

# The Challenge of the So-Called Electron Configurations of the Transition Metals

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**Abstract:** Quite different meanings are attached by chemists to the words element, atom, orbital, order of orbitals or configurations. This causes conceptual inconsistencies, in particular with respect to the transition-metal elements and their atoms or ions. The different meanings will here be distinguished carefully. They are analyzed on the basis of empirical atomic spectral data and quasi-relativistic density functional calculations. The latter are quite reliable for different average configuration energies of transition-metal atoms. The so-called “configurations of the chemical elements”, traditionally dis-

played in periodic tables, are the dominant configurations of the *lowest spin-orbit levels* of the free atoms. They are chemically rather irrelevant. In many-electron systems the *ns* and *np* AOs are significantly below the more hydrogen-like *nd* ones. Even  $(n+1)s$  is below *nd* for all *light* neutral atoms from C onwards, but only up to the

first elements of the respective long rows! The most common orbital order in *transition-metal atoms* is  $3p \ll 3d < 4s$  etc. The *chemically* relevant configuration in group *g* is always  $d^g$  instead of  $d^{g-2}s^2$ . Conceptually clear reasoning eliminates apparent textbook inconsistencies between simple quantum-chemical models and the empirical facts. The empirically and theoretically well-founded Rydberg  $(n-\delta_l)$  rule is to be preferred instead of the historical Madelung  $(n+l)$  rule with its large number of exceptions.

**Keywords:** Aufbau principle • density functional calculations • electron interaction • electronic configurations • orbitals • transition metal atoms

## 1. Introduction

Among the most basic theoretical tools of chemistry are the concepts of chemical elements, of the periodic system and its representations by different periodic tables, of atomic orbitals (AOs), and electron configurations. Many-electron atoms in compounds are described in general chemistry with the help of single-electron orbital functions.


The way of thinking about the electronic structure of atoms has strongly been influenced by the historical writings of Madelung and of Pauling.<sup>[1,2]</sup> Their ideas about the order of valence AOs have penetrated into all chemistry textbooks, either in the form of acceptably simplified theoretical models (e.g.<sup>[2-5]</sup>)—or more common in oversimplified or even inappropriate forms (e.g.<sup>[6,7]</sup>). Some logically inconsistent ideas have become particularly popular, for instance the belief that in a transition metal atom, *4s* is occupied before *3d*, but *4s* is also easier to ionize.

More than one third of all elements belong to the *d* block of the periodic system. It is known since the early days of ligand field theory<sup>[8]</sup> that the chemical, spectroscopic, and magnetic properties of transition-metal complexes are dominated by the *nd* shells, with little influence of the  $(n+1)s$  shells. Complex chemistry is *d*-shell chemistry.

Nevertheless, most chemists and physicists believe in the so-called Madelung or  $n+l$  rule [Eq. (1)], with *nd* valence shifted above  $(n+1)s$  Rydberg, while chemical experience, as codified in periodic tables, corresponds to some quite different orders such as that given in expression (2), in which  $(n+1)s$  Rydberg is stabilized with respect to the hydrogenic value, though in most cases *not* below *nd* valence.

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The Madelung ( $n+l$ ) rule from textbooks:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p \quad (1)$$

The Rydberg ( $n-\delta_l$ ) rule from chemical and spectroscopic experience:

$$1s \ll 2s < 2p \ll 3s < 3p \ll 3d < 4s < 4p \ll 4d < 5s < 5p \ll 4f < 5d < 6s < 6p \ll 5f < 6d < 7s < 7p \quad (2)$$

To understand this paradoxical situation, the different meanings attached to the words element, atom, orbital, configuration, order of orbitals or configurations are clarified in Section 2. The correct energies and orders of orbitals and of configurations, in well-defined senses, are determined and described in Section 3 on the basis of *available experimental data and of present density functional calculations*. The conclusions are summarized in Section 4. Some cases are studied in detail in the Appendix, Section 5.

## 2. Clarification of Concepts

**Different meanings of “chemical element”:** The common meaning of “chemical element” is *basic sub-stance*, standing “under or behind” (latin “sub”) real chemical matter and obeying the law of mass conservation. In this sense benzene or fullerene contain the element carbon. The second meaning of “element” is *simple stuff* such as diamond or the fullerenes. In textbook discussions of the electron configurations in the periodic table, however, “element” means an isolated non-charged *independent atom*. Atomic vacuum spectroscopy is dominated by diffuse Rydberg orbitals. (The term Rydberg orbital has been popularized in the NBO analysis misleadingly with a completely different meaning.)<sup>[11,12]</sup> On the other hand, chemically *bonded atoms* in condensed phases and in multiatomic molecules are perturbed by the compact atomic environment. The diffuse orbitals of free atoms become destabilized. Furthermore, transition-metal atoms are positively charged in many compounds, the ionic charge stabilizing the  $nd$  shell relative to the  $(n+1)s$  shell. Therefore, higher s-AOs are less important in chemistry.

**Different meanings of “electron configuration”:** The concept of electron orbital configuration assumes that the wave function  $\Psi$  of the  $N$ -electron system can be approximated by (a symmetry-adapted sum of) products of one-electron orbital functions  $\phi$  (the orbital or Fock approximation; expression (3)),<sup>[32]</sup>

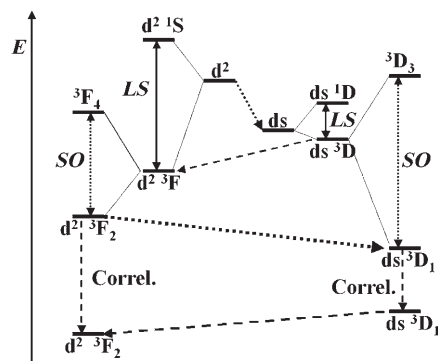
$$\Psi(X_1, \dots, X_N) \approx A \{ \phi_a(X_1) \cdot \phi_b(X_2) \cdot \dots \cdot \phi_\omega(X_N) \} \quad (3)$$

$A$  is the symmetrization operator guaranteeing the fulfillment of the Pauli principle and further spatial and spin sym-

metry requirements of the correct  $N$ -electron wave function  $\Psi$ .  $\Psi$  depends on the positional and spin coordinates  $X_i$  of electrons  $i$ ,  $i=1$  to  $N$ .  $\Psi$  is approximated with the help of one-electron orbitals  $\phi_j$ ,  $j=a$  to  $\omega \geq N$ . Configuration means the *set of occupied orbital shells* and the (*partial*) *occupation numbers of the shells*, such as  $B 2s^2 2p^1$ . Approximation (3) works reasonably well for many states of low energy.

One can clearly speak of the state of lowest energy of an isolated noninteracting atom. It has a well-defined configuration within approximation (3), provided the mixing with functions of same symmetry from other configurations is weak. If the configuration contains partially occupied degenerate or near-degenerate shells with same or similar orbital energies, such as  $2p$  (spin-orbit split into  $2p^{1/2}$  and  $2p^{3/2}$ ) or  $3d-4s$  (such with rather similar energies), several states emerge from such an open shell. There are, for instance, six individual states of  $B 2s^2 2p^1$  or nearly seven thousand ones of  $Sm^* 4f^7 6s$ . Provided none of those states strongly mixes with states from other configurations, the average energy of all states of the configuration is also a well-defined number.

The energy level splittings of open-shell configuration averages into individual energy levels is schematically sketched for a hypothetical case of  $d^2$  and  $ds$  in Scheme 1.

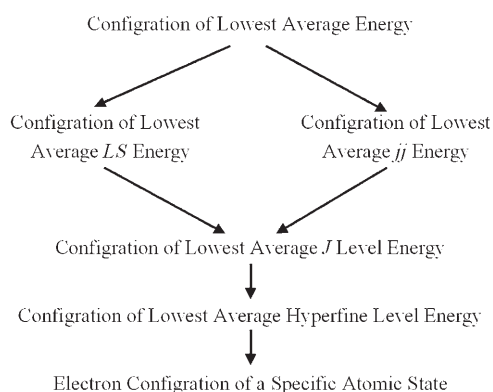


Scheme 1. Schematic energy levels of hypothetical configurations  $d^2$  and  $ds$ . They are split and shifted by  $LS$  and  $SO$  couplings and by many-electron correlations.  $E_F$  means the energy at the Fock orbital approximation,  $E$  means the correlation-corrected or experimental values. The case shown has  $E_F(ds) < E_F(d^2)$ , after  $LS$ -splitting  $E_F(d^2 3F) < E_F(ds 3D)$ , after further  $SO$ -splitting  $E_F(ds 3D_1) < E_F(d^2 3F_2)$ , and with correlation  $E(d^2 3F_2) < E(ds 3D_1)$ . Further hyperfine splittings are neglected here.

For the upper rows of the periodic table it is appropriate to account at first for the instantaneous Coulomb repulsions (comprising direct and exchange parts) between the different orbitals of the partially filled shells. This yields the splitting into  $LS$ -term averages, for example, for  $d^2$  into  $LS$  terms  $3F$ ,  $1G$ ,  $3P$ ,  $1D$ ,  $1S$ . Next the relativistic spin-orbit interactions are to be considered.  $3F$ , for example, is split into three different  $J$ -level averages  $3F_2$ ,  $3F_3$ ,  $3F_4$ . If the nucleus has non-vanishing spin and is not approximated by a structureless Coulomb charge, the  $J$  levels are split into *hyperfine sublevels*,<sup>[10]</sup> for example, the  $^{13}C s^2 p^2 3P_1$  into  $F=1/2$  and  $3/2$ . These may be finally split into *individual states* by additional electromagnetic fields. At each type of averaging, a different

configuration may correspond to the lowest energy, as sketched in Scheme 1. And at each type of averaging, one may account, or not, for electron correlation, by mixing different configurations, that is, orbital occupation schemes (CI). Thereby one goes from the orbital approximation to a more accurate level (i.e. accurate theory or experiment). If CI is strong, the very concept of a 'leading configuration' loses its meaning.

