

The corresponding classical result for $\theta = \pi/2$ would be $2|f(\pi/2)|^2$. Thus for exchange-symmetric particles the scattering at 90° would be just twice as intense as a classical calculation would predict. This is precisely what experiment shows with alpha particles; see Figure 13-4, which shows an angular distribution of alpha particles scattered by helium.

13-8 STATES OF THE HELIUM ATOM

Energy Levels of the Helium Atom

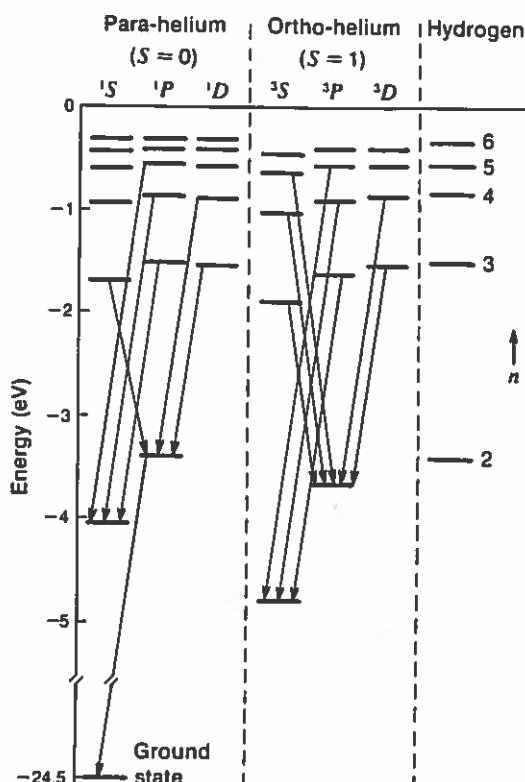
The helium atom provides us with the clearest example of a system of two identical particles in a common potential. The components of the neutral helium atom are two electrons bound in the field of a nucleus consisting of two protons plus either two neutrons (the principal isotope, helium-4) or one neutron (helium-3: relative natural abundance 0.00013 percent). The analysis of the optical spectrum of helium shows that the spectral lines can be classified with the help of two virtually separate energy-level diagrams (Figure 13-5), with almost no transitions taking place from an energy level in one set to levels in the other set.

At one time it was believed that these separate sets of levels belonged to two different and distinct elements, which were given the names ortho-helium and para-helium. But with the discovery of electron spin, it came to be realized that ortho-helium and para-helium were not two distinct substances, but were simply the manifestation of two different classes of energy levels into which the states of any helium atom could be divided, according to whether the electron spins were parallel ($S = 1$) or antiparallel ($S = 0$). The total angular momentum J of any state is then the vector combination of the resultant spin S with the resultant orbital angular momentum L of the two electrons.⁴ For $S = 0$ this gives only one possibility ($J = L$) but for $S = 1$ there are (except for $L = 0$) three possibilities ($J = L - 1, L, L + 1$) with slightly different energies. Combined electron states having $S = 0$ are thus singlets, whereas states having $S = 1$ are in general *triplets*.

This hypothesis concerning the energy-level structure of

⁴Here we are using the italic capital letters L , S , and J to denote the quantum numbers associated with the orbital, spin, and total angular momentum of a two-electron system. The *vectors* L , S , J are the actual angular momenta so that, for example, $|L| = \sqrt{L(L+1)}\hbar$.

Fig. 13-5 Energy levels of helium, showing the transitions observed in its optical spectrum. The zero of the energy scale corresponds to singly-ionized helium (He^+) in its ground state, plus a free electron with zero kinetic energy. Hydrogen energy levels are shown for comparison.



the helium atom was further justified when fine structure of the "triplet lines" was detected. The effectively complete separation between the para-helium ($S = 0$) and ortho-helium ($S = 1$) systems of energy levels is the result of the lack of any efficient radiative mechanism by which electrons of a helium atom, after once being excited to a state having $S = 1$, can find their way back to a state with $S = 0$ (or vice versa). Any such transition must involve a "spin flip" which (as we shall see in Chapter 14) is a very improbable process compared to the electric dipole transitions through which almost all optical spectra are produced.

The problem of accounting in detail for the energy level structure of helium is a complicated one, but is worth discussing because it illustrates so clearly the quantum-mechanical consequences of identity. However, because of the complexity of the problem, we shall approach it via some simpler models which, although less accurate, provide a useful background to, and are consistent with, the more rigorous analysis.

Our discussion begins with simple semiclassical models, first for the ground state and then for the excited states. We will then present the formulation and the main results of the quantum-mechanical theory of the helium atom.

Helium Ground State: Simplest Models

In the ground state of helium, both electrons are in a lowest possible energy state, corresponding in first approximation to the state described by $n = 1$, $l = 0$, and $m_l = 0$ for a single-electron system. This situation requires a *symmetric* space function for the two electrons together, since an antisymmetric space function with equal quantum numbers n , l , m_l would be identically zero (Eq. 13-5b). A symmetric space function is possible provided that the combined spin function is antisymmetric. This means that the ground state of helium belongs to the para-helium ($S = 0$) energy-level structure, as is shown in Figure 13-5. The ionization energy of helium—the energy required to remove one electron from an atom initially in the ground state—is observed to be 24.5 eV. This is the first quantitative result that any theoretical model of the helium ground state must produce.

If we could regard the helium atom as consisting of two electrons each interacting with the central charge $2e$, but having no interaction with one another, then the energy levels would correspond simply to the combination of two hydrogen-like states. The energy of an individual electron would be that of the hydrogen-like ground state⁵ with $Z = 2$:

$$E_n = -\frac{Z^2 me^4}{2\hbar^2} \cdot \frac{1}{n^2} = -13.6 \frac{Z^2}{n^2} \text{ eV}$$

Thus for the ground state, with $n = 1$ for both electrons, we should have

$$E = -54.4 \text{ eV} \quad (\text{for either electron})$$

The energy needed to ionize the atom by removing one electron would then be 54.4 eV. The fact that this is in profound disagreement with the actual ionization energy (24.5 eV) is not surprising since the Coulomb interaction between the two

⁵In this discussion we shall, for simplicity, be using cgs units only.

the point of view of the excited electron, is highly concentrated.

A better analysis, in terms of electron wave functions rather than Bohr orbits, will recognize the fact that the energy levels will depend to some extent on the l value, as well as the n value, of the excited electron. In particular, for $l = 0$, the wave function (as we saw in discussing the Coulomb model in Chapter 12) gives a significant electron probability density at the position of the nucleus; this corresponds, in physical terms, to some penetration through the screening provided by the inner electron. In consequence the electron having $n > 1$ but $l = 0$ will be more fully exposed to the attractive potential of the full nuclear charge, and its energy will be lowered accordingly. This effect is apparent in Figure 13-5; the levels for which both electrons have $l = 0$ are pulled down significantly compared to the corresponding levels in hydrogen.

