17

The Electronic States of Atoms. II. Higher-Order Approximations for Multielectron Atoms

OBJECTIVES

After studying this chapter, the student should:

1. Understand the basic ideas behind the variation method, the perturbation method, and the self-consistent field method;
2. be able to solve simple problems using the variation and perturbation methods;
3. understand the Aufbau principle and its relationship to the periodic table of the elements;
4. be able to solve problems related to electron configurations and term symbols of multielectron atoms.

PRINCIPAL FACTS AND IDEAS

1. The interelectron repulsions are included in approximation methods that go beyond the zero-order orbital approximation.
2 The variation theorem allows calculation of upper bounds to ground-state energies.
3. The perturbation method allows approximate calculations of energies and wave functions for any states.
4. The self-consistent field method allows generation of the best possible orbital wave function, leaving only the error due to neglect of electron correlation.
5. The electronic structure of multielectron atoms can be described in terms of the approximation schemes.
6. The structure of the periodic table of the elements can be understood in terms of higher-order orbital approximations.

17.1 The Variation Method and Its Application to the Helium Atom

The zero-order orbital approximation that was employed in Chapter 16 neglects the interelectron repulsions, with the result that each electron is independent of the other electrons and occupies a hydrogenlike orbital in a product wave function. There are three principal approximation schemes that go beyond this approximation. The first scheme is the **variational method**, which is based on the **variation theorem**.

The Variation Theorem

The expectation value of the energy for a state corresponding to a wave function ψ is given by Eq. (15.4-1):

$$\langle E\rangle = \frac{\int \psi^* \hat{H}\psi\, dq}{\int \psi^*\psi\, dq} \tag{17.1-1}$$

where $\hat{H}$ is the correct Hamiltonian operator for the system and where the coordinates of all of the particles of the system are abbreviated by q. The integration is to be done over all values of all coordinates.

The variation theorem states: *The expectation value of the energy calculated with any function φ obeying the same boundary conditions as the correct system wave functions cannot be lower than E_{gs}, the correct ground-state energy eigenvalue of the system:*

$$\frac{\int \varphi^* \hat{H}\varphi\, dq}{\int \varphi^*\varphi\, dq} \geq E_{\mathrm{gs}} \quad \text{(variation theorem)} \tag{17.1-2}$$

where φ is any function obeying the same boundary conditions as the correct wave functions and depending on the same coordinates and where $\hat{H}$ must be the correct Hamiltonian. The expectation value is equal to E_{gs} if and only if the function φ is the same function as the correct ground-state energy eigenfunction. The proof of the theorem is assigned in Problem 17.10.

The Variation Method

The variation theorem suggests the **variation method** for finding an approximate ground-state energy and wave function. First choose a family of possible approximate wave functions. The second step is to calculate the expectation value of the energy using the different members of the family of functions. This expectation value is called the **variational energy**, and is usually denoted by W. Next, find the member of the family that gives a lower (more negative) value of W than any other member of the family. Since W can never be more negative than the correct ground-state energy, this value of W is a better approximation to the ground-state energy than is obtained from any other member of the family of functions. The theorem does not guarantee that this function is a better approximation to the correct wave function than any other member of the family, but it is likely to be so. A typical application of the variation method uses a family of functions that can be represented by a single formula containing one or more variable parameters. Such as family of functions is called a **variation function** or a

variation trial function. The variational energy W is calculated as a function of the parameters, and the minimum value of W is found by the methods of calculus.

Application of the Variation Method to the Helium Atom[1]

Let us first use the zero-order orbital wave function of Eq. (16.3-28) as a variation trial function. This is a single function, so no minimization can be done. It is normalized so that the variational energy is

$$\begin{aligned} W = \frac{1}{2}\int & \psi_{100}(1)^*\psi_{100}(2)^*[\alpha(1)\beta(2) - \beta(1)\alpha(2)]^*\hat{H}\psi_{100}(1)\psi_{100}(2) \\ & \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\, dq_1'\, dq_2' \end{aligned} \tag{17.1-3}$$

where $\hat{H}$ is the correct Hamiltonian operator, and where dq_1' and dq_2' indicate integration over space and spin coordinates. The space orbital ψ_{100} is a hydrogenlike $1s$ orbital with $Z = 2$.

Since the helium-atom Hamiltonian operator is independent of the spin coordinates, the spin factor is not operated on and the integral over the spin coordinates can be factored from the space coordinate integration. Because of the normalization and orthogonality of the spin functions, integration over the spin coordinates gives a factor of 2, which cancels the normalizing constant 1/2. We could have omitted the spin factor and the spin integration from the beginning. The result is

$$W = \int \psi_{100}(1)^*\psi_{100}(2)^*\left[\hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\psi_{100}(1)\psi_{100}(2)\, dq \tag{17.1-4}$$

where we use the symbol dq to stand for $d^3\mathbf{r}_1\, d^3\mathbf{r}_2$. The entire Hamiltonian, not the zero-order approximate Hamiltonian, must be used in Eq. (17.1-4).

The $\hat{H}_{\mathrm{HL}}(1)$ and $\hat{H}_{\mathrm{HL}}(2)$ terms in the Hamiltonian operator give ground-state energy eigenvalues for a hydrogenlike atom.

Exercise 17.1

Show that the $\hat{H}_{\mathrm{HL}}(1)$ term in Eq. (17.1-4) yields a contribution to W equal to $E_1(\mathrm{HL})$ and that the $\hat{H}_{\mathrm{HL}}(2)$ term yields an equal contribution.

We now have

$$W = 2E_1(\mathrm{HL}) + \int \psi_{100}(1)^*\psi_{100}(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_{100}(1)\psi_{100}(2)\, dq \tag{17.1-5}$$

Evaluation of the integral in this equation is tedious and we given only the result:[2]

$$W = 2E_1(\mathrm{HL}) + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = 2E_1(\mathrm{HL}) - \frac{5}{8}\langle\mathscr{V}\rangle_{\mathrm{HL}(1s)} \tag{17.1-6}$$

where $\langle\mathscr{V}\rangle_{\mathrm{HL}(1s)}$ is the expectation value of the potential energy for the hydrogenlike atom in its ground state. The variational energy is, using Eq. (16.2-12),

$$W = -2\frac{Z^2e^2}{2(4\pi\varepsilon_0 a)} + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = -108.8\,\mathrm{eV} + 34.0\,\mathrm{eV} = -74.8\,\mathrm{eV} \tag{17.1-7}$$

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[1] Our treatment follows that in J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, pp. 221ff.

[2] I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N. J., 1991, pp. 230ff.

where we have put in the value $Z = 2$ in the calculation of the numerical value. This result is more positive than the correct value of -79.0 eV, as the variation theorem guaranteed. The error is approximately 4 eV, which is much better than the error of -30 eV obtained with the zero-order approximation. This improvement in the energy value was not obtained by changing the wave function. Our wave function is still the zero-order wave function obtained by complete neglect of the interelectron repulsion. The improvement came from using the complete Hamiltonian operator in calculating the variational energy. The zero-order energy was calculated using only the zero-order Hamiltonian, and is not required to conform to the variation theorem.

We now use a variational trial function that represents a family of functions. We replace the nuclear charge Z in the hydrogenlike $1s$ orbitals by a variable parameter, Z'. The modified $1s$ space orbital is

$$\psi'_{100} = \psi'_{100}(Z') = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a}\right)^{3/2} e^{-Z'r/a} \tag{17.1-8}$$

where a is the Bohr radius. The orbital depends on the value of Z', and we label it with a prime ($'$). It is still normalized. The variation trial function is

$$\varphi = \varphi(Z') = \psi'(1)\psi'(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{17.1-9}$$

where we omit the subscripts on the orbital symbols. There is a physical motivation for choosing this variation function. As an electron moves about in the atom, there is some probability that the other electron will be somewhere between the first electron and the nucleus, "shielding" the first electron somewhat from the full nuclear charge and causing it to move as though the nucleus had a smaller charge. Therefore, a value of Z' smaller than 2 should produce a better approximation than the value $Z = 2$ used to obtain the value of -74.8 eV in Eq. (17.1-7).

