4s is Always Above 3d!

or, How to tell the orbitals from the wavefunctions

Textbook diagrams showing that the energy of an electron in a 4s “level” is less than that of an electron in a 3d “level” for atoms of atomic number 19 and above have no rigorous basis in experiment or in bona fide quantum theory.

Many textbooks of general chemistry contain a diagram—either with the chapter on atomic electronic structure, or the chapter on the periodic table—said to represent the energy levels of electrons within an atom. The diagram invariably shows that the energy of an electron in a 4s “level” is less than in a 3d “level” for atomic numbers of 19 and above. Yet, such a diagram has no rigorous basis either in experiment or in bona fide quantum theory. First, individual electrons in many-electron atoms do not exist in energy levels—at least not in the sense of stationary quantum states—and second, when orbital energies (as the electron “levels” are properly termed) are correctly defined, the 4s orbital energy is always above the 3d orbital energy.

The chemist’s model of the many-electron atom is based on many features of the exact solution of the nonrelativistic Schrödinger equation for the hydrogen atom. In this special case there is only a single electron moving in the field of the nucleus and the solutions labelled 1s, 2s, 2p—refer to stationary quantum states of the atom. Unfortunately, chemical educators have been careless in the development of the concepts needed in building up a qualitative model of an atom containing more than one electron; the role played by the additional electron(s) is not as trivial and disposable as usually assumed. In particular, terms such as orbital, orbital energy, energy level, and wavefunction either have been misused or employed in rather vague ways. Consequently, although chemists frequently allude to the Schrödinger equation as their ultimate authority—and sometimes even display it in freshmen texts in full differential attire!—they invariably proceed to develop a model for atomic electronic structure which not only is in variance with various quantum mechanical principles but contains internal inconsistencies as well. Anyone who has tried to teach the rigorous quantum mechanical basis of the orbital approximation to upperclass or beginning graduate chemistry students knows how much has to be unlearned.

The wavefunction of an atom or molecule is a mathematical quantity which contains all possible relevant information about the system. Strictly speaking, only an isolated system can be described by a wavefunction. The simplest satisfactory quantum mechanical model of a many-electron atom assumes that the electronic wavefunction may be approximated by a Slater determinant of one-electron distribution functions which contain both spatial and spin coordinates of the electrons. For the special case of an atom with an even number of electrons (2N), all in closed shells, the determinantal wavefunction is customarily assumed to have the special form

$$\psi(1,2,\ldots,2N) = \frac{1}{\sqrt{(2N)!}} \left| \begin{array}{c} \phi_1(1)\phi_2(1)\ldots\phi_N(1) \\ \phi_1(2)\phi_2(1)\ldots\phi_N(2) \\ \vdots \end{array} \right|$$

(1)

where $\phi_\mu(\mu)$ is the spatial part of the one-electron distribution function used to describe the behavior of electron $\mu$. The quantities $\alpha(\mu)$ and $\beta(\mu)$ are the spin parts of the one-electron distribution functions. The determinantal form is required in order to satisfy the important fundamental antisymmetry principle of quantum mechanics. The physical interpretation of the determinantal wavefunction is that of a superposition of $2N$ single-electron distribution functions to serve as an approximation to a single $2N$-electron distribution function. The form of the approximate wavefunction is such that each electron is as likely to be described by a particular function $\phi_\mu$ as by any other; this is necessary in order to avoid implying distinguishability of electrons.

At this point, the one-electron distribution functions—or specifically, their spatial portions—are completely arbitrary; following Mulliken they are given the general name of orbitals. Since orbitals describe a single electron under the average influence of the other electrons, they certainly are not wavefunctions. Individual electrons in a many-electron atom (or molecule) are not isolated systems and, consequently, have no wavefunctions. Only the atom (or molecule) as a whole (assuming it is isolated) can have a wavefunction.