The configurations given in periodic tables are the leading configurations of the lowest experimental *J*-level averages of the free atoms (comprising  $2J+1$  states). The implicit assumption that the single-configuration approach still makes sense is justified in most cases. Some authors (e.g.,<sup>[9]</sup>) have suggested to refer to *LS* averages instead of *J* averages. However, relativistic interactions become more important than Coulomb interactions in the valence shells of the most heavy atoms. Then it is more appropriate to consider the adjacent *J* levels corresponding to *jj*-term averages. In the case of  $d^2$  those are  $d^{3/2^2}$ ,  $d^{3/2}d^{5/2}$ ,  $d^{5/2^2}$ . The *LS* and *jj* schemes just correspond to two different partitionings of the whole set of *J* levels of the configuration. The different kinds of configurations are sketched Scheme 2. Whether none or



Scheme 2. Different meanings of "lowest configuration".

some choice or choices are appropriate depends on the particular case. In correlated intermediate coupling cases, any reference of a *J* level to some *LS* term, or to some *jj* term, or even to some configuration, may be inappropriate because of strong term or configuration mixings. For instance, the conventional *LS* nomenclature of *J* levels of lanthanoid atoms often has no physical significance.<sup>[22]</sup>

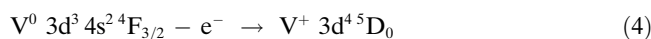
The Hamiltonian of a free atom is rotationally symmetric, and the coupling of orbital and spin angular momenta is important for atomic spectra. These couplings are partially quenched in molecules and solids by strong nonspherical fields.<sup>[33]</sup> Consequently, many atomic *J*-levels are mixed in the molecules. That is, several lower atomic configurations determine the chemistry of the element, not just the one corresponding to the lowest *J* level of the free atom. For several transition metals the lowest *J* level configuration even does not at all belong to the chemically relevant ones. For instance, the lowest *J*-level average of the free Ni atom

has  $3d^8 4s^2$  as leading configuration, the lowest *LS* level average has  $3d^9 4s^1$ , and chemically bound  $Ni^0$  has  $3d^{10}$ . Some case studies are presented in the Appendix.

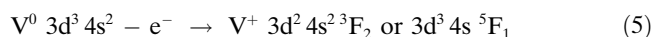
**Different kinds of atomic orbitals:** The wave function  $\Psi$  of the stationary ground state of an isolated *N*-electrons atom is uniquely defined (up to a gauge-dependent phase-factor). However, the atomic orbital set  $\{\varphi_i\}$  to approximate  $\Psi$  according to Equation (3) can be precisely defined in different manners. The AO concepts must be distinguished in three respects.

- 1) The AOs depend somewhat on the approximation strategy. One must distinguish AOs as symmetry restricted or unrestricted AOs; as spin-orbit averaged or *SO*-split AOs; as optimized level or optimized average AOs; as ab initio single or multi-configuration self-consistent field or some kind of density functional AOs; as AOs optimized concerning the energy or the wave function overlap or some other property.
- 2) Depending on the atomic state and on the approximation procedure, there is more or less arbitrariness in choosing different equivalent sets  $\{\varphi'_i\}$  of hybrid AOs as linear combinations of the original set of occupied orbitals  $\{\varphi_i\}$ .
- 3) One must distinguish the AOs of atoms under different physical conditions: AOs of free atoms in vacuum from bonded atoms surrounded by other atoms; AOs of neutral atoms from those of charged atomic ions; AOs optimal for a specific state or for the average of some set of states. In any case, the AOs of the chosen kind are then uniquely determined by the physical nature of the state of the system.

**Different orbital energies and orbital filling rules:** We can ask different well-specified questions concerning one-electron aspects of *N*-electron systems. For instance, what is the change of energy and of electron density, when we eliminate one unit of charge from an atom A with minimal reorganization? A simple or direct one-electron (vertical) ionization  $A^0 \rightarrow A^+$  does not necessarily yield the ground state of  $A^+$ . For instance, it is known from spectroscopy<sup>[22]</sup> that the adiabatic ionization of the vanadium atom to its cationic ground state is, already at the lowest order of approximation, a two-electron "shake down" process (4):



The direct vertical one-electron ionizations from 3d or 4s [Expression (5)], are higher in energy.



According to a theorem of Koopmans,<sup>[13]</sup> energies and densities of occupied eigen-orbitals  $\phi$  of an appropriately formulated, canonical effective one-electron Fock operator

are reasonable approximations for *vertical* ionization processes.

Whether  $d^{a+1}s^b$  and  $d^a s^{b+1}$  is the *ground configuration*, that is, has lower configuration average energy, can be approximately predicted by comparing the two direct ionization processes [Expression (6)] with the help of the *ab initio Fock (F) orbital energies*<sup>[32]</sup>  $-\varepsilon_d^F(d^{a+1}s^b)$  and  $-\varepsilon_s^F(d^a s^{b+1})$ .

$$d^{a+1}s^b \rightarrow d^a s^b \leftarrow d^a s^{b+1} \quad (6)$$

That is, the ground configuration can be predicted from the order of orbital energies of the *two different* configurations. The energies of an orbital are different for configurations with different occupation schemes, even if we choose the same average orbital functions for the two configurations. For instance, for an s-AO, Expression (7) applies, where  $G_{ij}$  means the average repulsion energy between two electrons in shells  $i$  and  $j$ .

$$\varepsilon_s^F(d^{a+1}s^b) - \varepsilon_s^F(d^a s^{b+1}) = G_{ds} - G_{ss} \quad (7)$$

It is well known in ligand field theory<sup>[8]</sup> that a higher energy orbital level becomes occupied even if a lower orbital is not yet full (e.g.  $d_{eg} > d_{t2g}$  in  $O_h$  symmetry) if the orbital energy difference is smaller than the difference of some electron repulsion integrals  $G_{ij}$ . At the level of the average orbital approximation with the same set of orbitals for the different states,  $d^a s^{b+1}$  is below  $d^{a+1}s^b$  even if  $\varepsilon_d^F < \varepsilon_s^F$  ( $\varepsilon_s^F - \varepsilon_d^F = \Delta\varepsilon^F > 0$ ), *provided* the inequalities (8) hold. There, two Fock orbital energies of the *same* configuration are compared to two electron interaction integrals  $G_{ij}$ :

$d^a s^{b+1}$  below  $d^{a+1}s^b$ , if

$$\Delta\varepsilon^F(d^{a+1}s^b) < \delta G = G_{ds} - G_{ss} \quad (8a)$$

or

$$\Delta\varepsilon(d^a s^b) < \delta G + \Delta G = G_{dd} - G_{ss} \quad (8b)$$

or

$$\Delta\varepsilon(d^a s^{b+1}) < \Delta G = G_{dd} - G_{ds} \quad (8c)$$

A theorem by Janak<sup>[14]</sup> states that a simpler form of the Aufbau rule applies to *Kohn–Sham (KS) density functional orbital energies*.<sup>[34]</sup> Neglecting some details of the exchange functional and again using average orbitals, the ground configuration is given by (9), for:

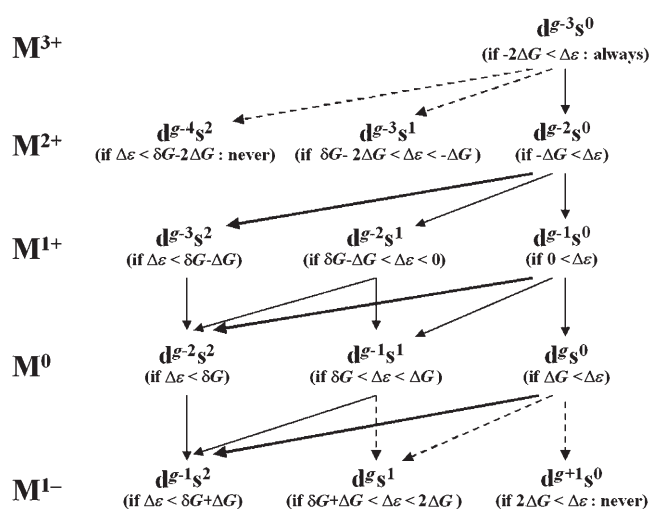
$$d^a s^0, \text{ if } \Delta\varepsilon^{KS}(d^a s^0) < 0 \quad (9a)$$

$$d^{a-1} s^1, \text{ if } \Delta\varepsilon^{KS}(d^{a-1} s^1) \approx 0 \quad (9b)$$

$$d^{a-2} s^2, \text{ if } \Delta\varepsilon^{KS}(d^{a-2} s^2) > 0 \quad (9c)$$

To be correct for the intermediate case, the fractional occupation number (FON) density functional formalism should be applied<sup>[15]</sup> yielding fractional s-occupations  $y$  between 0 and 2, with  $\Delta\varepsilon^{KS}(d^{a-y}s^y) = 0$ . Comparison of Equations (8) and (9) shows that the Fock orbital energies (describing ionization potentials) are in general more negative, and the orbital energy gaps are larger, than the Kohn–Sham ones (describing occupation schemes).<sup>[34]</sup> Since the  $nd$  shell is spatially more compact than the  $(n+1)s$  shell, the terms  $\delta G$  and  $\Delta G$  are positive. For case studies see the Appendix.

From rules (8,9) follow the possible ground configurations of transition-metal atoms  $M$  and their ions  $M^q$  (Scheme 3).



