

Transition Metals and the Aufbau Principle

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It is somewhat surprising that many qualitative discussions on the electronic structure of transition metal atoms do not cover the subject matter as correctly as one might expect on the basis of the available knowledge (1–3). Indeed, a number of comments in *this Journal*, as well as many textbooks contain certain misleading statements on the relative energy of 3d and 4s orbitals, and on the corresponding implications for the energy of the $3d^p4s^q$ configurations (4–10).

First of all, it should be stressed that the orbital energy problem—by its very nature—can only be discussed in the framework of approximate one-electron theories. In terms of the more exacting correlated wavefunctions (11–13), that are certainly in reach of present computational methods, the question partly loses its meaning. Nevertheless, as a first approach to the intricacies of the Aufbau-principle, it remains useful to take a global and more approximative view of the electronic structure of the transition metal series as a whole. From this perspective, Hartree–Fock theory appears to offer the safest way to proceed. Before doing so, however, two cautionary remarks should be made: 1. only the occupied orbitals should be included in a meaningful analysis of the orbital energies; the virtual orbitals of Hartree–Fock theory do not have a comparable physical interpretation; 2. because ultimately we are interested in the relative energy of the different configurations, we will discuss the Hartree–Fock solutions of *the average of each configuration*; the details describing the features of the individual multiplet states will not be taken into consideration.

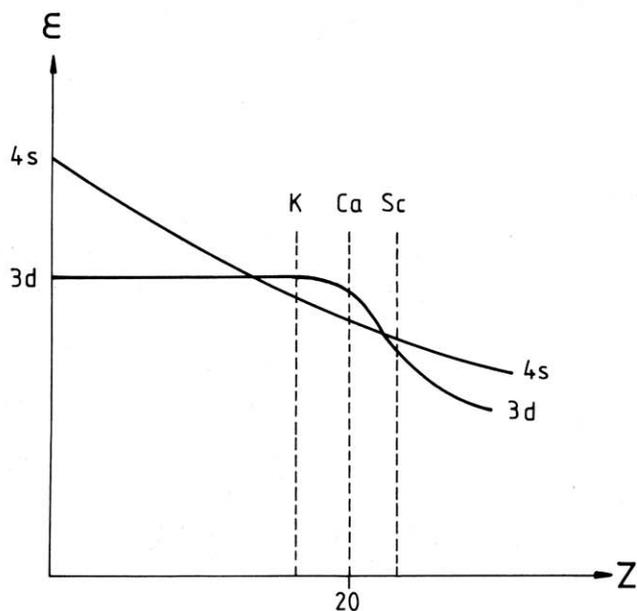


Figure 1. Schematic and partial orbital energy (ϵ)-diagram as a function of nuclear charge (Z) for the neutral atoms.

Orbital Energy Evolution

A diagram that seems to be central in many qualitative textbook discussions, is shown schematically in Figure 1. This diagram intends to show the evolution of the orbital energies ϵ_{4s} and ϵ_{3d} as a function of nuclear charge Z for the neutral atoms. Figure 1 is partly confirmed by Hartree–Fock calculations, carried out for the different atoms in their excited (...) $4s^1$ and (...) $3d^1$ configurations. The energy ϵ_{4s} decreases with increasing Z and drops below ϵ_{3d} already in the neighborhood of nitrogen ($Z = 7$). This phenomenon is reproduced—somewhat imperfectly—by Slater’s screening rules (14). For the 3d orbital, Slater’s rules prescribe $Z_{\text{eff}} = 1$ from H up to K ($Z = 19$) corresponding to the nearly constant ϵ_{3d} up to $Z = 19$: the inner shells are (almost) not penetrated by the 3d electron. For the 4s orbital, Slater’s rules prescribe $Z_{\text{eff}} = 1$ from H up to Ne ($Z = 10$) and a progressive increase of Z_{eff} from 1 to 2.2 between Ne and K. Obviously, the rules predict an ϵ_{4s} evolution that differs qualitatively from the Hartree–Fock results, in that they underestimate the penetration of 4s into the core. Yet, for K, Slater’s rules predict the correct result for the correct reason: 4s is well below 3d, because 4s is the better penetrator. Consequently, the K ground state has the $4s^1$ -configuration and the Ca ground state has the $4s^2$ configuration.

