lipkowitz and Boyd, 1990; Leszczynski, 1996; Von Ragué Schleyer, 1998; Truhlar and Morokuma, 1999; Yang and Liu, 2004; Domcke et al., 2004; Carr and Zachariah, 2004). While principle knowledge of theoretical physics of the 1930s is not easily acceptable among ordinary chemists and philosophers, at least these practical achievements of computational chemistry should form the background of philosophy of reaction chemistry.

The inventors of PTs started from the series of average atomic weights A , semi-empirically based on chemical stoichiometry (Meyer, 1864; Hinrichs, 1867; Mendelejev, 1869a, b, c). The orders of increasing A and Z do not agree in all cases. Remarkably Mendelejev arranged Te, I and the iron–platinum-group according to the order of Z (completely unknown at his time). Meyer and then Mendelejev ordered Co–Ni with $\Delta A = -0.24$ against the order of A . That the deeply physical parameter Z was intuitively felt in some sense by pure chemists at early times throws some light on the natural relation between chemistry and physics.

4.2. *Valences*

Z also determines the atomic orbitals (AOs), the shells and consequently the number g of valence electrons, which govern the properties of the CEs. The dependence of g on Z is quite involved. Accordingly, a PT representing the natural system of CEs should be at least 2-dimensional. Meyer (1864) and Newlands (1864, 1865) seem to have been the first to point that out.

Historically it was not clear at the beginning whether one should use the smallest, the most common, or the greatest valence number as the criterion, instead of or in addition to chemical similarity, for the construction of a natural map of CEs (van Spronsen, 1969). Meyer (1864), Newlands (1865) and Mendelejev (1869a, b, c) had chosen the greatest valence, g . Since this does not work well for the TMs, Meyer (1864) was still doubtful about the arrangement of those elements. Even nowadays the valence shells of the TMs seem mysterious.

The valence numbers and more so the chemical properties of the CEs form multidimensional concepts. The dimensionality of tabular forms of the natural system of CE is not uniquely determined by nature, nor the amount of information to be codified in the PTs. Further philosophical and chemometric case studies are needed to decide, whether a two-dimensional table is a natural one, or the simplest one, or just reflects the literacy of a human culture strongly resting on planar printing. A few really three-dimensional

‘periodic bodies’ were mentioned by Mazurs (1957, 1974), while mathematically two-dimensional tables of multi-connected topology (bent tables on cylinders or cones, with or without ears) are also often called three-dimensional by superficial investigators.

5. ELECTRONIC ORBITAL CONFIGURATIONS

5.1. *Basic quantum chemical concepts*

Since the invention of quantum mechanics, the concept of electronic configurations of atoms and elements has become an important ingredient of chemistry and of PTs. Since the respective philosophical, chemical and physical concepts differ so much, the basic physical quantum concepts must be reviewed. This is done in Appendix A.2. Here is a summary:

It depends on the case and our purpose, and on the environment, whether it makes sense to talk about individual molecules and orbitals. If orbitals can and are physically well-defined, then they can be measured, even if mathematically complex. The spin always occurs in the wave function. At the nonrelativistic level of approximation, there are no energy contributions due to spin. The so-called exchange energy is a part of the electric Coulomb energy and does not result from an additional exchange force.

5.2. *Orbitals*

For some material, some scientific question can be answered with the help of the concept that it is built up of weakly interacting atoms or molecules. For some nearly independent atom or molecule, described by matter-field Ψ , some question can be answered with the help of the concept that Ψ is *reasonably well approximated by an antisymmetrized product Φ of orbitals ϕ*

$$(3) \quad \Psi \approx \Phi = \mathcal{A} \{ \phi_a(X_1) \cdot \phi_b(X_2) \cdot \dots \cdot \phi_n(X_N) \} .$$

We distinguish between electrons i (with coordinates $X_i, i = 1, 2, \dots, N$) and orbitals φ_j ($j = a, b, \dots, n$). For simple cases, the numbers of electrons (N) and of orbitals (n) are equal, $N = n$. In the case of *open* shells, the number of orbitals is slightly larger, $N < n$. For instance, for the C atom with outer valence shell p^2 and $N = 2$, $n = 6$ spin-orbitals $p_x\alpha, \dots$ are needed for the 1S state:

$$(4) \quad \Psi \approx \Phi = \sqrt{3} \cdot |p_x\alpha, p_x\beta| + \sqrt{3} \cdot |p_y\alpha, p_y\beta| + \sqrt{3} \cdot |p_z\alpha, p_z\beta|.$$

An important consequence of Eq. (3) is that the set of orbitals $\varphi_a, \varphi_b, \dots, \varphi_n$ is not unique. Any linear-combined, hybridized set is equivalent. It makes no difference, whether

$$(5) \varphi_a \text{ and } \varphi_b \text{ or equivalently } c_a\varphi_a + c_b\varphi_b \text{ and } c_b^*\varphi_a - c_a^*\varphi_b$$

with arbitrary complex coefficients c_a, c_b are chosen. An atom in a given state may (or may not, depending on the case and question) *have a unique 'one-particle Hilbert space of occupied orbitals'*, spanned by any orbital set (5). It is the orbital set that matters.

5.3. Configurations

If Eq. (3) holds, we may say that *the atom in given state Ψ has orbital configuration Φ* . That an orbital configuration is a good tool to answer a given question is *a natural property of the respective state of the system*. The state 'has' orbitals.

There are states where at least *a few different configuration functions* are needed for any reasonable description. This happens quite frequently for excited states and for covalent bond breaking. The simplest example occurs for the Be atom. Its so-called $1s^2 2s^2$ ground state is of strongly mixed two-configuration type, approximately represented by

$$(6) \quad \Phi = 0.96 \cdot [1s^2 2s^2 \ ^1S] - 0.28 \cdot [1s^2 2p^2 \ ^1S],$$

corresponding to approximate orbital occupation $1s^2 2s^{1.84} 2p^{0.16}$ (namely: $2 \times 0.28^2 = 0.16$).

There are also states with a *very large number of configurations*, the largest coefficient of the ‘leading’ configuration being much smaller than the 0.96 in Eq. (6). In such cases the orbital approximation simply breaks down (Cederbaum et al., 1977). There are atomic states in nature where there are only a few ‘significantly’ occupied orbitals and very many weakly occupied ones.

5.4. Different meanings of the word ‘configuration energy’

The word ‘configuration energy’ is used with quite different meanings. When talking about configurations, we should at first specify our intended meaning. And we should investigate, whether this meaning is an appropriate concept in the given context for the given atomic state.

