

Why the 4s Orbital Is Occupied before the 3d

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An electron becomes less tightly bound when transferred from the 4s orbital of a ground-state configuration to a vacancy in the 3d shell—despite the fact that, in the ground-state configuration, the 3d electrons are more tightly bound than the 4s electrons.

In relating the periodic table to the electron configurations of the elements, a well-known problem of explanation arises in the first transitional series. The atoms of the first transition have, according to atomic spectroscopy, the general ground-state configuration $\text{Ar}(4s)^2(3d)^n$, with the exceptions of chromium and copper, which adopt $\text{Ar}(4s)(3d)^{n+1}$. The corresponding dipositive ions all have the general configuration $\text{Ar}(3d)^n$, which suggests that the 3d electrons are more tightly bound in the atom than the 4s. The problem is how, or indeed whether, one can explain both the preferential occupation of the 4s orbital and its preferential ionization using the same concept of orbital energy.

Koopmans' Theorem and the Definition of Orbital Energy

The problem largely disappears when orbital energies are consistently defined through Koopmans' theorem, not only in the ground-state configuration but in any alternative configuration as well. It then becomes possible to express the difference between the total energies of two configurations as a difference between orbital energies. This is an important conclusion of the work (1, 2) of Vanquickenborne, Pierloot, and Devoghel (VPD). We reach the same conclusion in this paper, which we prepared unaware of ref 2. Our derivations are more detailed and more elementary than those of VPD, and therefore may be more accessible to the nonspecialist. The wavefunctions used are different, so the numerical results may prove an interesting comparison. In agreement with VPD, we find that an explanation of the preferential occupation of 4s originally given in *this Journal* (3) is unsound.

The Aufbau Scheme, Ionization Data, and SCF Calculations

First, it is necessary to dispose of the notion, still found in many textbooks at the general undergraduate level, that the order in which the orbitals are filled in ground-state configurations is directly determined by orbital energies. Apart from failing to account for the configurations of chromium and copper, which do not conform to a simple Aufbau scheme, the main objection to this approach is its lack of plausible explanation of the ionization data. In 1978 Pilar (3) advocated a diametrically opposed point of view in *this Journal*.

It is the ionization data that are directly explained by orbital energies, if one accepts the Self-Consistent Field (SCF) model of atomic structure. In SCF theory an orbital energy ϵ_i corresponds to the energy that an atom would lose if the orbital ϕ_i lost an electron while all the other orbitals remained "frozen". This result is known as Koopmans' theorem and suggests that the quantity $-\epsilon_i$ will approximate to an ionization energy. Agreement between $-\epsilon_i$

and experimental ionization energies is generally fair, but because there are cases where this is not so, we shall call $-\epsilon_i$ a "Koopmans ionization energy".

SCF calculations have shown that the 3d orbital energy, ϵ_d , is below the 4s orbital energy, ϵ_s , in all configurations where both orbitals are occupied. The same calculations show that the configuration of lowest total energy for a transition element always contains at least one 4s electron. This is not a paradox in SCF theory, but it is a puzzle that requires some explanation.

Determining the Ground-State Configuration

How does the SCF method determine several configurations, and not just the configuration where the partially filled orbitals have the same highest energy? The SCF method is a variational method and, as such, it determines approximate wavefunctions for ground states of specified symmetry or, for an atomic system, of specified angular momentum. The wavefunction for an electron configuration may be represented by an antisymmetrized product of atomic orbitals whose angular parts correspond to specific values of the l quantum number. The total energy of such a wavefunction is then minimized with respect to variations in the radial parts of the atomic orbitals. After each iteration of the variational process, a new set of orbitals emerges, with orbital energies given by the eigenvalues of an effective one-electron Hamiltonian.

Before each subsequent iteration, the orbitals are placed in groups of specific l quantum number and electrons are assigned preferentially to the lowest eigenvalues in each group. However, the distribution is subject to the restriction that the number of electrons with a given l value must correspond to the configuration whose total energy is being minimized. Thus, the occupation numbers need not be the same as those obtained if all the orbitals were filled according to their relative energies, subject only to the Pauli restriction. Several configurations with different values of the total angular-momentum quantum numbers may be determined in this way, and the overall ground-state configuration is identified as the one with the overall lowest total energy.