After this limited success in describing the energy-level structure of helium in very simple terms, we shall now turn to the more rigorous quantum-mechanical description. Here again we begin with the simplest possible model by initially ignoring electron spin and exchange effects. Later we shall add these effects to the analysis.

Quantum Model without Exchange Energy

Any acceptable solution for the electronic structure of helium must be based on the Schrödinger equation as it applies to this system. We have

$$\left[\left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{2e^2}{r_1} \right) + \left(-\frac{\hbar^2}{2m_2} \nabla_2^2 - \frac{2e^2}{r_2} \right) + \frac{e^2}{r_{12}} \right] \psi = E\psi \quad (13-7)$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators for the coordinates \mathbf{r}_1 and \mathbf{r}_2 of the separate electrons, respectively, and r_{12} is the (scalar) distance between the electrons. The presence of the interaction term between electrons, e^2/r_{12} , immediately prevents the equation from being separable in the coordinates of the individual electrons; therefore there is no closed analytic solution, only a process of numerical approximation. For the present we ignore electron spin and exchange effects (that is, the consequences of identity and antisymmetrization, to be examined later) and concentrate on approximation methods that

will allow a crude quantum estimate of the energies of lower levels in helium.

We apply first a technique known as *perturbation theory* that parallels closely the semiclassical Bohr analysis of helium given above. Starting with the initial assumption that the electrons do not interact allows us to use exact wave functions $\psi_i(\mathbf{r}_1)$ and $\psi_k(\mathbf{r}_2)$ for the separate electrons that are identical to the hydrogen atom solutions modified for the nuclear charge $2e$. Here i and k each specify values of n , l , and m_l for the separate states. By ignoring electron-electron interaction and the effects of spin, one can separate Eq. 13-7 if the wave function is written as a simple product $\psi_i(\mathbf{r}_1)\psi_k(\mathbf{r}_2)$ of the hydrogen-like solutions of the separate electrons. Then it is plausible, and more detailed analysis confirms,⁶ that the displacement of energy ΔE_1 caused by the electron-electron interaction is given, to first approximation, by multiplying the interaction energy $V(r_{12})$ by the probability that the electrons have the particular separation r_{12} , as given by $|\psi_i(\mathbf{r}_1) \cdot \psi_k(\mathbf{r}_2)|^2 d\tau_1 d\tau_2$, and then integrating over all the possible positions \mathbf{r}_1 and \mathbf{r}_2 . That is,⁷

$$\Delta E_1 \approx \iiint V(r_{12}) |\psi_i(\mathbf{r}_1) \cdot \psi_k(\mathbf{r}_2)|^2 d\tau_1 d\tau_2 \quad (13-8)$$

This perturbation technique is based on the principle that the effect of a small disturbing interaction can be calculated quite well by applying it to the undisturbed state of the system, ignoring the changes that the perturbing interaction causes in the state itself. (The method was extensively used, long before the advent of quantum mechanics, to deal with comparable problems in classical mechanics, for example the effect of the gravitational interaction between two planets, assuming in the first instance that each orbit is determined by the sun's attraction alone.) Since the functions ψ_i and ψ_k in Eq. 13-8 are known exactly, the integration can be carried out numerically to as high an accuracy as one is willing to pay for. The results are shown in column 3 of Figure 13-8, where ΔE_1 for the pair of states i and k is added to each energy in column 1. Notice

⁶See, for example, R. M. Eisberg, *Fundamentals of Modern Physics*, John Wiley, New York, 1961, Chaps. 9 and 12.

⁷We use $d\tau$ here for volume element (instead of dV) to avoid confusion with the use of V for potential energy.

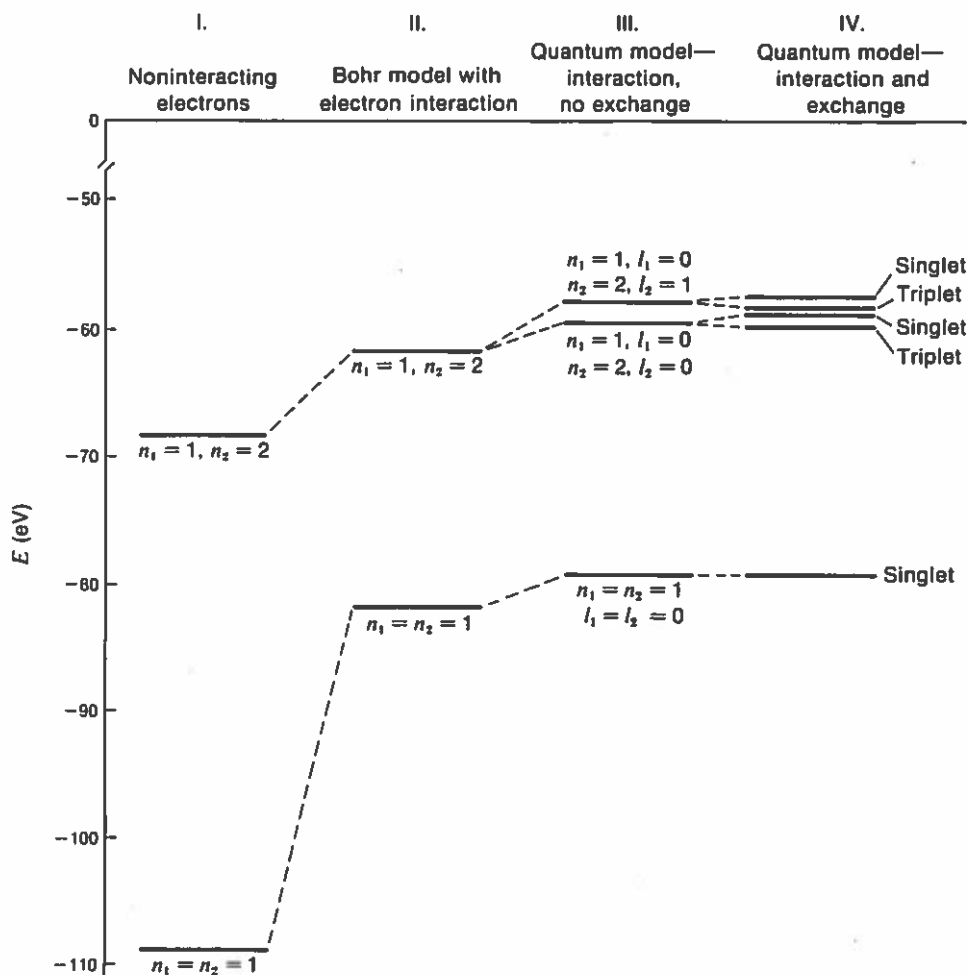


Fig. 13-8 Comparison of theoretical predictions for energy levels of the helium atom according to different models. The zero of energy in this diagram is not the same as in Fig. 13-5; it corresponds to complete separation of the atom into the helium nucleus (He^{++}) and two free electrons with zero kinetic energy. (Note also that the vertical energy scale is contracted relative to that in Figure 13-5.)

that the second level is split into two by this interaction. This is precisely the effect that we have already described qualitatively, namely the removal of the energy degeneracy between states of $l = 0$ and $l = 1$ (for the outer electron in its $n = 2$ states) by virtue of the reduced effectiveness of the electrostatic screening for the $l = 0$ state.