We discuss atomic electron configurations d^2 (comprising 45 individual states) and d^1s^1 (20 states) in Figure 3 (Condon and Shortley, 1935; Sobel’man, 1972). Let $E(d^2) > E(ds)$ for the energies of the two ‘**configuration averages**’. For the first two transition rows, the nonrelativistic description works reasonably well: the d^2 configuration is coarse-split into 5 ‘LS terms’. Due to the Coulomb repulsions between the different *compact* nd orbitals, the splitting is rather large. The lowest term is $d^2\ ^3F$ (21 states). The ds configuration is split into 2 LS terms. The Coulomb-exchange interaction between the compact nd and the *diffuse* $(n+1)s$ orbitals is comparatively small. The lower term

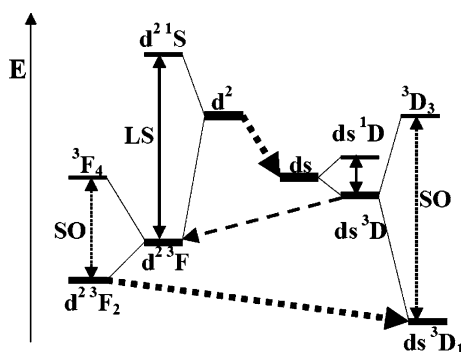


Figure 3. Schematic energy levels of a hypothetical atom with configurations d^2 and ds .

is $ds\ ^3D$ (15 states). In some real cases, $E(d^2\ ^3F) < E(ds\ ^3D)$ holds for the lowest '*LS term averages*'. Accounting also for relativistic effects such as spin-orbit coupling, the LS terms are fine-split into J levels. The lowest one of $d^2\ ^3F$ is $d^2\ ^3F_2$ (5 states), the lowest one of $ds\ ^3D$ is $ds\ ^3D_1$ (3 states). We neglect further hyperfine splittings. If $d^2\ ^3F$ and $ds\ ^3D$ are near in energy, it may happen that $E(d^2\ ^3F_2) > E(ds\ ^3D_1)$ for the lowest '*J level averages*'. For the heaviest atoms, spin-orbit splittings become more important than direct and exchange Coulomb splittings. The coarse splitting of the configuration is into '*jj term averages*'. In intermediate coupling cases, both LS and jj averaging make no sense.

5.5. *Meaning of 'configuration' in physics and chemistry*

In the hypothetical case of Figure 3, the *configuration* of lowest 'configuration average' is ds , of lowest 'LS term average' is d^2 , of lowest 'J level average' is ds . In high resolution *physical spectroscopy of free atoms*, the most appropriate concept for analyzing the nature of the atoms is the 'J level manifold of states'. The energetic ground state belongs to the lowest J level. To derive the lowest J level theoretically, one must apply highly sophisticated theoretical concepts of angular momentum coupling, relativistic spin orbit effects and electron Coulomb correlation.

In the *field of chemistry*, the natural situation is different. While the energy level schemes of free atoms are dominated by angular momentum couplings, the rotational motions of the electrons in bonded atoms are strongly perturbed by the fields of the adjacent atoms. The interactions between *bonded atoms* in compounds mix a large number of states of the free atoms, belonging to the ground and a few higher configuration averages. The 'deformed' carbon atoms in organic molecules can be represented as a hybridization of states from the s^2p^2 , sp^3 and p^4 configurations (Lu et al., 2004a, b). The lowest configuration average of a free atom is often, though not always, important for the bonded atom. The chemically dominant configuration, the lowest configuration average and the configuration of the

lowest J level are different for most TM atoms (Wang et al., 2006).

Obviously it is misleading to list the lowest J level configurations of free TM atoms in a PT for chemical applications, or to discuss the lowest spin-orbit split J levels with the aim to explain the PS of qualitative chemistry. Concerning general chemical teaching, where the basic Coulomb interaction effects between the different orbitals of open d and f shells are not mentioned, because it seems already too complicated, it makes no sense at all to mention and comment on the configurations of the lowest J levels, where one must also consider angular momentum and relativistic spin-orbit couplings. It is an interesting question of history of science how the discussion of the physical basis of chemistry and the periodic table could go so strongly astray.

6. ORBITALS

6.1. *Kinds of orbitals*

An orbital is a function depending on the coordinates of a single electron. What a single electron in a many-electron system means must be defined operationally (both in experiment or theory). What is changed, if an alkali metal atom absorbs a Vis-UV light quantum?: The s valence orbital. What is changed, if a laser pulse ionizes an electron off CH₄?: A delocalized 5-centric t_u HOMO. What corresponds to the chemical concept of a Lewis bond in CH₄?: A localized 2-centric C–H bond orbital. The shape of the orbital depends on the chosen physical process, and on the chosen theoretical approximation. Friedrich (2004) and Ostrovsky (2004b) have recently stressed that ‘approximation concepts’ form a constitutive ingredient of the harmonic marriage of experiment and theory in the ‘exact’ sciences.

For most states and processes, the respective orbitals vary with the theoretical approach (e.g. single- or multi-configuration Hartree–Fock, HF or density functional (DF) approaches). The Kohn–Sham DF approaches are based on one-electron density

and orbitals. Their aim is to correct for the defects of the *ab initio* HF one-electron orbital picture through approximate simulation of many-particle Fermi and Coulomb correlations. The latter contribute typically less or more than 50% to chemical bond energies.

The orbitals also vary somewhat with the state (e.g. free or bound atom, ground or excited state, charge of cation). One may choose a ‘complicated’ orbital picture with different AOs for any different state of the atom and its ions. Such approaches are applied in most quantum chemical calculations in order to obtain reliable numbers. Instead, one may use ‘more transparent’ orbital pictures for qualitative explanations, with only a single set of ‘averaged frozen’ AOs for all different states.

6.2. *Ab initio orbital calculations*

Sophisticated techniques, skills and equipments are needed to produce reliable results. For a reasonably accurate experimental picture of a complex nonstationary p-AO of Cs see Weihnacht et al. (1998/9). Orbital pictures are usually obtained with more reliable digits quantum-computationally. One can buy and run computers and programs at low cost, but the interpretation of the outputs by nonexperts is often inappropriate.

Simple approximate equations of quantum mechanics are the time-independent Dirac equation and the nonrelativistic approximation of Schrödinger. These differential equations possess exact analytical solutions (i.e. with complex derivatives nearly everywhere in space). This is so in particular for realistic potentials of extended nuclei, while the Coulomb potentials of point charges are a serious approximations in the case of heavy nuclei. *Accurate solutions* for the one-electron one-center case (AOs) are easily obtained *by numerical integration techniques*. For many-electronic states, iterative approximation techniques are required, such as MC-SCF-PT. The Hartrees (1927, 1958) applied numerical *finite difference* techniques already before World War 2 (Froese Fischer, 1977; Desclaux, 1973). Such numerical AOs can also be used in molecular calculations (Ozaki and Kino, 2004). More powerful *finite element* techniques (developed by engineers for classical macro- and

micro-structures: bridges, airplanes, tsunamis, weather forecast, nanotubes, etc.) are very efficient also for small molecules and their reactions.

Analytical expansion techniques are preferred for *approximate molecular calculations*. In the DF approach of Car and Parrinello (1985), the orbitals are expanded to the required numerical accuracy by complex *Fourier functions* $\exp(\pm i\zeta r)$, without empirical fitting. The finite element approach is an expansion with nonoverlapping *power functions*. In most molecular and crystal calculations, atom centered real *exponential functions*, Slater STOs $\exp(-\zeta r)$ or Gaussian GTOs $\exp(-\zeta r^2)$, with nonempirical exponents are sometimes combined with 2-electron $|r_1-r_2|$ terms (Hylleraas, 1930; Klopper, 1999; Fliegl, 2005).