The wave function of Eq. (17.1-9) is substituted into Eq. (17.1-1) to calculate the variational energy. The correct number of protons, $Z = 2$, not the value of Z', must be used in the Hamiltonian operator. The variational energy is

$$\begin{aligned} W = &\int \psi'(1)^*\psi'(2)^* \\ &\times \left[\hat{\mathscr{K}}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \hat{\mathscr{K}}(2) - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\psi'(1)\psi'(2)dq \end{aligned} \tag{17.1-10}$$

where $\hat{\mathscr{K}}$ is the kinetic energy operator for one electron. The kinetic energy operator of electron 1 operates only on the coordinates of electron 1, so that

$$\begin{aligned} \iint \psi'(1)^*\psi'(2)^*\hat{\mathscr{K}}(1)\psi'(1)\psi'(2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 &= \int \psi'(1)^*\hat{\mathscr{K}}(1)\psi'(1)\,d^3\mathbf{r}_1 \\ &= Z'^2\langle\mathscr{K}_\mathrm{H}\rangle_{1s} = -Z'^2E_1(\mathrm{H}) \end{aligned} \tag{17.1-11}$$

where $\langle\mathscr{K}_\mathrm{H}\rangle_{1s}$ is the expectation value of the kinetic energy of the hydrogen (not hydrogenlike) atom in the $1s$ state, and where we have used the fact that the expectation value of the kinetic energy equals the negative of the total energy (see Section 16.2). We have used the fact that the integral over the coordinates of particle 2 can be factored out, and the assumption that the orbital $\psi'(2)$ is normalized so that this integral equals unity. The factor Z'^2 comes from the fact that the orbital $\psi'(1)$ is the $1s$ orbital for an effective nuclear charge equal to $Z'e$.

The second term in the Hamiltonian operator in Eq. (17.1-10) gives

$$\begin{aligned}\text{Contribution to } W &= \int \psi'(1)^*\psi'(2)^* \frac{Ze^2}{4\pi\varepsilon_0 r_1} \psi'(1)\psi'(2)\,dq \\ &= ZZ'\langle \mathscr{V}_{\mathrm{H}}\rangle_{(1s)} = 2ZZ'E_1(\mathrm{H})\end{aligned} \tag{17.1-12}$$

where $\langle \mathscr{V}\rangle_{\mathrm{H}(1s)}$ is the expectation value of the potential energy of a hydrogen (not hydrogenlike) atom in the $1s$ state. We have a factor of Z from the original factor Z in the Hamiltonian, and a factor of Z' from use of the $1s$ orbital that corresponds to a nuclear charge of $Z'e$. The final equality comes from Eq. (16.2-27).

Exercise 17.2

Show that Eq. (17.1-12) is correct.

The next two terms in the Hamiltonian operator in Eq. (17.1-10) are just like the first two, except that the roles of particles 1 and 2 are interchanged. After the integrations are done, this interchange makes no difference, and these two terms give contributions equal to those of the first two terms. The last term is the same as in Eq. (17.1-6) except that the orbitals correspond to the nuclear charge of $Z'e$ instead of Ze, so that its contribution is

$$\int \psi'(1)^*\psi'(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi'(1)\psi'(2)dq = -\frac{5}{4}Z'E_1(\mathrm{H}) \tag{17.1-13}$$

The final result is

$$W = E_1(\mathrm{H})\left(-2Z'^2 + 4ZZ' - \frac{5}{4}Z'\right) \tag{17.1-14}$$

The variational energy is a function of a parameter, because our variation function was a family of functions expressed by a formula with a parameter.

Exercise 17.3

Verify eq. (17.1-14).

We find the minimum value of W by differentiating with respect to the variable parameter Z' and setting this derivative equal to zero:

$$0 = E_1(\mathrm{H})\left(-4Z' + 4Z - \frac{5}{4}\right)$$

This equation is satisfied by

$$Z' = Z - \frac{5}{16} \tag{17.1-15}$$

For $Z = 2$, $Z' = 27/16 = 1.6875$. Our optimized helium atom wave function corresponds to a shielding of the nucleus so that an electron moves as though there were an effective nuclear charge of 1.6875 protons instead of 2 protons. This is equivalent to saying that one electron has a 31.25% probability of being between the nucleus and the other electron. This electron density acts as though it were located at the nucleus, since a theorem of electrostatics asserts that a spherically symmetric distribution of charge

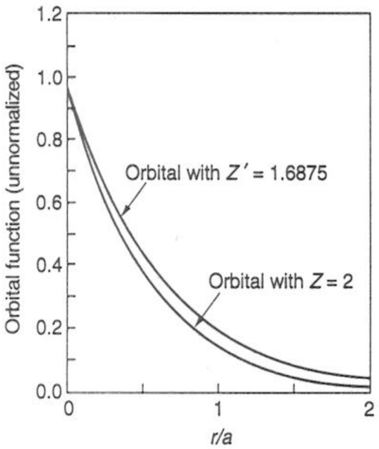

Figure 17.1. Zero-Order and Variationally Obtained Orbitals for the Ground State of the Helium Atom. This diagram shows how the two orbitals compare, with the effect of shielding making the variationally obtained orbital extend farther from the nucleus.

produces an electric field outside of the charge distribution exactly like that of a point charge of the same size as the total distributed charge. Figure 17.1 shows the zero-order $1s$ orbital (with $Z = 2$) and the variational orbital we have just obtained, with $Z' = 1.6875$. The variable on the horizontal axis is the distance from the nucleus divided by the Bohr radius a.

The minimum value of W is

$$W = (-13.60\,\text{eV})[-2(1.6875)^2 + 4(2)(1.6875) - \frac{5}{4}(1.6875)] \\ = -77.5\,\text{eV} \qquad (17.1\text{-}16)$$

This value differs from the experimental value of -79.0 eV by 1.5 eV, an error of 2%, corresponding to 145 kJ mol^{-1}. Our result is still not accurate enough for quantitative chemical purposes. More accurate values can be obtained by choosing more complicated variation functions. Hylleraas used the variation function[3]

$$\varphi = Ce^{-Z''r_1/a}e^{-Z''r_2/a}(1 + br_{12}) \qquad (17.1\text{-}17)$$

This is not an orbital wave function because of the dependence of the final factor on r_{12}, the distance between the electrons. This function gave a variational energy equal to -78.7 eV with a value of Z'' equal to 1.849 and a value of b equal to 0.364. This energy is in error by 0.3 eV, or about 0.4%. More elaborate variational functions have been used, and have given excellent agreement with experiment.[4]

The presence of the factor $(1 + br_{12})$ introduces a dependence on the interelectron distance. In a one-term orbital wave function, the probability density of each electron is independent of the position of any other electrons as in Eq. (16.3-24), and there is no electron correlation. The wave function of Eq. (17.1-17) gives a larger probability density for larger separations of the electrons. This inclusion of explicit dependence on interelectron distance is called **dynamical electron correlation**. An antisymmetrized orbital wave function can also exhibit correlation if it has an antisymmetric space factor like the triplet wave functions of Eq. (16.3-38) or Eq. (16.3-59), since an antisymmetrized space factor vanishes if two electrons are at the same location and has a small magnitude if they are near to each other. This effect is called **statistical correlation**.

Exercise 17.4

Consider the antisymmetrized orbital wave function

$$\Psi = C[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]$$

where ψ_1 and ψ_2 are any two different space orbitals. Show that the wave function vanishes if both electrons are at the same location.

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[3] E. A. Hylleraas, *Z. Physik*, **65**, 209 (1930).

[4] T. Koga, *J. Chem. Phys.*, **94**, 5530 (1991).

17.2

The Perturbation Method and Its Application to the Helium Atom

This method is the second of the three most commonly used approximation schemes. It is applied to a problem in which the Hamiltonian operator can be separated into two terms.

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \tag{17.2-1}$$

such that $\hat{H}^{(0)}$ gives a Schrödinger equation that can be solved:

$$\hat{H}^{(0}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \tag{17.2-2}$$

This equation is called the **unperturbed equation** or the **zero-order equation**. The wave function $\Psi^{(0)}$ and the energy eigenvalue $E^{(0)}$ are called the **zero-order wave function** or the **unperturbed wave function** and the **zero-order energy eigenvalue** or the **unperturbed energy eigenvalue.** The term $\hat{H}'$ in the Hamiltonian operator is called the **perturbation**. The best results are obtained if the perturbation term is small compared to other terms in the Hamiltonian operator.

For the helium atom, $\hat{H}^{(0)}$ is the same as the zero-order Hamiltonian in Chapter 16, and $\hat{H}'$ represents the interelectron repulsion energy. This energy in a helium atom is not small compared with the total energy, but we proceed. We first construct a new Hamiltonian operator in which the perturbation terms is multiplied by a fictitious parameter, λ:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}' \tag{17.2-3}$$

The new Schrödinger equation is

$$\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda) \tag{17.2-4}$$

where the energy eigenvalue and the energy eigenfunction now depend on λ. It seems at first that we are further complicating an already intractable problem by introducing a new independent variable. However, we will express energies and wave functions as power series in λ, and will sometimes obtain useful information by using only a few terms in the series.

