

LANTHANIDE CHEMISTRY AND ELECTRONIC CONFIGURATION

1 Niels Bohr and the lanthanide elements

Bohr suggested that the atoms of the elements lanthanum to lutetium had ground state configurations $[\text{Xe}]4f^n 5d^1 6s^2$ where n runs from zero to fourteen. He argued that these atoms were possessed of a very stable +3 oxidation state because the 4f sub-shell was an inner shell, being part of the inner xenon core. There were therefore three outer valence electrons, and these give rise to a very stable +3 oxidation state. We now know that most of the lanthanide atoms have configurations of the type $[\text{Xe}]4f^n 6s^2$. If Bohr's idea that the 4f electrons are part of the core were correct, then we would expect the outer electron configuration $6s^2$ in the atoms to give rise to elements that are divalent like barium. This is not the case. How do we reconcile the dominant atomic configuration $[\text{Xe}]4f^n 6s^2$ with tri-valency? Are the 4f electrons really inner electrons? These are two questions that we need to address. We shall do it by exploiting theories that appeared after Bohr's seminal work.

2 4f electrons in free lanthanide atoms

The outer electrons of the xenon core in lanthanide atoms are 5s and 5p. Bohr assumed that the 4f electrons in lanthanide atoms are inner electrons. If so they must spend most of their time closer to the nucleus than do the outer 5s and 5p electrons of the core. Quantum mechanics can give us an idea of where these three types of electron are to be found. We start with an early lanthanide element. Figure 1a shows the radial distribution functions of the 4f, 5s and 5p electrons in the praseodymium atom. They were obtained by what are known as self-consistent field calculations, and they show us the probability of finding each kind of electron at different distances from the nucleus.

- Do the distributions in Figure 1a suggest that, relative to the 5s and 5p electrons, the 4f electrons in the praseodymium atom are inner electrons?
- Yes; the 4f electron is most likely to be found at a distance that lies well inside the highest peaks in the 5s and 5p distributions. The 4f electron spends most of its time closer to the nucleus than either a 5s or 5p electron.

