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This sequence only involves permutation of the first four indices. To obtain $|P|$ we must rearrange the sequence (4, 1, 2, 3) in the form of the original sequence (1, 2, 3, 4) through exchanges of two integers only and count the minimum number of such exchanges which do the job.

$$(4, 1, 2, 3) \to (1, 4, 2, 3) \to (1, 2, 4, 3) \to (1, 2, 3, 4)$$

Three exchanges suffice so that $(-1)^{|P|} = -1$. We conclude that the preceding product wavefunction carries a minus sign, as written.

Each such N-particle product function is an eigenstate of $\hat{H}$ corresponding to the degenerate eigenenergy (12.32), whence the determinantal form (12.33), which is merely a linear combination of these product states, is also an eigenstate of $\hat{H}$ corresponding to the eigenenergy (12.32).

Orthonormality

The second property that the determinantal states (12.31) have is that they form an orthonormal sequence. That is,

$$\langle \varphi_A | \varphi_A \rangle = \frac{1}{N!} \sum_P \langle \varphi_{\nu_1}(1) \cdots \varphi_{\nu_N}(N) | \varphi_{\nu_1}(1) \cdots \varphi_{\nu_N}(N) \rangle$$
$$= 1$$

since there are $N!$ terms of unit value in the sum. Furthermore, owing to the orthogonality of single-particle eigenstates,

$$\langle \varphi_{A(\nu_1, \ldots, \nu_N)} | \varphi_{A(\nu_1', \ldots, \nu_N')} \rangle = 0$$
$$(\nu_1, \ldots, \nu_N) \neq (\nu_1', \ldots, \nu_N')$$

This establishes the orthogonality of these states.

Antisymmetry

The third property concerns the symmetry of φ_A. If $\hat{\mathfrak{X}}_{ij}$ denotes the exchange of the ith-particle coordinates with those of the jth particle, then

$$\hat{\mathfrak{X}}_{ij} \varphi_A(i, j) = \varphi_A(j, i) = -\varphi_A(i, j)$$

Exchanging particle coordinate numbers in φ_A, as given by (12.31), is effected by an exchange of two rows of the determinant. But a determinant changes sign under

interchange of two rows. It follows that $\varphi_A(i, j) = -\varphi_A(j, i)$. For example, for the exchange of particles 1 and 2,

$$\hat{\mathfrak{X}}_{1,2} \begin{vmatrix} \varphi_{\nu_1}(1) & \varphi_{\nu_2}(1) & \cdots & \varphi_{\nu_N}(1) \\ \varphi_{\nu_1}(2) & \varphi_{\nu_2}(2) & \cdots & \varphi_{\nu_N}(2) \\ \vdots & \vdots & & \vdots \\ \varphi_{\nu_1}(N) & \varphi_{\nu_2}(N) & \cdots & \varphi_{\nu_N}(N) \end{vmatrix} = \begin{vmatrix} \varphi_{\nu_1}(2) & \varphi_{\nu_2}(2) & \cdots & \varphi_{\nu_N}(2) \\ \varphi_{\nu_1}(1) & \varphi_{\nu_2}(1) & \cdots & \varphi_{\nu_N}(1) \\ \vdots & \vdots & & \vdots \\ \varphi_{\nu_1}(N) & \varphi_{\nu_2}(N) & \cdots & \varphi_{\nu_N}(N) \end{vmatrix}$$
$$= -\begin{vmatrix} \varphi_{\nu_1}(1) & \varphi_{\nu_2}(1) & \cdots & \varphi_{\nu_N}(1) \\ \varphi_{\nu_1}(2) & \varphi_{\nu_2}(2) & \cdots & \varphi_{\nu_N}(2) \\ \vdots & \vdots & & \vdots \\ \varphi_{\nu_1}(N) & \varphi_{\nu_2}(N) & \cdots & \varphi_{\nu_N}(N) \end{vmatrix}$$

This property establishes the antisymmetry of the state φ_A.

Exclusion Principle

Finally, we note that if particle 2 has the same quantum numbers as particle 1, then $\varphi_A = 0$. This property also follows from the determinantal structure of φ_A: namely, if two particles are in the same eigenstate, then two columns of the determinant (12.31) are equal and φ_A vanishes. Thus φ_A written in the Slater determinant form is consistent with the Pauli exclusion principle.

PROBLEMS

12.26 Which purely determinantal properties related to the Slater determinant are involved in: (a) the antisymmetry of φ_A; (b) the Pauli exclusion principle?

12.27 Two spin-$\frac{1}{2}$ neutrons move in a two-dimensional box of edge length L and impenetrable walls. If the neutrons do not interact with each other, construct the antisymmetric determinantal spin and coordinate-dependent energy eigenstates for the system.

12.6 APPLICATION OF SYMMETRIZATION RULES TO THE HELIUM ATOM

We have already found the Pauli principle to be an important rule in forming the periodic chart of the elements and in construction of properly antisymmetrized wavefunctions for atomic electrons in the central field approximation.