Consider a particular energy eigenfunction Ψ_n and its energy eigenvalue E_n, assumed to be nondegenerate. We assume that the energy eigenvalues and energy eigenfunctions can be represented by a power series in λ:

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots \tag{17.2-5}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots \tag{17.2-6}$$

We use superscripts on the coefficients instead of subscripts because we already have subscripts on our eigenvalues and eigenfunctions. The idea of the perturbation method is to obtain only a few coefficients (often just two) in Eqs. (17.2-5) and (17.2-6) and to hope that a partial sum containing these terms gives a useful approximation to the entire series when we let $\lambda = 1$. Figure 17.2 shows schematically a typical energy eigenvalue as a function of λ and as represented by the first two partial sums of the series for values of λ between zero and unity.

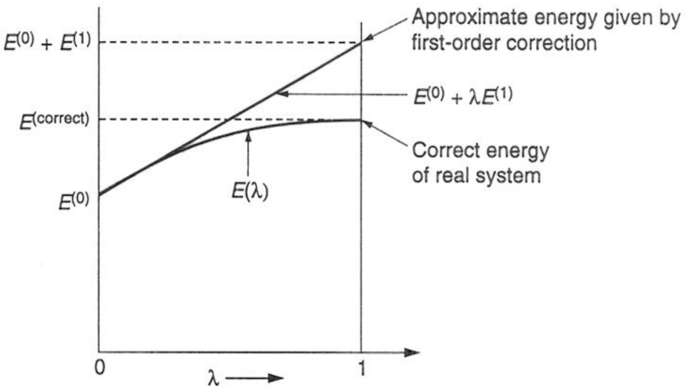

Figure 17.2. An Energy Eigenvalue as a Function of λ for a Hypothetical System. This diagram shows how the fictitious parameter λ is used in the perturbation method. Only the value $\lambda = 1$ has physical meaning, corresponding to the actual system. $\lambda = 0$ corresponds to a soluble problem with part of the Hamiltonian operator omitted (the zero-order problem).

Appendix G contains a derivation of the formula for the first-order correction to the energy, $E_n^{(1)}$. The result contains only the zero-order wave function:

$$E_n^{(1)} = \int \Psi_n^{(0)*} \hat{H}' \Psi_n^{(0)} \, dq \tag{17.2-7}$$

We now apply first-order perturbation to the ground state of the helium atom, for which

$$\hat{H}^{(0)} = \hat{H}_{\text{HL}}(1) + \hat{H}_{\text{HL}}(2) \tag{17.2-8}$$

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{17.2-9}$$

The zero-order ground-state energy $E_{1s1s}^{(0)}$ is given by Eq. (16.3-12) and $\Psi_{1s1s}^{(0)}$ is given by Eq. (16.3-28). Integration over the spin coordinates in Eq. (17.2-7) yields

$$E_{1s1s}^{(1)} = \int \psi_{100}(1)^* \psi_{100}(2)^* \left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right) \psi_{100}(1)\psi_{100}(2)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{17.2-10}$$

This result is the same as the integral in Eq. (17.1-5), so that our perturbation method result to first order is the same as the result we obtained with the variation method using the unmodified zero-order wave function as our variation function:

$$E_{1s1s}^{(0)} + E_{1s1s}^{(1)} = -108.8\text{ eV} + 34.0\text{ eV} = -74.8\text{ eV} \tag{17.2-11}$$

The first-order correction to the wave function and the second-order correction to the energy eigenvalue are more complicated than the first-order correction to the energy eigenvalue, and we do not discuss them. No exact calculation of the second-order correction to the energy of the helium atom has been made, but a calculation made by a combination of the perturbation and variation methods gives an accurate upper bound:[5]

$$E_{1s1s}^{(2)} = -4.3\text{ eV} \tag{17.2-12}$$

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[5] C. W. Scherr and R. E. Knight, *Rev. Mod. Phys.*, **35**, 436 (1963).

so that the second-order value of the energy is −79.1 eV, within 0.1 eV of the experimental value, −79.0 eV. Since the perturbation method is different from the variation method, the second-order energy can be lower than the correct energy. Approximate calculations through thirteenth order have been made, and have given values that agree with experiment nearly as well as the best results of the variation method.[6]

17.3

The Self-Consistent Field Method

The third general approximation method is the **self-consistent field** method (abbreviated SCF) introduced in 1928 by Hartree.[7] The goal of this method is similar to that of the variation method in that it seeks to optimize a wave function. It differs in two ways: first, the search is not restricted to any particular family of functions; second, it deals only with orbital wave functions. It allows the form of the orbital functions to be varied, and is capable of finding the best possible orbital approximation. The SCF method is extensively used in modern quantum chemistry. We do not discuss this method in detail, but illustrate its use by applying it to the ground state of the helium atom. The ground state of helium is a singlet state, and the antisymmetrization is in the spin factor of the wave function. We can proceed with the space factor of the wave function, omitting the spin factor, since the Hamiltonian contains no spin dependence.

The zero-order orbitals satisfied Eqs. (16.3-10) and (16.3-11), which omit the potential energy of electron–electron repulsion. We add a correction term to Eq. (16.3-10) to represent this potential energy. If electron 2 were fixed at location $\mathbf{r}_2$.

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\psi_1(1) = E_1\psi_1(1) \tag{17.3-1}$$

where r_{12} is the distance between the fixed position of electron 2 and the variable position of electron 1 and where E_1 is a new orbital energy. If electron 2 is not at a fixed position, but occupies the normalized orbital $\psi_2(2)$, then its probability of being found in the volume element $d^3\mathbf{r}_2$ is

$$(\text{Probability}) = \psi_2(2)^*\psi_2(2)\,d^3\mathbf{r}_2 = |\psi_2(2)|^2\,d^3r_2 \tag{17.3-2}$$

We now replace the electron–electron repulsion term in the Hamiltonian of Eq. (17.3-1) by a weighted average over all positions of electron 2, obtaining

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_2(2)|^2\,d^3r_2\right]\psi_1(1) = E_1\psi_1(1) \tag{17.3-3}$$

This is an **integrodifferential equation**, since it has both derivatives and an integral in it. After the integration, the integral term depends only on the coordinates of electron 1, so that the equation has a solution if the orbital for electron 2 is a known function. However, at this point both $\psi_1(1)$ and $\psi_2(2)$ are unknown functions (both are ψ_{1s} function if we are discussing the ground state).

The integrodifferential equation is solved by iteration (successive approximations). The first step is to replace the orbital under the integral by the zero-order function or

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[6] C. W. Scherr and R. E. Knight, *loc. cit.* (Note 5).

[7] D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24**, 89, 111, 426 (1928).

some other known function. The $\psi_{1s}(1)$ orbital that results from solving this equation is called the first-order solution $\psi_{1s}^{(1)}(1)$. The equation that it obeys is

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(1)}(1)-\frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(1)}(1)+\left[\int\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(0)}(2)|^2\,d^3r_2\right]\psi_{1s}^{(1)}=E_{1s}^{(1)}\psi_{1s}^{(1)}(1) \tag{17.3-4}$$

where $E_{1s}^{(1)}$ is a new approximation to the orbital energy. It is found that the integral in this equation depends only on r_1, not on θ_1 and ϕ_1, so the θ_1 and ϕ_1 dependence can be separated from the r_1 dependence. It is ordinarily not possible to solve Eq. (17.3-4) analytically, but an accurate numerical representation of $\psi_{1s}^{(1)}(1)$ can be obtained.

The next iteration (repetition) is carried out by replacing $\psi_{1s}^{(0)}(2)$ under the integral sign by $\psi_{1s}^{(1)}(2)$ and denoting the new unknown function by $\psi_{1s}^{(2)}(1)$. This equation is solved, and the resulting solution is used under the integral for the next iteration, and so forth. The equation for the jth iteration is

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(j)}(1)-\frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(j)}(1)+\left[\int\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(j-1)}(2)|^2\,d^3r_2\right]\psi_{1s}^{(j)}(1)=E_{1s}^{(j)}\psi_{1s}^{(j)}(1) \tag{17.3-5}$$

Successive approximations converge to the best possible orbital approximation. When additional iterations produce only negligible changes in the orbital function and the energy, we say that the integral term provides a self-consistent contribution to the force on electron 1, or a **self-consistent field**. At this point, the iteration is stopped and we assume that we are close to the best possible orbitals.

In the SCF method, the expectation value of the energy is not the sum of the orbital energies, because the potential energy of electron–electron repulsion has been included in Eq. (17.3-3) for each electron. Since both orbitals are obtained from this equation, the sum of the two orbital energies includes the interelectron repulsion energy twice. We correct for this double inclusion by subtracting the expectation value of the interelectron repulsion energy from the sum of the orbital energies. If n iterations have been carried out, the expectation value of the energy is

$$\begin{aligned}E(\text{atom})&=2E_{1s}^{(n)}-\int\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(n)}(1)|^2|\psi_{1s}^{(n)}(2)|^2\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2\\&=2E_{1s}^{(n)}-J_{1s1s}\end{aligned} \tag{17.3-6}$$

The integral J_{1s1s} is called a **Coulomb integral** because it represents at approximate expectation value of a Coulomb (electrostatic) repulsion energy between two electrons.