The "Frozen Orbital" Approximation for Excited Configurations

Although the SCF total energy is the quantitative discriminant of a ground-state configuration,¹ students would appreciate a qualitative explanation as to why the transfer of electron(s) from 4s to 3d can produce a less stable con-

¹Even the best SCF calculations do not always agree with the spectroscopic assignment of the ground-state configuration because correlation-energy differences may be of the same magnitude as total-energy differences and of opposite sign.

figuration for a transition element. Instead of representing each configuration by its own SCF wavefunction, we shall use the (variationally inferior) "frozen-orbital" approximation, in which the SCF orbitals from one particular configuration are used to construct wavefunctions for some other configurations.

Techniques for calculating the total energies of a selection of configurations, each derived from a "parental" SCF configuration, are well-known² in quantum chemistry. Recently Nelson (4) used these methods to investigate the relative stabilities of configurations of a transition element. Nelson deduced an expression for the difference ($E_z - E_x$) between the total energies of the Ar(3d)³ configuration (Z) and the Ar(4s)²(3d) configuration (X) of scandium, in terms of SCF orbital energies in the X configuration. He finds that ($E_z - E_x$) is $2(\epsilon_d - \epsilon_s)$ plus certain Coulomb and exchange repulsion integrals involving the 4s and 3d orbitals. According to data from Mann (5), the additional terms make a positive contribution that exceeds $2|\epsilon_d - \epsilon_s|$, and this confirms that the Ar(4s)²3d configuration is lower.

Differences between SCF Orbital Energies

Nelson's paper also makes the important point that the SCF definition of orbital energy is not the only one; there are other formulations in which the 4s orbital energy is actually below 3d. Nevertheless, because SCF orbital energies are so useful in explaining ionization data, one would like to know why differences between SCF orbital energies do not correctly indicate the relative stabilities of different configurations. In other words, one would like to know the source of the "additional" Coulomb and exchange repulsions.

This is not transparent from Nelson's paper. Pilar (3, 6) earlier suggested that the answer lies in the fact that the sum of the orbital energies is not equal to the total energy, and he implied that the additional terms originate in the double-counting of electron repulsions that occurs when orbital energies are summed. We shall show in the next section that, by itself, the "double-counting" explanation is unsound and leads to an incorrect assessment of total energy differences unless another factor is first taken into account: Orbital energies change when configurations change.

Redefining Orbital Energy for Each New Configuration

Orbital energies defined by the SCF equations for one configuration do not correspond to binding energies (i.e., ionization energies) in a different configuration. A more consistent approach would be to redefine the orbital energy for a given orbital in each new configuration so that the correspondence with an "orbital ionization energy" is maintained. Our term "orbital ionization energy" involves formally the same interactions as a "Koopmans ionization energy", but the orbitals have not been optimized by an SCF calculation on the configuration under discussion.

When the energy of each orbital corresponds to a binding energy in each new configuration, it turns out that the number of additional terms in the expression for the difference in total energy between two configurations is reduced. Indeed, where the two configurations differ in the assignment of one electron only, we shall show that the additional terms can be made to vanish altogether. Thus, the difference ($E_y - E_x$) between the total energies of the Ar(4s)(3d)ⁿ⁺¹ configuration (Y) and the Ar(4s)²(3d)ⁿ configuration (X) is not ($\epsilon_d - \epsilon_s$) where ϵ_d and ϵ_s are SCF orbital energies of configuration X. However, it can be expressed as ($\epsilon'_d - \epsilon_s$), where $-\epsilon'_d$ is an orbital ionization energy in

configuration Y, calculated using the SCF orbitals of configuration X.

Sets of Orbital Energies for Configurations

The need to relate orbital energies in excited configurations to ionization energies in excited states was noted by one advanced text of inorganic chemistry (7), but most textbooks talk of orbital energies as if there were only one set for all configurations. The simple proposal, that 4s is doubly occupied when $\epsilon_s < \epsilon'_d$, avoids the confusion that has come from discussing the relative stability of two configurations in terms of the orbital energies of the same configuration. Specifically, it avoids the suggestion, implicit in some accounts, that a less (or more) stable configuration can sometimes be obtained by transferring an electron from one orbital to another orbital where it will be more (or less) tightly bound. This simply cannot happen while the rest of the orbitals remain the same.