Scheme 3. Possible relations of *lowest* configuration energy averages of transition-metal atoms  $M^q$ , and ions  $M^q$ , at the average orbital level of the *ab initio* Fock orbital approach.  $\Delta\varepsilon = \varepsilon_s - \varepsilon_d$  refers to configuration  $d^{g-q-1}s^1$ ;  $G_{ss} < G_{ds}$ ,  $0 < \delta G = G_{ds} - G_{ss} < \Delta G = G_{dd} - G_{ds}$ . Cases with dashed arrow do not occur because the required  $\Delta G/\Delta\varepsilon$  relations do not occur for  $M^q$ . For instance, most  $M^{q+}$  have  $d^{g-q}s^0$  and  $M^-$  have  $d^{g-1}s^2$ .<sup>[17]</sup> For cases with bold arrow, electronic  $d \rightarrow s$  reorganization occurs due to  $e-e$  repulsion, that is,  $d^{g-2} + e \rightarrow d^{g-3}s^2$  ( $Y^{2+} \rightarrow Y^+$ ),  $d^{g-1} + e \rightarrow d^{g-2}s^2$  ( $Cr^+ \rightarrow Cr^0$ ) or  $d^g + e \rightarrow d^{g-2}s^2$  ( $Pd^0 \rightarrow Pd^-$ ).<sup>[22]</sup> Compare also Table 4.

For the higher charged cations  $M^{q+}$ ,  $nd$  is significantly below  $(n+1)s$ . The ground configuration of  $M^{3+}$  is  $d^{g-3}s^0$ ,  $g$  being the group number.  $\Delta\varepsilon$  in Scheme 3 means the Fock orbital energy differences  $\varepsilon_s^F - \varepsilon_d^F$  of the middle configuration  $d^{g-q-1}s^1$  of  $M^q$ . In general  $0 < \Delta\varepsilon$  ( $s$  above  $d$ ) and  $0 < \delta G < \Delta G$  ( $d$  more compact than  $s$ ). The tendency to occupy  $s$  instead of  $d$ , although  $d < s$ , is due to the small interelectronic repulsions of diffuse  $s$  orbitals. A few authors stated that “ $3d$  is always below  $4s$ !”.<sup>[8,16]</sup> However, experiment and theory both yield  $nd$  below  $(n+1)s$  in most though not all cases (see below). In these discussions one must also distinguish the orbital energies of the *ab initio* Fock and of the Kohn–Sham density functional pictures.<sup>[34]</sup>

### 3. Actual Values of Orbital and Total Energies

Since many graphs in the textbooks are misleading, we here present graphs based on reliable numerical values of orbital and configuration energies. We analyze their dependence on nuclear charge  $Z$  and quantum numbers  $n, l$ , and on the configuration of the other electrons in the atom.

**Numerical details:** Neutral atoms were calculated with the relativistic ZORA approximation,<sup>[18,32]</sup> using the Slater–Vosko–Becke–Perdew<sup>[19]</sup> density functional approach and extended Slater type basis sets.<sup>[20]</sup> The Amsterdam code ADF was applied.<sup>[21]</sup> This yields *configuration average energies* within a few tenths of an eV, that is, more accurate than individual open shell  $LS$ - or  $J$ -level values. Experimental configuration average energies from atom spectroscopy data are more accurate,<sup>[22]</sup> but only in cases where all  $J$  levels of the configuration are available. However, this is not always the case, in particular not for the central and the lower regions of the periodic table. Here the experimental average energies must be estimated, for example, with the help of Slater–Condon rules,<sup>[23]</sup> and then they may also be in error by up to a few tenths of an eV.

If not explicitly mentioned, all calculations were performed at the relativistic level (R), either averaging over spin-orbit splittings (AR) or taking  $SO$  splittings explicitly into account (SR). In a few cases the error of the nonrelativistic approximation (NR) was estimated.

To average over different orbital couplings, spin-restricted (re) calculations were performed. The two spin-orbitals  $\phi_+$  ( $r, s$ ) and  $\phi_-$  ( $r, s$ ) of a Kramers pair, for which  $r$  and  $s$  are position and spin direction, respectively, are then chosen to have the same spatial part and be equally (fractionally) occupied:  $\phi_+ = \psi(r) \cdot \alpha(s)$  and  $\phi_- = \psi(r) \cdot \beta(s)$  in the nonrelativistic case with real  $\psi$ ;  $\phi_+ = \psi \cdot \alpha + \xi \cdot \beta$  and  $\phi_- = \xi^* \cdot \alpha - \psi^* \cdot \beta$  in the spin-mixed relativistic case with complex  $\psi, \xi$ . These configuration averages govern the *short-range* bonding interactions between open shell atoms. Alternatively one can perform spin-unrestricted (un) calculations with different orbitals for  $\phi_+$  and  $\phi_-$ , and preferentially occupying the lower  $\phi$ . These calculations yield (averages over) lower energy high-spin states, which govern the *long-range* tails of interatomic interaction curves.

Linear  $Z$ - $\epsilon$  scales are not appropriate for plotting orbital energies  $\epsilon$  for large ranges of  $Z$  values and quantum numbers  $n, l, j$ . Therefore logarithmic or square root scales have been used in the literature:  $\epsilon$  versus  $Z^2$ ;  $\pm(-\epsilon)^{\pm 1/2}$  versus  $Z$ ; or  $\ln(-\epsilon)$  versus  $\ln Z$ . However, it is rather common in textbooks not to specify the chosen scales, or to use irregular scales. In the nonrelativistic, hydrogen-like, nuclear point charge approximation,  $\epsilon = -Z^2/n^2 \cdot [0.5 \text{ a.u.}]$ , that is,  $n = Z/\sqrt{-\epsilon/\text{Ry}}$ , where  $1 \text{ Ry} = 1/2 \text{ a.u.} \approx 13.6 \text{ eV}$ . For electrons of neutral atoms at large nuclear distances, the effective nuclear charge  $Z_{\text{eff}} \rightarrow 1$ .

We here define  $n_{\text{eff}}(Z, n, l) = 1/\sqrt{-\epsilon(Z, n, l)/\text{Ry}}$  and plot  $n_{\text{eff}}$  versus  $Z$ . A higher effective nuclear attraction  $Z_{\text{eff}}$  of core-penetrating AOs is represented by a lower effective

quantum number  $n_{\text{eff}}$ . The famous Rydberg rule (10) for the series of higher orbital energies  $\epsilon_{nlj}$  of a (neutral) atom states that the quantum defect  $\delta_{lj} = n - n_{\text{eff}}(Z, n, l)$  is nearly independent of  $n$  for given  $Z$  and  $l$ .<sup>[24]</sup>

$$\epsilon_{nlj} = -1 \text{ Ry}/(n - \delta_{lj})^2 \quad (10)$$

**Atomic orbital shells of light atoms:** *Dirac–Fock orbital energies* approximating spectroscopic *vertical ionization energies* of configuration averages are plotted in Figure 1 in

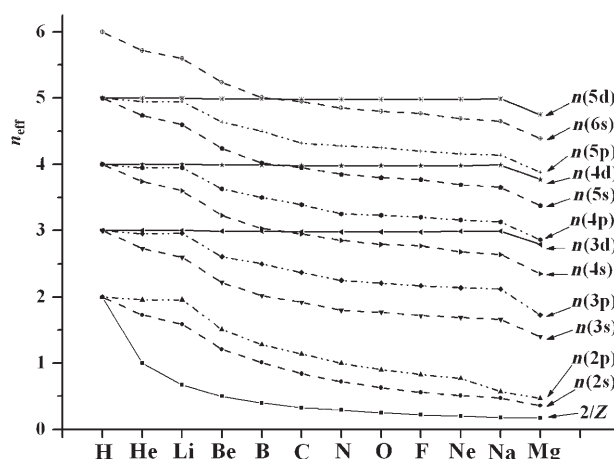


Figure 1. Experimental ionization energies or theoretical Dirac–Fock orbital energies<sup>[22,25]</sup> in terms of  $n_{\text{eff}} = 1/\sqrt{-\epsilon/\text{Ry}}$ , of neutral atoms with  $Z = 1$  to 12.  $1 \text{ Ry} = 0.5 \text{ a.u.} \approx 13.6 \text{ eV}$ . The lowest full line is for  $2sp$  in the unscreened hydrogen-like case,  $n_{\text{eff}} = 2/Z$ . (Differently shaped graphs in many scientific textbooks are due to artistic modifications of data.)

terms of  $n_{\text{eff}}$  for orbitals  $nl = 2s, 2p, \dots, 6s$  of the light neutral atoms H ( $Z = 1$ ) to Mg ( $Z = 12$ ).<sup>[22,25]</sup> An increase of nuclear charge with simultaneous filling of the inner  $1s, 2s, 2p$  shells hardly changes  $\epsilon$ ,  $n_{\text{eff}}$ , or  $Z_{\text{eff}}$  for outer AOs with *high* angular momentum  $l \geq 2$ . For penetrating AOs with *lower*  $l$ , the nuclear attraction becomes incompletely shielded, and  $\epsilon_s$  and  $\epsilon_p$  drop. The order of screening is  $s < p < d < f$ , as in Equation (2), corresponding to increasing quantum defect for decreasing  $l$ . Empirically  $\delta_l \approx a/(l+b)^k$  with parameters  $a, b, k$ . Around  $Z = 6$  (carbon), the  $(n+1)s$  drop below the  $nd$ , with  $(n+1) - \delta_s < n - \delta_d$  for all  $n = 3, 4, 5, \dots$ , in agreement with the Rydberg rule (10), though in contrast to typical textbook artwork. “ $nd$  is shifted above  $(n+1)s$ ” is also a somewhat misleading formulation.

The  $2s^2 2p^{g-2}, 2s^1 2p^{g-1}$  and  $2s^0 2p^g$  configuration average energies for the second row of the periodic table for group numbers  $g = 1$  (Li) to  $g = 7$  (F) are shown in Figure 2. The configuration energies vary smoothly, while the  $J$ -level splittings are somewhat irregular. The same holds for the first atomic ionization potentials (IPs) corresponding to  $J$  levels (Figure 3). The electronegativity values (EN), which govern the chemistry of the elements, show a more regular behavior. The irregular shape of the IP line changes when going down in the periodic table, because of increasing relativistic  $SO$  coupling (Figure 4).