Perturbation theory, which we have invoked in this analysis, assumes that for *small* interactive energies one can use wave functions that are exact in the absence of the interaction. Since the changes in energy between column 1 and column 2 of Figure 13-8 show that the electron-electron interaction energies are *not* small, we see that perturbation theory cannot yield accurate values of energy levels. More sophisticated perturbation methods can be employed, but the one we have described shows all essential features of this particular model and its consequences.

Quantum Model with Exchange Energy

Our discussion of the helium atom up to this point has, for the sake of simplicity, ignored the indistinguishability of the two electrons in the system. We have talked as if each electron could be assigned to a separate orbit or state. However, we cannot escape the fundamental fact that identity must be incorporated in the basic form of the wave function. We were not in fact justified in using descriptions of the kind "the first electron remains in its ground state and the second electron is raised to an excited state." All we can ever do is to speak of two identical electrons sharing a total state that may be based on two single-particle states. When we include this feature formally, there appears in the calculation of the total energy an *exchange term* that results in a difference of energies between symmetric and antisymmetric space states constructed from the same sets of space-state quantum numbers. It is the purpose of the present discussion to show how this correction comes about.

The Schrödinger equation for helium (Eq. 13-7) contains no explicit mention of the spin states of the electrons. However, the spin states play an essential role through the requirement that the space function ψ be either symmetric (for singlet states, $S = 0$) or antisymmetric (for triplet states, $S = 1$). These symmetry considerations place certain limitations (as expressed in the Pauli principle) on the values of n , l , and m_l that the two electrons may have. More importantly, however, they lead to the above-mentioned exchange term in the expression for the total energy of the system. The essential character of this energy difference can be understood along the lines of the earlier discussion of one-dimensional systems (Sections 13-3 through 13-5). If the electrons are in the spin state $S = 0$, which makes the space wave function symmetric, they tend to

huddle close together, whereas in the $S = 1$ state involving the same two sets of quantum numbers n, l, m (but in this case an antisymmetric space state) they tend to stay apart. Since the Coulomb energy of interaction between electrons is positive and increases with decreasing separation, the $S = 0$ state will be pushed somewhat higher in energy than the corresponding $S = 1$ state. (In addition, *both* states will be raised in energy with respect to what one would have in the absence of the electron-electron repulsion.)

To obtain a more formal description of these effects, suppose that the electrons are in space states labeled i and k , where these indices identify the complete sets of quantum numbers n, l, m_l . The normalized symmetric and antisymmetric space functions constructed from these are the following:

$$\begin{aligned}\psi_s &= \frac{1}{\sqrt{2}} [\psi_i(\mathbf{r}_1)\psi_k(\mathbf{r}_2) + \psi_i(\mathbf{r}_2)\psi_k(\mathbf{r}_1)] & \text{for } S = 0 \text{ (singlet)} \\ \psi_a &= \frac{1}{\sqrt{2}} [\psi_i(\mathbf{r}_1)\psi_k(\mathbf{r}_2) - \psi_i(\mathbf{r}_2)\psi_k(\mathbf{r}_1)] & \text{for } S = 1 \text{ (triplet)}\end{aligned}$$

(13-9)

As before, the probability that one electron is in a volume element $d\tau_1$ at \mathbf{r}_1 and the other in a volume element $d\tau_2$ at \mathbf{r}_2 is given by $\psi^*\psi d\tau_1 d\tau_2$ where ψ is ψ_s or ψ_a as the case may be. We can substitute from Eq. 13-9 into Eq. 13-8 and expand to obtain

$$\begin{aligned}\Delta E &= \frac{1}{2} \iint |\psi_i(\mathbf{r}_1)|^2 |\psi_k(\mathbf{r}_2)|^2 V(r_{12}) d\tau_1 d\tau_2 \\ &+ \frac{1}{2} \iint |\psi_i(\mathbf{r}_2)|^2 |\psi_k(\mathbf{r}_1)|^2 V(r_{12}) d\tau_1 d\tau_2 \\ &\pm \frac{1}{2} \iint \psi_i^*(\mathbf{r}_1)\psi_k(\mathbf{r}_1)\psi_k^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) V(r_{12}) d\tau_1 d\tau_2 \\ &\pm \frac{1}{2} \iint \psi_k^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_i^*(\mathbf{r}_2)\psi_k(\mathbf{r}_2) V(r_{12}) d\tau_1 d\tau_2\end{aligned}$$

where the \pm refer to the symmetric and antisymmetric space states, respectively. This looks like a very formidable expression, but the first two integrals are exactly equal to one another and, moreover, when added together equal the quantity ΔE_1 which we discussed (Eq. 13-8) in the case in which spin was ig-

nored. The last two terms are equal to one another also, since there is a complete symmetry between the roles of r_1 and r_2 . Thus we can put

$$\Delta E = \Delta E_1 \pm \Delta E_2 \quad (13-10)$$

where

$$\Delta E_1 = \iint |\psi_i(\mathbf{r}_1)|^2 |\psi_k(\mathbf{r}_2)|^2 V(r_{12}) d\tau_1 d\tau_2 \quad (13-11a)$$

and

$$\Delta E_2 = \iint \psi_i^*(\mathbf{r}_1) \psi_k(\mathbf{r}_1) \psi_k^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) V(r_{12}) d\tau_1 d\tau_2 \quad (13-11b)$$

The term ΔE_1 then represents a general upward shift of the energy levels as a result of the electron-electron repulsion, while the further correction, $\pm \Delta E_2$, is the exchange term, involving (as the explicit expression for it shows) the association of each electron with both of the component one-electron states. The resultant modification of energy levels is indicated in column 4 of Figure 13-8. The agreement with observation is good.