Total Energies and Orbital Energies

In general there are several atomic wavefunctions that arise from an electronic configuration, each corresponding to definite values of the L and S quantum numbers. For simplicity we shall consider only one wavefunction for each configuration, and that wavefunction will correspond to the largest M_L quantum number that is compatible with the largest M_S . In such a case the wavefunction Ψ consists of a single determinant where the singly occupied orbitals all have the same spin factor.

$$\Psi = [(\phi_1)^2(\phi_2)^2 \dots (\phi_k)^2 \phi_m \dots \phi_n] \quad (1)$$

Our notation implies, for example, that

$$[(\phi_k)^2 \phi_m] = \frac{|\phi_k(1) \bar{\phi}_k(1) \phi_m(1)|}{|\phi_k(2) \bar{\phi}_k(2) \phi_m(2)|} (3!)^{-1/2} \quad (1A)$$

where $\bar{\phi}_k$ has spin quantum number $m_s = -1/2$; and ϕ_k has $m_s = 1/2$.

Use of the Expectation Value

For the Ψ function given by eq 1 the expectation value of the total energy E may be expressed in the form

$$E = \sum_i v_i H_i + \frac{1}{2} \sum_i \sum_j v_i v_j (a_{ij} J_{ij} - b_{ij} K_{ij}) \quad (2)$$

where H_i is the sum of the kinetic energy and the bare nuclear attraction energy of an electron in orbital ϕ_i ; and J_{ij} and K_{ij} are the Coulomb and exchange repulsion integrals between orbitals ϕ_i and ϕ_j , defined in the usual way (8).

The coefficients a_{ij} and b_{ij} are equal to 1 and 1/2 when either v_i or v_j is 2; and a_{ij} and b_{ij} are both 1 when v_i and v_j are both 1. Where several orbitals have the same n and l quantum numbers (e.g., the 3d orbitals) the total Coulomb-exchange interaction between these orbitals is averaged over all of them, so that each electron in the shell is subject to the same repulsions regardless of the m_l quantum number.

The optimum forms of the orbitals are determined by minimizing E with respect to variations in the ϕ_i , which preserve their orthonormality. It can be shown (8, 9) that these orbitals satisfy the SCF equations

$$\hat{F}_i \phi_i = \epsilon_i \phi_i \quad (3)$$

²These techniques are the same as the methods used for calculating diagonal matrix elements in a Configuration Interaction calculation.

where we have assumed that the orthogonality of the ϕ_i can be preserved without introducing off-diagonal elements of ϵ , which would couple the SCF equations.

The SCF Hamiltonian $\hat{F}_i$ of which ϕ_i is an eigenfunction is given by

$$\hat{F}_i = \hat{H} + \sum_j v_j (a_{ij} \hat{J}_j - b_{ij} \hat{K}_j) \quad (3a)$$

and is the same for all orbitals in the same shell.³ (In other words, the subscript i in $\hat{F}_i$ would be redundant if there were no open shells).

The Coulomb and exchange operators $\hat{J}_j$ and $\hat{K}_j$ are one-electron operators implicitly defined by the relations

$$J_{ij} = \langle \phi_i | \hat{J}_j | \phi_i \rangle \quad (3b)$$

and

$$K_{ij} = \langle \phi_i | \hat{K}_j | \phi_i \rangle \quad (3c)$$

and $\hat{H}$ is the hydrogenlike Hamiltonian with nuclear charge Z .

$$H_i = \langle \phi_i | \hat{H} | \phi_i \rangle \quad (3d)$$

Calculating Orbital Energies

The eigenvalues in eq 3 are the orbital energies, and these are readily found from

$$\epsilon_i = \langle \phi_i | \hat{F}_i | \phi_i \rangle \quad (4)$$

$$\epsilon_i = H_i + \sum_j v_j (a_{ij} J_{ij} - b_{ij} K_{ij}) \quad (5)$$

Using the above definition and considering a singly occupied orbital, for example, ϕ_m in eq 1, it can be shown that $-\epsilon_m$ is the energy needed to remove an electron from ϕ_m while the other orbitals are "frozen": If the doubly occupied orbital ϕ_k lost one electron, the wavefunction for the ion would have ambiguous spin, depending on whether the electron remaining in ϕ_k had spin parallel or antiparallel to the electrons in the open shell. The quantity $-\epsilon_k$ therefore represents an ionization energy averaged over two values of M_S .