The historical name ‘AOs’ for those expansion functions is misleading. Typically 2–5 expansion functions for each occupied atomic s, p and d valence shell are applied in molecular calculations to reproduce the correct radial behavior of the orbitals. In addition, several functions of higher angular momentum are included in the expansion, for instance two p and one d type function on H, or two d and one f type function on O or P. These so-called pol(arization) functions account for the angular deformation of the atoms in the molecule, and for electron correlation in post-orbital approaches. These pol-functions have nothing to do with higher AOs in real atoms. Pauling’s ‘valence shell expansion’ of hypervalent metalloids and ‘outer shell complexes’ is now known to be a myth. It is also misleading to speak of the known exact solution for the hydrogen atom: the e^{-r} function is a nonrelativistic orbital approximation for an approximate point nucleus without magnetic moment, and the exponential is an approximate expansion of powers.

6.3. Chemically relevant AOs

Valence AOs are characterized by two different criteria, an energetic and a spatial one. The AO *energies* of the bonding atoms should be similar and of such an order of magnitude that a fraction of the orbital binding energy is of the order of typical

chemical bond energies. The latter are in the range of a few hundred kJ/mol = a few eV.

In order to form covalent or metallic bonds, the AO *radii* should be of the order of typical bond lengths, i.e. in the Å range. Smaller AOs, in particular the inner valence f orbitals, may participate in ionic, though not in covalent bonds. The more extended Rydberg orbitals are important in vacuum spectroscopy, but of minor relevance in chemistry. They are strongly perturbed and shifted upwards in energy by the surrounding atoms. This holds in particular for the $(n+1)s$ AOs of the nd elements, and for the nd AOs of the np elements. (The *so-called* NBO-Rydberg orbitals of Reed et al. (1983, 1985, 1988) denote the junk of the NBO prescription and have nothing to do with the established spectroscopic Rydberg concept.)

The equilibrium of chemically bonded atoms is determined by *vanishing* forces: the classical electric and quantum interference attractions of partially occupied overlapping valence AOs are compensated by the ‘Pauli’ repulsion of overlapping occupied core shells. The smallest, most strongly bound and the most extended, weakly bound valence and core AOs of s, p, d, and f types of atoms of all CE are listed in Table I. They were derived from ‘empirical’ data, obtained from quantum chemical ‘computer investigations’.

The atomic valence orbital radii are in the range of 0.4–2.5 Å. The alkali metal atoms have even bigger s AOs, but in most cases they become unoccupied in ionic compounds. Nearly all outer core radii are smaller than 1 Å. f valence shells are even smaller. So one distinguishes between outer and inner valence shells. The inner 4f shell of the lanthanids does not participate in covalent, but only in ionic bonding.

The atomic valence orbital energies range from –4 to –26 eV, while the outer core level energies are below –16 eV. That is, the valence orbital levels of strongly electronegative atoms from the right side of the PT are below the upper core levels of atoms from groups 1, 2, 12. The outer p and d core

TABLE I
Fock orbital energies (in eV) and orbital radii (in Å) of atomic valence shells and outer core shells
from relativistic quantum chemical calculations

Atomic valence shells	Most strongly binding atom	Orbital energy in -eV	Orbital radius in Å	Most weakly binding atom	Orbital energy in -eV	Orbital radius in Å
s	N ^a	26	0.7	Cs	4	3.2
p	F ^b	20	0.6	In, Tl	6	2
d	Cu	13	0.5	Ac	5	1.8
f	Lu	21	0.4	Pa	7	0.8

Atomic outer core shells	Smallest outer core shell	Orbital energy in -eV	Orbital radius in Å	Largest outer core shell	Orbital energy in -eV	Orbital radius in Å
s	N	425	0.1	O ^a	34	0.6
p	Cl	220	0.2	Fr	16	1.2
d	Br	85	0.3	Hg	16	0.8

^aThe 2s AOs of O and F are already too strongly bound to contribute significantly in chemical bonding. According to quantum molecular calculations, they are better counted as core shells.

^bThe outer p AOs of the noble gas atoms Ar to E118 are bound less than F2p. They are valence levels.

shells of the alkali metal, alkaline earth metal and group-12 atoms, respectively, participate in so-called core-shell binding. Another example elucidated by quantum chemical calculations is the valence-active $6p^6$ shell of the early actinids with $5f6d7s$ valence shell (e.g. Van Wezenbeek et al., 1991; Dyall, 1999). The outer d^{10} shell of the coinage metal atoms is strongly valence active. Concerning the same atom, however, there is always a *large energy gap between its core and valence shells*.

6.4. Energetic order of atomic valence orbitals

There is a unique definition for the orbital energy ε of a *one-electron* system: the energy of the system relative to the case without the electron. ε of hydrogen atoms is

$$(7) \quad \varepsilon/13.6 \text{ eV} \approx -1/n^2, \quad n = n_r + l,$$

$$(8) \quad \begin{aligned} &\text{Hydrogen atom: } 1s \ll 2s \approx 2p \ll 3s \approx 3p \approx 3d \ll 4s \\ &\approx 4p \approx 4d \approx 4f \ll 5s \approx 5p \approx 5d \dots, \end{aligned}$$

where n_r is the radial quantum number (number of zero-spheres of the AO), l the angular quantum number (number of zero-planes or -cones), and n is the so-called principle quantum number.

Interelectronic repulsions change order (8) in all *many-electron* atoms. Electrons with vanishing or small angular momenta ($l = 0$: s AOs; $l = 1$: p AOs) can come near to the nucleus. The centrifugal force prevents this for electrons with larger l (d and f AOs). When nuclear charge and number of electrons increase, the inner 1s, 2s and 2p AOs are filled at first: The ‘nonpenetrating’ d (and f) electrons do not feel the increased nuclear charge, which is shielded by the inner core electrons. The p, and especially the s electrons become more strongly bound. The outer orbital energies of neutral many-electron atoms are rather accurately reproduced by the famous empirical $(n - \delta)$ *Rydberg* formula (Duncan, 1971):

$$\varepsilon \approx -1/n_{\text{eff}}^2, \quad n_{\text{eff}} = n - \delta(l),$$

which also follows from *ab initio* quantum defect theory (Seaton, 1966, 1983). The ‘quantum defect’ δ increases for small l . (A rough model for the empirical data is $\delta(l) \sim a(Z)/(l + 1/2)^2$.) We can derive and explain from *first principles* that the energetic order has *qualitatively* changed:

$$(10) \quad ns \approx np \approx nd \approx nf \rightarrow ns < np < nd < nf.$$

Before discussing the energetic order in many-electron atoms *in quantitative detail*, we must specify which operationally defined type of orbital energy ε we are talking about. The theorem of Koopmans (1933) states that ionization energies for *minimal change* of electronic structure are approximated by the negative orbital energies ε^{F} of the *canonical* version of the Fock orbital approximation. The simplest form of canonical Fock approaches is obtained for the optimization of configuration averages. We will here use the respective particular experimental/theoretical definition of orbital energies as ‘simple ionization energies’. We note that the smallest ionization energies in common tables refer to the lowest spin–orbit J states, that they often refer to complicated electron rearrangement processes, and that orbital energies in Fock and DF approaches also have different meanings.