Roothaan modified the Hartree–Fock method by representing the orbitals by linear combinations of functions similar to Eq. (15.2-13) instead of by numerical representations.[8] Clementi and Roetti expressed the unknown orbitals as a linear combination of **Slater-type orbitals** (STOs). Each Slater-type orbital is a product of r raised to some power, an exponential factor, and the correct spherical harmonic angular functions. Using this expression instead of a numerical representation to evaluate the integrals in the self-consistent-field method, they obtained an energy for the ground state of the helium atom equal to −77.9 eV.[9]

The Slater-type orbitals are named after the same John C. Slater after whom the Slater determinants are named.

The self-consistent field method converges to the best orbital wave function, but it does not include any dynamical electron correlation. The difference between the best

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[8] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[9] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

energy calculated with an orbital wave function and the correct nonrelativistic energy is called the **correlation energy** or the **correlation error**. The 1.1 eV error of Clementi and Roetti is presumably an approximation to the correlation error. The "configuration interaction" method eliminates part of the correlation error by constructing a wave function that is a sum of terms, each of which corresponds to a different electron configuration. We discuss this method briefly later in this chapter and in the next chapter.

17.4 Excited States of the Helium Atom

Excited states of atoms are generally harder to treat than ground states. The variation theorem applies only to ground states, so it cannot be used for excited states in its original form. There is an **extended variation theorem**, which states that the calculated variational energy will be no lower than the correct energy of the first excited state if the variation trial function is orthogonal to the correct ground-state energy eigenfunction. It will be no lower than the energy of the second excited state if the variation trial function is orthogonal to both the ground state and the first excited state, etc.[10] Unfortunately, the correct ground-state energy eigenfunction is not generally known, so that a family of functions exactly orthogonal to it cannot be chosen. Some calculations have been made in which a family of functions is chosen that is orthogonal to an approximate ground-state variation function. This family of functions might be nearly orthogonal to the correct ground-state function and the minimum variational energy from this family might be a good approximation to the energy of the first excited state. In other cases, even if the ground-state wave function is not known, some known property, such as being a spherically symmetric function, might permit construction of a trial function that is exactly orthogonal to it.

Degenerate Perturbation Theory

The perturbation method as described earlier in this chapter does not apply to a zero-order state that has the same energy as other zero-order states of the system (the degenerate case). For example, the zero-order orbital energies of the $2s$ and $2p$ hydrogenlike orbitals are all equal, to that all of the zero-order states of the $(1s)(2s)$ and $(1s)(2p)$ helium configurations have the same energy. A version of the perturbation method has been developed to handle the degenerate case. We will describe this method only briefly and present some results for the first excited states of the helium atom.[11]

There is no guarantee that the wave functions that we first obtain with the zero-order solution are in correspondence with the correct wave functions in the degenerate case. If not, the smooth dependence on the parameter λ depicted in Figure 17.2 will not occur. The first task of the degenerate perturbation method is to find the **correct zero-order wave functions**, the ones that are in one-to-one correspondence with the exact wave functions. As the fictitious parameter λ is increased from a value of zero to a value of unity, each correct zero-order function smoothly turns into one of the exact functions

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[10] Levine, *op. cit.*, pp. 193ff (Note 2).

[11] Levine, *op. cit.*, pp. 241ff (Note 2).

without getting mixed up with other functions. We express the correct zero-order wave functions as linear combinations of the degenerate "initial" zero-order wave functions:

$$\Psi_{n(\text{new})}^{(0)} = \sum_{j=1}^{g} c_{nj}\Psi_j^{(0)} \tag{17.4-1}$$

In order to find the c_{nj} coefficients that define the correct zero-order functions, one must solve a set of homogeneous linear simultaneous equations that are somewhat similar to a set of equations described in Appendix H. Every equation of such a set consists only of terms each of which is proportional to one of the coefficients to be found. These equations are "trivially" satisfied if all of the coefficients equal zero. An equation that must be satisfied for a nontrivial solution of these equations to exist is called a **secular equation.**[12] Solution of the secular equation gives the first-order corrections to the energies as well as allowing solution of the equations for the c_{nj} coefficients for each correct zero-order function. It turns out that the wave functions of Eq. (16.3-38) are the correct zero-order functions for the $(1s)(2s)$ configuration, and three sets of similar functions are the correct zero-order functions for the $(1s)(2p)$ configuration.

Figure 17.3 shows the results of calculations to first order and to third orders for the energies of the four levels that result from the $(1s)(2s)$ and the $(1s)(2p)$ configurations.[13] We observe the following facts: (1) Each triplet state has a lower energy than the corresponding singlet state. (2) The $(1s)(2s)$ configuration gives states of lower energy than the $(1s)(2p)$ configuration. That is, the orbital energies of the $2p$ subshell are higher than the orbital energies of the $2s$ subshell. The same behavior is found by experiment generally to be true for atoms with more than two electrons, and it is also found in higher shells that the orbital energies of a d subshell lie higher than those of the orbital energies of the p subshell in the same shell, etc.

It is possible to explain the difference in the subshell energies on the basis of shielding. An electron in the $1s$ orbital of a ground-state helium atom moves as though the nuclear charge were reduced, due to the shielding of the positive nuclear charge by the negative charge of the other electron. Electrons in other shells are similarly shielded by other electrons that are present. An electron in a $2s$ orbital spends more time close to the nucleus than one in a $2p$ orbital, as shown in the radial distribution functions of Figure 16.13b. An electron in a $2s$ orbital will experience less shielding and its energy will be lower than one in a $2p$ orbital, in agreement with the results shown in Figure 17.3.

It is possible to explain the difference in the energies of the singlet and triplet states on the basis of statistical correlation. The singlet state wave functions have symmetric space factors, since the spin factors are antisymmetric. Statistical correlation is not found in symmetric space factors. In the triplet state wave functions, the spin factor is symmetric, so the space factor is antisymmetric, giving statistical correlation, as in Exercise 17.4. The electrons have lower probability of being found close together than of being far apart when the system is in a triplet state. Since close proximity of two electrons corresponds to higher potential energy, a triplet state has a lower energy than a singlet state with the same space orbitals. We will use these explanations involving shielding and statistical correlation again in discussing multi-electron atoms, although this analysis is oversimplified. It also is found that the antisymmetric space factor corresponds to lower probability that the electrons will be far apart, as well as to a lower

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[12] Levine, *op. cit.*, pp. 238ff (Note 2).

[13] Levine, *op. cit.*, pp. 247ff (Note 2).

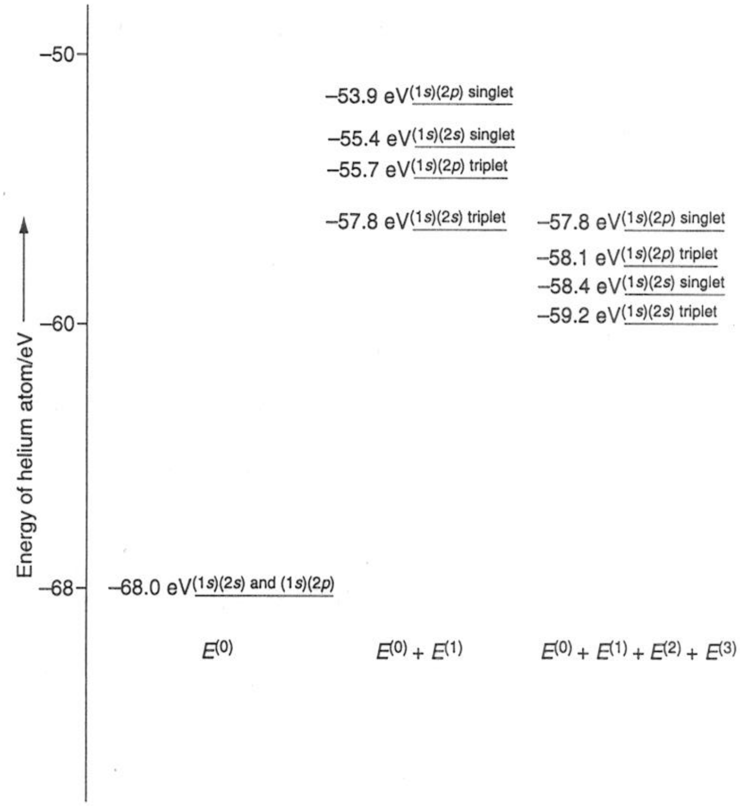

Figure 17.3. Approximate Energies of Helium Excited States. These excited state are the same as those found in perturbation theory. It is assumed that perturbation theory is capable of finding all of the actual states, even if the correct energies cannot be calculated exactly.

probability that they will be close together. There is also a higher probability that the electrons will be found close to the nucleus, and this fact may be a controlling factor.[14]

Exercise 17.5

Sketch a qualitative energy level diagram for the excited states of the $(1s)(3s)$, $(1s)(3p)$, and $(1s)(3d)$ configurations for the helium atom.