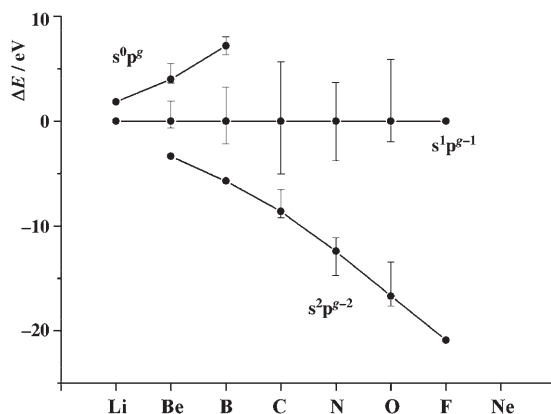


Figure 2. Relative experimental configurational energies  $\Delta E$  of second-row atoms [in eV]. Zero line is for  $s^1 p^{g-1}$ , upper line for  $p^g$ , lower line for  $s^2 p^{g-2}$ .  $g$  = Group number (Li: 1, F: 7). The vertical bars indicate the lowest and highest  $J$ -level energies. The bars are non-overlapping: configurational splittings are smaller than  $LS$  and  $SO$  splittings, in contrast to the transition-metal atoms (see Figure 8).

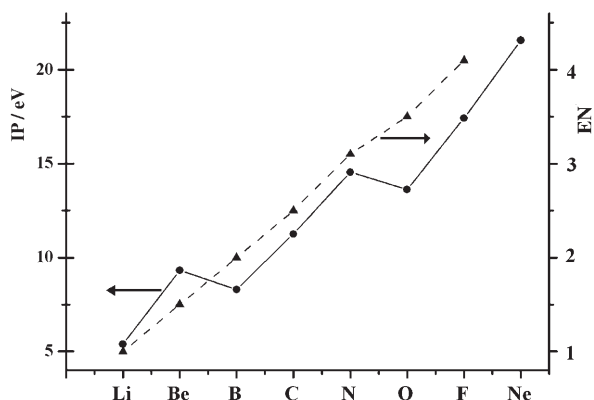


Figure 3. Experimental atomic IPs ( $\bullet$ , for  $J$  levels, left scale) and chemical electronegativities EN ( $\blacktriangle$ , dashed line, right scale) of second-row atoms. Note the IP maxima for Be  $s^2 1S_0$ , N  $p^3 4S_{3/2}$ , Ne  $p^6 1S_0$ .

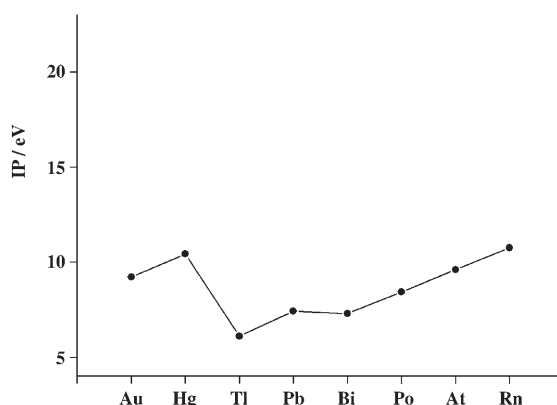


Figure 4. Experimental IPs ( $J$  levels) of sixth-row atoms  $A = \text{Au}$  to  $\text{Rn}$ . Compare with Figure 3 and note the IP maxima for Hg ( $s_{1/2}^2$ ) $^0$ , Pb ( $p_{1/2}^2$ ) $^0$ , Rn ( $p_{3/2}^4$ ) $^0$ . (The  $A \ell^k {}^s L_J$  nomenclature of light atoms must here be replaced by  $A (lj)^k J$ ).

**Variation of canonical Fock atomic orbital energies over the periodic table:** The canonical 3d, 4s, 4d, 5s orbital energies (corresponding to vertical IPs) from spectroscopic and/or Dirac-Fock data, of neutral atoms with “standard configuration”  $d^{g-2} s^2$ , are plotted in terms of  $n_{\text{eff}} = 1/\sqrt{-\epsilon/\text{Ry}}$  versus  $Z$  from 1 to 46 (Pd) in Figure 5. Two points are to be noted.

1) For small  $Z=1$  (H) to 5 or 6 (B,C), the orbitals are rather hydrogen-like with  $nd < (n+1)s$ . Then incomplete screening of s-AOs becomes so strong that  $(n+1)s < nd$  until  $Z=20$  (Ca) for  $n=3$ , until  $Z=38$  or 39 (Sr,Y) for  $n=4$ , and until  $Z=72$  (Hf) for  $n=5$ . The  $nd$  are particularly weakly bound for the alkali metal atoms ( $g=1$ ) at the beginning of the long rows.

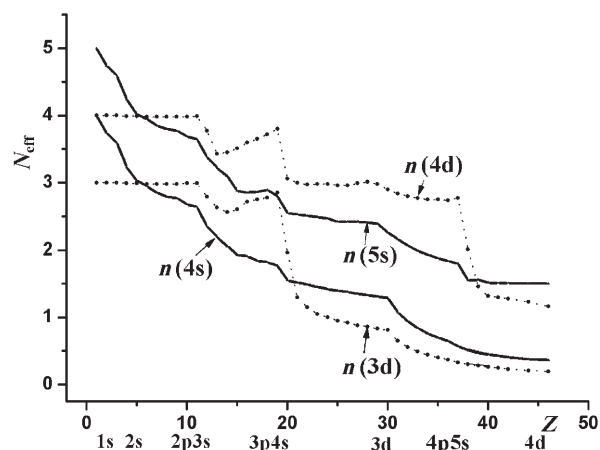


Figure 5. Effective quantum numbers  $n_{\text{eff}}$  of 3d, 4d (dotted lines) and 4s, 5s (full lines) from canonical Fock type orbitals of neutral atoms with  $Z=1-46$ . Below the  $Z$  values it is indicated which  $nl$  shells have been filled. Note the comparatively smooth variation of  $ns$ , and the sharp drops of  $nd$  at  $Z=11$  (Na), 19 (K), 37 (Rb), where inner and outer s-shells become occupied. Note the 3d maximum for K, with  $3d > 4s, 4p, 5s$ .

2) Incomplete screening of d-AOs develops, when overlapping or outer s-AO become occupied.<sup>[26]</sup> The d orbitals then shrink drastically, as shown in Figure 6. This is the so-called d-orbital collapse, known already for decades.<sup>[27]</sup> For all first-row transition metals from Sc onwards, the canonical 3d AO is again below 4s;  $4d < 5s$  for all second-row atoms from Zr onwards ( $\epsilon_d \approx \epsilon_s$  for Y); and  $5d < 6s$  for La and all third-row atoms from Ta onwards (i.e. except Lu; for Hf  $\epsilon_d \approx \epsilon_s$ ).

The overall behavior of orbital energies as displayed in Figure 5 is not new. For instance, Mazurs<sup>[28]</sup> plotted theoretical data of 1963.<sup>[29]</sup> Qualitatively correct plots can also be found in some of the textbooks.<sup>[4]</sup> Orbital energy plots show a more irregular behavior, if they refer to a series of configurations with different s populations.

**Variation of Kohn–Sham orbital energies of transition-metal atoms:** The energetic variation of Kohn–Sham density functional AOs is even more systematic (Figure 7). Compared to

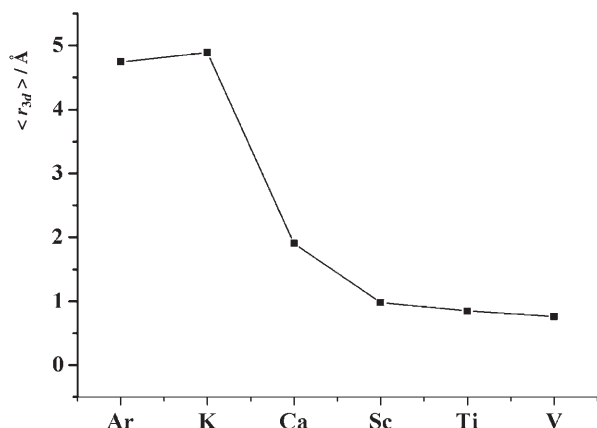


Figure 6. 3d orbital radii ( $\langle 3d | r | 3d \rangle$  in  $\text{\AA}$ ) of atoms Ar ( $Z=18$ ) to V ( $Z=23$ ).

the Fock AOs, the Kohn–Sham AOs of d-type are shifted upwards. While for the  $d^{g-2}s^2$  configurations of all neutral transition metal atoms,  $\varepsilon_{nd}^F < \varepsilon_{(n+1)s}^F$ ,  $\varepsilon_{(n+1)s}^{KS} < \varepsilon_{nd}^{KS}$  still holds in the Kohn–Sham picture for the early transition-metal atoms. On the other hand, for Rh and Pd at the end of the second row,  $\varepsilon_{nd}^{KS} < \varepsilon_{(n+1)s}^{KS}$  yields a populated d-shell with an empty s-shell for the lowest energy configuration. In the middle of the second row, configurations  $d^{g-2}s^2$ ,  $d^{g-1}s^1$  and  $d^g s^0$  are near in energy, with states of same  $LSJ$  symmetry showing strong configuration mixing.<sup>[22]</sup> This is represented by fractional  $s^v$  occupations, see the Appendix.

**Variation of configurational energies of the transition-metal atoms:** Configuration average energies (both, the ones determined from atom spectroscopic data,<sup>[22]</sup> and the ones from present relativistic density functional calculations) for the three configurations  $d^{g-2}s^2$ ,  $d^{g-1}s^1$ , and  $d^g s^0$  are displayed in Figure 8 and in the Appendix. The trends are quite regular as in the case of the main group elements. There is reasonable agreement between experiment and calculation, concerning both the trends and the energy variations. (Individual  $LS$ ,  $jj$ , or  $J$  energies are more difficult to obtain from quantum calculations than configuration averages). The resulting average ground configurations of the atoms are listed in Table 1. Experimental energies of the lowest  $J$  levels of the three configurations are displayed in Figure 9. They are somewhat irregular due to the large  $LSJ$  splittings. The configurations of the lowest  $J$  levels (listed in common periodic tables), of the lowest  $LS$  terms, of the lowest  $jj$  terms, and the lowest configuration averages are different in many cases (Table 2).