The problems start with scandium ($Z = 21$). The conventional textbook explanation goes as follows. Adding one more electron necessarily induces occupation of 3d, but at

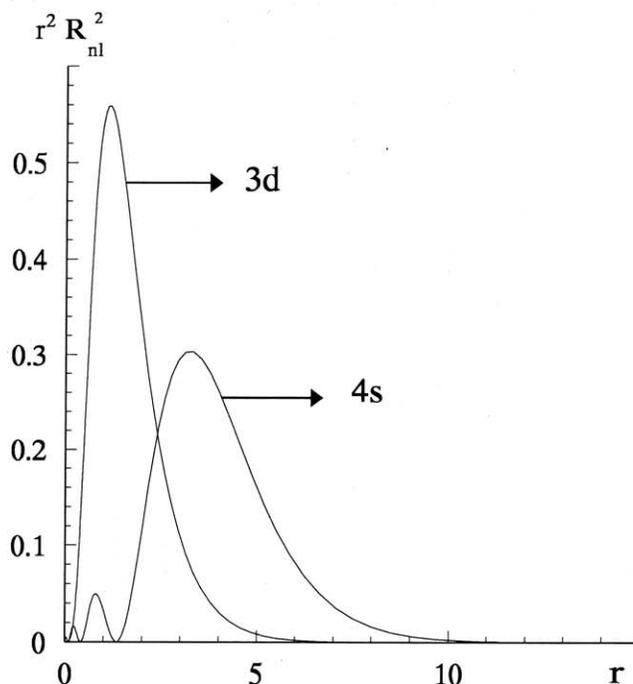


Figure 2. Probability density to find an electron at a given distance from the nucleus in a 3d, and a 4s orbital of the scandium atom (in the $4s^2 3d^1$ configuration); all quantities are in atomic units.

the same time 3d drops below 4s, the reason being found in Figure 2. Although the inner maxima of 4s are responsible for the strong penetrating power of this orbital, the maximum of 3d is closer to the nucleus than the outer maximum of 4s. Therefore, 3d feels the complete, nearly un-screened increase of Z by a full unit in going from K to Ca, and again from Ca to Sc. As a consequence, when we reach Sc, 3d is again below 4s, and it stays there for all the transition metals, being filled progressively with more electrons, as we move toward Cu and Zn. This is the evolution shown in Figure 1.

Although the above statements are basically correct, the question remains why scandium should maintain a ground state configuration of $4s^2 3d^1$. If $\epsilon_{4s} > \epsilon_{3d}$, shouldn't the ground state be $4s^0 3d^3$, obtained by dropping two electrons from the higher lying 4s into the lower 3d? The fact that 4s was "already" occupied in K and Ca, is utterly irrelevant to a scandium atom, that is characterized by its own increased values of Z and Z_{eff} , and by its own (reversed) orbital energy pattern.

The answer to the above question is not apparent from Figure 1. As a matter of fact, this diagram is inadequate to discuss the orbital energy evolution of transition metals. In the example of the scandium $4s^2 3d^1$ configuration, ϵ_{3d} is the energy of an electron moving in the field of the core and two 4s electrons. It is different from ϵ_{3d} in the $4s^1 3d^2$ configuration where it corresponds to the energy of an electron moving in the field of the core, one other 3d and one 4s electron. It is also different from ϵ_{3d} in the $3d^3$ configuration, where the valence surroundings of the electron in 3d consists of two other 3d-electrons. Similarly ϵ_{4s} is different in $4s^2 3d^1$ and in $4s^1 3d^2$ (we do not consider the virtual 4s orbital in $4s^0 3d^3$). Therefore, for Sc and all other transition metals, we have to discuss *five different orbital energies*, not just two as in Figure 1.

