The purpose of this article is to point out a misconception that is reinforced in many elementary as well as more advanced chemistry texts and to discuss the limitations of the orbital concept generally.

The misconception concerns the “building up” of the transition elements and their first ionization energies. It is frequently stated that for a certain value of atomic number, the orbital energies for the 3d and 4s orbitals cross over each other, so that 4s becomes lower than 3d. The two orbital energies are then said to cross again, thus reestablishing the original order whereby 4s is of higher energy. This feature is used to state the configurations of the elements in the first transition series beginning with scandium. A graph is usually produced, with little indication as to which quantity is plotted on the vertical axis and whether the data are obtained theoretically or empirically (1-7).

The notion that the 4s orbital ever has a lower energy than that of 3d is completely erroneous, as has been previously pointed out in this Journal (8). As Pilar states, this view has no basis in either bona fide quantum theory or experimental findings. The origin of the graph showing intersecting orbital energies (Fig. 1), lies in a paper written in 1955 by Latter (9). This author used the Thomas–Fermi approximation method in order to calculate the orbital energies in several many-electron atoms. The method is known to be rather crude, and several more accurate approaches are available (10). One of the most frequently used alternative methods consists of the Hartree–Fock approximation, which shows that the energy of the 4s orbital is always higher than that of 3d (11).

It is therefore a little surprising to find the persistent use of the graph originally obtained by Latter’s more inaccurate calculations. The reason for this state of affairs presumably lies in the fact that the Latter graph may be used to give the illusion of an explanation for the configurations and ionization energies of transition elements. A typically encountered explanation runs along the following lines although there are numerous variations: Since the energies for 3d and 4s cross each other for the element potassium, the 4s orbital is more stable and therefore preferentially occupied by the 19th electron according to the aufbau principle. At atomic number 21, or the element scandium, the energies have crossed again, but, since the 4s orbital already contains two electrons, the 21st electron enters a 3d orbital. This process is said to continue across the first transition series except for the cases of chromium and copper, where electron repulsion effects are invoked to account for the out-of-sequence configurations involving just one 4s electron (1).

In order to clarify this general procedure we refer to the box diagram representation for the outer shell configurations of potassium, calcium, and scandium, where the relative order of energies of the 3d and 4s orbitals is that given by the Latter calculations. In each case the final electron added to the atom is shown by a bold arrow. The case of scandium deserves special attention. The reason why it is only the final electron that enters a 3d orbital is usually attributed to the 4s orbital already being filled in the atom of calcium. We
return to this point below since it represents something of an anomaly in the scheme.

Now although the 4s orbitals appear to be more stable according to this type of argument, it emerges that the 4s electrons are also the ones most easily lost by ionization of transition metals (12). This apparently puzzling feature is explained away by referring once again to the graph or corresponding box diagram, which shows that the 4s electrons are indeed less stable for these atoms. In the case of calcium, the 4s electrons are also the first to be lost on ionization for the simple reason that this atom does not contain any 3d electrons.

The first of many objections to the above approach is that we can only obtain the configuration of scandium, say, if we already know the precise configuration of the previous element. If, however, we consider the scandium atom in isolation, the Latter graph suggests that the 3d orbitals should be occupied in preference to 4s in view of their greater stability.

Another serious fallacy fostered by the above naive approach is that ionization energies correspond to orbital energies. In truth, the orbital concept and hence orbital energies, rely on approximations made in order to facilitate calculations, whereas measurements of ionization energies reflect the actual interactions between electrons in any atom.

The Schrodinger equation may only be solved exactly for the case of the two-particle system in the hydrogen atom. As soon as we turn to the three-body problem, we must introduce approximations in order to proceed. In the crudest of all approximations, all interactions between electrons are completely neglected. The wave function of the atom is expressed as a linear combination of various products of one electron functions. This approximation yields hydrogenic orbitals whose energies may be obtained exactly. Clearly the orbital energies obtained in this way will fail to correspond to observed data on ionization energies in which inter-electron repulsions are a contributing factor.