**Chemically interacting atoms:** An important aspect of *free transition-metal atoms* is the competition of compact  $nd$  and diffuse  $(n+1)s$  orbitals. Atoms in chemical compounds are surrounded by other atoms, in particular by *chemically bound atoms* at standard bond distances, and by weakly interacting atoms at van der Waals or so-called non-bonded reduced distances. Closed atomic core shells repel overlap-

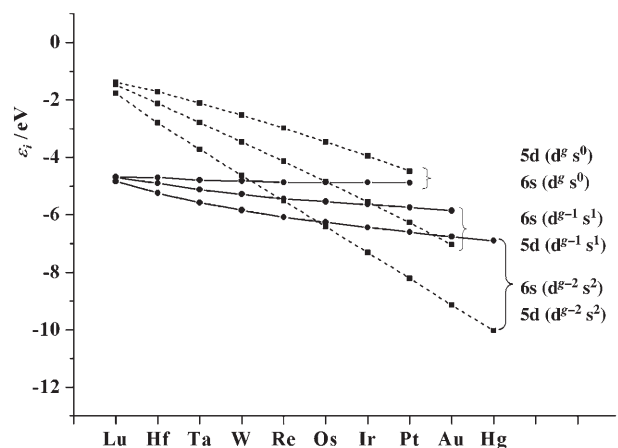
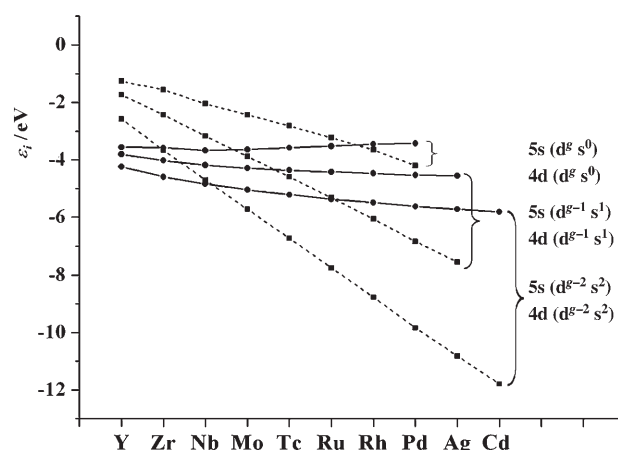
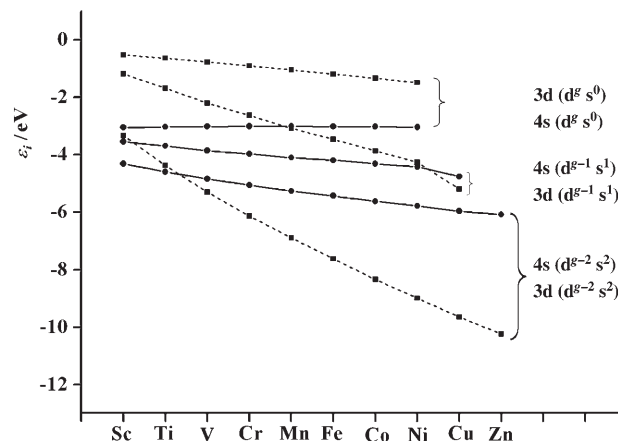


Figure 7. Kohn–Sham valence orbital energies of transition-metal atoms,  $\varepsilon_i$  (in eV), for  $nd$  (---) and  $(n+1)s$  (—) at the relativistic spin-averaged spin-restricted ZORA level: first row 3d,4s (top scheme), second row 4d,5s (middle), and third row 5d,6s (bottom), each for  $d^g s^0$  (upper lines),  $d^{g-1} s^1$  (middle) and  $d^{g-2} s^2$  configurations (lower lines).

ping orbitals of adjacent atoms according to the Pauli principle (corresponding to kinetic energy increase upon orbital orthogonalization). The diffuse  $(n+1)s$  AOs are thereby shifted energetically upwards, the more ligand atoms are surrounding the transition-metal atom.

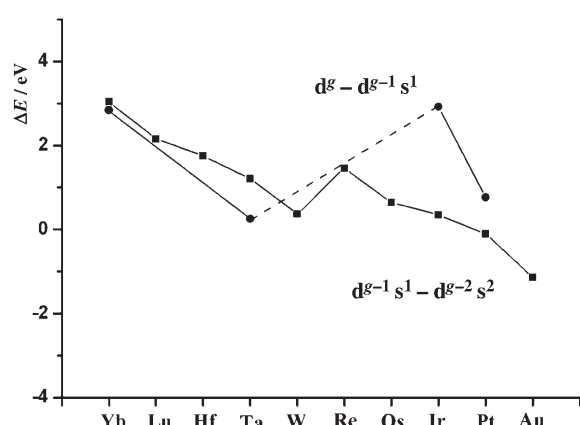
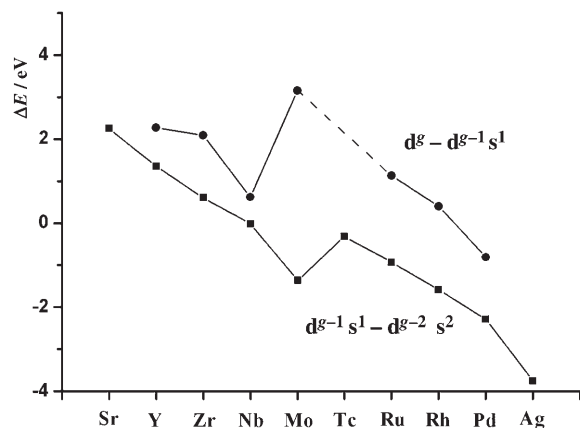
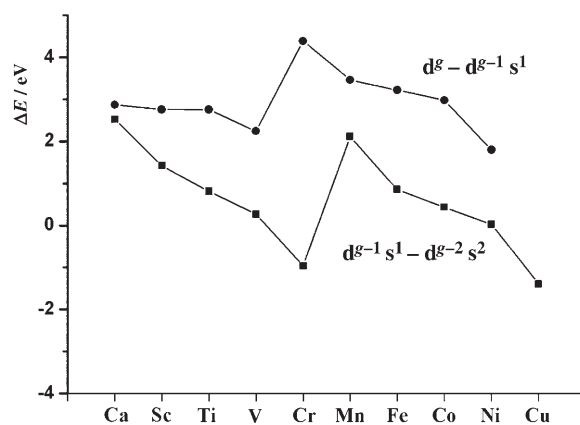
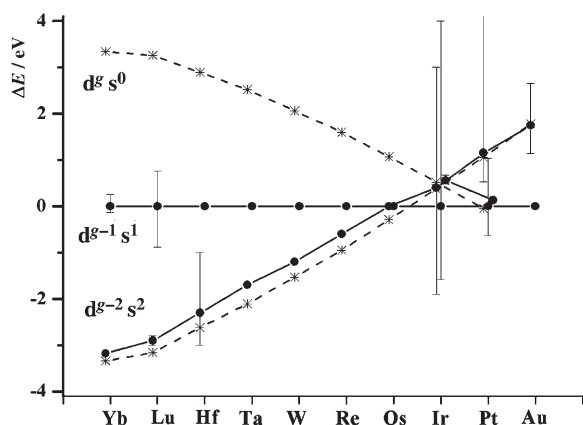
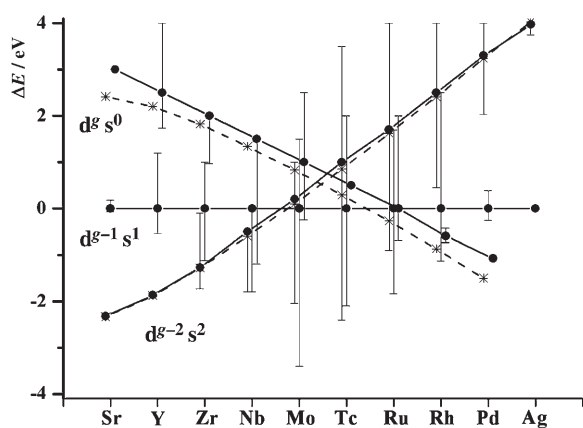
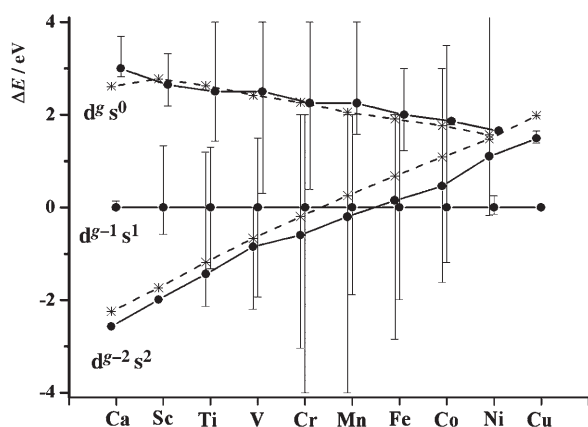


Figure 8. Configurational energy differences  $\Delta E$  of first- (top), second- (middle), and third-row transition-metal atoms (bottom), from density functional calculations (\*, dashed lines) and derived from experimental spectra ( $\bullet$ , full lines). Zero reference line is for  $d^{g-1}s^1$ , line decreasing in energy is for  $d^g s^0$ , line increasing in energy for  $d^{g-2}s^2$ ;  $g$  = Group number from 2 (Ca, Sr, Yb) to 11 (Cu, Ag, Au). Vertical bars indicate the lowest and highest experimental  $J$ -level energies. Due to the strong overlap of the bars, no simple rule holds for the configurations of the lowest  $J$ -levels. This is different from the main-group elements (Figure 2).