In general, for the $3d^p 4s^q$ configuration, it can be shown (3) that

$$\epsilon_{3d} = \omega_{3d} + (p-1)(3d,3d) + q(3d,4s) \quad (1)$$

and similarly

$$\epsilon_{4s} = \omega_{4s} + (q-1)(4s,4s) + p(3d,4s) \quad (2)$$

where ω is the effective one-electron energy of a valence (i.e., 3d or 4s) electron, moving in the average field of the core; (3d,3d) is the average repulsion of two electrons in the d shell; (3d,4s) is the average repulsion of one electron

¹It is interesting to realize that the configurational dependence of ϵ is, in fact, already suggested by Slater's simple rules. Indeed, for the neutral atoms, the rules predict

$$Z_{\text{eff}}(3d; 3d^p 4s^q) = 0.35 + (0.65)p + q$$

$$Z_{\text{eff}}(4s; 3d^p 4s^q) = 1.55 + (0.15)p + (0.65)q$$

From these equations a $4s \rightarrow 3d$ transition decreases Z_{eff} in both cases, suggesting an increase of both ϵ_{3d} and ϵ_{4s} – as in eq 5. It is true though that the equations for Z_{eff} are not able to reproduce the finer details of the orbital energy evolution; for instance, they suggest—incorrectly—that ϵ_{4s} is a more sensitive function of the 4s-population than ϵ_{3d} . Also, as a general rule, it does not appear to be a good idea to focus on Z_{eff} . Indeed, even in the cases where $Z_{\text{eff}}(3d) < Z_{\text{eff}}(4s)$, this inequality does not necessarily have direct implications for the relative energy of 3d and 4s, because both orbitals also differ in principal quantum number. As a matter of fact, discussions of Z_{eff} and the associated penetration effects are not nearly as illuminating for transition metals as they are for the neutral elements up to Ca (with $Z \leq 20$). Apart from the difficulties mentioned above, one also has to realize that there are other procedures to determine Z_{eff} , that do not always yield the same qualitative results as Slater's rules. See for instance Fischer, C. F. in *The Hartree-Fock Method for Atoms*; Wiley: New York, 1977.

in the d shell and one electron in the s shell; (4s,4s) is the (average) repulsion of two electrons in the s shell; $q = 0, 1$ or 2 in eq 1; whereas, $q = 1$ or 2 in eq 2. For a given number of valence electrons, $(p+q)$ is constant, and if we define

$$n = p + q - 2$$

the three relevant configurations can be designated as $3d^n 4s^2$, $3d^{n+1} 4s^1$ and $3d^{n+2} 4s^0$. The detailed evolution of the five orbital energies for the transition metals and their ions is discussed in reference 3. One of the main results from the numerical Hartree-Fock calculations is that—*within* one specified configuration—for any transition metal atom of the first series:

$$\epsilon_{4s} > \epsilon_{3d} \quad (3)$$

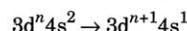
Much of the configurational problem now can be clarified by realizing that for scandium and the following elements, the 4s orbital is a much larger and more diffuse orbital than 3d. As a consequence two electrons distributed over the five 3d orbitals repel each other more strongly than two electrons in 4s. On the basis of numerical Hartree-Fock calculations, the following inequalities summarize the situation for any transition metal atom or ion in any configuration:

$$(4s,4s) < (4s,3d) < (3d,3d) \quad (4)$$

As a consequence of eqs 1, 2 and 4:

$$\begin{aligned} \epsilon_{3d}(3d^n 4s^2) < \epsilon_{3d}(3d^{n+1} 4s^1) < \epsilon_{3d}(3d^{n+2} 4s^0) \\ \epsilon_{4s}(3d^n 4s^2) < \epsilon_{4s}(3d^{n+1} 4s^1) \end{aligned} \quad (5)$$

The energies of *both* 4s and 3d are increasing functions of the 3d orbital population.¹ This is a somewhat unusual situation, especially for 4s, where the depopulation process



entails the replacement of one (4s,4s) interaction by one (4s,3d) interaction, thus leading to the rise of ϵ_{4s} , by virtue of eq 4.