The *quantitative* order for this choice of orbital energies can be derived from the *vast empirical data, equivalently experimental or computational* (Wang et al., 2006; Mann et al., 2000; Bills, 1998; Vanquickenborn et al., 1994, 1989; Levine, 2000, 1970; Pilar, 1968, 1990, 1979, 1978, and earlier). The energetic order of the valence shells of most atoms is

$$(11) \quad \begin{aligned} \text{Bound atoms: } &1s \ll 2s < 2p \ll 3s < 3p \ll 3d \leq 4s < 4p \\ &\ll 4d \leq 5s < 5p \ll 4f \leq 5d \leq 6s < 6p \\ &\ll 5f \leq 6d \leq 7s < 7p \dots \end{aligned}$$

Many textbooks present the different Madelung order,

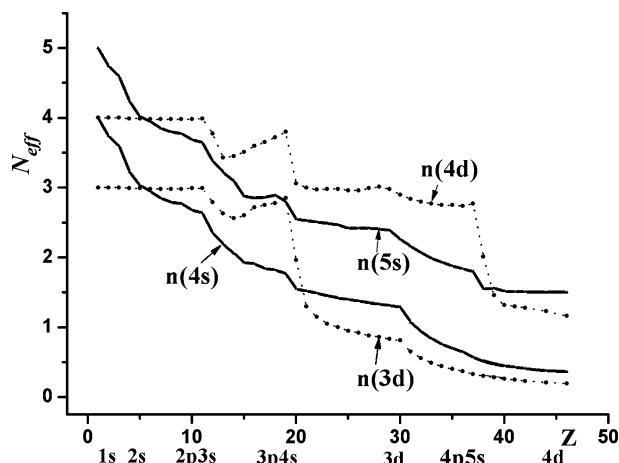


Figure 4. Effective quantum numbers $N_{\text{eff}} \sim 1/\sqrt{|\varepsilon^F|}$ of 3d, 4s, 4d, 5s for canonical Fock type orbitals of neutral atoms with $Z = 1-46$. Below the Z axis the filled nl -shells are indicated. Note the comparatively smooth variation of ns , and the sharp drops of nd after $Z = 11(\text{Na})$, $19(\text{K})$, $37(\text{Rb})$. Note the 3d ‘maximum’ for K with $3d > 5s$! From Wang et al. (2006).

$$(12) \text{ Textbook order: } 1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \\ < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d \dots,$$

and often present artistically modified graphical representations. *Qualitatively and quantitatively correct* ε^F values for the 3d, 4s, 4d, 5s orbitals of neutral atoms of the upper half of the PS are reproduced here in Figure 4 (Wang et al., 2006).

For elements in the neighborhood of the noble gases, the ns and np AOs are so strongly deshielded in comparison to nd , that $(n + 1)s$, and sometimes even $(n + 1)p$ and $(n + 2)s$ become more strongly bound than nd . The *alkali and alkaline earth metal atoms* of groups 1 and 2 form the ‘exceptional’ cases! The respective orbital order can also be explained qualitatively, but should not be used as the common rule. The fashionable $(n + l)$ *Madelung* rule (Karapetoff 1930; Madelung 1936) refers only to groups 1 and 2. In all other groups, in particular in the cations, “ $(n + 1)s$ is always above nd ” (Pilar, 1978), though not really always (Carlton, 1979)! For the atoms following ${}_6\text{C}$, until the respective TM atoms, $(n + 1)s$ is below

nd , for any n (again in contrast to many textbook graphics). The *minus* in the more general $(n - \delta)$ *Rydberg* rule also better reflects the fact that the orbitals in many-electron atoms are energetically *lowered* in comparison to the hydrogen case. Finally, the quantitative dependence on l is not linear as suggested by the Madelung rule, but of higher power ($\delta \sim 1/l^2$, see above).

The three main points to be remembered for chemistry and the PS are:

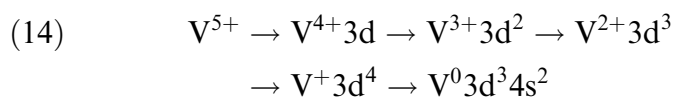
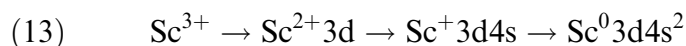
- (1) A large energy gap occurs between np and nd (and between $1s$ and $2s$). This causes the exceptional behavior of the noble gases (including He), and defines and explains the recurrence of similar elements in the PS. The groups of most similar elements are around the noble gases (group 0/18): the halogens (17) and chalcogens (16), and the alkali (1), alkaline earth (2) and rare earth metals (3).
- (2) For the particular case of weakly attracting atomic cores of groups 1 and 2, nd is even above $(n + 1)s$.
- (3) nf is even significantly above $(n + 1)p$, it is near $(n + 1)d$.

6.5. *Filling order of atomic valence orbitals*

Since electrons repel each, the total energy of an atom is not the sum of the orbital energies. A well-known rule in chemistry states that the ground state of a TM complex is obtained by filling the lowest orbital levels as long as the distance to the next higher level is larger than some electron interaction integral (Ballhausen, 1962; Griffith, 1962; Schl fer and Gliemann, 1967). A similar *correct Aufbau rule* holds for free atoms: If an atom has two energetically near-degenerate valence levels, the upper one becomes populated, too, if its energy distance is smaller than the difference of the respective electron repulsion energies (e.g. Pilar, 1968; N gadi and Kibler, 1992; Melrose and Scerri, 1996; Mann et al., 2000). The *oversimplified version of the Aufbau rule*, “The lowest energy orbitals are filled at first”, only holds for orbital level schemes with large gaps, i.e. for $1s < 2s < 2p < 3s < 3p < 3d$, though not for $3d \sim 4s$.

For the alkali (A) and alkaline earth (E) metal atoms, with $(n + 1)s < nd$, the ground configurations of A^0 and E^+ are s^1 , those of A^- and E^0 are s^2 . This trend changes from groups 3 or

4 onwards: $nd < (n + 1)s$ for the TM cations. The first electrons added to a TM^{g+} core are accommodated in the d shell. Because of the compactness of the d shell and the respectively strong inter-electronic Coulomb repulsion, it becomes in most cases more favorable for TM^0 to house 1 or 2 electrons in the s shell. Typical filling orders are:



We note the configurational rearrangement for V: when we add an electron to $\text{V}^{+}3d^4$, it does not only go to the slightly higher, diffuse 4s, but it also squeezes one of the 3d electrons up into the 4s, where the e–e repulsion is much smaller. Details are discussed in Appendix A.3 and by Wang et al. (2006).