Figure 9. Experimental differences  $\Delta E$  of lowest  $J$  levels of  $d^{g-1}s - d^{g-2}s^2$  and of  $d^g - d^{g-1}s$  configurations of first-, second-, and third-row transition-metal atoms. Note the extrema due to particularly stable  $J$  levels for  $d^5$  and  $d^{10}$ , while the average configurations  $d^3$  and  $d^{10}$  are not particularly stable (see Figure 8).

Table 1. Lowest average  $d^{g-y}s^y$  ground configurations of free transition-metal atoms ( $g$  = Group number or number of valence electrons of the neutral atom).

Transition row	$d^{g-2}s^2$ config. for:	$d^{g-1}s^1$ config. for:	$d^g s^0$ config. for:
1st	$g=2-7$ (Ca–Mn)	$g=8-11$ (Fe–Cu)	–
2nd	$g=2-5$ (Sr–Nb)	$g=6-8, 11$ (Mo–Ru, Ag)	$g=9, 10$ (Rh, Pd)
3rd	$g=2-8$ (Ba–Os)	$g=8-11$ (Os–Au)	–

Figure 10 shows the gap between the higher  $(n+1)s$  and the lower (averaged)  $nd$  levels of a  $Mn^+$   $d^5 s^1$  ion, symmetrically surrounded by two ( $D_{\infty h}$ ), six ( $O_h$ ), and twelve ( $I_h$ ) closed shell He atoms at various interatomic separations  $R$  (Mn–He). At separations  $R < 3 \text{ \AA}$ , the diffuse 4s Rydberg AO becomes energetically raised,



Table 2. The number  $y$  of  $s$  electrons in different kinds of experimental ground configurations  $d^{x-y}s^y$  of transition-metal atoms, depending on which sets of states are averaged: whole configuration, lowest  $jj$  term (for 3rd row), lowest  $LS$  term, or lowest  $J$  level.

Group	5	6	6	7	8	8	9	9	9	10
row	2nd	1st	3rd	2nd	1st	3rd	1st	2nd	3rd	1st
atom	Nb	Cr	W	Tc	Fe	Os	Co	Rh	Ir	Ni
config.	2	2	2	1	1	1;2 <sup>[a]</sup>	1	0	1	1
$jj$ term			2			2			1	
$LS$ term	1	1	1	2	2	2	2	1	2	1
$J$ level	1	1	2	2	2	2	2	1	2	2

[a] Some experimental data for Os are missing, the estimated experimental configuration energies are comparable.

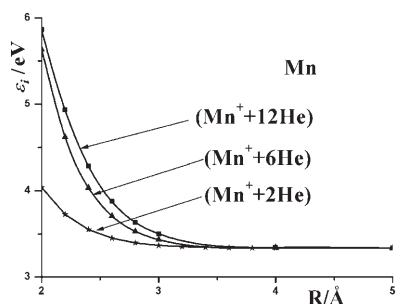


Figure 10. Energy gap  $\Delta\epsilon$  (in eV) between lower 3d average and upper 4s Kohn-Sham AOs of  $Mn^+ d^5s$ , symmetrically surrounded by 2, 6, and 12 He atoms, versus internuclear separation  $R(Mn-He)$  in Å.

while the 3d valence AO is significantly perturbed only for  $R < 2 \text{ \AA}$ . At  $R \approx 2 \text{ \AA}$  a compact ligand shell has increased the 3d–4s gap by about 2 eV. As a general rule, the  $(n+1)s$ -AO of coordinated transition-metal atoms is destabilized and therefore becomes less important for bonding at ordinary equilibrium bond lengths.

The relative raising of 4s had already been detected spectroscopically a long time ago.<sup>[31]</sup> Optical bands corresponding to 3d  $\rightarrow$  4s electronic excitations of divalent first-row cations in fluoride host crystals observed at 5.5 to 8.5 eV, were 0.3 to 0.6 eV higher than in the free cations. The 3d–4s gap of  $Cu^+$  in LiCl is raised even by 2.5 eV from 2.8 to 5.3 eV.

#### 4. Summary

To obtain a clear picture of chemistry, one must distinguish between concepts that are different. One must distinguish:

- between “basic” elements in chemical compounds, “simple” elemental materials, and completely atomized matter,
- between a free atom and a chemically perturbed atom in compounds and condensed phases,
- between the atomic configuration of the lowest Coulomb (direct and exchange) and spin-orbit split  $J$ -level and the chemically relevant configuration(s) of a low energy ensemble average,

- between Kohn–Sham density functional orbitals, fulfilling a simple Aufbau rule and describing the lowest experimental configuration averages, and canonical Fock orbitals, describing experimental vertical ionizations and obeying the more complex Aufbau rule known for low-spin/high-spin complexes,
- between the lowest adiabatic ionization potential, sometimes corresponding to a rearrangement of the cationic configuration, and the vertical direct one-electron orbital ionization, sometimes leading to an excited cationic configuration,
- between changes of orbital energies and orbital occupations from one neutral atom to the next one in the periodic system, and changes from one ion to the next one of the same atom.

The filling order of orbitals cannot be derived directly from orbital ionization energies, neither experimentally nor theoretically, because there is no general simple relation owing to possible orbital reorganizations. The values of any kind of orbital energies strongly depend on the ionic charge and on the orbital occupation scheme. For instance, the order of a given kind of  $nd$  and  $(n+1)s$  energies changes from  $d^{g-2}s^2$  to  $d^{g-1}s^1$  to  $d^g$ . The configuration of lowest average energy, that is, the ground configuration, is obtained by occupying the lowest energy Kohn–Sham orbitals; or equivalently by occupying the corresponding canonical Fock orbitals, which are not necessarily the lowest in energy. In the Fock picture, the order of total energies differs from the order of orbital energies by (direct and exchange) Coulomb energy differences  $\delta G$  or  $\Delta G$ .

Occupied inner  $s$ ,  $p$ ,  $d$ , and  $f$  shells exert different nuclear screening powers on  $s$ ,  $p$ ,  $d$ , and  $f$  valence orbitals. The order of orbitals varies quite regularly along the periodic table, as long as the same type of reference configurations are considered. Concerning theoretical Fock or experimental direct ionization energies, the  $(n+1)s$  are above the  $nd$  for  $Z < 5$  or 6. Then the  $(n+1)s$  drop below  $nd$ . However, after the respective rare gas atoms, the  $nd$  become also stabilized and contracted and suddenly collapse below the  $(n+1)s$  at the beginning of the transition rows: 3d at Sc, 4d at Zr, 5d at Hf. The hydrogen-like tendency of  $nd < (n+1)s$  is even more pronounced for transition-metal cations and for chemically bound atoms.

The ground states of free atoms are determined by the Coulomb and spin-orbit couplings of the open  $nl$  orbital shells. If one wants to explain the configurations of the lowest atomic states, one must do this at a highly sophisticated theoretical level, which is not appropriate in general chemistry. These typically atomic couplings are significantly damped by the intramolecular fields and are of little importance for most chemical phenomena. A chemically rather unimportant small spin-orbit energy shift by a few  $\text{kJ mol}^{-1}$  can result in a different atomic ground level and a different corresponding configuration, as for example, for Cr or Ni. Energetic near degeneracy of two different configurations is better described by fractional occupation schemes, which

change from atom to atom in small steps. This is in accord with the concept of partial occupations and partial charges of atoms and AOs in molecules. Average configuration energies vary quite smoothly over the periodic table and can be explained most easily and satisfactorily at the density functional orbital approximation.

So-called exceptions and irregularities occur in the periodic table, if one compares data of neighbor atoms referring to non-analogous configurations. Or if the data depend on couplings and nondynamic correlations specific for the free atoms. Parameters that have a more direct meaning for the chemical behavior of the elements, such as configuration average energies, electronegativities, or covalent, ionic and van der Waals radii, vary more regularly over the periodic table. Half filled shells are not particularly stable, but they give rise to a particularly low atomic  $LS$  term. The separation of different  $ns^y np^{g-y}$  configurations of main-group atoms is much larger than that of  $nd^{g-y} ns^y$  configurations of transition-metal atoms. Therefore, the order of configurational energies of main-group atoms does not depend on  $LS$ ,  $jj$ , and  $SO$  couplings and different state averagings, as in the case of the transition metal atoms.

All trends from the first- to the second- to the third-transition row are non-monotonous. This reflects the well-known “secondary periodicity”:<sup>[19–24]</sup> The first 3d-row is built on a  $3s^2 3p^6$  core, the second 4d-row on a  $3d^{10} 4s^2 4p^6$  core, and the third 5d-row on a  $4d^{10} 5s^2 5p^6 4f^{14}$  core. The insertion of the  $f^{14}$  shell not only causes the lanthanid contraction, also the relativistic effects increase strongly. That is because of the large increase of  $Z$  from the second to the third row and because relativity varies with a high power of  $Z$ .<sup>[33]</sup>

The stabilization of AOs by incomplete nuclear screening and the resulting deviations of the order of AOs from the hydrogenic order is reasonably described by the Rydberg “ $-1/l^2$ ” rule,  $n_{\text{eff}} = n - \delta_l$  with  $\delta_l \sim a/(l+b)^2$ . The popular Madelung  $n+l$  (“ $+l$ ”) rule has two defects: 1) the plus presumes a rise of  $d$  and  $f$  instead of the lowering of  $s$  and  $p$ , 2) squaric rules like  $n - a/(l+b)^2$  can simulate correct orders of AOs, but not a linear  $n+l$  rule.