The self-consistent-field method must also be modified in order to treat excited states of the helium atom, because two different space orbitals can be involved. In this case two simultaneous integrodifferential equations must be solved by iteration. Furthermore, an antisymmetrized wave function requires two terms in the space factor of the wave function. The original self-consistent-field method of Hartree did not provide for antisymmetrization. The method was modified by Fock[15] to include antisymmetrization.

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[14] Levine, *op. cit.*, pp. 303ff (Note 2).

[15] V. Fock, *Zf. Phys.*, **61**, 126 (1930).

17.5 Atoms with More Than Two Electrons

The discussion of other atoms is similar to that of helium. In zero order, electron–electron repulsions are neglected, and in higher-order calculations these repulsions are treated with the same approximation methods as in the helium atom.

Higher-Order Approximations for the Lithium Atom

The zero-order wave function for the ground state of the lithium atom was written in Section 16.4. An application of the variation method to the lithium atom ground state uses an orbital wave function containing hydrogenlike orbitals with variable orbital exponents (variable effective nuclear charges) similar to that used with helium except that different effective nuclear charges are used in the $1s$ and $2s$ orbitals. The minimum in the variational energy, -201.2 eV, is found to occur with effective nuclear charges of 2.686 protons for the $1s$ orbitals and 1.776 protons for the $2s$ orbital.[16] This variational energy differs from the correct value of -203.5 eV by 1%. The difference in the two effective nuclear charges corresponds to the fact that an electron occupying a $2s$ orbital is on the average farther from the nucleus than an electron occupying a $1s$ orbital, so that there is a larger probability that other electrons are found between it and the nucleus than is the case with a $1s$ electron. The effective charge for the $2s$ orbital corresponds to 1.224 electrons being found between the nucleus and the $2s$ electron, while a $1s$ electron appears to have 0.314 electron between itself and the nucleus.

The effective nuclear charge seen by the $1s$ electrons is nearly the same as would be seen by the $1s$ electrons in a heliumlike atom with three protons in the nucleus, since the minimum in the variational energy of Eq. (17.1-14) occurs at $Z' = 2.6875$ if $Z = 3$. A $1s$ electron in a lithium atom is shielded primarily by the other $1s$ electron, and sees almost no shielding due to the $2s$ electron. Since the $2s$ electron on the average is found farther away from the nucleus than the $1s$ electron, this result is plausible.

*Exercise 17.6

a. Find the value of $\langle r \rangle$ for an electron in a hydrogenlike $1s$ orbital with $Z = 2.686$.
b. Find the value of $\langle r \rangle$ for an electron in a hydrogenlike $2s$ orbital with $Z = 1.776$.

In further variational calculations, the $2p$ orbital is found to be higher in energy than the $2s$ orbitals, so that the ground configuration is $(1s)^2(2s)$, not $(1s)^2(2p)$. The $2p$ electron is more effectively screened from the nuclear charge than is a $2s$ electron. However, an electron in a $2p$ orbital is not on the average farther from the nucleus than one in a $2s$ orbital for the same nuclear charge (see Problem 16.35). It is not just the average distance from the nucleus, but the entire radial probability distribution that determines the effectiveness of the shielding. The $2s$ orbital is nonzero for $r = 0$, while the $2p$ orbitals vanish for $r = 0$, so an orbital in a $2s$ orbital has a greater probability of being found close to the nucleus, where the shielding is least effective, than does an electron in a $2p$ orbital. Figure 16.10b shows that the radial probability distribution for the $2s$ orbital has a "hump" close to the nucleus that the $2p$ orbital does not have. We say that the $2s$ orbital is more "penetrating" toward the nucleus than are the $2p$ orbitals.

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[16] Levine, *op. cit.*, pp. 274ff (Note 2).

The **ionization potential** can be used to obtain an estimate of the effective nuclear charge for the outermost electron in an atom. The first ionization potential is defined as the energy required to remove one electron from an isolated neutral atom. If the orbitals for the other electrons are not changed much by the removal of one electron, the ionization potential is nearly equal to the magnitude of the energy of the orbital occupied by the outermost electron.[17] In the case of lithium, we have already seen that the effective charge seen by the $1s$ electrons is nearly unaffected by the presence of the $2s$ electron, so this condition is fairly well met.

EXAMPLE 17.1

Find the effective nuclear charge seen by the $2s$ electron in lithium from the ionization potential, which is 124 kcal mol^{-1}. Compare this value with the value of 1.776 obtained with the variational method.

Solution

The ionization potential in electronvolts is

$$(\mathrm{IP}) = \frac{(124000\ \mathrm{cal\,mol^{-1}})(4.184\ \mathrm{J\,cal^{-1}})}{96485\mathrm{J\,mol^{-1}\,eV^{-1}}} = 5.38\ \mathrm{eV}$$

The energy of the $2s$ orbital is given by Eq. (16.2-10) as

$$E_2 = -\frac{(17.6\ \mathrm{eV})Z'^2}{4}$$

where Z' is the effective nuclear charge. Setting this energy equal to 5.38 eV gives $Z' = 1.26$, which is in only rough agreement with the value of 1.776 obtained by the variational calculation.

When the perturbation method is applied to the lithium atom, the first-order correction to the ground-state energy is equal to 83.5 eV, resulting in an energy through first order equal to -192.0 eV. This value is considerably less accurate than the value obtained by the simple variational calculation.[18] The Hartree–Fock method is the most successful of the three common approximation methods. A careful Hartree–Fock–Roothaan calculation leads to a ground-state energy of -202.3 eV, differing from the correct value by only 0.6%.[19] This error is presumably a good approximation to the correlation error.

One way to include dynamical electron correlation in an orbital wave function is to construct a wave function that is a linear combination of several Slater determinants corresponding to different configurations, a method that is known as **configuration interaction**, abbreviated CI. For example, for the ground state of the lithium atom, one could use

$$\Psi = c_1\Psi_{1s1s2s} + c_2\Psi_{1s2s2s} + c_3\Psi_{1s1s3s} + \cdots \tag{17.5-1}$$

where c_1, c_2, and c_3, etc., are variable parameters and the Ψs represent Slater-determinant wave functions with the given configurations. The variational energy is minimized with respect to these parameters. Although it is not obvious from inspection of Eq. (17.5-1) that Ψ includes dynamical correlation, it does in fact depend on

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[17] Levine, *op. cit.*, p. 475 (Note 2).

[18] Levine, *op cit.*, p. 274ff (Note 2).

[19] F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, p. 336.

interelectron distances, a fact that we discuss briefly in the next chapter. Unfortunately, the process converges slowly, so that many configurations must be used to get good accuracy. Using large computers, atomic and molecular calculations have been constructed with as many as a million configurations.

Atoms with More Than Three Electrons

The higher-order approximate treatment of the other atoms is similar to the helium and lithium treatments. All three approximations schemes can be applied, but the most accurate work has been done with the Hartree–Fock–Roothaan method and configuration interaction. The optimum orbitals appear to be in one-to-one correspondence with the hydrogenlike orbitals. Figure 17.4 shows approximate orbital energies in neutral atoms, obtained by an approximation scheme called the Thomas–Fermi method. This method gives orbital energies that generally agree with those from the Hartree–Fock method. Notice that logarithmic scales are used in the figure. Several things are apparent: First, the orbitals in the same shell but in different subshells have different energies, with higher values of *l* corresponding to higher energies; second, all of the orbitals in a given subshell have the same energy; third, the energies depend strongly on the nuclear charge, with some pairs of curves crossing and recrossing as a function of