An apparently simple solution to the problem of making specific choices of orbitals to use in the determinantal wavefunction is to use the eigenfunctions of the hydrogen atom. In fact, atomic spectra and other experimental measurements suggest that atoms are often hydrogen-like in behavior. Also, theory shows that if the repulsions between electrons could be ignored, then the determinantal wavefunction using hydrogen-like orbitals would indeed be the exact wavefunction of the atom. Nevertheless, hydrogen atom wavefunctions do not turn out to be good orbitals for many-electron atoms.

Considerable improvement results by modifying the hydrogen wavefunctions by using the nuclear charge $Z$ as an adjustable parameter. One way of interpreting the effect of varying $Z$ is in terms of a shielding or screening of nuclear charge by the electrons; this is a crude and incomplete way of taking electron repulsions into account. Nevertheless, most fixed sets of orbitals generally lead to certain internal inconsistencies, especially for large-$Z$ atoms.

1. In general, for $N$ electrons ($N$ odd or even), a linear combination of two or more Slater determinants may be needed. However, most of the qualitative aspects of the model do not depend on this generalization.

2. Since the exact wavefunction must be antisymmetric with respect to exchange of the full coordinates (space and spin) of any pair of electrons, approximate wavefunctions will be all the better if they also obey the antisymmetry principle. Incidentally, the Pauli exclusion principle is not a fundamental principle of quantum mechanics. It arises only because of the particular form (a determinantal product) of the approximate wavefunction employed to satisfy the antisymmetry principle.

3. For example, they are not a complete set of basis functions and they do not lead to satisfaction of the quantum mechanical virial theorem. In addition (and partly as a consequence of the latter) they give very poor approximations to the atom’s total energy and do not correlate well with ionization energies and X-ray and spectral term values.
...the total energy of the atom is not simply the sum of the orbital energies...

notably, that if a single electron is assumed to have a charge distribution implied by an orbital \( \phi_i \), then use of this orbital to define an effective Hamiltonian for the electron—one taking into account the average effect of the other \( 2N - 1 \) electrons—leads to the implication that the electron distribution is not given by the assumed \( \phi_i \) but by some modified orbital \( \phi_i \). It was the genius of the Hartrees (father and son) to suggest a way of obtaining orbitals free of this inconsistency. Such orbitals are now known as SCF (for self-consistent field) or Hartree-Fock orbitals. What at first appears to be an entirely different approach is to use the quantum mechanical variation theorem to select the orbitals which make the total energy of the atom a minimum. Somewhat surprisingly, the two methods can always be transformed into each other without affecting the energy or the intrinsic nature of the model.

The SCF orbitals can always be chosen to satisfy the pseudoenergy equations known as the Hartree-Fock or self-consistent field equations

\[
\mathcal{J} \phi_i = \epsilon_i \phi_i
\]

where \( \mathcal{J} \) is the Hartree-Fock or SCF operator and \( \epsilon_i \) is called the orbital energy. The operator \( \mathcal{J} \) may also be written

\[
\mathcal{J} = h + V^{\text{eff}}
\]

where \( V^{\text{eff}} \) represents the average or effective potential of a single electron moving in a field of \( 2N - 1 \) other electrons. The operator \( h \) (in atomic units) is given by

\[
h = -\frac{1}{2} \nabla^2 - \frac{Z}{r}
\]

and is simply the hydrogen-atom-like Hamiltonian operator of a one-electron atom with nuclear charge \( Z \). The orbital energy \( \epsilon_i \), which is an eigenvalue of \( \mathcal{J} \), represents three contributions to the energy of an electron when its probability density is described by the orbital \( \phi_i \). These are: the kinetic energy of the electron, the potential energy of the electron’s interaction with the nucleus, and the potential energy due to coulombic repulsion between the electron and the effective field provided by the \( 2N - 1 \) other electrons. Since each electron interacts with all the other electrons, individual electrons do not constitute isolated systems. Consequently, the orbitals \( \phi_i \) are not wavefunctions (as they are often called) and the orbital energies \( \epsilon_i \) do not represent energies of quant states of electrons. Although the Hartree-Fock equations bear a strong resemblance to a Schrödinger equation for a single electron, it is important not to confuse the SCF operator with the correct Hamiltonian operator of the atom. The latter has the general form