The Hartree–Fock method provides a better orbital approximation since it includes the effect of inter-electronic repulsions, but only does so in a time-averaged manner. This method fails to account for the instantaneous changes in the configuration of an atom. The energy contribution due to this effect, or correlation energy, is the focus of much attention in modern theoretical chemistry (13). Correlation effects are responsible for the London dispersion forces, which are important in the context of chemical structure and bonding, such as the solidification of iodine.

In order to account for correlation effects we are forced to abandon the orbital concept altogether; that is, the wave function for an atom may no longer be taken as the product of one-electron functions. An alternative, fuller approach was first applied to the helium atom by Hylleraas (14, 15), and it remains as the basis for some of the most accurate atomic wave functions that have been computed (16).

We turn now to a deeper and more general objection to the use of orbitals. The orbital approach consists in attributing a set of four quantum numbers to each electron in an atom, as was suggested by Pauli when he formulated his exclusion principle (17). Very shortly afterwards the advent of the new quantum mechanics showed that electrons are not in stationary states, but only the atom as a whole can be said to have stationary states. It follows that the use of four quantum numbers in the characterization of individual electrons is illegitimate, with the exception of the hydrogen atom. Modern chemistry and physics textbooks, however, routinely produce tables of electronic configurations of each element, while most invariably fail to emphasize the approximate nature of this classification.

The manner in which quantum mechanics dispels the view that each electron is in a stationary state is understood as follows: If we consider the Hamiltonian operator for the system \( H \), together with any other operator which may be denoted by \( H \), then Heisenberg’s equation of motion, which is equivalent to the Schrödinger equation, may be written as

\[
\frac{\text{d}\psi}{\text{d}t} = \frac{i}{\hbar} [A, \psi]
\]

If these two operators commute, it follows that the dynamical variable associated with the operator \( A \) is a constant of the motion, or in other words a time-independent property. If we consider the quantum numbers for individual electrons, it can be shown that their operators do not commute with the Hamiltonian (18). It follows that these numbers are not constants of the motion for many-electron atoms. The quantum numbers for the atom as a whole on the other hand do correspond to operators that commute with the Hamiltonian. When the spin-orbit interaction is included, however, even the overall quantum numbers of \( L \) and \( S \), representing total orbital and spin angular momenta, respectively, fail to commute with the Hamiltonian (19). The only quantum number that remains “good” in this sense is the overall angular momentum numbered denoted by \( J \). Furthermore, spectral evidence on atoms must be interpreted in terms of a set of overall quantum numbers obtained by the coupling of individual electron quantum numbers, contrary to the orbital model. It would appear that the orbital model accords neither with quantum mechanical theory nor experimental fact.

Post, a philosopher of science, has written about the unquestioning allegiance to a particular scientific model, which he sees as increasingly prevalent (20). Traditional models have been either deductive or inductive. Deductive ones are approximations to a more general theory without logical contradiction, while inductive models originate in empirical evidence and point the way to a new, as yet incomplete theory. According to Post, a third, weaker type of model has arisen in recent times, whose failings, however, are not generally appreciated. He calls this class the “floating” models, since they are neither strictly derived from a theory nor are they based on experimental observation. He cites as an example the atomic orbital model, which is allegedly based on quantum mechanics but which stems from approximations that logically contradict the theory. He also claims a lack of direct experimental evidence for atomic orbitals, since experiments observe the interaction between electrons, which is denied by the simple atomic orbital model. As we saw earlier, even more sophisticated orbital models cannot account for dynamic correlation effects between electrons, which must be artificially introduced into the orbital approach in order to obtain agreement with experimental atomic energies.

Many chemists would choose to ignore these purist objections, however, since the orbital model does provide a reasonably good approximation and serves to rationalize a considerable body of knowledge on the structure and bonding of elements. It also serves as a good starting point for the classification of spectral terms. It would clearly not be desirable to abandon the model, but it is essential for educators and writers of textbooks to stress the limitations of the orbital approximation.

Returning to our opening discussion of the relative energies of the 3d and 4s orbitals, it seems that in this case there is no justifiable reason for continuing to teach this point by referring to the Latter diagram as well as all the inconsistencies that were pointed out previously. If we must be pragmatic and accept the usefulness of orbitals, then we should at least recognize their poorer relative energies rather than compounding a situation that is already philosophically unsound with further inconsistencies.

**Literature Cited**