Using perturbation theory for the lower-energy levels and a hydrogen-like approximation for the higher-energy levels, we have obtained a respectable description of the electronic structure of helium. More accurate approximation methods have been developed that yield results very much closer to the observed energies. As important as the energy values, however, are the physical arguments in our analysis that accounted qualitatively for the various energy splittings. These arguments will have further application in the analysis of multielectron atoms.

Classification of Helium Levels

We end this discussion of the helium atom with a brief description of the spectroscopic classification of the energy levels. The basic feature is that the classification is in terms of the resultant angular momenta of the two electrons, not their individual angular momenta. The vector model for the combination of *orbital* angular momenta, as discussed in Chapter 11 (Section 11-6) applies equally well here. If the states of the individual electrons correspond to orbital angular momentum quantum numbers l_1, l_2 , then the resultant orbital angular

momentum is characterized by the quantum number L , where

$$|l_1 - l_2| \leq L \leq l_1 + l_2$$

The *total* angular momentum J of the two electrons together is then obtained by the vector combination of the orbital angular momentum, $L(|L| = \sqrt{L(L+1)}\hbar)$ with the total spin angular momentum. For the singlet spin states ($S = 0$) we of course have $J = L$ simply, but for the triplet spin states ($S = 1$) there are in general three different values of J for each value of L (other than $L = 0$). To take a specific example, consider the various states that might be based on the single-electron states $n_1 = n_2 = 2$, $l_1 = l_2 = 1$. Then we can have

$$L = 0, 1, 2$$

For $S = 0$ we thus have

$$J = 0, 1, 2$$

Using the spectroscopic notation, we designate the possible states as 1S_0 , 1P_1 , 1D_2 , where (remember) S , P , D refer to the total orbital angular momentum numbers $L = 0$, 1 , and 2 , respectively, the superscript (equal to $2S + 1$) indicates that the level is a spin singlet, and the subscript gives the value of J . For $S = 1$ the possibilities are considerably more numerous:

$$\begin{aligned} L = 0: & \quad J = 1 \quad ({}^3S_1) \\ L = 1: & \quad J = 0, 1, 2 \quad ({}^3P_0, {}^3P_1, {}^3P_2) \\ L = 2: & \quad J = 1, 2, 3 \quad ({}^3D_1, {}^3D_2, {}^3D_3) \end{aligned}$$

The energy levels of helium are identified in this notation on Figure 13-9. The energy differences between states of the same L and S but different J are quite small, and they are not shown as separate in the level scheme of the figure.

To complete the classification of these two-electron states in helium, it is convenient to introduce an *effective principal quantum number* n such that $n = 1$ for the lowest state of the atom (a 1S_0 state). We can do this by defining

$$n = n_1 + n_2 - 1$$

In crudest approximation, the levels for all the different values

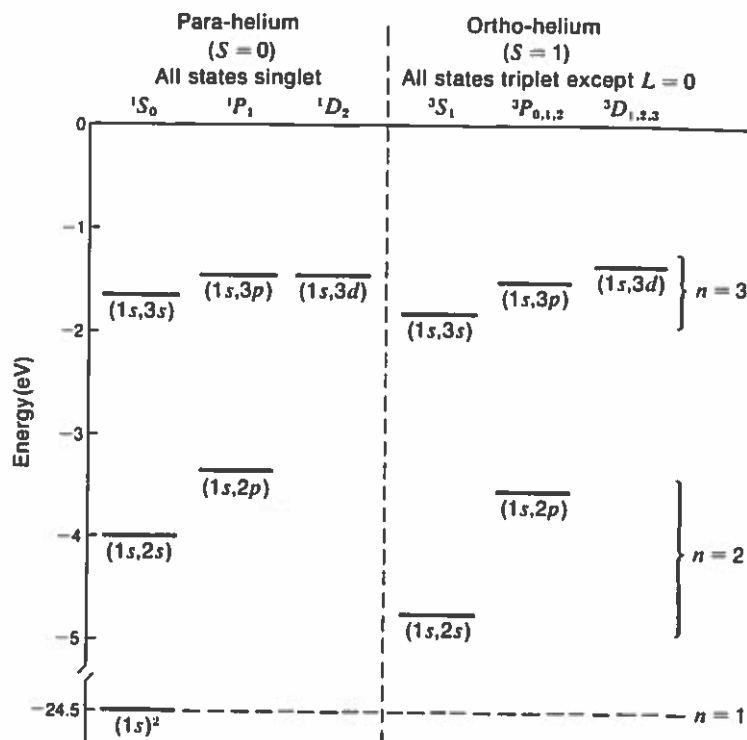


Fig. 13-9 Classification of the lowest-energy states of the helium atom. (Same energy scale as Figure 13-5.)

of L and S can then be grouped as belonging to $n = 1$, $n = 2$, $n = 3$, and so on. This, too, is indicated on Figure 13-9. The effectiveness of this classification in terms of n is due, as we mentioned earlier, to the fact that the states shown in Figure 13-9 all derive from the excitation of one electron only, leaving the other one in the lowest state ($n_1 = 1$, $l_1 = 0$) to screen the nuclear charge, and thus yielding a hydrogen-like configuration that is increasingly accurate for higher levels of excitation of the outer electron.

13-9 MANY-ELECTRON ATOMS

The Self-Consistent Field Method

The analysis of the two-electron system in helium is already complicated. The detailed consideration of electron states in atoms with still more electrons is prohibitively difficult if one tries to proceed along similar lines. There are, however, other approaches that thrive on the old principle that

"there's safety in numbers." These methods all make use in one way or another of the assumption that, in a many-electron atom, any one electron finds itself in a spherically symmetric field due to the combined effect of the nuclear charge and all the other electrons.

All such methods must contain a considerable element of trial and error, because a knowledge of the potential $V(r)$ in which any one electron finds itself requires knowledge (or at least an assumption) about the radial distribution of electric charge density that corresponds to the position probability distributions for all the other electrons. But these latter, in turn, must represent acceptable solutions of the Schrödinger equation for the potential $V(r)$. Thus the analysis involves the search, through successive approximations, for what is called a *self-consistent field*. Starting from some assumed form of $V(r)$, we can calculate the spatial probability distribution of the electrons, but then the resulting probability distribution, which defines an electric charge distribution, must—if the analysis is self-consistent—generate the potential $V(r)$ that we assumed. Techniques for handling such problems were first developed about 1928 by E. Fermi, D. R. Hartree, and L. H. Thomas.