\[
\hat{H} = \sum_{i=1}^{N} \frac{1}{2m} \nabla_i^2 + V_{\text{pot}}(r_{ij}) + V_{\text{exchange}}(r_{ij})
\]

where \( \hat{H} \) is a hydrogen-atom Hamiltonian (of the same form as eqn. (4)) and the \( 1/r_{ij} \) terms represent electron-pair repulsions. Whereas the Hamiltonian \( \hat{H} \) determines the total energies of the stationary quantum states of the atom, the Hartree-Fock operator (an effective monoelectronic Hamiltonian) has no role save to generate the self-consistent orbitals.

The electron distributions represented by the SCF orbitals bear some resemblance to the electron distributions represented by hydrogen-atom wavefunctions but the differences are significant. Although the SCF orbitals are customarily identified by so-called “quantum numbers” \( n \) and \( l \), these quantities no longer refer to anything which is truly quantized and thus are better regarded as simply convenient labels. One way in which hydrogen-atom wavefunctions differ from SCF orbitals is that the latter no longer exhibit all of the “degeneracy” characteristic of the former. Whereas the hydrogen-atom wavefunctions \( 2s \) and \( 2p \) are degenerate, the SCF \( 2s \) and \( 2p \) orbitals are associated with different orbital energies; this removal of degeneracy is due to the inclusion of electron repulsion.

The total energy of an atom whose wavefunction is approximated by a Slater determinant of the form of eqn. (1) and which has the Hamiltonian given in eqn. (5) may be written in the form

\[
\langle \psi | \hat{H} | \psi \rangle = 2 \sum_{i=1}^{N} \epsilon_i - G
\]

where \( G \) is the electron repulsion energy given by

\[
G = \sum_{i=1}^{N} \sum_{j>i} (2J_{ij} - K_{ij})
\]

The quantities \( J_{ij} \) and \( K_{ij} \) are coulombic and exchange integrals, respectively. For example, \( J_{ij} \) is just the energy due to electrostatic repulsion between two electrons, one with a charge distribution \( |\psi_i|^2 \) and the other with a charge distribution \( |\psi_j|^2 \). The exchange energy, although an electrostatic repulsion energy, has no simple physical interpretation since it arises as a mathematical consequence of antisymmetry.

It is important to note that the total energy of the atom is not simply the sum of the orbital energies as is often stated or implied; the sum of the orbital energies includes the electron repulsion energy \( G \) twice so that \( G \) must be subtracted once in order to obtain a correct total energy.

4British physicists William and Douglas Hartree developed their self-consistent field method for wavefunctions which were not antisymmetric; the Russian V. A. Fock modified the procedure to include antisymmetry.

5The so-called Slater orbitals resemble SCF orbitals much more closely than do H-atom wavefunctions. From SCF orbitals cannot be expressed in simple functional form but rather as tables of density values. Slater orbitals are functions of simple analytical form which duplicate some of the general features of SCF orbitals.
The physical significance of the orbital energy is made clear by Koopman’s theorem... An alternative expression for the total energy is
\[
\langle \psi | H | \psi \rangle = 2 \sum_{j=1}^{N} \epsilon_j^0 + G
\]
where \(\epsilon_j^0\) is given by
\[
\epsilon_j^0 = \epsilon_j - \sum_{j=1}^{N} (2d_{ij} - K_{ij})
\]
The quantity \(\epsilon_j^0\) is also given by
\[
\epsilon_j^0 = \langle \psi | h | \psi \rangle
\]
Thus, physically, \(\epsilon_j^0\) is the energy an electron would have if it had a probability distribution given by the orbital \(\phi_j\) and the other \(2N - 1\) electrons were not present. If the role of the \(2N - 1\) other electrons in determining \(\phi_j\) is ignored, \(\epsilon_j^0\) may be considered as the energy of an independent electron moving in the field of the nucleus.  