Equations 3–5 summarize the essential points on the relative energy of the five relevant orbitals. Figure 3 shows that our basic inequality (eq 3) does not imply that "dropping" one or two 4s electrons into the 3d orbitals should necessarily lead to a global stabilization. Indeed, in agreement with eq 5, the $4s \rightarrow 3d$ transition entails a significant increase of the corresponding orbital energies. As a consequence, for nearly all the neutral atoms (except for Ni and

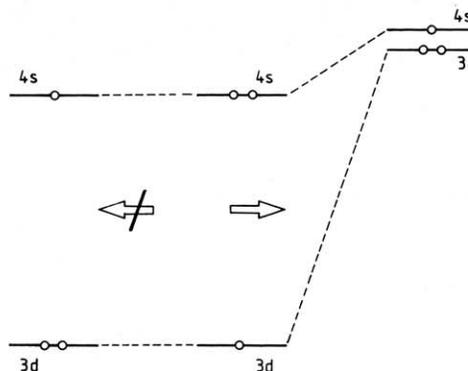


Figure 3. Schematic representation of the transition $3d^1 4s^2 \rightarrow 3d^2 4s^1$ in scandium. The left-hand side shows a hypothetical process, where $4s \rightarrow 3d$ transition is depicted as if the orbital energy were not a function of the occupation numbers. The right-hand side shows the result of an actual Hartree-Fock calculation: the conceivable energy gain accompanying the $4s \rightarrow 3d$ drop is more than offset by the increase in energy of the 3d and 4s orbitals.

Cu), the Hartree-Fock ground state configuration turns out (1, 3) to be $3d^n 4s^2$.

In order to place this remark into proper perspective, it is well to stress that the transition energy represented schematically in Figure 3 is, of course, not simply related to the sum of the orbital energies; its calculation requires the full formalism of the Hartree-Fock procedure for configuration averages. It can be shown (3) that to a good approximation

$$\Delta E_{av}(4s \rightarrow 3d) \cong (\epsilon_{3d} - \epsilon_{4s}) + [(3d,3d) - (3d,4s)] \quad (6)$$

where ΔE_{av} is the total energy difference between the two configuration averages, involved in the $4s \rightarrow 3d$ orbital transition, and where the quantities at the right-hand side of the equation refer to the $3d^{n-1} 4s^1$ configuration. Equation 6 shows that the $4s \rightarrow 3d$ transition can be an energy-demanding process, even if $\epsilon_{3d} - \epsilon_{4s} < 0$ (eq 3). Indeed, the term in square brackets is positive because of eq 4 and turns out to be the dominant term for the neutral metal atoms. Although Figure 3 does not reveal the details of eq 6, it captures the essence of the phenomenon: the increased valence repulsion is responsible for the fact that an otherwise favorable orbital transition does not take place.

Orbital Energies in Transition Metal Ions

In order to rationalize the electronic structure of the ions, one often simply refers (again) to Figure 1. Because 4s is the highest occupied orbital, it is supposed to be reasonable to expect that ionization takes place from 4s. This is a correct conclusion on the basis of the wrong reason. Indeed, if it were obvious that the higher lying 4s is depopulated upon ionization, wouldn't it be equally obvious that 4s should be depopulated in the neutral atom by releasing electrons into the lower lying 3d? Yet, from the previous section we know that this does not happen. The same problem can be rephrased alternatively by asking why the greater stability of $3d^n 4s^2$ (with respect to $3d^{n+1} 4s^1$) in a given atom should not lead to a larger stability of $3d^{n-1} 4s^2$ (with respect to $3d^n 4s^1$) for the corresponding ions.

