



ELECTRONIC CONFIGURATIONS vs ORBITAL ENERGIES

INTRODUCTION

Comparison of electronic configurations of ground state atoms with orbital energies reveals interesting features as the atomic number varies, for the transition elements. In fact, it is not possible, in some cases, to correctly predict the electronic configuration of an atom by simply filling its manifold of orbitals, ordered by their increasing energies (aufbau principle), with the use of the Pauli exclusion principle. For instance, the ground state electronic configuration of scandium is neither $[\text{Ar}]3d^3$ nor $[\text{Ar}]3d^24s^1$ but $[\text{Ar}]3d^14s^2$, despite the fact that $\epsilon_{3d} < \epsilon_{4s}$ (fig. 1), where $[\text{Ar}]$ represents the argon

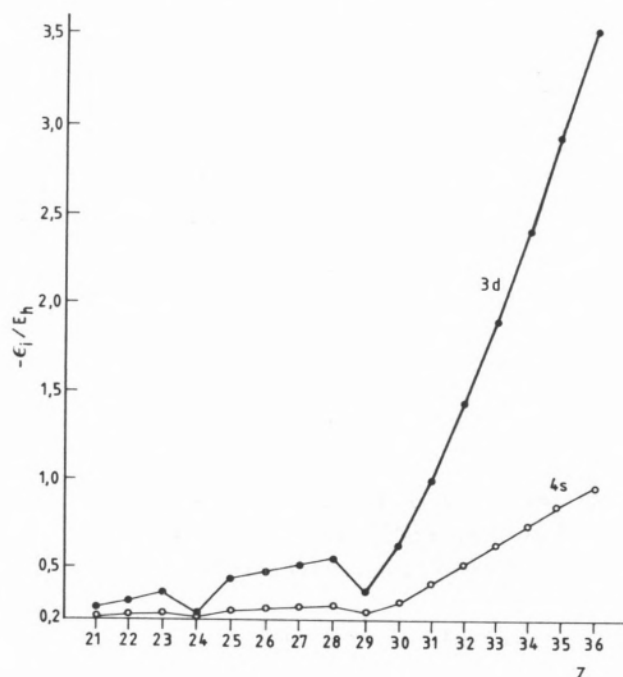


Fig. 1

3d and 4s orbital energies for the third row elements of the periodic table [1] ($E_h = 4.3598 \times 10^{-18}$ J, Hartree energy)

core and ϵ stands for an orbital energy. For yttrium, the ground state electronic configuration is $[\text{Kr}]4d^15s^2$ although $\epsilon_{4d} < \epsilon_{5s}$ (fig. 2).

Being a one-electron function useful for constructing many-electron wavefunctions and interpreting the periodic properties of elements, an atomic orbital has a rigorous and clear-cut definition in the context of self-consistent field methods. Besides being the most rigorously defined of all types of orbitals, the self-consistent field orbital is the

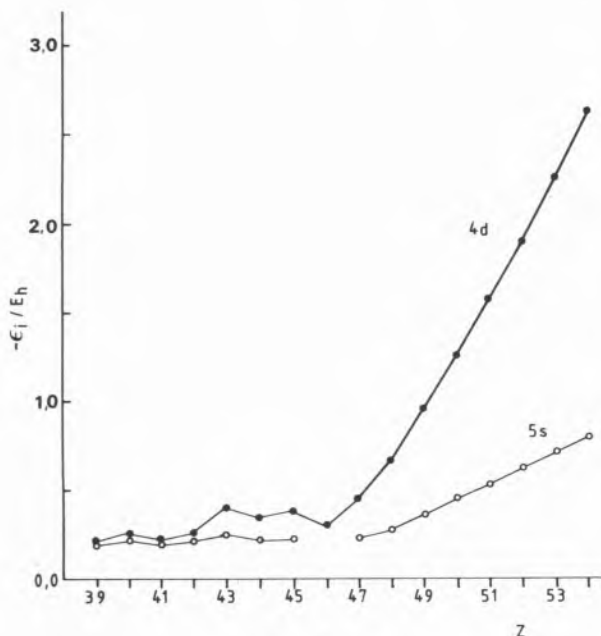


Fig. 2

4d and 5s orbital energies for the fourth row elements of the periodic table [1]. For $Z=46$ the 5s orbital occupancy is zero, in the ground state. Therefore, ϵ_{5s} is not indicated

one whose energy is most closely related to experimental photoelectronic energies through Koopmans' approximation.