The physical significance of the orbital energy \(\epsilon_j\) is made clear by Koopman’s theorem (1, 2) which shows that the \(\epsilon_j\) are approximations to experimental ionization energies, X-ray term values, and spectral term values of atoms. For example, if \(\phi_j\) is the highest energy orbital used to describe the ground state wavefunction of an atom X, then \(-\epsilon_j\) is an approximation to the minimum energy needed to produce the ion X\(^+\); that is, \(-\epsilon_j\) is an approximation to the first ionization energy of atom X. This also means that the ground state energy of an ion X\(^+\) is given by \(E(X^+) = E(X) - \epsilon_j\) where \(h\) is the orbital of highest energy. The fact that X-ray wavelengths may be interpreted in terms of a single electron dropping from one orbital to another does not necessarily mean that electrons themselves are in bona fide quantum states. What it does mean is that the quantum states of the cation may be described quite well in terms of the same orbitals used for the ground state of the neutral atom. The energies \(\epsilon_j\) have no comparable relationship to any experimental quantity. As shown in Figure 1, accurate Hartree-Fock calculations clearly show that \(\epsilon_{3s}\) is above \(\epsilon_{3d}\) for all of the elements of the third full period. More recent Hartree-Fock calculations by Wachters (3), using a totally different calculational approach, show the same general results. Furthermore, as pointed out by Herman and Skillman (4), the Hartree-Fock orbital energies are in excellent agreement with the experimental values and, thus, lend credence to Koopman’s theorem. As a general rule, orbital energies \(\epsilon_j\) increase as \(n\) increases and for the same \(n\) value, the higher \(l\) value has the higher energy.

\[\text{(Ar)} \, 3d \quad 2^2D_{5/2} \quad \text{and} \quad 2^2D_{3/2}\]

\[\text{(Ar)} \, 4s \quad 2^2S_{1/2}\]

\[\text{(Ne)} \, 4s \quad 2^2S_{1/2}\]

\[\text{(Ne)} \, 3d \quad 2^2D_{5/2} \quad \text{and} \quad 2^2D_{3/2}\]

\[\text{Figure 2. Energy level diagram of potassium for the states arising from the (Ar)}3d\text{ and (Ar)}4s\text{ electron configurations.}\]

\[\text{SODIUM}\]

\[\text{Figure 3. Energy level diagram of sodium for the states arising from the (Ne)}3d\text{ and (Ne)}4s\text{ electron configurations.}\]

If \(\epsilon_{4s}\) is always above \(\epsilon_{3d}\), how does one account for the fact that a 4s orbital must be used before 3d in order to obtain electron configurations in accord with the periodic table? The explanation follows quite simply from the variational basis of the SCF model: Since it is the total energy and not the sum of the orbital energies which is minimized, there is no a priori reason to expect that using the lowest energy orbitals necessarily leads to the lowest total energy. In other words, a minimum value of \(2 \sum_{j=1}^{N} \epsilon_j\) does not guarantee a minimum value of \(2 \sum_{j=1}^{N} \epsilon_j - G\) (5). It is true that the sum of the orbital energies is lower when 3d orbitals are used instead of 4s orbitals, but when the electron repulsion term \(G\) is subtracted from the orbital energy sum, the total energy becomes lower when 4s is used instead of 3d. This happens because the repulsions between an argon core 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^2\)3p\(^6\) and 4s are greater than between an argon core and 3d. As noted even by those employing the incorrect model, the 4s electron distribution is more penetrating (spread out more throughout the argon core region) than is the 3d electron distribution so that the former leads to a greater overall electron repulsion—enough greater to more than compensate for the difference in 4s and 3d orbital energies. As a consequence of the above interrelationships, the quantum states of potassium implied by the electron configuration (Ar)4s and (Ar)3d turn out as shown in Figure 2. Misinterpretation of the diagram, due partly to the fact that the quantum states are often labelled 3d and 4s (all this labelling means is that the states arise from configurations with 3d and 4s), leads to the commonly accepted statement that