6.6. Ground configurations of free atoms

The ground configuration averages (e.g. d^{g-q} for bonded TM ions TM^{q+}) are more relevant for general chemistry than the ground J levels of atoms in vacuum. The so-called exceptional ground J level configurations of Cr, Cu, etc. of chemical textbooks and philosophical discussions are determined by specific orbit–orbit and spin–orbit couplings. For instance, free Cr^0 has a particularly large negative Coulomb-exchange energy contribution for its lowest LS term from the d^5s^1 configuration manifold. The chemically ‘normal’ configuration of Cr^0 , however, is d^6 , for instance $(d-t_{2g})^6$ in $\text{Cr}(\text{CO})_6$.

The energies of the three configurations $d^g s^0$, $d^{g-1} s^1$ and $d^{g-2} s^2$ of 1st row transition metal atoms Ca to Cu are shown in Figure 5. They were determined on the basis of available experimental vacuum spectroscopic data (Moore, 1949ff, NIST, 2000, 2003) and calculated by a first-principles DF approach without any specific empirical data (Wang et al., 2006). We note the reasonable agreement of the configuration energies between

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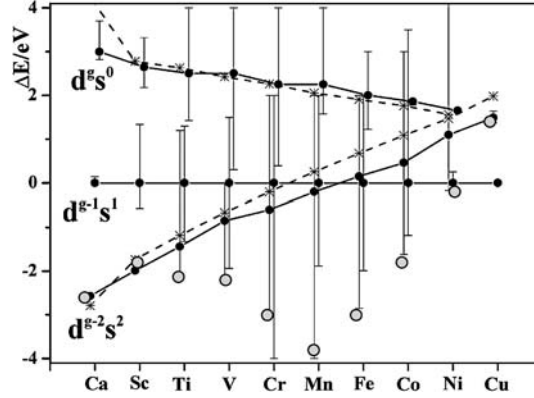


Figure 5. Energies ΔE (in eV) of $d^g s^0$ (upper lines), $d^{g-1} s^1$ (zero energy reference) and $d^{g-2} s^2$ configuration averages (up-going lines) of 1st row TM atoms from Ca to Cu. Experimental estimates: \bullet , full lines; ab-initio calculation: \times , dashed lines. The vertical bars indicate the lowest and highest experimental J-level energies of the three configurations. The lowest spin-orbit-J-level of $d^{g-2} s^2$ is marked by \circ . If some bar ends lower, the lowest J-level has another configuration (From Wang et al., 2006).

experiment and theory. We also note the rather smooth ‘exceptionless’ trends over the row. The lowest and highest experimental J-level energies of the three configurations are indicated by vertical bars, which strongly overlap. The lowest spin-orbit-J-levels of $d^{g-2} s^2$ are marked by \circ . Because of the theoretically complicated, numerically irregular orbit-orbit and spin-orbit splittings, the lowest J-levels of Cr and Cu belong to $d^{g-1} s^1$, and in the case of Ni, the lowest J-levels of $d^{g-2} s^2$ and $d^{g-1} s^1$ are nearly equal. While the energetic parameters of the atoms vary systematically over the period, there are specific integer jumps in the coupling effects from free atom to the next free atom. This is another topic of future philosophical reflection.

7. SUMMARY AND CONCLUSIONS

7.1. Origin and basis of PTs

The concept of a natural PS of CEs represented by PTs began as a two-dimensional classification of macroscopic matter

according to chemical properties. CEs as conserved essences of materials must be distinguished from elemental materials as well as from free independent atoms in vacuum. Chemical properties comprise dynamic, reactive, relational and static, physical, reflexive ones. The properties chosen as relevant for a PT depend on one side on the practical and epistemological interests of the scientist, on the other side on the property values given by nature. Often materials under ‘normal’ conditions are chosen, that is temperatures in the range of 300 K and pressures in the range of 1 at, which evolved in the chaotic cosmic history towards human life on earth.

In the course of history of the PTs, a large number of vaguely defined chemical properties was compacted into chemical similarity fields with vertical and horizontal extensions and finally replaced by just two natural numbers referring to chemically bound atoms. The basic structure of the PS is nowadays defined by the nuclear charge Z , increasing 1 by 1 ‘horizontally’, and by the number g and the type of valence electrons, being constant ‘vertically’. All well-defined numerical properties of the CEs are exactly determined by Z through *ab initio* quantum physics of the valence shells. The latter are characterized by number, symmetry, *spatial and energy ranges* of the valence-active atomic orbitals. The basis of the PS has become less empirical, less chemical, less ‘reactive’ and more theoretical, more physical, more ‘atomic’. However, atoms here do not mean free but chemically bound ones. The PS is well determined by the physics *and* chemistry of deterministic nature under ‘normal conditions’. Its representation in PTs is not unique.

7.2. *Chemistry, physics and the PS*

The relations between chemistry, physics and the PTs suggest three fields of inquiry:

- (1) How deterministic or constructivistic (though still within the limits of the laws of nature) are the relations between chemical experience of *nature*, and *the model* concept of PTs systematizing it?

- (2) What are the *intrinsic characteristics of those models*, representing the PS of CE?
- (3) Which relations exist between basic *physical theory and the chemical concept* of a PS?

Ad (1) The recent quantitative chemometric researches require extension: How many important ‘principal chemical properties’ of the CE exist? How strongly interest-laden are they (for somewhat different classification schemes see e.g. Stone, 1979; Pettifor, 1984, 2003 or King, 2004)? Are there chemically adequate concepts of measurable similarity of CEs? How quantifiable are parts of qualitative chemistry? Can PTs emerge as selforganizing maps automatically? To which extent are dimension and structure of the different PTs determined by nature? These are the main points to be addressed by a philosophy of the PS in the 21st century.

Ad (2) The apparent structure of PTs has been simulated by group theoretical means (Novaro, 1973; Négadi et al., 1992; Kibler, 2006). So far the series of ground states when going from one free neutral atom to the next one was considered. In the future, a turn towards chemistry is welcome. First, the chemically most relevant structure of the inert core shells, and the structure of the valence shells of atoms bound in molecules, should become the center of interest. Second, the natural systematics of *chemical experiences* as coded in traditional PTs should attract more interest in investigations of the internal structure of the PS.

Ad (3) Computational chemistry can reproduce or predict the numerical properties of matter. Atomic valence orbitals have binding energies of 5–25 eV and orbital radii below 2.5 Å. Spatially diffuse and weakly bound Rydberg AOs are chemically less significant. The most important aspect of the AO order are the *energy gaps between core and valence shells*. That determines the quasi-periodicity of the PS. The true empirical (measured or computed) orbital orders were presented above. The orders change steadily from the hydrogenic order (8) over the most common order (11) and the ‘alkali’ order to the somewhat different $(n + l)$ Madelung order (12) in the textbooks.