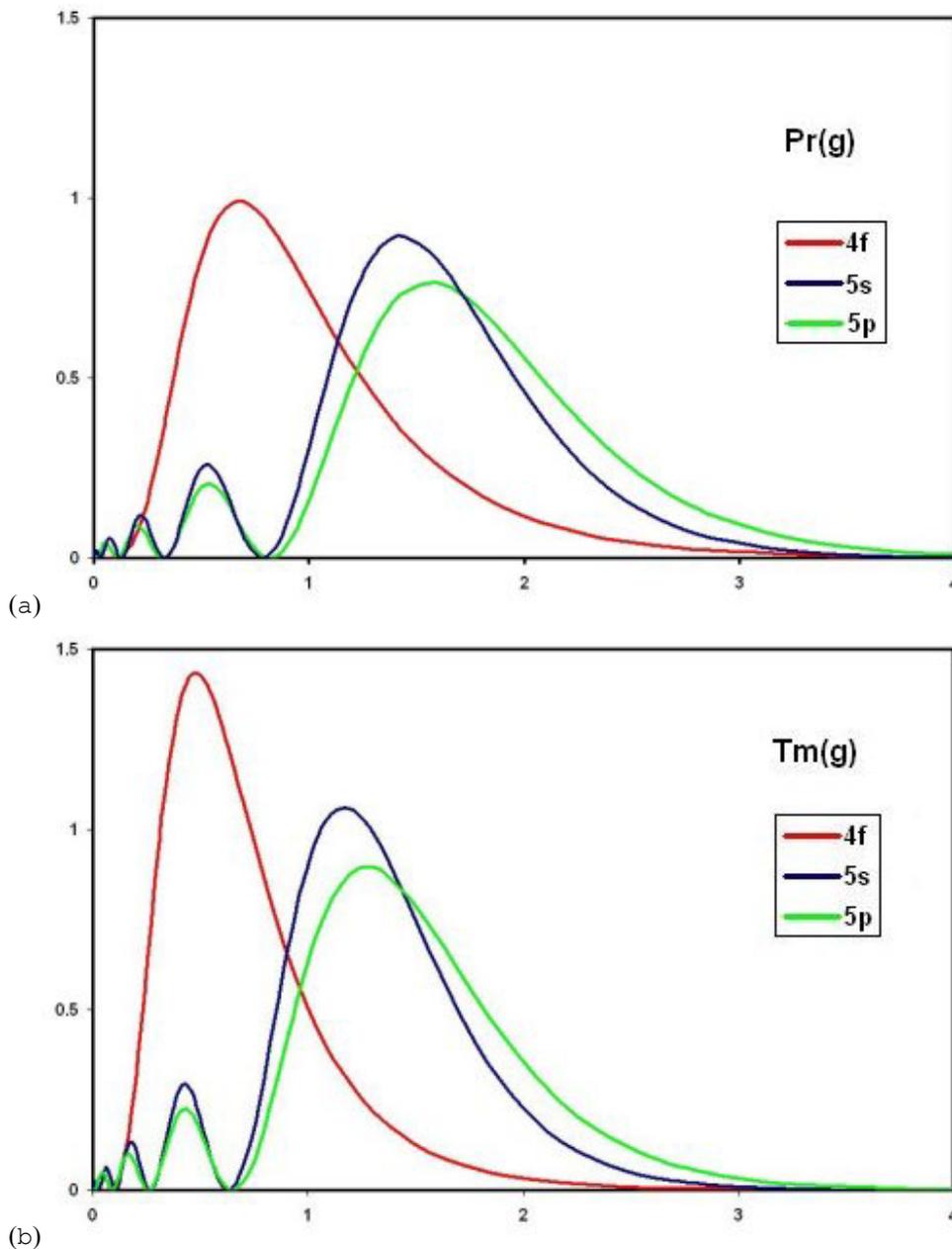


Figure 1 Radial distribution functions for 4f, 5s and 5p electrons in (a) the praseodymium atom and (b) the thulium atom.

Figure 1b shows that this is also true in the thulium atom. Whether we choose an atom from the early or the later part of the lanthanide series, the 4f electrons spend most of their time inside the outer electrons of the xenon core.

These more modern calculations therefore suggest that Bohr was right. In the lanthanide atoms, the 4f electrons are inner electrons and lie well inside the noble gas core. But this discovery makes the disparity between the dominant $[\text{Xe}]4f^n6s^2$ configuration and the

stable +3 oxidation state even more disturbing. The thulium atom for example has the ground state configuration $[\text{Xe}]4f^{13}6s^2$. When it forms compounds in its common oxidation state of +3, three thulium electrons are needed to form the bonds. The outer 6s electrons provide two of them but the third must be taken from the 4f sub-shell. An electron that Figure 1 shows to be well inside the noble gas core in a spatial sense must be used to form bonds.

Why does this seem surprising? In Figures 1a and 1b, the maximum in the 4f distribution lies inside the outer maxima in those of 5s and 5p. This agrees with an idea that we introduced when discussing electronic configurations in the introductory program, *Chemical Periodicity and Electron Structure*: electrons of higher principal quantum number tend to be found at greater distances from the nucleus. But we also suggested that, because they are further from the positively charged nucleus, electrons of higher principal quantum number are more easily lost, either by ionization processes, or in forming bonds with more electronegative elements. It is this second assumption that fails us here. When three electrons on the lanthanide atom are used to form compounds in the most stable oxidation state of +3, one of them is taken from the 4f sub-shell. Despite its location well inside the xenon core and its lower principal quantum number, the 4f electron is easier to remove than the outer 5s and 5p electrons of the xenon core. Why is this?

3 Penetration

Plots like those in Figure 1 tell us something about the motion of a particular type of electron in an atom. That motion is determined by the combined influence of the positively charged nucleus and the other negatively charged electrons. Consider the thulium atom which is the subject of Figure 1b. The atomic number is 69: the nucleus carries a positive charge of $+69e$. Around this nucleus move 69 electrons. The two outermost electrons are 6s. Their distributions are not included in Figure 1b but they will usually be found outside the xenon core. So in a thulium atom, the outer 6s electrons will spend most of their time outside a spherical charge cloud containing the 67 electrons of the xenon core and 4f sub-shell with the nucleus at its centre. This intervening charge cloud protects the 6s electrons from the full force of the $+69e$ nuclear charge. One way of looking at this is to say that the like-charged cloud repels them. Another is to say that the cloud *shields* them so that they experience an *effective* nuclear charge which is much less than the raw value of $+69e$. For example, if we imagine a situation in which one 6s electron is, as usual, well outside the core while the other is, unusually, *inside* it, then a charge cloud of 68 electrons will shield the outermost electron from the nuclear charge of $+69e$. The laws of electrostatics then tell us that the outermost electron would move under the influence of an *effective* nuclear charge of only $+e$.