6However, the \(2N - 1\) other electrons—via the average field they provide in \(J\)—do determine \(\phi_j\) and, consequently, have some effect on \(\epsilon_j\).  
7Experimental values of orbital energies have been tabulated (12).  
8Details of the explanation may be obtained from the author.  
9Another possibility is that in the pre-computer age, SCF calculations were difficult to do and were often approximated by a classical model known as the Thomas-Fermi method. Such calculations predicted that \(\epsilon_{3d}\) was above \(\epsilon_{4s}\) at higher atomic numbers (13).  
10If the orbital occupation diagram indicates a change of spin in the "promoted" electron, the negative sign between the determinants in eqn. (15) changes to a plus sign and the state represented is the triplet state 2\(^3\)S\(_1\). The latter stationary quantum state is slightly lower in energy than is the 2\(^1\)S\(_0\) state, a fact which is readily explainable on the basis of the correct theoretical energy expressions (the basis of Hund’s rule of maximum multiplicity).
3d lies above 4s. The correct interpretation is: in spite of the fact that \( \epsilon_{3d} \) is of higher energy than \( \epsilon_{4s} \), the energy due to the (Ar)3d configuration is lower than that due to the (Ar)3p configuration. Similarly, if energy values are worked out for excited states of sodium based on the configurations (Ne)3d and (Ne)4s, the resulting energy level diagram is as shown in Figure 3. In this case the state based on (Ne)4s lies above that based on (Ne)3d since repulsion between a neon core (1s\(^2\)2s\(^2\)2p\(^6\)) and a single electron is not enough different between 3d and 4s to change the energy minimization stemming from the orbital sum alone.

The correct quantum mechanical model also makes it clear why an ion such as Ti\(^{2+}\) is (Ar)3d\(^2\) rather than (Ar)4s\(^2\); i.e., why Ti\(^{2+}\) is not isoelectronic with Ca (Ar)4s\(^2\); according to Koopmans’ theorem, the energy of Ti\(^{2+}\) must have the general form

\[ E(Ti^{2+}) = E(Ti) - 2\epsilon_{4s} \]

If \( E(Ti^{2+}) \) is to be minimized, it is necessary that \( K \) is 4s rather than 3d since \( \epsilon_{4s} \) is greater than \( \epsilon_{3d} \). One might ask: Why doesn’t 4s/(Ar) repulsion again dominate the total energy term to make (Ar)4s\(^2\) lower in energy, as it does in calcium? The answer is that 1) the aufbau principle (the order of filling) applies only to neutral atoms, and 2) the greater effective nuclear charge of Ti\(^{2+}\) (Z\(_{eff}\) \( \approx \) 22 – 18 = 4) separates \( \epsilon_{4s} \) and \( \epsilon_{3d} \) more than it does in Ca (Z\(_{eff}\) \( \approx \) 20 – 18 = 2). The difference between \( \epsilon_{4s} \) and \( \epsilon_{3d} \) varies roughly as (Z\(_{eff}\))^2. \(^{8}\)

It should be noted that \( \epsilon_{4s} \) is less than \( \epsilon_{3d} \) at the same time that \( \epsilon_{4s} \) is greater than \( \epsilon_{3d} \). This follows from the relationships

\[ \epsilon_{4s} = \epsilon_0 + \frac{\hbar^2}{8m} (2J_{4s} - K_{4s}) \]

\[ \epsilon_{3d} = \epsilon_0 + \frac{\hbar^2}{8m} (2J_{3d} - K_{3d}) \]

and the fact that the summation term in the former is of greater magnitude than in the latter. It may be that it is the \( \epsilon_0 \) and not the \( \epsilon_i \) that some people have in mind when employing the incorrect model,

1) The new orbital energies are neither \( \epsilon_i \) nor \( \epsilon_0 \) and do not correspond very accurately to any experimental quantities. The most glaring discrepancy occurs for the 4s and 3d orbitals; experimental ionization energies clearly show that 4s is above 3d.