The trend (10) in the orbital energy orders is due to angular momentum dependent core shielding, best described by the well-founded $(n - \delta)$ quantum defect Rydberg formula. The energy order and the occupation order of AOs is not always the same. Going from one atom to the next, and adding electrons to the same atomic cation can also yield different orders. The ‘correct Aufbau rule’ of the orbital model is: The lowest orbitals are occupied in the ground state, *provided* inter-electronic repulsion does not prevent it. This correct rule is well known in ligand field theory. Orbital occupation as well as chemical binding depend on energy *and* spatial extension of the orbitals. This all is both intuitively understandable and numerically correctly computable with the help of the ‘quantum theory of the theoretical experts’.

7.3. *Quantum chemical and philosophical models*

Our discussions were based on chemical experience and physical theory, the latter reproducing the data of the former at the kJ/mol level. The recent literature on the PS starts from theoretically influenced traditional models of ordinary chemists and philosophers and combines it with high resolution spectroscopy of independent atoms in vacuum. However, the simplistic chemical model approaches cannot describe the complex pattern of individual free atomic states. Anyhow the latter are of small relevance for qualitative chemistry of condensed materials.

Even simple (but still theoretically consistent) forms of orbital models seem already somewhat difficult for chemists. Electronic interactions must often be accounted for explicitly already at the qualitative level. The chemically relevant atomic configuration averages vary very regularly and understandably without exceptions. There is no mystical stability of filled or half-filled shells of free atoms in chemical compounds. It is well known that a d^5 shell does *not* govern the chemistry of Cr. The noble gas shell of O^{2-} is *not* stable, except if stabilized by surrounding counterions (O^{2-} cannot appear in vacuum). As Schmid (2003) coined it: The noble gas configuration is not the driving force but the rule of the game.

The $(n + l)$ order of chemical textbooks is a typical example of a ‘fact historically created in the community’ of chemists (compare Fleck, 1935). Modified versions of PTs are suggested from time to time to the chemical community, based on hypothetical numerological, esthetic or group theoretical speculations. We suggest keeping the traditional forms of PTs, which are based on chemical empirics and on empirically founded quantum chemistry.

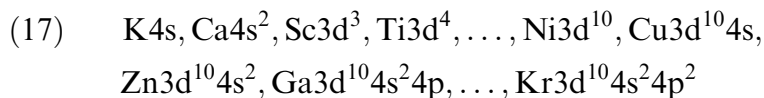
In undergraduate teaching the structure of the PS of CE may be explained as follows: Start from the *energy* order (8) of hydrogenic orbitals. Explain the trend of change (10) due to electronic repulsion in many-electron atoms, resulting in gaps after 1s and the *np*. Present the most common orbital order (11). Also mention the different orbital *radii* orders, which determine the AO overlaps and the strengths of covalences:

$$(15) \quad \text{Hydrogen atom:} \quad 1s \ll 2p < 2s \ll 3d < 3p < 3s \\ \ll 4f < 4d < 4p < 4s \dots$$

$$(16) \quad \text{Most atoms:} \quad 1s \ll 2s \approx 2p \ll 3s < 3p < 3d \\ \ll 4s < 4p < 4d < 4f < 5s \dots$$

Note that the orbital radii, though not the energies, are mainly determined by the principle quantum number n . Apply the ‘simplified Aufbau rule’ as long as complex chemistry and chemistry of free atoms are not touched. Derive the structure of the PT on the basis of the core-valence energy gaps, which explains the exceptional role of rare gases including He. Mention the particularly large deshielding (10) for the first two groups, where $(n + 1)s < (n - 1)f$, *nd* results. Since the $ns - np$ and $nd - (n + 1)s$ gaps are not large in the valence shells, closed s^2 or d^{10} shells are not particularly stable, but can form sp or ds hybrids, while closed p^6 shells are easily stabilized by larger Z values (alkali and alkaline earth metal cations) or by surrounding cations (halogen and chalcogen anions).

For the 4th row, for instance, one obtains the following correct electron configurations for chemically *bonded* atoms:



TM complex chemistry, which is d-chemistry, can now be easily explained with the ligand field MO model. One may mention that due to specific Coulomb orbit–orbit and magnetic spin–orbit couplings, the ground states of most *free neutral* atoms have other configurations than the chemically dominant ones in line (17).

Our present discussions (see also Schwarz, 2004; Wang et al., 2006) are in a sense orthogonal to the mainstream (e.g. Scerri, 2001, 2003, 2004a, b, 2005; Bensaude-Vincent, 2001; Ostrovsky, 2001, 2003a, b, 2004a; Kibler, 2004, 2006). In essence, we suggest to base discussions of the chemical PS on electron configurations of chemically bonded atoms, on chemical experience and on theoretical arguments consistent with physical quantum theory.

7.4. *Physically oriented aspects*

When Dirac (1929) said, chemistry *can* be reduced to physics in principle, he was wrong, but not in the sense usually mentioned, but because some very basic qualitative chemical concepts are so vaguely defined and therefore not easily reduced to physics. Physicists must know more chemistry, and chemists must know more physics, to arrive at converging and logically consistent interpretations. According to Lichtenberg (1793), those who understand nothing else than chemistry, don't understand chemistry either.

It depends on the *details of the case*, whether an approximation concept represents a real structure of the investigated complex system. Many, though not all, states of N -electron atoms 'have' N occupied spin–orbitals. Experimental data are helpful to find out, which approximations must be rejected. However, this is not sufficient. The basic theory itself is the yardstick to decide whether a model is a theoretically well-founded 'reducing' model, or whether it is only a fit that accidentally seems to work. For instance, the $(n - \delta)$ Rydberg rule is

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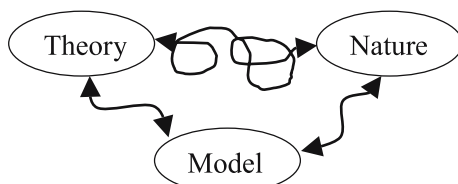


Figure 6. The inductive/reductive path between experimentally investigable nature and basic theory is quite involved. A shorter bypass through a simplified theory-based model helps understanding.

not just preferable over the $(n + l)$ Madelung rule, because the latter has too many exceptions, but because the former has a grounding in quantum defect theory. From the physical point of view, we must distinguish between purely empirical fit models and theory-based approximation models (Figure 6). Theory-based models are the ones that supply us with understanding and weak reduction (Ostrovsky, 2004b/5). The concept of the PS evolved as an empirical model of chemistry. It is now in the transition phase towards an understandable model based in physical theory, ‘qualitatively *and* theoretically correct’.

7.5. From theoretical physics to empirical chemistry

The basic well-corroborated stance of quantum mechanics is that every ‘material-specific parameter’ that can be measured definitely, can also be calculated definitely from a few empirical ‘natural constants’. The latter relate the atomic units of nature to the conventional SI units chosen by more and more societies since the French revolution. One step towards understanding nature is the semiempirical rationalization by models *post factum*; another step is the approximate *ab initio* quantum mechanical deduction of the phenomenological structure and their specific parameters.