The expression for ϵ_i brings out in a formal way the point made earlier:

The energy of an orbital depends upon all the occupation numbers including its own. If any occupation numbers are changed, then all the orbital energies will be changed.

This is still true even when the same functions ϕ_i 's are used to describe the new configuration, so that the energy integrals remain the same. The other point brought out by eq 5 is that empty orbitals—solutions to the SCF equations with occupation number zero—have energies that include an additional Coulomb-exchange repulsion and thus do not have the same physical meaning as occupied orbital energies. These virtual orbitals resemble more the orbitals of the anion than those of the neutral atom. Vacant orbitals with the same n and l quantum numbers as occupied orbitals (e.g., 3d orbitals) are said to be equivalent (9) to occupied orbitals and are not regarded as virtual.

³For example, in $[\text{Ar } 4s(3d)^{n+1}]$ the argonlike core, the 4s orbital, and the 3d orbitals are regarded as separate shells.

Computing the Total Energy of an Alternative Configuration

Once an open-shell configuration has been computed by the SCF method, trial wavefunctions for the alternative configurations may be constructed by transferring electrons from the closed to the open shell. The total energy (E') of an alternative configuration may be computed by either of the following two methods.

- Use the same orbitals and therefore the same energy integrals as in the original SCF calculation, but modify the total energy expression to take account of the new occupation numbers.
- Reoptimize the orbitals through a new set of SCF equations and compute the new total energy expression with slightly different values of the energy integrals.

The second approach is the more reliable way to compare the energies of configurations; but the frozen-orbital method can be acceptable where total energy differences are large, or where E' is found to be below E , in which case the variation theorem says that an SCF calculation would only make E' lower still. If a frozen-orbital approach is used, an SCF calculation on a closed-shell configuration is not a suitable starting point because then it would be necessary to use virtual orbitals to build wavefunctions of the open-shell configurations. Indeed SCF theory as developed for a closed shell is not a suitable background for a discussion (3) of the relative stability of open-shell configurations.

Formulating Total Energy with Orbital Energies

Orbital energies are not needed for the calculation of total energies; this emphasizes that they are not fundamental in determining the stability of a configuration. It is, however, possible to formulate the total energy in a way that does involve orbital energies if this is desired. From eqs 2 and 5 one finds

$$E = \sum v_i \epsilon_i - G \quad (6)$$

where

$$G = \frac{1}{2} \sum_i \sum_j v_i v_j (a_{ij} J_{ij} - b_{ij} K_{ij}) \quad (7)$$

Pilar (3, 6) has suggested that a formulation like eq 6 can give a useful insight into why 4s is preferred to 3d in the lowest configuration. The use of the 4s rather than the 3d will give a higher value to the summation of orbital energies. However, Pilar claims that this will be counteracted by an increased value of G because repulsions between the 4s electron and the core orbitals are greater than the repulsions between a 3d electron and the core.

In fact, as Mann's tables of integrals (5) show, this claim is false: The repulsions between the 3d and the core orbitals are very much greater than those between 4s and the core. The fallacy in Pilar's argument lies in the use of eq 6 to assess the total energies of two configurations while regarding the ϵ_i as constant.

The calculation of the total energy (E') of an alternative configuration is not just a matter of inserting different values of v_s and v_d into eqs 6 and 7: It is also necessary to recalculate the orbital energies via eq 5. The correct expression for E' is

$$E' = \sum v'_i \epsilon'_i - G' \quad (8)$$

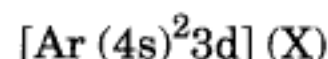
from which not much can be learned without a full calculation. The use of 3d at the expense of 4s raises all the orbital energies (i.e., $\epsilon'_i > \epsilon_i$), and this gives a higher value to the orbital-energy summation, despite the change in occupa-

tion numbers. At the same time electron repulsion is increased ($G' > G$). It is then not obvious which of E or E' will be lower.⁴

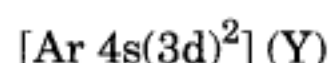
The "corrected orbital-energy summation" method is not a convenient way to assess energy differences. There are many cancellations when E is subtracted from E' , including the repulsions between 4s and the core and between 3d and the core. As Nelson's results confirm, these repulsions are not involved in total-energy differences except in so far as they are involved in the definitions of ϵ_s and ϵ_d .