2) The electron repulsion energy is not trivial. Qualitatively, it accounts for the removal of degeneracy and quantitatively, it is of appreciable magnitude. For example, in He:\(^1s^2\), \( \epsilon_1 = -0.918 \) au and the total energy is \(-2.862 \) au. Thus, the electron repulsion energy is \( 2(-0.918) + 2.862 = 1.026 \) au—certainly not a negligible value! Consequently, it is not surprising that \( G \) plays such a crucial role in determining ground state electron configurations of third row elements.

3) The variation principle applies only to the correct Hamiltonian, that is, the Hamiltonian containing the electron repulsions. Neglect of electron repulsion implies an effective Hamiltonian which, in turn, ignores the very important variation theorem of quantum mechanics.

4) Neglect of electron repulsion also implies that the Slater determinantal form of the wavefunction may be replaced by a simple product of orbitals (6). Such a wavefunction is not antisymmetric as required by a basic principle of quantum mechanics and implies that one electron is distinguishable from another.

5) The virial theorem, another important theorem of quantum mechanics, requires that the average kinetic energy of the atom equals the negative of one-half the potential energy (7). Neglect of electron repulsions makes it impossible to satisfy this theorem even in principle except by use of unconvincing subtractions.

6) The incorrect model causes undesirable confusion in the minds of students concerning the correct meanings of stationary quantum states, orbital energies, orbitals, and wavefunctions.

It should be clear from the quantum model of atomic electronic structure that diagrams showing the promotion of an electron from one orbital to another are not literal representations of transitions between stationary quantum states. This is one of the hardest things to teach; even advanced students continue to confuse orbitals with wavefunctions and orbital occupation diagrams with quantum state diagrams. As a simple example, consider the transition between the ground state and first excited singlet state of the helium atom. The diagram illustrating this transition is

\[ E_j = E_i \pm 2\epsilon_s \]

As well known, the frequency of radiation which is needed to carry out this transition is given by

\[ \nu = \frac{2\epsilon_s}{h} \]

Now consider the orbital occupation diagram

\[ \begin{array}{c|c|c|c} \hline & 1s^2 & \hline & 1s^1 \end{array} \]

Although this diagram utilizes the form of an energy level diagram, it is simply a mnemonic device that tells one to use the electron configuration 1s\(^2\) to construct the approximate helium atom wavefunction

\[ \psi(1s) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1s(1) & 1s(2) \end{bmatrix} \]

This wavefunction represents the 1S\(_0\) ground state of helium shown as the lower level in the first diagram. Now if one “promotes” an electron from 1s to 2s without changing electron spins, the orbital occupation diagram becomes

\[ \begin{array}{c|c|c|c} \hline & 1s^1 & \hline & 1s^0 \end{array} \]

This tells us only that the lowest singlet excited state of helium may be approximated by the electron configuration 1s2s and the wavefunction (8).

\[ \psi(1s2s) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1s(1)2s(1) & 1s(2)2s(1) & 1s(1)2s(2) & 1s(2)2s(2) \end{bmatrix} \]

This wavefunction represents the 2S\(_0\) excited state of helium shown as the upper state in the first diagram. \(^{10}\) Note that whereas \( E_2 - E_1 \) in the first diagram corresponds to the frequency of the exciting radiation (and thus to a spectroscopic transition of helium) the quantity \( \epsilon_2 - \epsilon_1 \) is not simply related to any observable energy. In fact, one can show that

\[ E_2 - E_1 = \epsilon_3 - \epsilon_4 - 2\epsilon_2 + 2K \]

(16)

Only if the coulombic and exchange integrals (which represent electron repulsions) can be ignored, is it a good approximation to relate differences in orbital energies to differences in quantum state energies. In the above case, the electron repulsions contribute over 14% of the total energy difference. This in itself may be small enough to neglect, but in some cases neglect of electron repulsions leads to qualitative errors similar to those involving the relative values of \( \epsilon_{3d} \) and \( \epsilon_{4s} \).