Within the Hartree-Fock self-consistent method, the total electronic energy of a many-electron atom is not simply the sum over the electrons of orbital energies. Under the non-relativistic hamiltonian approximation, the total electronic energy of an atom whose wavefunction is approximated by a Slater determinant is given by

$$E = \sum_{i=1}^n \epsilon_i - G \quad (1)$$

where n is the number of occupied spin-orbitals and G is the electronic repulsion energy expressed in terms of Coulomb and exchange integrals. In this general form, (1) applies also to non-closed subshells.

Accurate Hartree-Fock wavefunctions [1, 2] enable us to interpret the electronic configurations of atoms and to understand the periodic properties of the elements [3]. Herewith we present Hartree-Fock results for a few electronic configurations of a scandium atom and its monovalent ion as well as for a neutral yttrium atom. The objective nature of these

results speaks for itself, exempting us from wandering among less well founded predictions as it has been previously done quite so often. These values not only reveal important trends for the orbital and repulsion energies but also clarify the interpretation of ground state electronic configurations in terms of the atomic orbital concept [4, 5] on a well founded and objective basis. For the motivation of this article the reader is referred to [4].

Before starting with the analysis of Hartree-Fock results for ground state atoms, it is necessary to remark on an important, albeit frequently forgotten, point. Comparison of orbital energies should be limited to configurations where the compared orbitals are simultaneously occupied. In fact, while an occupied spin-orbital refers to the field of the nucleus and the $n-1$ other electrons, an unoccupied spin-orbital should be considered instead as the solution of the Hartree-Fock equations for an nonexistent ghostlike charge acted upon by all the other n electrons in the atom.

2 — HARTREE-FOCK RESULTS ON SCANDIUM AND YTTRIUM ATOMS

Tables 1 and 2 show Roothaan-Hartree-Fock results for a few electronic configurations of a scandium neutral atom (Table 1) and its monovalent ion (Table 2).

The first interesting conclusion worth extracting from these tables is that small variations in the total electronic energy result from a critical balance of two large and approximately equal numbers: the variation in the sum over all orbital energies, $\sum \epsilon_i$, and in the electronic repulsion energy, G . Under these conditions, it may be difficult or even impossible to single out a particular and specific effect for the interpretation of any observed energy trend.

A second and equally important point is the appreciable variations exhibited by the 3d and 4s orbital energies upon alteration of the electronic configuration of the valence electrons (when an electron changes from 3d to 4s), in spite of a fixed atomic number. This is a relevant point not so much mentioned before as general attention is paid instead to the variation of orbital energies as functions of atomic number for ground state atoms.

In order to analyse the energy terms involved in a particular scheme of partitioning the atom in different groups of electrons, like core and valence elec-

Table 1
Roothaan-Hartree-Fock energies for two electronic configurations of scandium [2] $E_h = 4.3598 \times 10^{-18}$ J (Hartree energy)

Electronic Configuration	ϵ_{3d}/E_h	ϵ_{4s}/E_h	$\Sigma\epsilon_i/E_h$	G/ E_h	E/ E_h
[Ar]3d ² 4s ¹ (I)	-0.21529	-0.19537	-476.46291	283.23569	-759.69860
[Ar]3d ¹ 4s ² (II)	-0.34357	-0.21014	-479.31765	280.41787	-759.73552
$\Delta(I-II)$	0.12828	0.01477	2.85474	2.81782	0.03692

Table 2
Roothaan-Hartree-Fock energies for different electronic configurations of Sc⁺ [2]

Electronic Configuration	ϵ_{3d}/E_h	ϵ_{4s}/E_h	$\Sigma\epsilon_i/E_h$	G/ E_h	E/ E_h
[Ar]3d ² (I)	-0.45481	—	-480.71988	278.78986	-759.50974
[Ar]4s ² (II)	—	-0.48719	-488.29584	271.16613	-759.46197
[Ar]3d ¹ 4s ¹ (III)	-0.59990	-0.44926	-484.14304	275.39597	-759.53901
$\Delta(I-III)$	0.14509	—	3.42316	3.39389	0.02927
$\Delta(II-III)$	—	-0.03793	-4.15280	-4.22984	0.07704

trons, one should not forget that a particular sum of Hartree-Fock orbital energies over some or all of the occupied orbitals includes the electronic repulsion interactions twice, therefore requiring subtraction of the corresponding repulsion energy according to an equation like (1). However, the repulsion energy G cannot be rigorously partitioned in several terms, unlike any sum of orbital energies which are one-electron quantities. While we are aware of this fact it is nevertheless worth mentioning the appreciable variations observed in the sum of extracore orbital energies as they are of the order of magnitude of ϵ_{4s} or ϵ_{3d} .