In what follows, we do not discuss self-consistent field methods in any depth or detail. Rather, we shall simply indicate how the picture of a many-electron atom can be approximated in terms of the solutions to the one-electron problem, in conjunction with the Pauli exclusion principle. There will be no attempt to construct antisymmetrized wave functions as such. Instead, the Pauli principle is used simply as a basis for determining how many electrons can be accommodated in a "shell" made up of electrons all having the same principal quantum number. (The reason why it is appropriate to speak of electron shells will become apparent in the course of the discussion.) Our concern will be with the ground state of a neutral atom of atomic number Z . The energy of this state will be the lowest possible energy of a system made up of the central charge Ze together with the Z electrons—subject, of course, to the limitations imposed by the Pauli principle. For the purposes of finding this lowest level, we can imagine building up the atom from scratch, as it were, starting with the nucleus alone and adding the electrons, each of which falls into the lowest available level.

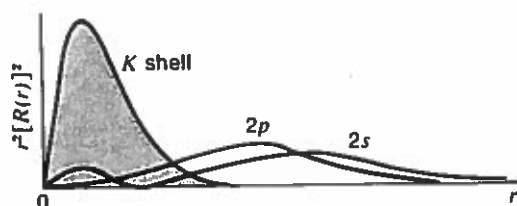
The K Shell

From our discussion of the helium atom, it is clear that the first two electrons will fall into the $1s$ level (each with $n = 1$, $l = 0$), with their spins antiparallel. This completed inner level is called the *K shell*. Addition of a third electron to the $1s$ state is impossible because it would be obliged to have the same set of quantum numbers (including spin) as one of the two electrons already present. Thus the third electron must enter a state with $n = 2$ and $l = 0$ or 1 . Before considering the energy of this third electron, we note that the energy of the first two electrons is not quite as negative as it would be if each moved alone in the field of the central charge. A single $1s$ electron would have a characteristic distance $a_1 = a_0/Z$ from the nucleus, a potential energy $-Ze^2/a_1 = -Z^2e^2/a_0$ and a radial wave function of the form e^{-r/a_1} . The presence of the second electron will raise the energy of each, and will also keep each electron farther from the nucleus, on the average, than it would otherwise be. Both of these effects can be approximately described, so far as either electron is concerned, in terms of a partial screening of the nuclear charge by the other electron. If the screening were complete, the effective value of the central charge would be reduced to $Z - 1$, and the parameter a_1 increased to $a_0/(Z - 1)$. We can anticipate that a more careful self-consistent field calculation will yield results somewhere between the no-shielding and the complete shielding limits discussed here.

The L Shell

When we consider, now, the energy of the third electron, it is not far from the truth to say that it "sees" a central charge $(Z - 2)e$ unless it penetrates within the tiny charge cloud represented by the first two electrons in the *K shell*. However, to the degree that it does penetrate, it will be exposed more nearly to the full positive charge Ze of the nucleus and its energy will be lowered. If the third electron is in a $2s$ state, for which ψ remains nonzero at $r = 0$, we have such penetration (see Figure 13-10). We can thus infer that the third electron will fall into the $2s$ state ($l = 0$) rather than the $2p$ state ($l = 1$), which has zero probability at the nucleus. The fourth electron will also fall into the $2s$ state, with spin antiparallel to the third

Fig. 13-10 Comparison of K-shell penetration by 2s and 2p radial probability densities.

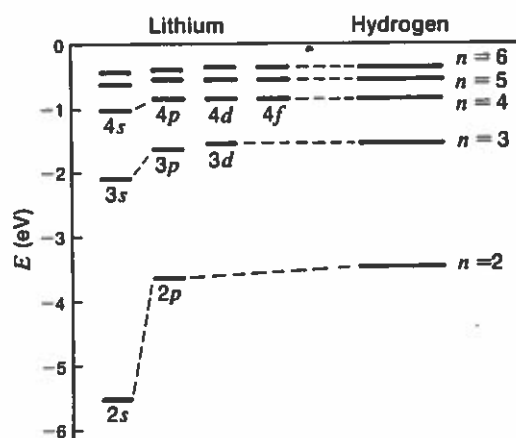


electron. After this point the Pauli principle again intervenes, and the fifth electron will go into the slightly higher 2p state ($n = 2, l = 1$).

The energy difference between 2s and 2p levels can be further illuminated if we backtrack for a moment and consider the case $Z = 3$ (lithium). For lithium the third electron completes a neutral atom and the ground state can be described by the notation $(1s)^2 (2s)$, where the superscript tells the number of electrons in each state and the absence of superscript implies only one electron in that state. The first excitation of the lithium atom will be obtained by raising the third electron to the relatively nonpenetrating state 2p, and the energy of this state will correspond quite closely to that of the $n = 2$ states in a hydrogen atom, since in both cases the electron moves in the field of an effective central charge $+e$. Figure 13-11 illustrates this point. (The situation is like the one we discussed in connection with excited states of the helium atom.)

Returning now to the case where Z is large enough to accommodate many electrons, we can see that it is at least plausible that the filling of the two 2s states will be followed by the

Fig. 13-11 Energy levels of lithium compared with hydrogen. Note that for higher orbital angular momentum of the valence electron in lithium its energy more nearly equals the corresponding energy in hydrogen.



filling of the $2p$ levels. There will be six of these latter (two states of opposite spin for each of the three substates for $l = 1$: namely, $m_l = +1, 0$, and -1). Figure 13-12 indicates how the mean radii of the position probability distributions depend much more on n than on l . Thus, for $n = 2$, the two $2s$ electrons and the six $2p$ electrons form, in effect, a "shell" of electric charge, significantly further out from the nucleus than the $1s$ electrons, and characterized roughly by a Bohr-atom orbit radius calculated for $n = 2$, with a central charge $(Z - 2)e$. This completed second set of levels is called the L shell.

Sodium

The screening of the nuclear charge by the L shell, when this is completely filled, has an important effect on the energies