Originally there were only very few clamps between physical and chemical concepts, although textbooks of ‘physics for chemists’ were on the market since the birth of modern scientific chemistry (e.g. Scholz, 1815; Buchner, 1825). After physics has been largely unified (Heisenberg, 1969; Von Weizsäcker,

1985, 1992; Hawking, 1988; Weinberg, 1993) the next natural step and aim in the development of science are tighter conceptual relations between physics, chemistry and biology.

One obstacle is that scientific achievements from specialist's fields are not easily presented in a sufficiently simplified but conceptually *undeformed* manner to the broader audience. Many skeptical questions in the literature against *ab initio* quantum mechanical explanations of atomic and macroscopic phenomena have been positively answered in the specialist's literature of previous decades. The analysis of typical misunderstandings of physical theory by chemists, the clarification of the common concepts of chemists, and interdisciplinary exchanges will lead towards sensible philosophical interpretations.

Even extreme physical reductionists such as Weinberg (1993) believe that special fields of complex matter (e.g. chemistry) require specifically adequate concepts and procedures. The (weak) reduction to physical concepts or the emergence from physics just proves the autonomy of those fields as matured fields of serious natural inquiry. Fields of complex matter demand for fuzzy qualitative concepts in an otherwise completely unorganized field of phenomena. Both chemical empirism and physical reductionism are needed.

7.6. *The road*

The essence of chemistry as created by the practicing chemists is (i) *fuzzy classification of compounds* (of organic and inorganic chemistry) according to their chemical properties and reactions, and (ii) the *strict physical and fuzzy chemical laws* of properties and their changes (physical and general chemistry). One type of classification concerns the PS of CE. As in any classification of (nearly) continuous phenomena, one must introduce somewhat arbitrary borders of distinction, which necessarily makes sense only far from the border region of similar things.

The ultimate and constitutive aim of natural science is the creative finding of structures and laws of different domains of nature, at first inside the domains and then relating the domains. This comprises the understanding of reductive and emergent

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relations. The way towards this aim consists of two steps, (i) finding out what should be done, what has been achieved already and what is still missing and (ii) then going as far as possible.

The complex direct path between chemistry and physics can be made more transparent by finding bypasses through theory-based approximate models (Figure 6). Concerning the PS, there are two problems, a more serious chemical one and a less serious physical one. The chemical one is the elucidation of the fuzzy relations between chemistry and the PS. Here, more must be achieved in history, philosophy and theory of chemistry. Important recent steps are the works of Cahn, Khramov, Restrepo, Sneath and Zhou from the last 5 years.

Concerning the relations between the PS and physics, the successful achievements of the last 40 years will be continuing along the paths of normal research in quantum chemistry. Three aims should be pursued. (i) In physics and quantum chemistry: relating the *chemical* essence of the PS to approximate models of *ab initio* quantum chemistry. (ii) In chemical education: didactical simplification of the quantum chemical achievements, for instance concerning the ‘true’ order of AOs, the importance of gaps and the chemically relevant atomic configurations. (iii) In scientific writing: the presentation of basic quantum chemical and quantum mechanical wisdom in such a manner that it can be better absorbed in the communities

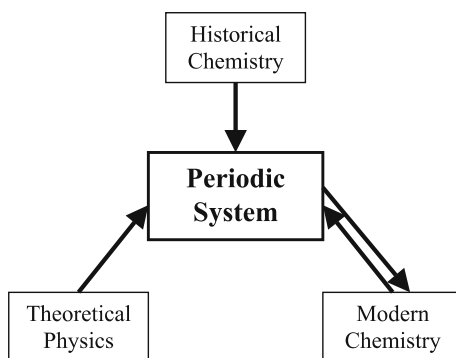


Figure 7. History, physics, chemistry and the periodic system of CEs.

of ordinary chemists and chemically oriented metascientists (Figure 7).

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APPENDIX

A1 Main component analysis of the properties of CEs

Be V_{pc} the matrix of empirical values of properties $p = 1$ to P of CEs $c = 1$ to C . Since the different properties are defined on different scales, property scales ‘on an equal footing’ with adapted zeros and units are introduced, with the values scattering around zero with unit mean variation:

$$(A1.1) \quad \Sigma_c V_{pc} = 0, \quad (\Sigma_c V_{pc}^2)/(C - 1) = 1.$$

Assuming approximately linear property-correlations (otherwise nonlinear scale transformations are required before), correlation matrices of properties and elements can be defined:

$$(A1.2) \quad M_{pp'} = \Sigma_c V_{pc} \cdot V_{p'c}, \text{ in matrix form } \mathbf{M} = \mathbf{V} \times \mathbf{V}^\dagger,$$

$$(A1.3) \quad N_{cc'} = \Sigma_p V_{pc} \cdot V_{pc'}, \quad \mathbf{N} = \mathbf{V}^\dagger \times \mathbf{V}.$$

\mathbf{M} and \mathbf{N} have the same set of nonzero eigenvalues λ . If there are only F eigenvalues $\lambda_f > 0$ ($f = 1$ to $F \ll P$), then all empirical properties of all CEs can be approximately represented by a few liner combinations of measured properties:

$$V_{pc} \approx \sum_f L_{pf} S_{fc}, \mathbf{V} \approx \mathbf{L} \times \mathbf{S}.$$

S_{fc} is the value or score of the so-called ‘main component’ or ‘principal property’ f of CE c . L_{pf} is the weight or loading of the observable property p in/on the combined principal property f .

$\mathbf{L}_f = (L_p)_f$ and $(S_c^\dagger)_f$ are the f th eigenvectors of \mathbf{M} or \mathbf{N} ,

$$(A1.5) \quad \mathbf{M} \times \mathbf{L} = \mathbf{L} \times \lambda \quad \text{and} \quad \mathbf{S} \times \mathbf{N} = \lambda \times \mathbf{S}.$$

The definition of the individual principal properties by Eq. (A1.4), i.e. $|\mathbf{V} - \mathbf{L} \times \mathbf{S}|$ minimal, is not unique. This is as with the molecular orbitals: Only the set of occupied orbitals is well defined by nature; the most convenient (fully equivalent) linear combinations from this set depend on one’s purpose (e.g. delocalized ‘canonical’ orbitals or localized ones or somehow hybridized ones). One can ‘rotate’ the ‘canonical’ principal properties \mathbf{L}_f from Eq. (A1.5) by a unitary transformation matrix \mathbf{U} (with $\mathbf{U} \times \mathbf{U}^\dagger = \mathbf{1}$) and form an equivalent set of principal properties $\mathbf{L}'_f = \mathbf{L}_f \times \mathbf{U}$ as linear combinations (sums and differences) of the canonical ones. Criticism against ‘rotation’ seems to stem from the ‘softer’ sciences, but makes less sense in the harder sciences, where the empirical data are well-defined and better understood. So far the analysis of rotated principal properties in chemistry is completely missing.