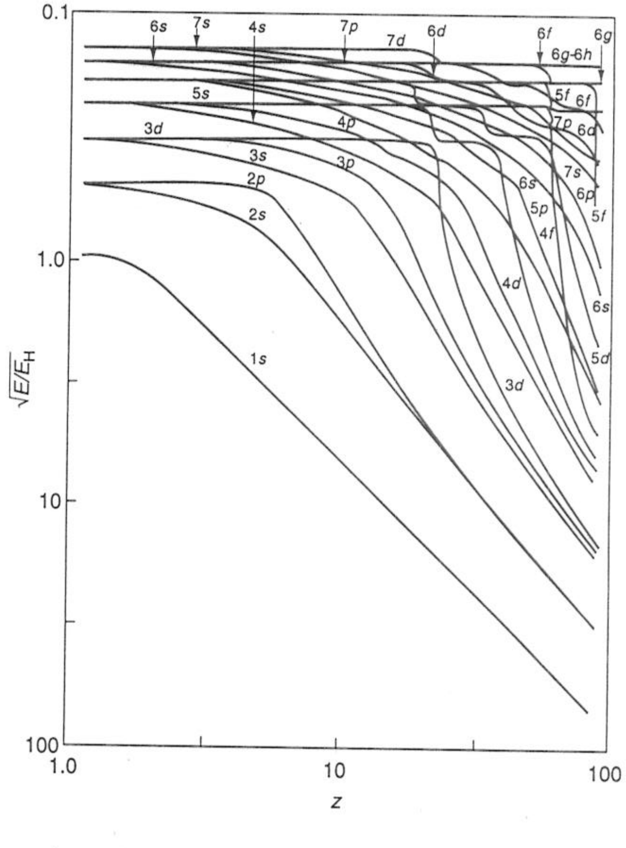

Figure 17.4. **Approximate Orbital Energies in Neutral Atoms.** The axes in this diagram are logarithmic. The order of occupation of subshells can only approximately be determined from this diagram. From R. Latter, *Phys. Rev.*, **99**, 510 (1955).

the nuclear charge. The energy differences between subshells in the same shell can be ascribed to differences in shielding. An electron in an s orbital spends more time close to the nucleus than an electron in a p orbital and is less effectively shielded from the nucleus by other electrons, giving it a lower orbital energy. Similarly, an electron in a p orbital is less effectively shielded than an electron in a d orbital, and so on. All of the orbitals in a subshell have the same orbital energy because they all contain the same radial factor.

Using Figure 17.4 or some equivalent source of orbital energies, it is now possible to determine the ground-level configuration for any neutral atom, using the Aufbau principle that was introduced in Chapter 16. This principle states that the ground-state configuration is obtained by choosing the lowest-energy set of orbitals compatible with Pauli exclusion. For the first 18 elements, the subshell energies lie in the increasing order $1s$, $2s$, $2p$, $3s$, $3p$. For example, the subshell configuration of the ground state of argon is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$. From Figure 17.4 we see that beyond atomic number 15, the $3d$ orbital energy is higher than that of the $4s$. Therefore, elements 19 (potassium) and 20 (calcium) in their ground states have the $4s$ orbitals occupied in preference to the $3d$ orbitals. Beyond atomic number 23, the figure shows the $4s$ energy above the $3d$ energy. However, it is found experimentally that most of the transition elements from scandium (element 23) through zinc (element 30) have two electrons occupying the $4s$ spin orbitals in their ground levels, although chromium (element 24) and copper (element 29) have only one $4s$ electron. Assuming the energies in the figure to be essentially correct, it appears that other factors besides orbital energy, principally the correlation energy, are important in determining the ground-level configuration.

The correct ground-level configuration for most elements can be obtained from the scheme of Figure 17.5, which shows the "**diagonal mnemonic device**" or the "**diagonal rule**." To determine the order of orbitals for the Aufbau principle, one follows the diagonal paths from upper right to lower left, moving top to bottom from one diagonal to the next. The number of spin orbitals in each subshell is listed at the top of the figure, so that one can tell when enough subshells have been chosen to be occupied by the electrons of a given atom. The diagonal mnemonic device is equivalent to the "**$n + l$ rule**," which states that subshells of a given value of $n + l$ are occupied

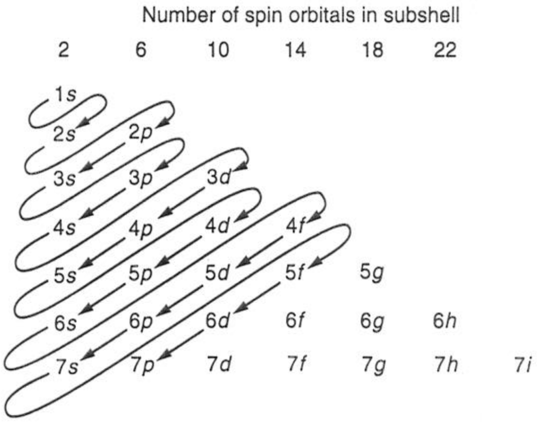

Figure 17.5. The Diagonal Mnemonic Device for Applying the Aufbau Principle to Neutral Atoms. Following the arrows in the diagram gives the order of occupation of subshells in neutral atoms. Exceptions are given in Table 17.1.

before those of the next higher value of $n + l$, and that within a given value of $n + l$, the subshells are occupied in the order of increasing n.

EXAMPLE 17.2

Give the ground-level configuration of (a) Al, (b) Mn.

Solution

a. Al (13 electrons): $(1s)^2(2s)^2(2p)^6(3s)^2(3p)$

b. Mn (25 electrons): $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^5(4s)^2$

Configurations are often abbreviated by giving an inert gas configuration as part of the configuration. The Mn configuration is sometimes abbreviated as $[\mathrm{Ar}](3d)^5(4s)^2$, where [Ar] stands for the ground-level configuration of argon.

*Exercise 17.7

Give the ground-level configuration of the elements: (a) S, (b) Ta, (c) Hg.

Table 17.1 lists the known exceptions to the diagonal rule through element 103. Some of the prominent exceptions are Cr, Cu, Mo, Ag, and Au. In each of these cases, there is d subshell having 5 or 10 electrons instead of having 4 or 9 electrons. These exceptions to the rule apparently correspond to the fact that a half-filled or filled subshell is more stable than otherwise expected, possibly because the orbital regions of the real d orbitals are well separated from each other, allowing electrons to have a fairly

Table 17.1 Exceptions to the Diagonal Mnemonic Rule

Atomic no.	Symbol	Ground configuration
24	Cr	$[\mathrm{Ar}](3d)^5(4s)^1$
29	Cu	$[\mathrm{Ar}](3d)^{10}(4s)^1$
41	Nb	$[\mathrm{Kr}](4d)^4(5s)^1$
42	Mo	$[\mathrm{Kr}](4d)^5(5s)^1$
44	Ru	$[\mathrm{Kr}](4d)^7(5s)^1$
45	Rh	$[\mathrm{Kr}](4d)^8(5s)^1$
46	Pd	$[\mathrm{Kr}](4d)^9(5s)^1$
47	Ag	$[\mathrm{Kr}](4d)^{10}(5s)^1$
64	Gd	$[\mathrm{Xe}](4f)^7(5d)^1(6s)^2$
65	Tb	$[\mathrm{Xe}](4f)^8(5d)^1(6s)^2$
66	Dy	$[\mathrm{Xe}](4f)^9(5d)^1(6s)^2$
67	Ho	$[\mathrm{Xe}](4f)^{10}(5d)^1(6s)^2$
68	Er	$[\mathrm{Xe}](4f)^{11}(5d)^1(6s)^2$
78	Pt	$[\mathrm{Xe}](4f)^{14}(5d)^9(6s)^1$
79	Au	$[\mathrm{Xe}](4f)^{14}(5d)^{10}(6s)^1$
90	Th	$[\mathrm{Rn}](6d)^2(7s)^1$
91	Pa	$[\mathrm{Rn}](5f)^2(6d)^1(7s)^2$
92	U	$[\mathrm{Rn}](5f)^3(6d)^1(7s)^2$
93	Np	$[\mathrm{Rn}](5f)^4(6d)^1(7s)^2$
94	Cm	$[\mathrm{Rn}](5f)^7(6d)^1(7s)^2$
103	Lr	$[\mathrm{Rn}](5f)^{14}(6d)^1(7s)^2$

low energy of repulsion when occupying these orbitals in preference to another choice of orbitals. There has been some discussion about whether lanthanum and actinium are also exceptions to the diagonal mnemonic rule. Lanthanum has sometimes been assigned a $5d$ electron in the ground level, and actinium has been assigned a $6d$ electron. However, from an analysis of spectroscopic observations, it appears that lanthanum has a $4f$ electron in its ground state and that actinium has a $5f$ electron, as predicted by the diagonal rule.[20]

The diagonal mnemonic rule does not necessarily apply to ions, since the shielding is different for ions than for neutral atoms. For example, the iron atom has six $3d$ electrons and two $4s$ electrons, in conformity with the diagonal rule. The Ni^{2+} ion, with the same number of electrons, has eight $3d$ electrons and no $4s$ electrons. The correct electron configuration for positive ions can usually be obtained by finding the configuration of the neutral atom and then removing electrons from the outer shell instead of the subshell to which the last electrons were added.

For those elements with partially filled subshells, the detailed configuration and the values of the quantum numbers L and S of the ground level can be predicted, using rules due to Hund. **Hund's first rule** is: *For the same value of L, the level with the largest value of S has the lowest energy.* **Hund's second rule** is: *For a given value of S, the level with the largest value of L has the lowest energy.* Hund's second rule is applied only after the first rule has been applied. These rules are quite reliable for ground levels, but less reliable for other levels.[21] There is also a third rule, which states that for subshells that are more than half filled, higher values of J correspond to lower energies, and that for subshells that are less than half filled, lower values of J correspond to lower energies.