Energy Differences between Configurations of the First Transition

We begin by showing how the energy difference between two low-lying configurations of scandium,



and



may be expressed in terms of orbital energies. The total energy of the configuration X is first formulated according to the principles behind eq 2.

$$E_x = E_{\text{core}} + 2 \sum_i (2J_{is} - K_{is}) + 2H_s + (2J_{sd} - K_{sd}) + H_d + \sum_i (2J_{id} - K_{id}) \quad (9)$$

where

$$E_{\text{core}} = \sum_i \sum_j (2J_{ij} - K_{ij}) + \sum_i 2H_i \quad (9a)$$

and indices i and j now refer exclusively to the orbitals of the argonlike core.

We now introduce the SCF definitions of ϵ_d and ϵ_s for the X configuration.

$$\epsilon_d = H_d + \sum_i (2J_{id} - K_{id}) + (2J_{sd} - K_{sd}) \quad (10a)$$

and

$$\epsilon_s = H_s + \sum_i (2J_{is} - K_{is}) + J_{ss} + (J_{sd} - \frac{1}{2}K_{sd}) \quad (10b)$$

Coulomb-Exchange Repulsion in the Open Shells

The last term in eq 10b is the average value of the Coulomb-exchange repulsion between a 4s electron and the 3d electron, taken over both values of the m_s quantum number of the 4s orbital. Substituting for ϵ_d and ϵ_s , we get from eq 9

$$E_x = E_{\text{core}} + 2\epsilon_s + \epsilon_d - (2J_{sd} - K_{sd}) - J_{ss} \quad (11)$$

where the last two terms in eq 11 were subtracted to ensure that electron repulsions (between 4s and 3d orbitals and within the 4s orbital) are not counted twice. These terms cancel when the energy difference ($E_y - E_x$) is taken.

The total energy of configuration Y is given by

$$E_y = E_{\text{core}} + \sum_i (2J_{is} - K_{is}) + H_s + (2J_{sd} - K_{sd}) + 2 \sum_i (2J_{id} - K_{id}) + 2H_d + (J_{dd} - K_{dd}) \quad (12)$$

The last term in eq 12 is the Coulomb-exchange repulsion between different d orbitals⁵ of the same spin. In order to make the calculation of the excitation energy $E_y - E_x$ consistent with the calculation of the ionization energy implicit in the definition of ϵ_s , we have again averaged the repulsion between the 4s orbital and the 3d shell over two values of m_s for the 4s electron. In terms of orbital energies, eq 12 may be written

$$E_y = E_{\text{core}} + \epsilon_s - (J_{ss} + J_{sd} - \frac{1}{2}K_{sd}) + 2\epsilon_d + J_{dd} - K_{dd} - (2J_{sd} - K_{sd}) \quad (13)$$

Again, the bracketed terms represent interactions included in $\epsilon_s + 2\epsilon_d$ that are not required according to eq 12.

Upon subtracting eq 11 from eq 13, we find

$$E_y - E_x = (\epsilon_d + J_{dd} - K_{dd} - J_{sd} + \frac{1}{2}K_{sd}) - \epsilon_s \quad (14)$$

Interpreting the Energy Change

Now eq 14 allows a very simple interpretation. An electron is first removed from 4s while all orbitals are frozen. The energy lost is ϵ_s . The electron then enters the 3d shell. The energy gained is not ϵ_d because the incoming electron does both of the following.

- It "gains" a repulsion ($J_{dd} - K_{dd}$) with the d electron already present, which is not included in the definition of ϵ_d .
- It "loses" a repulsion ($J_{sd} - \frac{1}{2}K_{sd}$) because the definition of ϵ_d assumes that the 4s orbital is doubly occupied.