A2 Some basic quantum chemical concepts

According to Cao (2003), fields are the basic ontological entities. Any experimentally completely specified ‘pure’ state of a molecule or nano-system with N electrons is completely described by its matter-field or wave function $\Psi(X_1, \dots, X_N)$. The approximation concept of a well defined number of electrons works well in the no-pair approximation of traditional relativistic quantum theory. In the case of thermodynamic or reactive ‘mixed’ ensembles, the density kernel $D(X_1, \dots, X_N; X'_1, \dots, X'_N)$ must be used instead of Ψ . For a pure state $D = \Psi(X) \cdot \Psi^*(X')$. $X_i = (r_i, s_i)$ represents the positional (r_i) and spin-directional (s_i) vectors of indistinguishable electrons i in space. Here we used the so-called position representation,

which is distinguished over other (e.g. momentum) representations, because the two-particle interactions are particularly simple: the Coulomb interaction energy of two charges q_1 and q_2 in position representation is $q_1 \cdot q_2 / |r_1 - r_2|$. While Ψ or D always contain the spin, the nonrelativistic approximation to the *energy* depends only on the position-dependent part of the wave function.

Because of Pauli exclusion, most or all of the possible spin factors are excluded from being coupled to a given positional factor. Except for external magnetic potentials or relativistic spin effects, there do not appear any direct energetic spin contributions. Different energies for singlet and triplet spin states of open shells are not caused by some specific spin-energy: Different positional states have different Coulomb energies, and are connected to different spin states. An extended analysis of the respective Hund rules has been carried out by Kutzelnigg and Morgan (1996). They have shown that the relation between spin and energy is much more involved than usually suggested, but without any magic. The ‘direct’ and ‘exchange’ energies are both pure Coulomb energies, without and with exchanged indices in the respective integrals.

Dirac’s matter-field for a single electron is a bi-quaternionic function of eight real components. Neglecting relativistic effects and the spin, a two-component complex function survives. In time-independent, stationary, nonreacting cases, a real one-component function is sufficient. There is no reason for any fear of multi-component functions in experimental sciences: position, electric and gravitational fields have three components; the electromagnetic potential has four components; the geometric structure of an N-atomic nonlinear molecule is represented by a point in $(3N-6)$ -dimensional space. A complex function is nothing else than two real functions, coupled in a specific manner to each other. A complex function is easier measurable than two independent real functions.

If operationally well-defined, orbitals can be ‘measured’, i.e. constructed from phase-sensitive interference measurements, holographically or tomographically. The measurability of wave functions and orbitals has been discussed in the literature

(Wang and Schwarz, 2000; Schwarz, 2001b, 2006). At present it is easier and more reliable to calculate them from Schödinger or Dirac type quantum equations.

A3 On electron configurations

Different ground configurations occur for most TMs in different contexts (Wang et al., 2006). Ni is an example. Most compounds are derived from $\text{Ni}^{2+} 3d^8$. In nonpolar compounds such as $\text{Ni}(\text{CO})_4$ the configuration is $3d^{10}$ (Hay, 1977). The lowest *average* configuration of *free* neutral Ni atoms is $3d^9 4s^1$ (spectroscopic energies from Russell (1929), Moore, (1949ff)). $3d^8 4s^2$, ‘the textbook configuration’ of Ni, is about *100 kJ/mol above* $3d^9 4s^1$. The Coulomb-exchange coupling of the compact 3d hole with the diffuse 4s of $3d^9 4s^1$ is small, the 3D term is lowered by only 8 kJ/mol. The Coulomb coupling of the two compact 3d holes of $d^8 s^2$ is large, the lowest LS term 3F being lowered by about 110 kJ/mol: 3F of $d^8 s^2$ is then *only 2.9 kJ/mol above* the lowest LS term 3D of $d^9 s$. Since the SO splitting of Ni d^8 3F (in the 10 kJ/mol range for 1st row TM atoms) is bigger than that of Ni $d^9 s$ 3D (Condon and Shortley,

TABLE A.3.I

The five different filling orders of lowest configuration averages of free transition metal ions (examples derived from spectroscopic data of Moore (1949ff))

Case	Example	Lowest configuration averages	Filling order
1	Rh	$\text{Rh}^{9+} \rightarrow \text{Rh}^{8+} 4d \rightarrow \dots$ $\rightarrow \text{Rh}^{+} 4d^8 \rightarrow \text{Rh}^0 4d^9$	$\dots + d+d+d$
2	Fe	$\text{Fe}^{8+} \rightarrow \text{Fe}^{7+} 3d \rightarrow \dots$ $\rightarrow \text{Fe}^{+} 3d^7 \rightarrow \text{Fe}^0 3d^7 4s$	$\dots + d+d+s$
3a	V	$\text{V}^{5+} \rightarrow \text{V}^{4+} 3d \rightarrow \dots$ $\rightarrow \text{V}^{+} 3d^4 \rightarrow \text{V}^0 3d^3 4s^2$	$\dots + d+d+(2s-d)$
3b	Y	$\text{Y}^{3+} \rightarrow \text{Y}^{2+} 4d \rightarrow$ $\text{Y}^{+} 5s^2 \rightarrow \text{Y}^0 4d 5s^2$	$+d+(2s-d)+s$
3c	Ti	$\text{Ti}^{4+} \rightarrow \text{Ti}^{3+} 3d \rightarrow \text{Ti}^{2+} 3d^2 \rightarrow$ $\text{Ti}^{+} 3d^2 4s \rightarrow \text{Ti}^0 3d^2 4s^2$	$\dots + d+s+s$

TABLE A.3.II
Lowest *average* energy electron configurations of free neutral atoms
(element symbol with group number g in parentheses)

Ground configuration	$d^{g-2}s^2$	$d^{g-1}s^1$	$d^g s^0$
1st TM row	Ca(2)–Mn(7), Zn(12)	Fe(8)–Cu(11)	
2nd TM row	Sr(2)–Nb(5), Cd(12)	Mo(6)–Ru(8), Ag(11)	Rh(9), Pd(10)
3rd TM row	Yb(2)–Re(7), Hg(12)	Os(8)–Au(11)	

Note the deviation from the configurations of the lowest free atomic J states, and from those of chemically bound atoms.

1935), the lowest J level 3F_4 of d^8s^2 comes *2.5 kJ/mol below* the lowest J level 3D_3 of d^9s . This reason seems unknown to most authors discussing d^8s^2 as ‘the configuration of Ni’ in a chemical context.

Since the statement “ $(n + 1)s$ is always above nd !” (Pilar, 1978, 1979) holds for all chemically bound TM atoms and ions, and also for most free species, the d-shell is filled first as in case 1 in Table A.3.I. Because the d–d repulsion is much larger than the d–s repulsion, the last electron is sometimes filled into the $(n + 1)s$ of free atoms (case 2). Sometimes, this electron even repels the penultimate electron also into the $(n + 1)s$ leading to s^2 for the neutral atom, as in case 3a. This may happen already for the cation M^+ , while the last electron again goes to nd (case 3b). The last two electrons may also go directly into $(n + 1)s$ as in case 3c. The average ground configurations can be derived without sophisticated discussions of direct and exchange Coulomb integrals and relativistic spin–orbit integrals (Wang et al., 2006). They are collected in Table A.3.II.

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