On the other hand, the sum of core orbital energies ($\Sigma\epsilon_i$)_{core}, easily computed from the tables by subtracting from $\Sigma\epsilon_i$ the sum of the valence electron energies, exhibit variations of the same order of magnitude as $\Sigma\epsilon_i$ (see Table 1 and 2). This legitimately suggests that the corresponding intracore repulsion energies should also balance variations in ($\Sigma\epsilon_i$)_{core}, therefore further stressing the importance of the variations in the valence electron energies, at least in relative terms. Now, as the orderings of $\Sigma\epsilon_i$ values for the various configurations of Sc and Sc⁺ are due to core orbital contraction when an electron changes from 3d to 4s (see fig. 3), the same effect should

also cause an increase in the intracore repulsion energies.

Another interesting observation, although purely factual and made in passing, can also be taken from the Sc⁺ results shown in Table 2: the smallest values quoted for $\Sigma\epsilon_i$ and G do not correspond to the ground state configuration ([Ar]3d¹4s¹), not even to the configuration with the largest number of 3d electrons, but to [Ar]4s².

By analysing Table 3 for two electron configurations of the yttrium atom, the reader can easily recognize several trends which are similar to those observed in the case of Sc and Sc⁺ atoms, therefore exempting us from specific comments on that case. The preceding results enable us to answer an usual and practical question on the transition elements electronic configurations which we particularize for the scandium atom: why does this atom "prefer" the ground state configuration [Ar]3d¹4s² to [Ar]3d²4s¹, despite the fact that $\epsilon_{3d} < \epsilon_{4s}$?

A possible answer, based on a simplistic and somewhat imprecise idea, attributes the stability of [Ar]3d¹4s² relative to [Ar]3d²4s¹ to a large 4s-[Ar] repulsion, hypothetically considered to be greater than the corresponding 3d-[Ar] interaction. Then, the argument continues, the difference between $\Sigma\epsilon_i$