The bracketed quantity in eq 14 is ϵ'_d , where

$$\epsilon'_d = \epsilon_d + (J_{dd} - K_{dd}) - (J_{sd} - \frac{1}{2}K_{sd}) \quad (15)$$

or, expressed differently,

$$\epsilon'_d = H_d + \sum_i (2J_{id} - K_{id}) + (J_{sd} - \frac{1}{2}K_{sd}) + (J_{dd} - K_{dd}) \quad (15a)$$

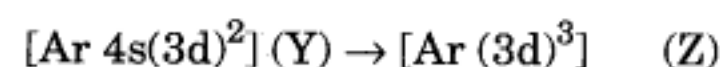
It is not difficult to see that ϵ'_d is the difference between the energy of the $\text{Ar}(4s)(3d)^2$ configuration of scandium and the $\text{Ar}(4s)(3d)$ configuration of Sc^+ averaged over two possible spins of the 4s electron. Thus, eq 14 is simply

$$E_y - E_x = \epsilon'_d - \epsilon_s \quad (16)$$

Using data from Mann's tables (5), we have (in atomic units), $\epsilon_s = -0.210$; $\epsilon_d = -0.344$; $(J_{dd} - K_{dd}) = 0.511$; and $(J_{sd} - \frac{1}{2}K_{sd}) = 0.281$. It then follows from eq 15 that $\epsilon'_d = -0.114$, which is above ϵ_s . The underlying reason for $\epsilon'_d > \epsilon_s$ and for the preferential occupation of 4s, is that the repulsion between the pair of 3d electrons is much greater than the repulsion that it "replaces": the repulsion between 4s and 3d.

Calculating the Energy Change in a Double Excitation

Similar methods may be used to calculate the energy change in a double excitation, whose last stage is



The total energy of the Z configuration is given by

$$E_z = E_{\text{core}} + 3\epsilon_d - 3(2J_{sd} - K_{sd}) + 3(J_{dd} - K_{dd}) \quad (17)$$

whereupon subtracting eq 13 and substituting for ϵ'_d from eq 15 we obtain

$$E_z - E_y = (\epsilon'_d + J_{dd} - K_{dd} - J_{sd} + \frac{1}{2}K_{sd}) - (\epsilon_s - J_{ss} + J_{sd} - \frac{1}{2}K_{sd}) \quad (18)$$

⁴The sum of the kinetic energy and the nuclear-attraction energy is lower for a 3d orbital than it is for a 4s orbital, that is, $H_d < H_s$, just as it is in the hydrogen atom.

⁵We choose the orbitals with $m_l = 2$ and $m_l = 1$ when calculating the d^2 configuration. For the d^3 configuration orbitals with $m_l = 2, 1$ and 0 are chosen to be consistent with Nelson.

$$= \epsilon'_d - \epsilon'_s \quad (18a)$$

where ϵ'_d and ϵ'_s are orbital energies in the Z and Y configurations calculated using orbitals of the X configuration.

The overall energy change, X→Z, is given by adding eqs 16 and 18a.

$$E_z - E_x = (\epsilon'_d - \epsilon'_s) + (\epsilon'_d - \epsilon_s) \quad (19)$$

The above expression gives exactly the same energy difference (0.399) for the double excitation, as found by Nelson.⁵ The transfer of the second 4s electron produces a much greater change in energy than the first.

Other Elements of the First Transition Series

The extension of these ideas to the other elements of the first transition series is relatively straightforward. For titanium, vanadium, manganese, iron, copper, and nickel the difference in energy between $[\text{Ar}(4s)(3d)^{n+1}]$ and $[\text{Ar}(4s)^2(3d)^n]$ is still given by eq 16 but, the generalization of eq 15 is

$$\epsilon'_d = \epsilon_d + 2 \left(\frac{\Gamma_{n+1}}{n+1} \right) - 2 \left(\frac{\Gamma_n}{n} \right) - (J_{sd} - \frac{1}{2}K_{sd}) \quad (20)$$

where Γ_{n+1} and Γ_n are the Coulomb-exchange repulsions within the 3d shell when the numbers of d electrons are $n+1$ and n .

The energy integrals and the values of ϵ_d and ϵ_s are all given by Mann for the $[\text{Ar}(4s)^2(3d)^n]$ configurations. To be consistent with Mann's calculation of ϵ_d , each Γ term should be calculated as an average over all the microstates arising from the appropriate configuration. Fortunately, there is a very simple way of carrying out this calculation. According to Slater (10) the difference between

$$\frac{2\Gamma_{n+1}}{n+1}$$

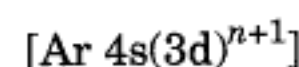
and

$$\frac{2\Gamma_n}{n}$$

is precisely the average value of the Coulomb-exchange repulsion between a pair of d electrons.