Calculations using the radial distribution function in Figure 1b suggest that the *average* effective nuclear charge experienced by a 6s electron in a thulium atom is considerably larger than this. The value obtained is $+11.8e$. The main reason for the increased value is that the 6s electrons do not spend all their time outside the core. As we saw in our

program on *The Inert Pair Effect*, they *penetrate* the core and pass close to the nucleus. During this time, there are many fewer electrons between them and the nucleus, so the shielding is reduced and they then experience a nuclear charge closer to $+69e$. Consequently, the average value of the effective nuclear charge is raised to the value we have just quoted.

4 Penetration by 4f, 5s and 5p electrons

At first sight, the sketch of the idea of penetration that we gave in Section 3 does not solve our problem. We want a reason why the 4f electrons are more easily removed than the outer 5s and 5p electrons of the xenon core. But in Figures 1a and 1b, the maximum in the 4f distribution lies well inside the large outer maxima in the 5s and 5p distributions. This suggests that, for most of the time, the 4f electrons penetrate more deeply into the core than the 5s and 5p. There are therefore fewer electrons to shield them from the nuclear charge, so they should be more tightly bound.

- Now make a more careful comparison of the three distributions in Figure 1b. Can you see any grounds for opposing this argument?
- The 4f distribution contains just one maximum. Although the largest maxima in the 5s and 5p distributions lie outside it, there are other lesser maxima that do not. In the case of 5s there are four lesser maxima of this type; in the case of 5p there are three. Unlike the 4f electrons, the 5s and 5p electrons sometimes penetrate deeply into the core and spend an appreciable time very close to the nucleus.*

The potential energy for interaction between charges of $+Ze$ and $-e$ is $-Ze^2/r$. We have seen that, during their motion, the 5s and 5p electrons spend a significant part of their time very close to the nucleus where they experience very large values of Z at very small distances r . This makes the energies of the 5s and 5p electrons more negative than the 4f and, of the three types of electron, 4f is much the most easily removed from the atom. Because the 4f electrons are short on penetration, they can make a contribution to the bonding in lanthanide compounds in spite of their position inside the xenon core.

5 The oxidation state profile

As the program has shown, every lanthanide element forms a +3 oxidation state which is very stable to oxidation or reduction. In keeping with its stability, this oxidation state is very easily made. For example, the metals all dissolve readily in acid to form tri-positive aqueous ions. But going beyond +3 is very difficult. There are a few scattered examples of the +4 state, cerium(IV) being much the most stable example, but oxidation states of

* The number of maxima in the radial distribution function for an orbital of a particular type is $(n - l)$ where n is the principal quantum number and l is the second or azimuthal quantum number. Thus for a 5p electron, $n = 5$ and $l = 1$ so the number is 4; for 4f, $n = 4$ and $l = 3$ so it is one.

five or above have never been made. Let's compare this behaviour with that of a normal transition series.

In *Chemistry of the Transition Elements*, you saw that scandium, the first element in the first transition series, has a highest oxidation state of +3. The highest oxidation state then rises in steps of one unit until we reach the fifth element, manganese. There the value reaches +7 in the permanganate ion before steadily falling back to two at zinc. The lanthanide series starts with lanthanum where, as with scandium, the highest oxidation state is +3. It rises to +4 at the second element, cerium, but the increase then stops. For the final 12 elements praseodymium to ytterbium, the highest oxidation state undergoes no further increase; it is usually three, occasionally four, but never five or above.

Let's relate this behaviour to the electronic configurations of the atoms. Again we'll use the example of thulium which, like most lanthanide elements has a highest oxidation state of +3. The electronic configuration of the atom is $[\text{Xe}]4f^{13}6s^2$. Thulium reacts readily with chlorine to form TmCl_3 , a chloride in oxidation state +3. Let's think of this chloride as ionic. Three electrons are removed from each thulium atom to form a Tm^{3+} ion and create the ionic bonding. These three are provided by the two outer 6s electrons and one of the 4f electrons, leaving the Tm^{3+} ion with the configuration $[\text{Xe}]4f^{12}$. In forming TmCl_3 therefore, one 4f electron has contributed to the bonding, and the reaction has occurred readily. What is striking about the lanthanide elements is that it is very difficult to go further. Occasionally one more 4f electron can be persuaded to make a bonding contribution but certainly not more than one. Consequently the highest observed oxidation state for the whole series is only +4, and the +3 state is very stable to oxidation.