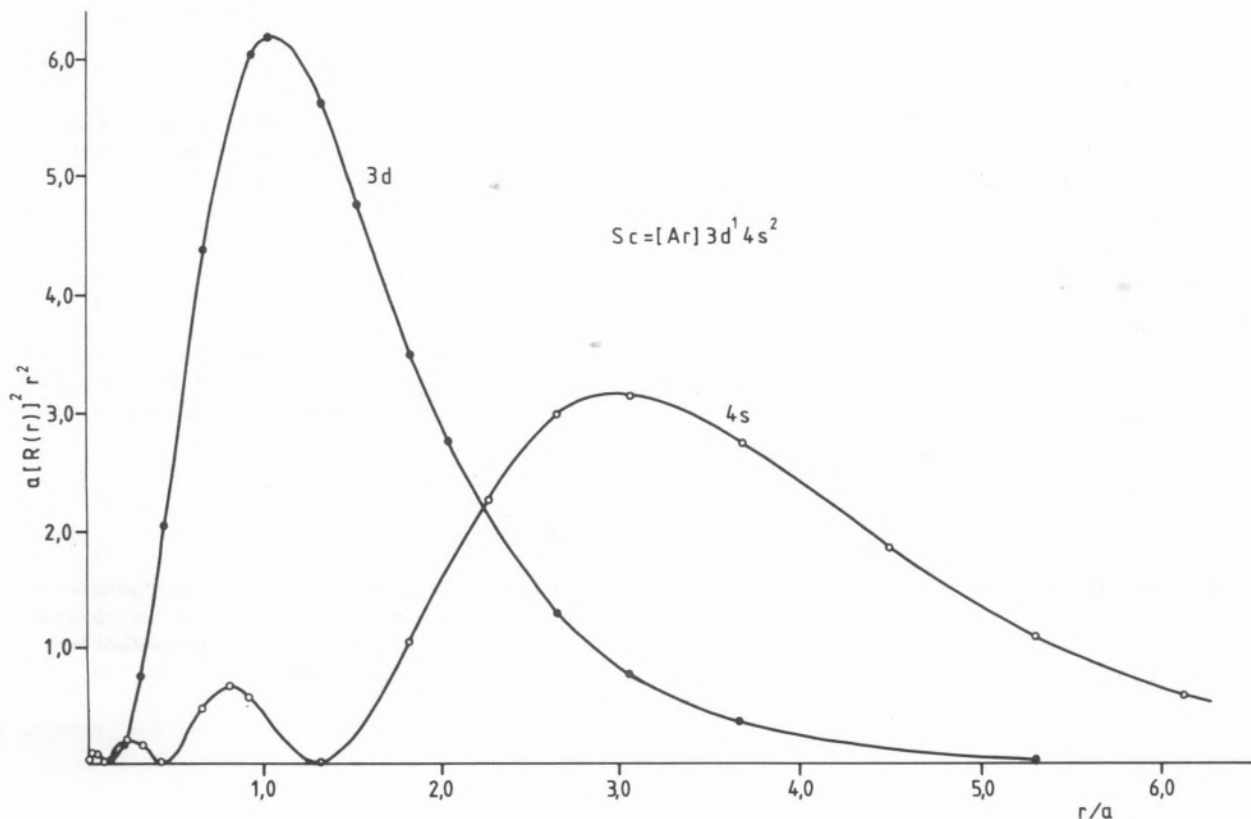


Fig. 3

Radial distribution functions for the 3d and 4s electrons of scandium [1] ($a_0 = 5.2918 \times 10^{-11} \text{ m}$, Bohr radius)

and G in (1) turns out to be smaller in the configuration with the largest possible number of 4s electrons which is 2, because of a larger G value.

Now, the results of Tables 1 and 2 show that both the premise — sum of orbital energies over all occupied spin-orbitals, $\Sigma \epsilon_i$, (wrongly) considered to be insensitive to the configuration of the outer electrons — and the conclusion — 4s-[Ar] repulsion assumed to be greater than 3d-[Ar] interaction — lack a well founded basis, at least within the Hartree-Fock methods which undoubtedly provide the best definition of the atomic orbital concept. In

fact, quite on the contrary, the 3d-[Ar] repulsion energy should be greater than that for 4s-[Ar] interaction, as it is qualitatively suggested by the observed increase of the G values as the number of 3d electrons increases in the electronic configurations considered (Tables 1 and 2). Furthermore, by plotting the radial distribution of 3d and 4s electrons in a scandium atom in its ground state electronic configuration, one can conclude that the existence of radial nodes in a 4s orbital is not enough to assume a 4s-[Ar] repulsion greater than the 3d-[Ar] interaction (see fig. 3).

Table 3
Roothaan-Hartree-Fock energies for two electronic configurations of yttrium [2]

Electronic Configuration	ϵ_{4d}/E	ϵ_{5s}/E_h	$\Sigma \epsilon_i/E_h$	G/E_h	E/E_h
[Kr]4d ² 5s ¹ (I)	-0.19375	-0.19233	-2050.01337	1281.64163	-3331.6550
[Kr]4d ¹ 5s ² (II)	-0.24987	-0.19578	-2053.51973	1278.15147	-3331.6712
Δ (I-II)	0.05612	0.00345	3.50636	3.49016	0.0162

3 — CONCLUSION

The self-consistent field orbital is a one-electron function rather useful for constructing many-electron wavefunctions and interpreting the periodic properties of elements. Accurate Hartree-Fock results for atoms yield a correct and well founded basis for interpreting ground state electronic configurations in terms of the orbital concept. By taking the scandium and yttrium atoms as examples of the above mentioned considerations, this article provides objective answers to several previously and yet unanswered questions raised on the relative stability of different electronic configurations interpreted in terms of orbital energies.

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ABSTRACT

A controversial point on the interpretation of electronic configurations of atoms in relation with orbital energies is reanalysed in the light of previously published accurate Hartree-Fock results.

RESUMO

A controvérsia suscitada na interpretação das configurações eletrónicas de átomos em relação com as energias das orbitais atómicas é reanalisada à luz de resultados de Hartree-Fock bastante precisos e previamente publicados.