With several electrons, the operators for the squares of the total orbital and spin angular momentum are complicated, since the angular momenta are vector sums. We will not discuss them, but will work with the z components. The operators for the z components are algebraic sums of the one-electron operators:

$$\hat{L}_z = \sum_{i=1}^{Z} \hat{l}_{iz}, \qquad \hat{S}_z = \sum_{i=1}^{Z} \hat{s}_{iz} \tag{17.5-2}$$

The quantum numbers M_L and M_S are also algebraic sums:

$$M_L = \sum_{i=1}^{Z} m_i \tag{17.5-3}$$

$$M_S = \sum_{i=1}^{Z} m_{si} \tag{17.5-4}$$

For any given detailed configuration, the possible values of M_L and M_S can be determined by algebraic addition as was done in Chapter 16. The addition is simplified by the fact that contributions to both M_L and M_S from filled subshells vanish. The possible values of L and S and the Russell–Saunders term symbols can be found from the fact that M_L ranges from $-L$ to $+L$, and that M_S ranges from $-S$ and $+S$. The ground-level term can then be determined from Hund's rules.

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[20] W. B. Jensen, *J. Chem. Educ.*, **59**, 635 (1982).

[21] Levine, *op. cit.*, pp. 303ff (Note 2).

EXAMPLE 17.3

Using Hund's first and second rules, find the ground-level term symbol for the nitrogen atom.

Solution

The ground-level configuration is $(1s)^2(2s)^2(2p)^3$. Applying Hund's first rule, we seek the largest value that S can have. The filled $1s$ and $2s$ subshells make no net contribution to L or S, because the subshells are filled and their m_s values add to zero. The three electrons in the $2p$ subshell can have their spins parallel if they occupy different space orbitals, so that the largest value of M_S is $+3/2$, and the smallest is $-3/2$. Therefore, the largest value of S is 3/2, and this will be the ground-level value.

Since we are looking for values of M_L, we use the space orbitals that are eigenfunctions of the $\hat{l}_z$ operators, the ψ_{2p1}, ψ_{2p0}, and $\psi_{2p,-1}$ orbitals. Each of these is occupied by one electron, so $M_L = 1 + 0 - 1 = 0$, and the only value of L is zero. The term symbol is ^{4}S (quartet S). There is no need to apply Hund's second rule, since only one value of L can occur with the value of S that we found.

***Exercise 17.8**

Find the ground-level term symbols for (a) Be, (b) B, (c) C, (d) O, and (e) F.

The explanation of Hund's first rule is the same as the explanation for the fact that the triplet levels were lower in energy than the singlet levels in helium, discussed in Chapter 16. The higher values of S correspond to more electrons occupying states of parallel spins, which means that they occupy a larger number of space orbitals. Occupying different orbitals lowers the probability that the electrons will be found close together, thus lowering the potential energy.

The Periodic Table of the Elements

Dmitri Mendeleev, 1834–1907, was a Russian chemist who correlated valence with atomic mass. Julius Lothar Meyer, 1830–1895, was a German chemist who correlated atomic volume with atomic mass.

The periodic table was invented independently by Mendeleev and Meyer. Both noticed that if the elements were listed in increasing order of atomic mass, there was a repetition, or periodicity, of chemical and physical properties. For example, lithium, sodium, potassium, rubidium, and cesium all form oxides with the formula M_2O and chlorides with the formula MCl, while beryllium, magnesium, calcium, strontium, and barium all form oxides with the formula MO and chlorides with the formula MCl_2, where we abbreviate the symbol for the metal with the letter M.

Inside the front cover of this book is a modern periodic table. The elements are listed in order of atomic number, instead of atomic mass, except that some elements are listed separately at the bottom of the table. Elements in any given column exhibit similar chemical properties. There are several ways of numbering the columns, and the two most common ways are shown. One scheme, which is supposed to become the standard scheme, is to number the 18 columns from 1 to 18. The other is to number the columns 1A through 8A and 1B through 8B, as indicated. Three columns are grouped together as column 8B. This numbering corresponds closely to the numbering scheme used by Mendeleev, although the A and B columns were not distinguished in his table, which had only eight columns, with iron, cobalt and nickel together in one column. There is also another numbering scheme in which some of the A and B designations are interchanged. The elements in the columns labeled A are called **representative elements**, and those in the columns labeled B are called **transition elements** or

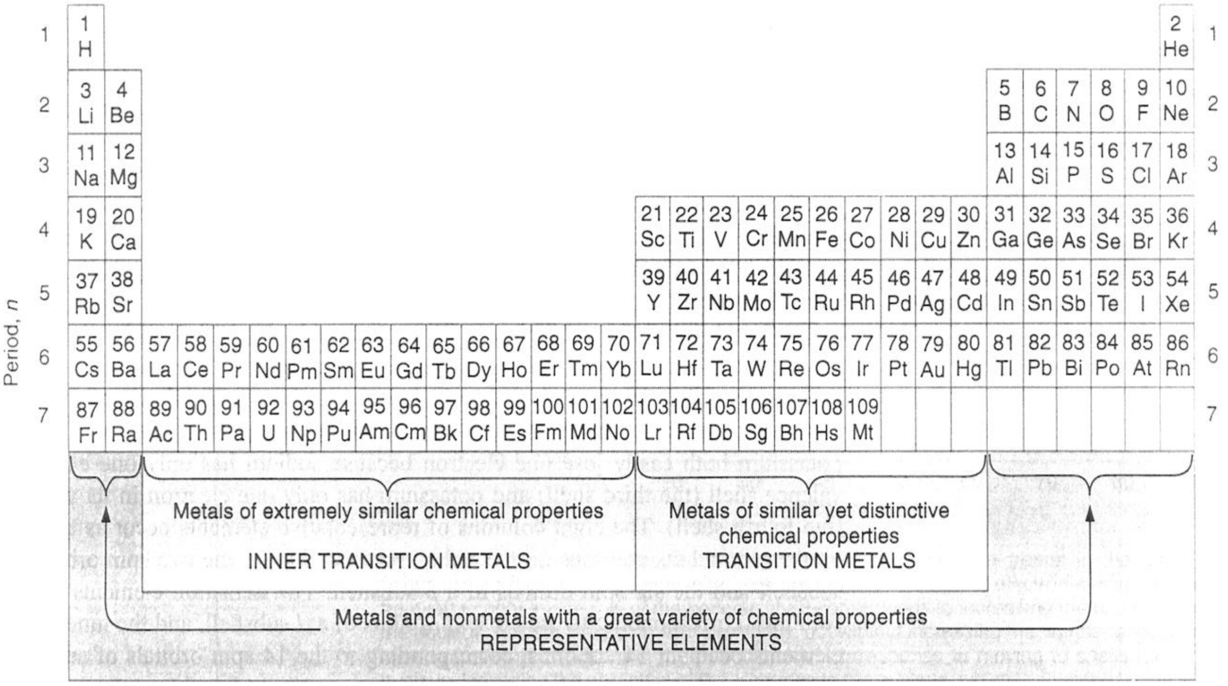

Figure 17.6. A Periodic Table of the Elements. This table is different from the periodic table inside the front cover in that all elements are listed in order of atomic number. The inner transition elements are given their own columns in the body of the table, instead of being placed underneath the body of the table.

transition metals. The two sets of 14 elements at the bottom of the chart are called **inner transition elements** or **inner transition metals**. Figure 17.6 shows a periodic table in which all elements are listed in order of increasing atomic number.

The elements following uranium (U, element 92) in the table do not occur in the earth's crust, but have been synthesized in nuclear reactors.[22] The elements after lawrencium, element 103, were given temporary names: element 104 was unnilquadrium, element 105 was unnilpentium, etc., based on the Latin version of the atomic numbers. Some of these names have been replaced, although there has been disagreement about what the names should be. The names of elements 104–109 that have been accepted by the International Union of Pure and Applied Chemistry are[23]

Atomic number	Symbol	Name
104	Rf	Rutherfordium
105	Db	Dubnium
106	Sg	Seaborgium
107	Bh	Bohrium
108	Hs	Hassium
109	Mt	Meitnerium

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[22] *Chem. Eng. News*, March 13, 1995, p. 35.

[23] *Chem. Eng. News*, August 21, 1995, p. 4, IUPAC news release, August 30, 1997.

Many elements were unknown at the time of Mendeleev. These elements included the inert gases, most of the inner transition elements, and others scattered about the table, such as scandium, gallium, and germanium. However, Mendeleev had sufficient confidence in the periodicity principle that he left blank spaces in the table for undiscovered elements. Mendeleev listed the elements in order of atomic mass, because the concept of atomic number was unknown. There are cases in which a larger atomic mass occurs before a small atomic mass (Ar and K, Co and Ni, Te and I). However, Mendeleev had an incorrect value for the atomic mass of tellurium, he listed Fe, Co, and Ni together in his column 8, and argon had not been discovered. He might have been unaware of these reversals of order.