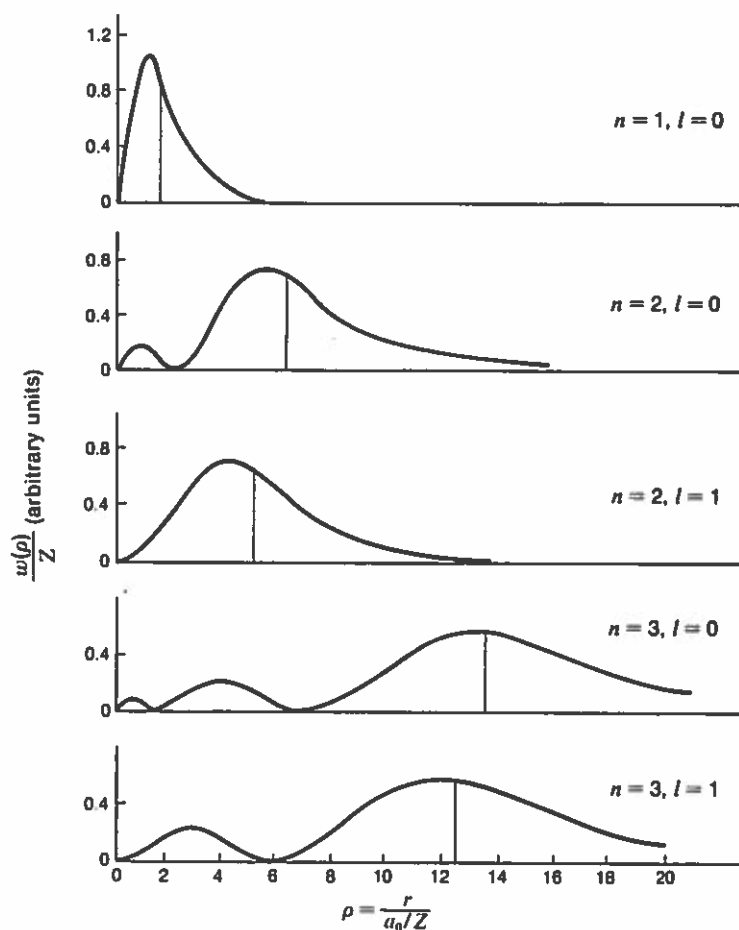


Fig. 13-12 Radial probability densities w for various n and l for hydrogen-like systems, showing that l has less effect than n on mean radius. (Mean radius in each case shown by vertical line.) The horizontal axis is in units a_0/Z .

of electrons added still later. Together with the charge $-2e$ represented by the K shell, it reduces the effective central charge to $(Z - 10)e$ with respect to any electron that does not penetrate the K and L shells. However, the first electron to be added after the $n = 2$ states are all filled will be a $3s$ electron which penetrates the K and L shells, yielding a more negative interaction energy with the nucleus than a nonpenetrating state would do. In the case of sodium ($Z = 11$) the addition of this electron yields a neutral atom, and the $3s$ electron plays the role of valency electron in the atom, being loosely bound compared to any of the others. (The energy needed to remove the outer $3s$ electron from sodium is 5.14 eV ; the energy required to remove a second electron is nearly 10 times greater— 47.3 eV .)

In the above description of sodium, we talk about the "outer electron in the $3s$ state" as if it were distinguishable from other electrons in the atom. In reality, we know, electrons are indistinguishable, so that the correct wave function must combine the one-electron wave functions in such a way as to yield an overall wave function antisymmetric with respect to exchange of any two electrons. As mentioned at the end of Section 13-6, we are justified in ignoring this necessity to the extent that the electron wave functions for the respective states do not overlap. When this overlap is small, the practical consequences of explicitly recognizing the identity of electrons and setting up an antisymmetric total wave function are then quite slight because the overlap integrals that express the exchange energies—similar to energy ΔE_2 in Eq. 13-10—become very small.

Higher Shells

By this point in the argument the main features of the "Aufbau" of the electron systems in atoms are fairly clear. By and large the electron states will be filled in order of increasing n , and in order of increasing l for each n . However, the pulling down of energy for the penetrating s states becomes more and more important as the central charge Ze increases, and ultimately this has the effect that an s state for a certain n has a lower energy than that of states of larger l belonging to $n - 1$. The first example of this effect occurs with potassium ($Z = 19$) after completion of the "subshell" of six electrons in the $3p$ states, giving 18 electrons up to this point. The next

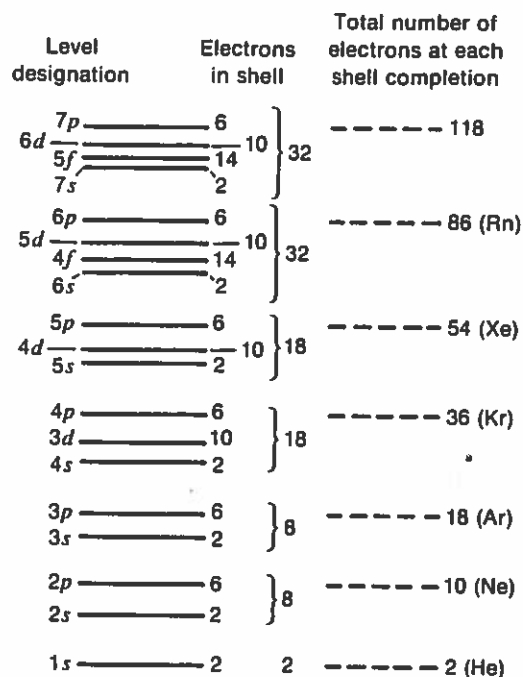


Fig. 13-13 Electronic shell structure.

electron to be added (the nineteenth) enters a $4s$ state instead of $3d$, and is the valency electron of the potassium atom. Thereafter as Z increases beyond potassium a certain amount of competition goes on between several possible subshells for each new electron added. However, the configurations at completion of particularly stable structures, as represented by the noble gases, are well defined and correspond to the ordering of levels shown in Figure 13-13. It is in these completed structures (Table 13-2) that we see the groupings that characterize the periodic table of the elements, marked by the noble gases themselves at $Z = 2$ (He), 10 (Ne), 18 (Ar), 36 (Kr), 54 (Xe), and 86 (Rn).

TABLE 13-2 Electron Shell Structure

Values of (n, l)	Shell Capacity	Cumulative Total
(1, 0)	2	2
(2, 0) + (2, 1)	8	10
(3, 0) + (3, 1)	8	18
(3, 2) + (4, 0) + (4, 1)	18	36
(4, 2) + (5, 0) + (5, 1)	18	54
(4, 3) + (5, 2) + (6, 0) + (6, 1)	32	86

In terms of observable physical properties, the approach to a major shell closure is marked by an increase in the first ionization potential of the atom [(the energy required to remove one electron from the neutral atom—see Figure 13-14a). The ionization potential then drops to an especially low value for each element for which Z corresponds to a closed shell plus one electron. These elements are the alkali metals (Li, Na, K, Rb, Cs); they represent systems in which the last electron finds itself mainly outside a relatively tightly bound structure that has a net charge of $+e$. The valency electron, in consequence of being weakly bound, also has a tendency to be especially far from the center of the atom. As a