Although few chemists can (or care to) do SCF calculations, nevertheless, the chemistry community accepts the SCF
model of electronic structure as the legitimate, rigorous basis of the orbital approximation. Even though few of us ever use optimized orbitals explicitly, we still must recognize that the SCF method constitutes a bona fide quantum mechanical model in accord with a large number of fundamental quantum mechanical principles (e.g., antisymmetry, virial theorem, Hellmann-Feynman theorem, correct spin-eigenfunction form, etc.). Consequently, the SCF method—at the very least—ought to establish the ground rules, vocabulary, and concepts employed by chemists when describing the orbital model of electrons in atoms and molecules. Does this mean that all chemistry teachers must now master the intricacies of quantum mechanics in order to be qualified to teach even high school chemistry? Not at all. All that is necessary is that the teacher has a clear conceptual understanding of those topics virtually all chemistry majors are presently exposed to anyway. Perhaps the key things to know are: the difference between an orbital and a wavefunction, the difference between orbital energies and stationary quantum states, and qualitative understanding of the quantities which contribute to the total energy of an atom. An outline of an approach suitable for general chemistry might be as follows.

1) The atom's electronic charge cloud is approximated by a superposition of one-electron charge clouds bearing some resemblance to those of the quantum states of hydrogen.
2) The one-electron charge clouds are called orbitals. An orbital is a subunit of a wavefunction (the total charge cloud of the atom) and describes how a single electron behaves in the field of a nucleus while interacting with one or more other electrons.
3) The total energy of an atom has the general form: $E = F - G$ where $F$ is the sum of the orbital energies and $G$ is the electron repulsion energy. The orbital energies increase as $n$ increases and, for equal $n$ values, increase as $l$ increases.
4) The order of superposition (filling) depends on the minimization of $E$; orbitals which minimize the $F$ part of $E$ may not necessarily minimize $E$ itself (the standard mnemonic device for the order of filling in neutral atoms should be introduced here and the $4s$ versus $3d$ case used as an example).
5) Superposition of orbitals may be designated by electron configurations, box diagrams, or orbital occupation diagrams. If the latter are used, care should be taken not to confuse them with energy level (quantum state) diagrams.

6) Koopmans' theorem: If an atom $X$ has a ground state energy $E_g$, then the ion $X^+$ has the ground state energy $E = E_g$ where $E_g$ is the energy of the highest occupied orbital in the neutral atom. Thus, the orbital energy is simply the negative of the energy needed to remove an electron from a neutral atom to form an ion whose electron configuration does not contain that orbital.

An important argument for basing electronic structure models on the correct SCF model is that nothing is introduced which has to be unlearned or abandoned when and if the orbital approximation is studied at a sophisticated level later in the student's career. Furthermore, even if the student never does become exposed to the latter, he almost certainly will encounter some form of molecular orbital theory, for example, the Hückel approximation, which is perhaps the worst-taught model in the entire spectrum of alleged quantum theoretical models used by chemists. The student may not be able to do anything more with the correct version of the model than is possible with the current incorrect one, but he certainly should be able to place it into a better perspective with respect to bona fide quantum theory. In particular, use of the correct SCF model makes it possible to teach the Hückel approximation on a much sounder basis than is usually done. Most of the crude assumptions and approximations used to justify the Hückel model—especially by organic chemists—are totally unnecessary. The same general results can be obtained in a cleaner and neater fashion by simply using a few key concepts correctly (11).

Literature Cited

7) Ref. (2), pp. 159 and 183 ff.
11) Ref. (2), Chapter 18.