## 5. Appendix

**Continuous variation of ground configurations:** For the early transition metals with  $nd^{g-2} (n+1)s^2$  ground configurations,  $\epsilon_{(n+1)s}^{\text{KS}} < \epsilon_{nd}^{\text{KS}}$  holds for the Kohn–Sham orbital energies. When  $Z$  increases and  $nd$  begins to drop again below  $(n+1)s$ , electronic charge flows from the diffuse  $(n+1)s$  into the more compact  $nd$ . At the density functional level one then obtains a fractionally occupied  $nd^{g-y} (n+1)s^y$  ground configuration corresponding to a mixed ensemble. This indicates strong configuration mixing of atomic states

(both in vacuum and in molecular environment).<sup>[15]</sup> As long as  $nd^{g-2} (n+1)s^2$  is the experimental atomic ground configuration average, the density functional  $s$ -population is 2 or a little smaller; for  $1.5 \geq y \geq 0.5$ , the experimental ground configuration is usually  $nd^{g-1} (n+1)s^1$ ; and for vanishing or small  $y$ , the ground configuration is  $nd^g$ . The respective  $s$  occupations, obtained from FON density functional calculations, and those derived from experimental atomic energies, are displayed in Figure 11 and Table 3. They agree reasonably well with each other and vary systematically over the three rows.

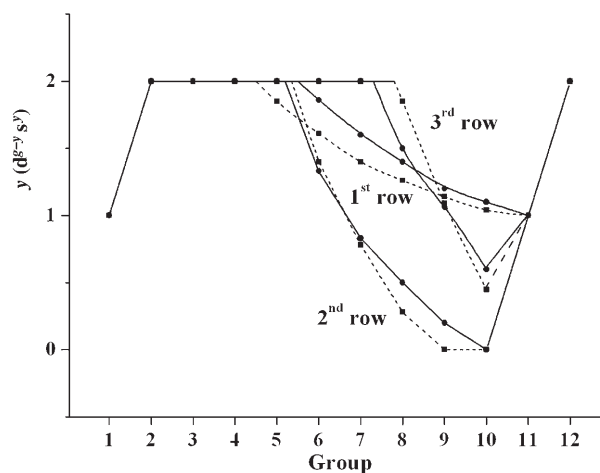


Figure 11. Fractional  $(n+1)s$ -AO population  $y$  of ground configuration  $d^{g-y}s^y$  of first-, second-, and third-row transition metal atoms. -----: FON density functional calculations ( $\epsilon_d = \epsilon_s$  for partially occupied  $s$ - $d$  shells); —: parabolic interpolation of experimental average configuration energies.

Table 3.  $(n+1)s$  occupancy of ground configuration averages of free transition-metal atoms from FON-DFT calculations ( $g$  = Group number = number of valence electrons of the neutral atom).

Transition row	$s^0$	$s^1$	$s^2$	“Fractionally” occupied $s$
1st	–	K, Cu ( $g=1, 11$ )	Ca to Ti, Zn ( $g=2-4, 12$ )	$V^{[a]}$ to Ni ( $g=5-10$ )
2nd	Rh <sup>[a]</sup> , Pd ( $g=9, 10$ )	Rb, Ag ( $g=1, 11$ )	Sr to Nb, Cd ( $g=2-5, 12$ )	Mo to Ru ( $g=6-10$ )
3rd	–	Cs, Au ( $g=1, 11$ )	Tm to Re, Hg ( $g=7-12$ )	Os, Ir <sup>[a]</sup> , Pt ( $g=8-10$ )

[a] The FON-DFT and experimental  $s$ -occupancies, respectively, are: for V 1.9 and 2.0; for Rh 0.0 and 0.2; for Ir near to 1.0.

### Order of ground configurations upon electron attachment:

It had been pointed out in Scheme 3 that configurational reorganization can be induced by adding electrons. The six possible cases of configurational sequences of transition-metal cations from  $M^{g+}$  to  $M^0$ , with explicit examples, are displayed in Table 4.

### Different orbital levels for different configurations and the Aufbau rule (example: Group 10):

In Figure 12 the Kohn–Sham spin-unrestricted orbital levels of  $d^{g-2}s^2$ ,  $d^{g-1}s^1$ , and  $d^g s^0$  configurations of the transition-metal atoms of Group 10 are shown. Five points may be noted.

- 1) The ground configuration of Ni(!) and Pt is  $d^9 s^1$ . In accordance with Janak’s simple Aufbau rule,<sup>[14]</sup> the lowest

Table 4. Six different filling orders of lowest configuration averages of some transition metal atoms M, derived from spectroscopic data.<sup>[22]</sup>

Atom	Lowest ionic configuration averages	Filling order	Case
Ca	$\text{Ca}^{2+} \rightarrow \text{Ca}^+ 4s \rightarrow \text{Ca}^0 4s^2$	+s+s	1
Sc <sup>[a]</sup>	$\text{Sc}^{3+} \rightarrow \text{Sc}^{2+} 3d \rightarrow \text{Sc}^+ 3d 4s \rightarrow \text{Sc}^0 3d 4s^2$	+d +s+s	2
Ti <sup>[a]</sup>	$\text{Ti}^{4+} \rightarrow \text{Ti}^{3+} 3d \rightarrow \text{Ti}^{2+} 3d^2 \rightarrow \text{Ti}^+ 3d^2 4s \rightarrow \text{Ti}^0 3d^2 4s^2$	+d+d +s+s	2
V	$\text{V}^{5+} \rightarrow \text{V}^{4+} 3d \rightarrow \text{V}^{3+} 3d^2 \rightarrow \text{V}^{2+} 3d^3 \rightarrow \text{V}^+ 3d^4 \rightarrow \text{V}^0 3d^3 4s^2$	+d+d+d+d + (2s-d)	3 <sup>[b]</sup>
Cr	$\text{Cr}^{6+} \rightarrow \text{Cr}^{5+} 3d \rightarrow \dots \rightarrow \text{Cr}^{2+} 3d^4 \rightarrow \text{Cr}^+ 3d^5 \rightarrow \text{Cr}^0 3d^4 4s^2$	+d+d+d+d+d + (2s-d)	3 <sup>[b]</sup>
Mn	$\text{Mn}^{7+} \rightarrow \text{Mn}^{6+} 3d \rightarrow \dots \rightarrow \text{Mn}^{2+} 3d^5 \rightarrow \text{Mn}^+ 3d^6 \rightarrow \text{Mn}^0 3d^4 4s^2$	+d+d+d+d+d+d + (2s-d)	3 <sup>[b]</sup>
Fe	$\text{Fe}^{8+} \rightarrow \text{Fe}^{7+} 3d \rightarrow \dots \rightarrow \text{Fe}^{2+} 3d^6 \rightarrow \text{Fe}^+ 3d^7 \rightarrow \text{Fe}^0 3d^7 4s$	+d+d+d+d+d +s	4
Co <sup>[c]</sup>	$\text{Co}^{9+} \rightarrow \text{Co}^{8+} 3d \rightarrow \dots \rightarrow \text{Co}^{2+} 3d^7 \rightarrow \text{Co}^+ 3d^8 \rightarrow \text{Co}^0 3d^8 4s$	+d+d+d+d+d+d +s	4
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	5 <sup>[d]</sup>
Rh	$\text{Rh}^{9+} \rightarrow \text{Rh}^{8+} 4d \rightarrow \dots \rightarrow \text{Rh}^{2+} 4d^7 \rightarrow \text{Rh}^+ 4d^8 \rightarrow \text{Rh}^0 4d^9$	+d+d+d+d+d+d +d	6

[a] Zn also belongs to case 2. [b] Configurational reorganization occurs upon adding an electron to  $\text{M}^+ d^{s-1}$ , yielding  $\text{M}^0 d^{s-2} s^2$ , although  $d < s$ . [c] Ni(!) and Cu, too, belong to case 4. [d] For Y, configurational reorganization upon adding an electron occurs already at  $\text{Y}^{2+}$ , and for  $\text{Y}^0 5s^2 4d$  we have the exceptional order  $s < d$ .

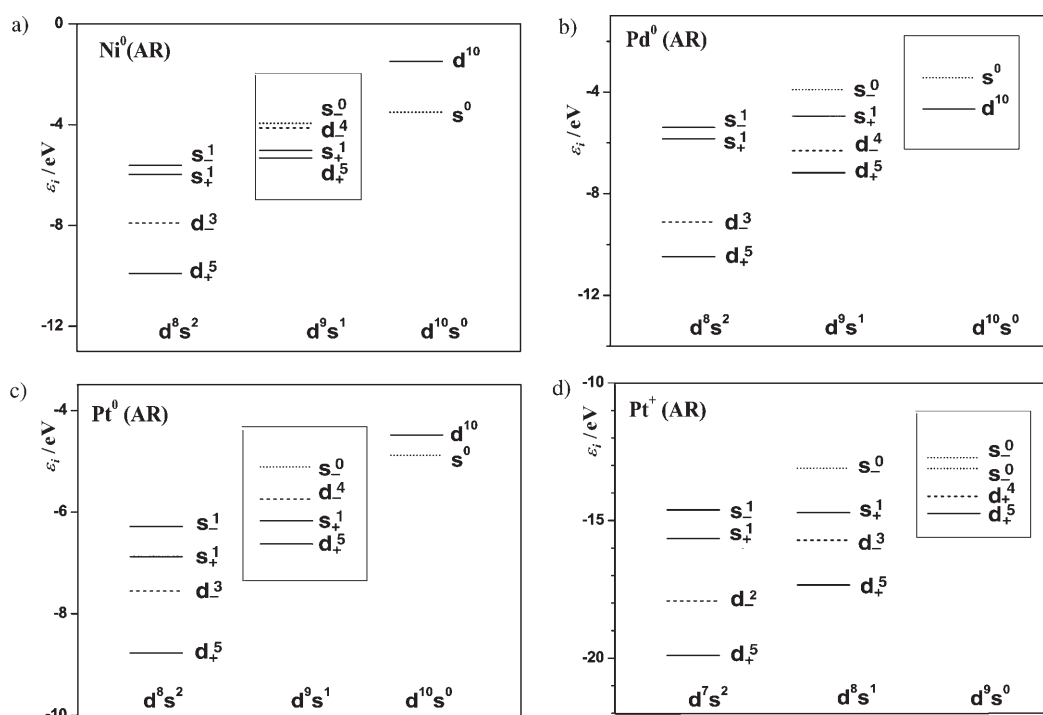


Figure 12.  $nd$ - and  $(n+1)s$ -AO energy levels  $\epsilon_i^{\text{KS}}$  (in eV) of Group 10 atoms, occupied ones (—), partially occupied ones (----), empty ones (.....), each for  $d^{s-2}s^2$ ,  $d^{s-1}s^1$ , and  $d^s s^0$  configurations, from spin-unrestricted  $SO$ -averaged relativistic (AR) density functional calculations: a)  $\text{Ni}^0$ , b)  $\text{Pd}^0$ , c)  $\text{Pt}^0$ , d)  $\text{Pt}^+$ . The ground configurations (in boxes) fulfill Janak's theorem.<sup>[14]</sup>

orbital levels are occupied, that is full  $d_+ < \text{full } s_+ < \text{partially occupied } d_- < \text{empty } s_-$ . For Ni  $3d^8 4s^2$  the partially occupied  $d_+^3$  is below the occupied  $s_+^1$  and  $s_-^1$ . Therefore  $3d^8 4s^2$  is *not* the ground configuration, in accordance with experimental energies, but is about  $100 \text{ kJ mol}^{-1}$  above  $3d^9 4s^1$ , and  $3d^{10}$  (with empty  $s$  below full  $d$ ) is even higher, see Figure 8. Why, then is  $3d^8 4s^2$  usually given for Ni?