The Configurations for Chromium and Copper

Chromium and copper are considered separately because Mann's SCF calculations refer to the spectroscopic ground-state configuration in every case, and for chromium and copper this is the "Y" configuration,



The energy difference ($E_y - E_x$) is still $\epsilon'_d - \epsilon_s$, but now ϵ'_d and ϵ'_s are SCF orbital energies in the "Y" configuration, and $-\epsilon_s$ is an orbital ionization energy in the "X" configuration.

$$\epsilon_s = \epsilon'_s + J_{ss} - (J_{sd} - \frac{1}{2}K_{sd}) \quad (21)$$

In terms of eq 21 the stability of the sd^5 configuration in the case of chromium is explained as follows. The rearrangement $sd^5 \rightarrow s^2d^4$ reduces the 4s orbital energy from ϵ'_s to ϵ_s but not by enough to take its value below ϵ'_d . A better explanation in terms of eq 20 would be that the rearrangement of $s^2d^4 \rightarrow sd^5$ raises the energy of the 3d orbital from ϵ_d to ϵ'_d but not by enough to take its value above ϵ_s . It is a pity that SCF calculations are not provided for the "X" con-

Orbital Energies (in atomic units)

Element	ϵ_s	ϵ_d	ϵ'_d	$(\epsilon'_d - \epsilon_s)$
Sc	-0.210	-0.343	-0.114	0.096
Ti	-0.222	-0.406	-0.130	0.092
V	-0.232	-0.461	-0.143	0.090
Cr	-0.269 ^a	—	-0.322 ^b	-0.053
Mn	-0.251	-0.611	-0.165	0.086
Fe	-0.260	-0.608	-0.175	0.085
Co	-0.268	-0.653	-0.183	0.085
Ni	-0.277	-0.697	-0.191	0.086
Cu	-0.319 ^a	—	-0.491 ^b	-0.172

^aCalculated from eq 21.

^bSCF values

figuration $[\text{Ar}(4s)^2(3d)^n]$ throughout the series because it would be more convincing, from a variational point of view, if we could show that the Y configuration of chromium or copper is lower than the X configuration when both configurations are computed with the X orbitals. What we have shown is that the X configuration is higher than the "Y" when both are computed with "Y" orbitals.

Alternative and Less Stable Configurations

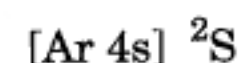
In the table all the values of $(\epsilon'_d - \epsilon_s)$, which give the total energy differences ($E_y - E_x$), are in favor of the configuration for which the SCF orbitals were computed by Mann. The magnitudes of the energy differences are not quite large enough to be sure in every case that an SCF calculation on the alternative configuration would not lead to its having lower total energy than the (spectroscopic) ground-state configuration assumed here. Indeed, calculations by VPD suggest that the alternative configuration provides the SCF ground state for both chromium and nickel. SCF values of ϵ'_d , as indicated by results for chromium and copper, can be expected to be considerably lower than the frozen-orbital values; but it must be remembered that $(\epsilon'_d - \epsilon_s)$ does not represent a difference in total energy between two atomic wavefunctions unless the same set of orbitals is used to build both wavefunctions.

If the choice between s^2d^n and sd^{n+1} is finely balanced energetically, there is little doubt about the relative instability of the s^0d^{n+2} configurations. As was shown for scandium, the voiding of the 4s orbital produces a great increase in energy. For chromium the energy of the d^6 configuration relative to sd^5 is given by $(\epsilon'_d - \epsilon'_s)$, where ϵ'_d is the 3d orbital energy in the d^6 configuration computed with the orbitals of the sd^5 configuration, and ϵ'_s is an SCF orbital energy in the sd^5 configuration. The value of ϵ'_d is actually positive (0.078). The orbital energies that are not the direct results of SCF calculations should not be taken too seriously as (negative) ionization energies. The important point however is that ϵ'_d is far above ϵ'_s (-0.207).

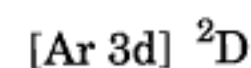
Thus, from our results, if the orbitals are optimized for a spectroscopic ground-state configuration, the transfer of an electron from 4s to 3d produces a less stable configuration in every case. (This statement cannot be applied in the case of copper, where the 3d shell is full.)