As the 4f electrons are to be found in the xenon core, an explanation of this striking property must be sought in changes that take place within the core itself when the oxidation state increases. All we shall do here is to point to one possibility. We first look for other sub-shells that might have high electron densities in the same region as 4f. An obvious choice is other filled sub-shells with the same principal quantum number. These are 4s, 4p and 4d. Figure 2a shows the radial distribution functions for these electrons in the praseodymium atom of Figure 1a. It has the electron configuration $[\text{Xe}]4f^36s^2$. The single maximum for the 4f electrons and the large outer maxima for the 4s, 4p and 4d electrons all occur close together but that for 4f lies a little further from the nucleus than the other three. Now let's move towards the end of the series. Figure 2b shows the situation in the thulium atom. The raw nuclear charge has increased by $+10e$ and all four distributions have been pulled in towards the nucleus. However, the maximum in 4f has been pulled in more and now lies just *inside* those of 4s, 4p and 4d.

When the thulium atom of Figure 2b forms compounds in oxidation state +3, we expect these electrons to experience a further increase in effective nuclear charge. How do the distributions change? An indication of the kind of change that occurs can be obtained by looking at the situation in the Tm^{3+} ion. This is shown in Figure 2c. There has been a

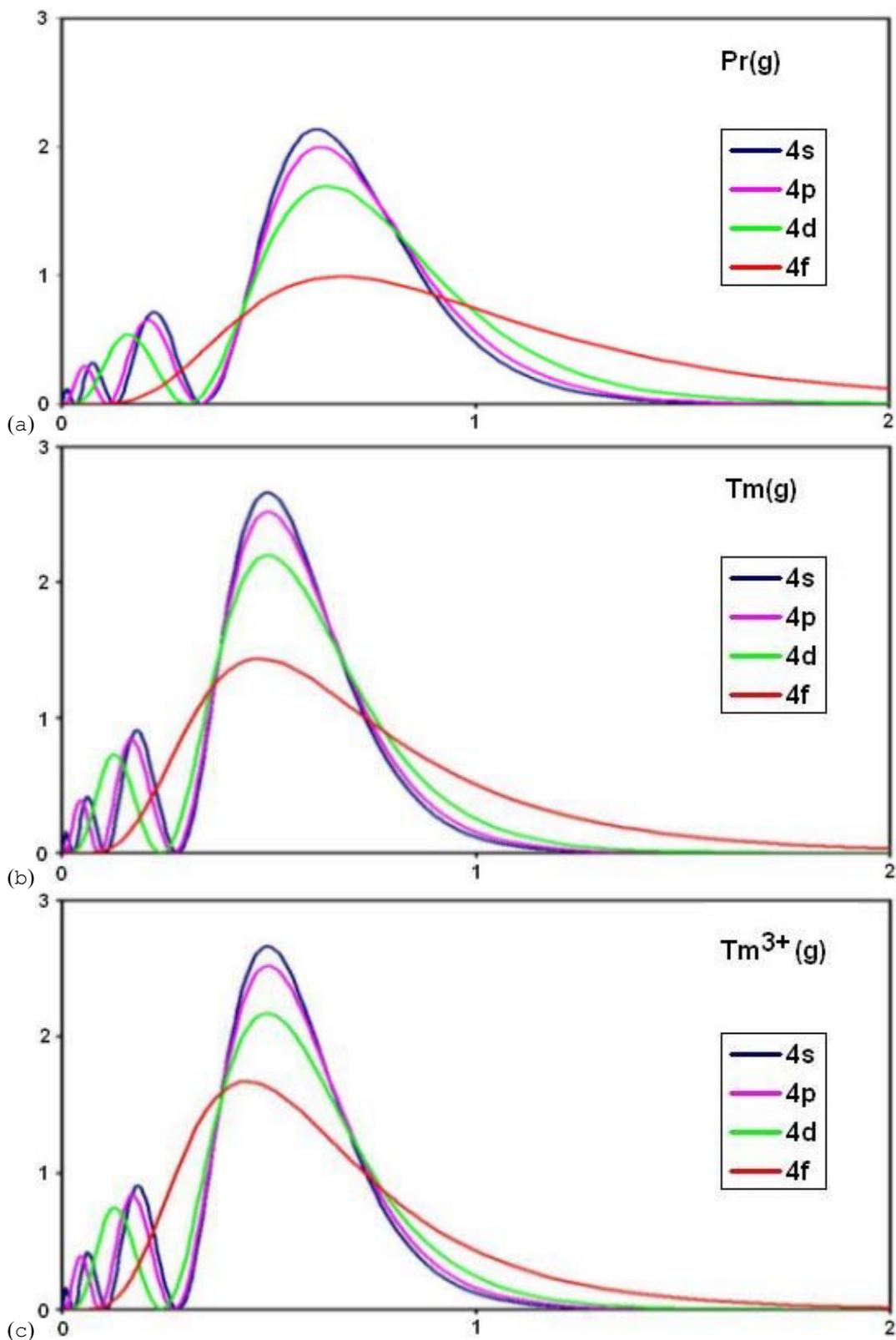


Figure 2 Radial distribution functions for 4s, 4p, 4d and 4f electrons in (a) the praseodymium atom; (b) the thulium atom; (c) the tri-positive thulium ion.

further contraction of the 4f distribution relative to the other three. Its maximum is close to breaking out to the left from under the umbrella provided by the outer maxima of the 4s, 4p and 4d distributions. A significantly larger proportion of the 4f electron density now lies between the umbrella and the nucleus where it is exposed to a considerably greater nuclear charge.

This contraction in the 4f electron distribution with increasing effective nuclear charge might explain why it is hard to obtain lanthanide oxidation states greater than +3. Because there are 18 electrons in the 4s, 4p and 4d sub-shells, the contraction occurs through a region of especially high electron density. With increase in oxidation state, the nuclear charge experienced by the remaining 4f electrons therefore increases especially sharply and at an early stage they become too tightly bound to engage in further bonding.