- 2) Subtle and chemically irrelevant energy splittings must be considered to obtain the  $d^8 s^2 {}^3F_4$  ground level of Ni. First, the Coulomb exchange coupling of the compact  $3d$  hole with the diffuse  $4s$  of  $3d^9 4s^1$  is small, while the Coulomb coupling of the two compact  $3d$  holes of  $3d^8$  is large. Accordingly, the lowest  $LS$  term  ${}^3F$  of  $d^8 s^2$  is

strongly stabilized and is then *only*  $3 \text{ kJ mol}^{-1}$  above the lowest  $LS$  term  ${}^3D$  of  $d^9 s$  (lower ends of the vertical bars for Ni in Figure 8 are similar). Second, since the (small)  $SO$  splitting of  $d^8 {}^3F$  is also bigger than that of  $d^9 s {}^3D$ ,<sup>[23]</sup> the lowest  $J$  level  ${}^3F_4$  of  $d^8 s^2$  is finally  $2.5 \text{ kJ mol}^{-1}$  below the lowest  $J$  level  ${}^3D_3$  of  $d^9 s$ .

- 3) Due to the electron repulsions increasing from  $s$ - $s$  to  $d$ - $s$  to  $d$ - $d$ , the orbital energies rise from configuration  $d^{s-2} s^2$  to  $d^{s-1} s^1$  to  $d^s s^0$ , in particular the compact  $nd$  level (see also Figure 7). For instance,  $nd$  is above  $(n+1)s$  for the excited  $d^{10}$  configurations of Ni and Pt (Figure 12).
- 4) The trends from Ni to Pd to Pt are non-monotonous, as mentioned in the Summary. Owing to the large relativistic  $SO$  splittings, the collection of  $J$  levels into  $jj$  terms

(instead of *LS* terms) is more appropriate for Pt. The lowest *J* level of  $d^9s$  is ( $d_{5/2}s_{1/2}$ )  $J=3$ , and Pt  $d^8s^2$  ( $d_{5/2}^2$ )  $J=4$  is still  $10 \text{ kJ mol}^{-1}$  higher. At the level of the nonrelativistic approximation, a wrong ground configuration would result for Pt, namely  $d^{10}$ , as for Pd.

- 5) When the number of valence electrons is reduced, forming atomic cations, the compact *d* levels are more stabilized than the diffuse *s* levels. For singly ionized  $\text{Ni}^+$ ,  $\text{Pd}^+$  and  $\text{Pt}^+$ ,  $nd$  is already significantly below  $(n+1)s$ , and the *s*-AO remains empty throughout. The ground configurations of bound atoms  $A^{q+}$  are always  $d^{g-q}$ .

**Averages over different sets of *J* levels; fractional orbital occupations (example: Group 6):** Another interesting case is Group 6 (Figure 13), with the so-called exceptional configurations  $d^5s^1$  for Cr and Mo and a so-called regular  $d^4s^2$  one for W. Spin-restricted spin-averaged relativistic (re-AR) calculations yield configuration energies averaged over all states of the configuration. Spin-unrestricted (AR) and/or *SO* split (SR) calculations yield energy averages over specific selections of lower states.

For Cr, the lowest experimental average configuration energy corresponds to  $d^4s^2$  with 210 states in 34 *J* levels. The lowest  $d^4s^2$  *J* level  $^5D_0$  is stabilized by  $\sim 2.5 \text{ eV}$ . The  $d^5s^1$  average (504 states, 74 *J* levels) is  $\sim 0.66 \text{ eV}$  above the  $d^4s^2$  ground configuration. But its lowest *J* level  $d^5s^1 \ ^7S_3$  is split down by more than 4 eV and thus forms the ground level of Cr (see Figure 8 and Table 2). Since the two configurations  $d^4s^2$  and  $d^5s^1$  have similar energies for Cr (and also for the following atoms Mn and Fe), strong configuration mixing occurs for several states.<sup>[22]</sup> In such cases, the lowest energy from Kohn–Sham calculations is obtained for some inter-

mediate fractional occupation scheme,<sup>[15]</sup>  $d^{4.4}s^{1.6}$  for Cr. Quadratically interpolating the experimental configuration energies yields  $d^{4.2}s^{1.8}$  (Figure 11). Any integer occupation Scheme for Cr violates Janak's Aufbau rule (Figure 13a).

AR calculations of  $\text{Cr}(d_+)^4(s_+)^1(s_-)^1$ ,  $\text{Cr}(d_+)^5(s_+)^1$  and  $\text{Cr}(d_+)^5(d_-)^1$  yield averages of the low-energy *J* levels of Cr  $d^4s^2 \ ^5D_{0,1,2,3,4}$ , Cr  $d^5s^1 \ ^7S_3$ , and Cr  $d^6s^0 \ ^5D_{0,1,2,3,4}$ , respectively, that is, the lowest *LS*-term averages. Figure 13b shows that Cr  $d^5s^1$  fulfills the Aufbau rule, that is, the lowest *LS* term of Cr has configuration  $d^5s^1$ . The situation for Mo is similar.

Owing to the lanthanoid contraction and increased relativistic effects in the sixth row,  $d^4s^2$  is again the ground configuration of W, more than 1 eV below  $d^5s^1$  (Figure 8 and 13c). However, because of the larger *LS* and *SO* splittings of  $d^5s^1$ , the lowest terms or levels of  $d^5s^1$  and  $d^4s^2$  are near to each other. As in Ni, the lowest *J* level of W just 'accidentally' happens to correspond to  $s^2$ . The AP and SR calculations (Figure 13d and 13e) reproduce this situation.

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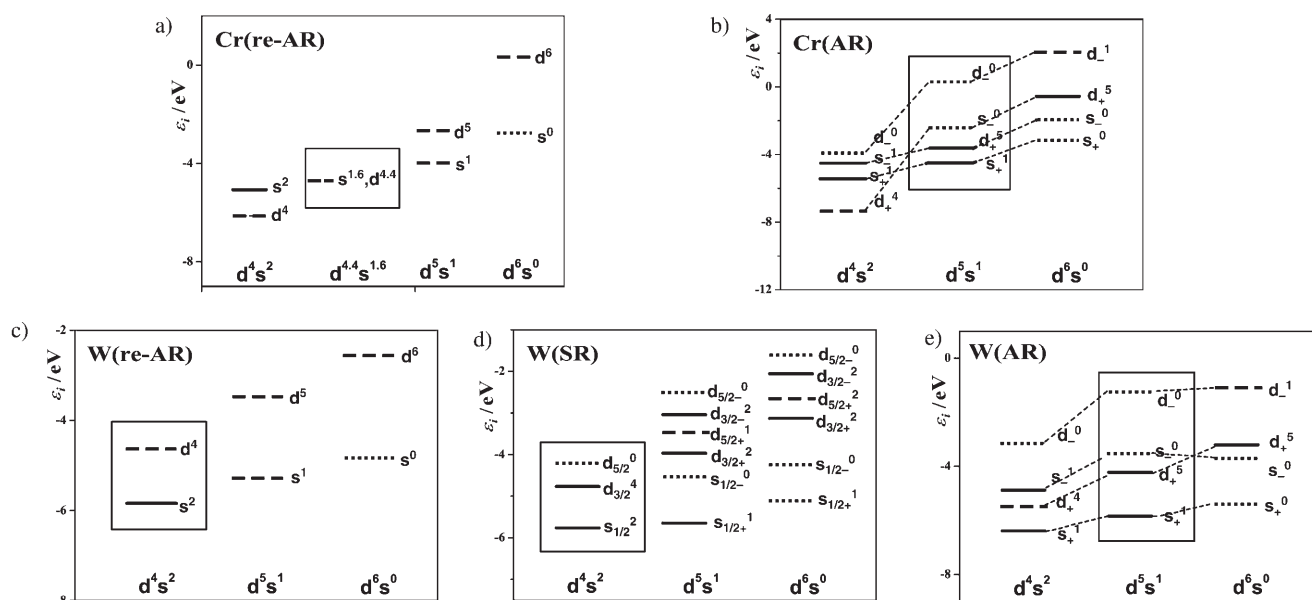


Figure 13. *nd*- and  $(n+1)s$ -AO energy levels  $\epsilon_i$  (in eV) of group 6 atoms Cr and W, occupied levels (—), partially occupied ones (-----), empty ones (.....), each for ground (in box) and excited configurations, from spin restricted (re) or unrestricted (—), spin averaged (A) or split (S) relativistic (R) density functional calculations.

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