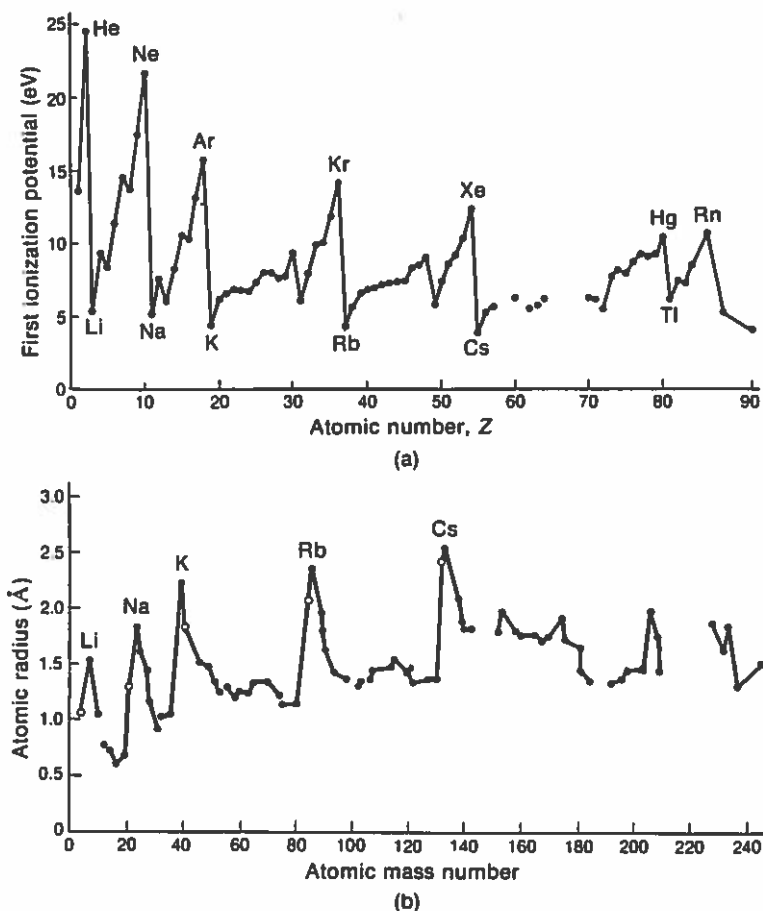


Fig. 13-14 (a) First ionization potential as a function of Z . (b) Atomic radius as a function of atomic mass number.

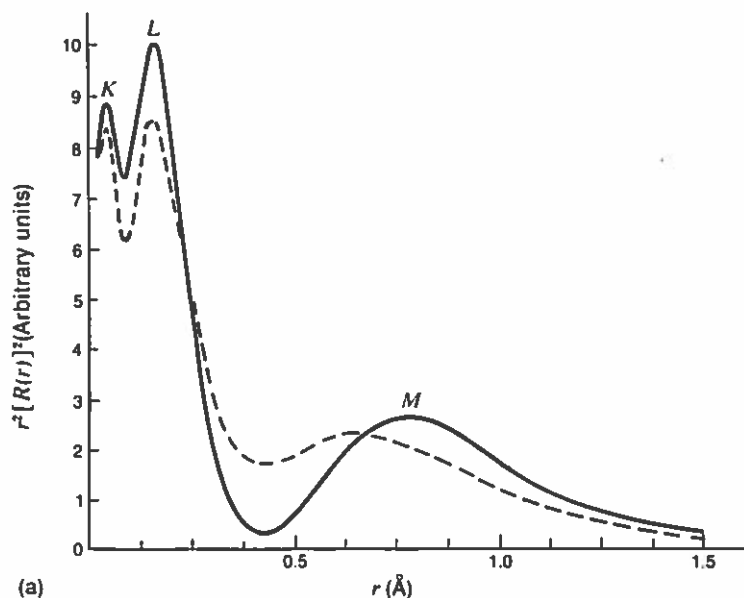
result the alkalis are the largest of the atoms in the periodic table (Figure 13-14b).

It is worth noting that, although there are clear periodicities in atomic radii, the atoms—all the way from hydrogen to uranium—show remarkably little variation in size, and in particular no important tendency to be bigger if they are more massive. In a very qualitative way, this can be understood as a consequence of the large central charge pulling the electrons into orbits of much smaller radius than the corresponding ones in hydrogen, so that even though shells belonging to $n > 1$ are involved, the outer radius of the overall charge distribution is not much affected.

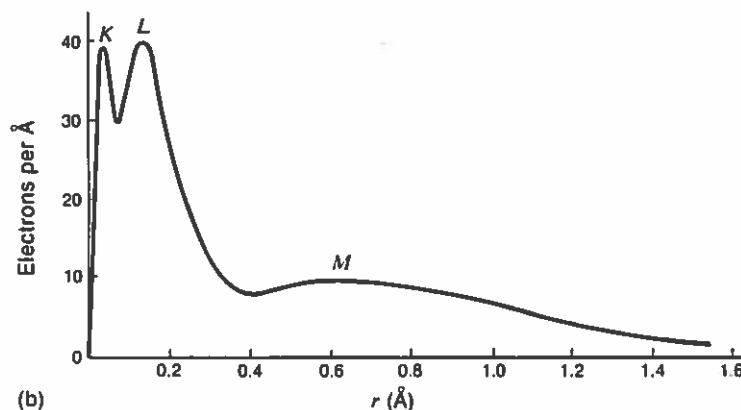
The picture of groups of electrons forming shells or subshells at fairly well-defined radii is well grounded theoretically and has also been verified experimentally. Figure 13-15a shows the results of some calculations of the radial probability distribution (and hence the charge distribution) for the complete set of 18 electrons in the argon atom. One curve in the figure shows the result of a crude calculation in which the electrons in any one shell are assumed to have hydrogen-like wave functions defined for a central charge Ze diminished by the charge of the electrons in completed shells nearer the nucleus. A second curve in the figure shows the result of a better calculation embodying the requirements of the self-consistent field. The difference between the two curves is not great, but it is significant. Figure 13-15b shows the result of an experiment in which the radial charge distribution in argon was derived from a study of the scattering of electrons from the atoms in argon gas (similar to an x-ray diffraction analysis). The agreement between experiment and the better theoretical distribution is very good. Thus in various ways one finds reason to believe that the theory of many-electron atoms, using quantum mechanics, is a reflection of reality. In fact our brief account here does not begin to do justice to the extent to which the detailed physical properties of atoms (and especially their spectra) have been successfully interpreted with the help of quantum theory.

13-10 GENERAL STRUCTURE OF A MASSIVE ATOM

To bring together the results discussed above, it may be helpful to consider the complete picture of a particular mas-



(a)



(b)

Fig. 13-15 Total radial distribution of electrons in the argon atom.

(a) Theoretical. Solid curve: simple shell model. Broken curve: self-consistent field approximation. (b) Experimental, deduced from electron scattering. [After L. S. Bartell and L. O. Brockway, *Phys. Rev.* **90**, 833 (1953)]

sive atom with many electrons. Let us take the most abundant isotope of tin, with $Z = 50$, $A = 120$.