For all transition metal ions, 4s is above 3d (eq 1 remains valid), but the effective nuclear charge has increased significantly, both for 4s and 3d. As a consequence, the stabilization energy of both orbitals, as well as their energy difference, increases considerably. Indeed, all these quantities are roughly proportional to Z_{eff}^2 . The corresponding energy diagram is shown schematically in Figure 4. If the orbital energy difference

$$\Delta\epsilon = \epsilon_{4s} - \epsilon_{3d}$$

reaches a critical threshold value, which from eq 6 is seen to be equal to $[(3d,3d) - (3d,4s)]$, dropping one or two electrons from 4s into 3d eventually does become favorable (3). Numerical calculations show that this turns out to be the case for *all* transition metal ions. The increased valence repulsion, accompanying the 3d population is no longer sufficient to keep the electrons in 4s.

Conclusion

The present paper shows why the ground state configuration of the neutral transition metals is in most cases $3d^n 4s^2$, and why the ground state configuration of the corresponding ions is obtained by preferentially removing the 4s electrons. It does so by introducing the five relevant orbital energies of 3d and 4s. We show that for the neutral atoms, the population of 4s is necessary to keep the energy

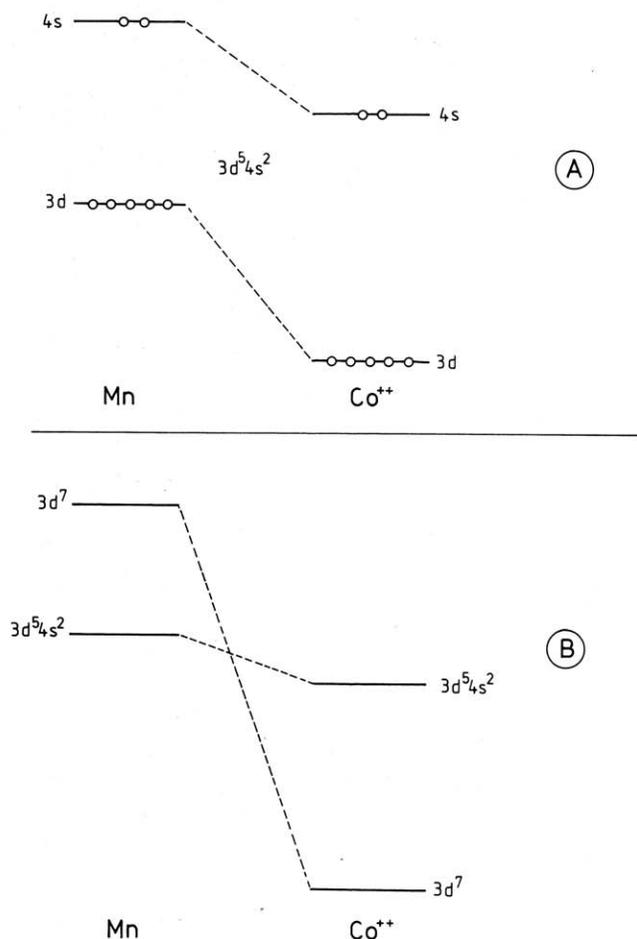


Figure 4. (A) Comparison of the 3d and 4s orbitals in the $3d^5 4s^2$ configuration of Mn (left) and Co^{2+} (right). (B) Inversion of the configuration energies of $3d^5 4s^2$ and $3d^7$ between Mn (left) and Co^{2+} (right).

of 4s and 3d as low as possible. For the ions, $\epsilon_{4s} - \epsilon_{3d}$ becomes so large that the 4s-depopulation becomes favorable *in spite* of the increase of both ϵ_{3d} and ϵ_{4s} .

In this paper, we only consider configuration averages, not the individual states. More specifically, we do not explicitly consider Hund's rules. The fact that for instance in Cr the ground state is a 7S state, corresponding to the $3d^5 4s^1$ configuration, is perfectly compatible with $3d^4 4s^2$ being the lowest average energy configuration—as predicted by Hartree-Fock theory.

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