In Section 4 of the program, *Chemistry of Transition Elements*, we provided a possible reason why the highest oxidation states of the first row transition metals fall below the number of outer electrons beyond manganese. We suggested that the increase in effective nuclear charge, both across the series and with increasing oxidation state, led to a contraction of the 3d electron distribution relative to those of 3s and 3p. Consequently, the 3d electrons are drawn more into the argon core where they become unavailable for bonding. Our explanation of the reluctance of lanthanide oxidation states to rise above +3 is obviously related to this. There are two main differences. Firstly, in the transition series the contraction occurs at the boundary between the argon core and valence electrons, but in the lanthanide series it occurs within the xenon core itself. Secondly, in the transition series, we considered a contraction with respect to eight other electrons (3s and 3p). In the lanthanides this number was eighteen (4s, 4p and 4d). We have suggested that this difference might explain the unusually low oxidation state threshold in the lanthanide series. Both the connections and differences between the two explanations make an attractive story. However, in the case of the lanthanides, the internal structure of the core is very intricate and it is possible that another and better explanation may be found!

6 Samarium; an example

Let's end by using what we have found to discuss the chemistry of a particular lanthanide element. The samarium atom has the electronic configuration $[\text{Xe}]4f^66s^2$. The 6s sub-shell is full and contains two outer electrons; the six 4f electrons lie almost entirely within the xenon core. If the atom is converted to the Sm^{2+} ion, it is the two outer 6s electrons that are lost: the ground state of the ion is $[\text{Xe}]4f^6$. In aqueous solution, this ion is well-known. It is blood-red, and you saw it formed in Section 2 of our program when samarium metal was dissolved in acid.

The two outer 6s electrons spend most of their time outside the xenon core, so their loss causes only a modest increase in the effective nuclear charge experienced by the inner 4f electrons. Thus, when a further electron is needed for bonding it can be taken from the 4f sub-shell. In aqueous solution, $\text{Sm}^{2+}(\text{aq})$ is unstable, and can easily be persuaded to

surrender a 4f electron to become $\text{Sm}^{3+}(\text{aq})$. Again, you watched this in Section 2 where the blood-red dipositive ion was quickly decomposed as it was oxidized by hydrogen ions to pale yellow $\text{Sm}^{3+}(\text{aq})$ with the electronic configuration $[\text{Xe}]4f^5$.

Unlike the loss of the outer 6s pair, the removal of the first inner 4f electron causes a considerable increase in the effective nuclear charge that is experienced by the five 4f electrons that remain. The process outlined in the previous section has therefore begun. In $\text{Sm}^{3+}(\text{aq})$, the 4f electrons have been drawn more deeply into the core than those in the 4s, 4p and 4d sub-shells and their shielding from the raw nuclear charge has been critically reduced. The resulting increase in effective nuclear charge is so marked, that no one has yet succeeded in preparing compounds of samarium(IV), where a further 4f electron has been drawn into bonding and the electronic configuration is $[\text{Xe}]4f^4$.