The nucleus of this atom has a charge of $+50e$; it contains 50 protons and a number of neutrons equal to $A - Z$, i.e., 70, but the nuclear structure is not our concern here. Closest to the nucleus (on the average) are two electrons in states with $n = 1$; these electrons are exposed to almost the full force of the nuclear electric field. According to the simple theory of hydrogen-like atoms, the energy of an electron in the field of an effective central charge Qe is given by

$$E(Q,n) = -\frac{2\pi^2 m Q^2 e^4}{n^2 \hbar^2} = -13.6 \frac{Q^2}{n^2} \text{ eV} \quad (13-12)$$

Thus, for $n = 1$, $Q \approx 50$, each electron would be bound with a negative energy equal to almost 2500 times the binding energy of the electron in the hydrogen atom (13.6 eV). This would be on the order of 30 keV. Direct measurements show that it takes x rays with a quantum energy of 29.2 keV to dislodge an electron from this innermost shell. The average distance of these electrons from the nucleus is comparable to the orbit radius calculated from the Bohr theory for $n = 1$, $Q = 50$; this is about 0.01 \AA , or 10^{-12} m —about 150 times the nuclear radius of tin.

Going to the next electron shell (cf. Table 13-2), we have eight electrons for which $n = 2$ and for which the nuclear charge is significantly shielded, first by the two inner-most electrons, secondly by the other electrons in this same shell, and thirdly by penetrating electrons from shells still farther out. The effective central charge is not easy to estimate in this case, but experiment shows that x rays of about 4 keV can eject electrons from this shell. (For experimental evidence of this, see the graph of x-ray absorption edges in Chapter 1, Figure 1-18.) Actually, this and subsequent shells have a substructure, based on the involvement of two or more values of the quantum number l , that we shall not go into here. Putting $n = 2$ in Eq. 13-12, and using the observed electron binding energy of about 4 keV, one would infer an effective central charge of about $35e$ and a mean shell radius of about 0.06 \AA .

Proceeding in the same way, one finds that the third shell (8 electrons, $n = 3$) has a critical x-ray absorption energy of about 0.9 keV, corresponding to $Q \approx 24$, $r \approx 0.2 \text{ \AA}$; and the fourth shell (18 electrons) has a critical x-ray absorption energy of about 120 eV, corresponding to $Q \approx 12$, $r \approx 0.7 \text{ \AA}$.

This accounts for 36 out of the 50 electrons in the atom. The remaining 14 belong to the fifth electron shell, which can accommodate up to 18 electrons. The situation in this region of the atom is complicated, but we know that these electrons are the main contributors to the outer parts of the atomic charge cloud, which extends to a radius of about 1.5 \AA (see Figure 13-14b). To remove one of these electrons requires an energy of 7.3 eV (the first ionization potential of tin). Thus we see that the energy-level structure within the Sn atom

ranges all the way from weakly bound electrons (less than 10 eV) to very tightly bound electrons (tens of keV).

The chemical and spectroscopic characteristics of an element depend on the details of the quantum state of its outermost electrons. In particular, the chemical valence depends upon the extent to which the total number of electrons in an atom represents an excess or a deficit with respect to the more stable configuration of a completed shell. In the case of tin, for example, the total of 50 electrons is four short of completing the fifth shell of Table 13-2. In these terms one can understand why tin is quadrivalent (although it takes a study of finer details to understand in physical terms why it also exhibits divalency). In such matters as these, however, although the properties certainly have their complete basis in electric forces and quantum theory, the theoretical analysis is at best semi-empirical.

EXERCISES

13-1 Unlike particles in a box. Consider two dissimilar particles, of masses m_0 and $4m_0$ (for example, a neutron and an alpha particle) confined in the same one-dimensional box of length L . Ignoring their mutual interactions, write down and solve the Schrödinger equation for this system and obtain an expression for the total energy. Consider the conditions for energy degeneracy of the system (that is, different combinations of quantum numbers resulting in the same total energy).

13-2 Like particles in a box: I.

(a) Consider two particles of the same mass in a one-dimensional box of length L . Sketch the "contour map," analogous to Figure 13-1, for the two possible wave functions associated with having one particle in the state $n = 1$ and the other particle in the state $n = 3$.

(b) Now impose the condition that the particles are identical and construct the contour maps of probability density, analogous to Figure 13-2, for the symmetric and antisymmetric space states belonging to the same pair of quantum numbers.

13-3 Like particles in a box: II. Two particles in a one-dimensional box are in a combined quantum state belonging to the quantum numbers $n = 1$ and $n = 2$.

(a) Ignoring the need to make the total wave function either symmetric or antisymmetric, calculate the probability that *both* particles are within a distance $\pm L/20$ of the point $x = L/4$.

(b) Assume now that the total space wave function must be symmetric, and calculate the probability in this case.

(c) Compare the results of (a) and (b) with the corresponding probability for two classical Newtonian particles simply bouncing back and forth between the ends of the box with incommensurable constant speeds.

13-4 Combined spin states.

(a) Consider the combined spin states for a particle of spin 1 and a particle of spin $\frac{1}{2}$. Tabulate all the possible z components of the resultant spin and show that they correspond to the array of spin states arising from total spins of $\frac{3}{2}$ and $\frac{1}{2}$.

(b) Suppose that the particles in question are a deuteron and a neutron. The deuteron is the combination of a proton with a neutron, and with the addition of another neutron it forms the nuclide hydrogen-3 (tritium). Taking account of the Pauli principle, what possible spin(s) would you predict for the tritium nucleus in its ground state and in a state in which one of the three nucleons is raised to an excited energy level?

13-5 *Antisymmetric wave functions and the Pauli principle.* Consider a wave function for two electrons written explicitly as the product of a symmetric space function and an antisymmetric spin function, or vice versa:

$$\begin{aligned} \psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) &\sim [\psi_A(\mathbf{r}_1)\psi_B(\mathbf{r}_2) \pm \psi_B(\mathbf{r}_1)\psi_A(\mathbf{r}_2)] \\ &\times [\alpha(1)\beta(2) \mp \beta(1)\alpha(2)] \end{aligned}$$

The quantities σ_1, σ_2 denote "spin coordinates" corresponding to the single-particle spin functions α and β . Multiply out this expression and show that it can be rewritten as the sum of two expressions each of the form

$$\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)$$

where the subscripts A and B now refer to a complete set of quantum numbers (space + spin) for one particle. This gives an alternative way of verifying that the total wave function vanishes identically if A and B represent identical sets of space and spin quantum numbers.

13-6 *Pauli's principle and the energy of a many-particle system.* The Pauli principle allows two electrons (or other spin- $\frac{1}{2}$ particles) with opposite spins to occupy the same space state and hence have the same energy.

(a) Compare the minimum possible *total* energy for 10 electrons confined within a single one-dimensional box to the total energy for 10