The form of the periodic table was first explained by Niels Bohr, who also introduced the modern "long" form of the chart with 18 columns. The similarity of chemical properties of the elements in a given column is due to the similarity of their electron configurations in the outermost shell (**the valence shell**). For example, sodium and potassium both easily lose one electron because sodium has only one electron in its valence shell (the third shell) and potassium has only one electron in its valence shell (the fourth shell). The eight columns of representative elements occur as two columns on the left and six columns on the right, corresponding to the two spin orbitals of an s subshell and the six spin orbitals of a p subshell. The transition elements occur in 10 columns, corresponding to the 10 spin orbitals of a d subshell, and the inner transitions elements occur in 14 columns, corresponding to the 14 spin orbitals of an f subshell.

The general chemical behavior of an element can be predicted from its first ionization potential and its electron affinity. The **ionization potential** (also called ionization energy) is the energy required to remove one electron. The **electron affinity** is the energy required to remove the extra electron from a singly charged negative ion of the element. It is therefore equal to the amount of energy given off in forming a negative ion, and is positive if a gaseous atom spontaneously attracts an electron. Those with relatively high ionization potential will also have relatively high electron affinities (except for the inert gases). Those elements with relatively small values of the ionization potential will tend to lose electrons when combining chemically. Those elements with high electron affinities will tend to gain electrons when combining chemically.

Figure 17.7 shows the first ionization potential of the elements as a function of atomic number. The elements with the highest ionization potentials are the inert gases, which have eight electrons in the valence shell (except for helium). A similar graph of the electron affinity would show that the elements of column 7A, the halogens, have the greatest electron affinity. In other words, if the halogen achieves the same configuration as an inert gas by gaining an electron, it becomes relatively stable. The elements with the lowest ionization potentials are the elements in column 1A, the alkali metals, which have a single electron in the s subshell of the valence shell. It is relatively easy to remove an electron from an atom of an alkali metal, giving the inert gas configuration in the shell just below the valence subshell.

Figure 17.7 shows several additional elements, such as beryllium, nitrogen, magnesium, phosphorus, zinc, and mercury, which have higher ionization potentials than their immediate neighbors. All of these elements have ground-level configurations with all subshells completely filled (beryllium, magnesium, zinc, and mercury), or with all subshells filled except for a half-filled valence subshell (nitrogen and phosphorus). We conclude that not only is a filled subshell relatively stable, but also that a half-filled subshell is relatively stable. We have already mentioned this behavior in some exceptions to the diagonal rule, such as chromium and copper.

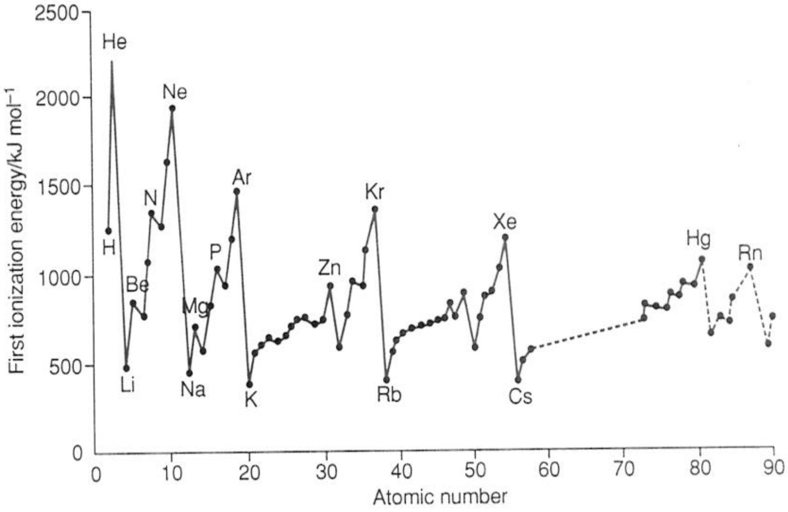

Figure 17.7. First Ionization Potentials of the Elements. The trends in the table and their relation to position in the periodic chart are understood in terms of electron configurations. Moving from left to right in one row of the periodic chart corresponds to increasing the number of protons in the nucleus, holding the electrons more tightly, but without increasing the number of occupied shells. Moving from top to bottom in the periodic chart corresponds to moving to shells farther from the nucleus, lessening the attraction of the electrons to the nucleus, which is shielded by the electrons in the inner shells.

By Hund's first rule, a subshell that is half full or less than half full in the ground level will have each electron occupying a different space orbital, in order to have parallel spins, resulting in the state of maximum M_S. A half-filled subshell therefore has one electron occupying each space orbital, and has the same electron charge distribution as a full subshell except for having only half as much total charge. **Unsöld's theorem** asserts that the charge distribution in a filled hydrogenlike subshell is spherically symmetric (independent of θ and ϕ). This theorem also must hold for a half-filled subshell.

Exercise 17.9

For hydrogenlike orbitals, show that

$$|\psi_{2p1}|^2 + |\psi_{2p0}|^2 + |\psi_{2p-1}|^2$$

is independent of θ and ϕ, as asserted by Unsöld's theorem.

There are a number of additional chemical and physical properties, including atomic size, melting temperature, and electronegativity, that can be correlated with electron configuration and thus with position in the periodic table.

Summary of the Chapter

This chapter introduced three approximation schemes and discussed their application to atoms with two or more electrons. The first approximation scheme was the variation method, in which a variation trial function is chosen to minimize the approximate ground-state energy. A simple orbital variation trial function was found to correspond to a reduced nuclear charge in the helium atom. This result was interpreted to mean that each electron in a helium atom shields the other electron from the full charge of the nucleus. A better approximation corresponds to introduction of electron correlation, a dependence of the wave function on the interelectronic distance.

The next approximation method discussed was the perturbation method. To apply this method, the Hamiltonian must be written as $\hat{H}^{(0)} + \hat{H}'$, where $\hat{H}^{(0)}$ represents a Hamiltonian of a Schrödinger equation that can be solved. The term $\hat{H}'$ is called the perturbation term. The perturbation term is arbitrarily multiplied by a fictitious parameter λ, so that $\lambda = 1$ corresponds to the actual case. The method is based on representations of the energy eigenvalues and energy eigenfunctions as power series in λ and approximation of the series by partial sums. In the helium atom treatment the interelectronic repulsive potential energy was treated as the perturbation term in the Hamiltonian operator. The method gave useful results for excited states.

The third approximation scheme was the self-consistent-field method of Hartree and Fock. In this method an optimum orbital wave function is sought without restricting the search to a single family of functions. For the helium atom the interelectronic replusive energy is represented by assuming the probability density for the second electron to be given by an earlier approximate orbital and solving the resulting integrodifferential equation by iteration.

In the orbital approximation, the energies of the orbitals in multielectron atoms depend on the angular momentum quantum number as well as on the principal quantum number, increasing as l increases. The ground state is identified by the Aufbau principle, choosing orbitals that give the lowest sum of the orbital energies consistent with the Pauli exclusion principle.

Hund's first rule is that the largest value of S corresponds to the lowest energy in a configuration. The second rule is that for fixed value of S, the largest value of L, the quantum number for the total orbital angular momentum, corresponds to the lowest energy. The first rule correlates with the fact that the larger values of S correspond to lower probability for small interelectron distances, lowering the potential energy.

The form of the periodic table is determined by electron configurations. Elements with the same number of electrons in the outer (valence) shell have similar chemical properties. For example, all of the inert gases have eight electrons in the outer shell, corresponding to the stable configuration with fully occupied s and p subshells.

PROBLEMS

Problems for Section 17.1

17.10. Prove the variational theorem. Assume that all of the energy eigenfunctions and energy eigenvalues are known, and write the variation function as a linear combination of the energy eigenfunctions:

$$\varphi = \sum_{i=1}^{\infty} c_i \psi_i$$

Substitute this expression into the formula for the variational energy and use eigenfunction and orthogonality properties.

17.11. Calculate the variational energy of a particle in a one-dimensional box of length a, with the following trial functions:

- ***a.** $\varphi(x) = Ax(a - x)$
- ***b.** $\varphi(x) = Ax^2(a^2 - x^2)$
- **c.** $\varphi(x) = Ax^3(a^3 - x^3)$

Calculate the percent error for each trial function.

17.12. Calculate the variational energy of a harmonic oscillator using the trial function $\varphi(x) = A/(b^2 + x^2)$, where b is a variable parameter. Minimize the energy and find the percent error from the correct ground-state energy.