The Case of Potassium

It is interesting to ask why the buildup of the 3d shell does not begin with potassium. The relevant configurations are



and



and the total energies are given by

$$E(^2S) = E_{\text{core}} + \epsilon_s$$

and

$$E(^2D) = E_{\text{core}} + \epsilon_d$$

The orbital energies are given by

$$\epsilon_s = H_s + \sum_i (2J_{is} - K_{is})$$

and

$$\epsilon_d = H_d + \sum_i (2J_{id} - K_{id})$$

If the orbitals of the argonlike core are the same in each case, then the preference for the ^2S configuration must indicate $\epsilon_s < \epsilon_d$. However, it should be stressed that these orbital energies cannot both be results of the same SCF calculation, and the general rule that 3d is below 4s in the same configuration is not broken. There are two ways in which the ^2S configuration could be the lower one: Either E_{core} is lower in the presence of 4s than it would be in the presence of 3d, or the 4s electron really is more tightly bound than a 3d electron would be outside the same core. The calculations of VPD have shown that the 4s electron is more tightly bound.

Orbital Energies Are Still Not Energy Levels

We have shown that the relative stability of two configurations that differ by a one-electron substitution may be inferred correctly from the energies of their differentiating orbitals, provided that each of these corresponds to a binding energy in its own configuration. Although differences between orbital energies defined in this way do approximately represent excitation energies, it would be wrong to regard these orbital energies as energy levels. To each excited-state orbital energy defined in this way there is only one possible excitation, that is, only one possible substitution of a ground-state orbital.

The idea that orbital energies are energy levels is one of those attractive but ultimately misleading ideas that students acquire very easily and shed with difficulty. It is first encountered with the hydrogen atom, where the story of quantum theory and spectroscopy begins, and where the idea is perfectly correct. As Pilar has pointed out (3), the extension of the idea to the many-electron atom—encouraged by many elementary textbooks—is inconsistent with quantum mechanics. Only isolated systems, like the hydrogen atom, have energy levels. An electron in a many-electron atom is not isolated. We make the same point in a slightly different way. The Schrödinger equation defines the energy levels of the hydrogen atom without regard to which level may be occupied, whereas the SCF equations define orbital energies in the many-electron atom only with reference to a particular set of occupation numbers.

A crucial difference between the concepts of orbital energy and energy level arises in the meaning of degeneracy. Students tend to think of the 3d shell as an energy level with a 10-fold degeneracy that can accommodate just 10 electrons due to the Pauli principle. If $\epsilon_d < \epsilon_s$, it seems incomprehensible that a higher level can be used while the "degenerate level" is incompletely filled. In fact, only the 3d orbitals actually occupied have the same energy ϵ_d ; this energy is not acquired by further electrons entering the vacant 3d orbitals. It is therefore misleading to speak of occupied and vacant orbitals as being "degenerate". A more appropriate designation would be "spatially equivalent" or "spin-equivalent" in the sense of Nesbet (9).

Conclusions

Although an elaborate treatment of SCF theory is beyond a first- or even a second-year course in atomic structure, the following points may be made without a great deal of mathematical background.

1. Orbital energies correspond approximately to ionization energies, not energy levels, in the many-electron atom.
2. Orbital energies depend upon the particular electron configuration under consideration: They may therefore be changed by an electronic transition.
3. The 4s orbital is ionized before 3d because ϵ_s is above ϵ_d , when both orbital energies are defined in the same configuration.
4. The 4s orbital is occupied instead of 3d because the 4s orbital energy in the (spectroscopic) ground configuration is below the 3d orbital energy in the alternative configuration, which uses the same orbitals but an extra 3d orbital instead of a 4s.

Points 1 and 3 are Pilar's explanation of the preferential ionization of the 4s orbital, whereas points 2 and 4 are the explanation of its preferential occupation. Nelson explains the latter by pointing to the increase in the total electron-repulsion energy that occurs when 3d is used at the expense of 4s. This is sound, but we prefer to regard this increase in electron repulsion as part of a change in orbital binding energy rather than as an extraneous consideration.

Nelson also observes, correctly, that the transition elements provide examples of ground-state configurations where "higher orbitals are occupied despite vacancies in lower ones". Students could accept this more readily if it were pointed out that, without orbital relaxation, the vacant orbitals are not available at an energy lower than that of the highest orbital actually occupied.

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