In this and the next section we will further demonstrate the important role played by symmetrization principles in analysis of two elemental systems in nature. The first of these is the helium atom, which has two outer electrons. Among other properties we will find how the Pauli principle influences the coupling between these

electrons in the construction of properly antisymmetrized wavefunctions for the atom. The second example is the deuterium molecule, whose two deuteron nuclei are bosons. Consequently, the nuclear component of the molecular wavefunction must be symmetrized with respect to exchange of space and spin coordinates. Construction of such properly symmetrized states leads very simply to intensity rules for emission.

The Helium Atom

The Hamiltonian of helium, in a frame where the nucleus is at rest, is

$$\hat{H} = \left(\frac{\hat{p}_1^2}{2m} - \frac{2e^2}{r_1}\right) + \left(\frac{\hat{p}_2^2}{2m} - \frac{2e^2}{r_2}\right) + \frac{e^2}{r_{12}} + \hat{H}_{SO} \tag{12.34}$$
$$= \hat{H}_0(1) + \hat{H}_0(2) + \hat{H}_{ES} + \hat{H}_{SO}$$

The last term, H_{SO}, is written for the spin-orbit interaction between the electrons and the nucleus, while H_{ES} is written for the electrostatic interaction, e^2/r_{12}, between the two electrons. The interelectron displacement is

$$r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$$

(Fig. 12.11). If the electrostatic as well as spin-orbit terms are neglected, $\hat{H}$ reduces to the sum of two hydrogenic Hamiltonians (each with $Z = 2$).

$$\hat{H}_0(1, 2) = \hat{H}_0(1) + \hat{H}_0(2) \tag{12.35}$$

This Hamiltonian (as well as the total Hamiltonian) is symmetric with respect to the interchange of the two electrons

$$[\hat{\mathcal{X}}_{12}, \hat{H}_0(1, 2)] = 0 \tag{12.36}$$

This merely reflects the indistinguishability of the two electrons. This property must be maintained in the eigenstates that we construct for $\hat{H}_0(1, 2)$. With the abbreviations

$$\nu_1 \equiv (n_1, l_1, m_{l_1}); \qquad \nu_2 \equiv (n_2, l_2, m_{l_2})$$

these symmetrized eigenstates of $H_0(1, 2)$ appear as[1]

$$\varphi_{S,A}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\varphi_{\nu_1}(1)\varphi_{\nu_2}(2) \pm \varphi_{\nu_1}(2)\varphi_{\nu_2}(1)] \tag{12.37}$$

The plus sign gives a symmetric state, φ_S, while the minus sign gives an antisymmetric state, φ_A. The energy eigenvalue corresponding to either of these states is

$$E^{(0)}_{n_1,n_2} = -4R\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) = -2mc^2\alpha^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \tag{12.38}$$

[1] In the event that $\nu_1 = \nu_2$, then $\varphi_S(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{\nu_1}(1)\varphi_{\nu_1}(2)$.

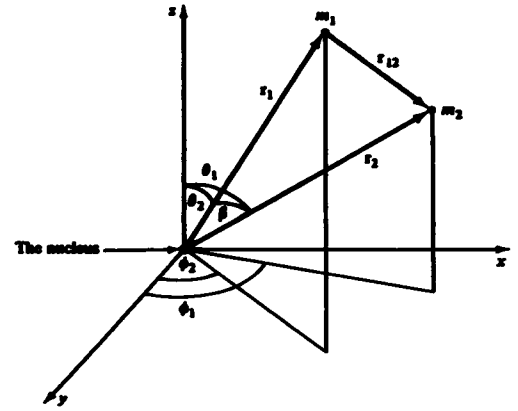

FIGURE 12.11 The coordinates of the two electrons in helium. The six-dimensional volume element $(d\tau_1\, d\tau_2)$ is given by

$$d\tau_1\, d\tau_2 = r_1^2\, d\Omega_1\, dr_1\, r_2^2\, d\Omega_2\, dr_2 = r_1^2 r_2^2\, dr_1\, dr_2\, d\cos\theta_1\, d\cos\theta_2\, d\phi_1\, d\phi_2$$

The potential of interaction between electrons is given by

$$V = \frac{e^2}{r_{12}} = \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\beta}}$$

(See Fig. 9.16 for addition formulas connecting β to $\theta_1, \theta_2, \phi_1, \phi_2$.)

Separation of Multiplets Due to Spin Symmetry

Although the spin-orbit correction to the Hamiltonian of helium is small [$\Delta E_{SO}/E \sim \alpha^2$; see (12.13)] and may well be neglected in a first approximation, the spin of the electrons still has an important influence on the properties of helium. This occurs through a combination of Pauli antisymmetrization requirements on wavefunctions with respect to exchange of space and spin coordinates and the relatively large electrostatic interaction between electrons (see Problem 12.28). In what follows, first we will construct the properly antisymmetrized space-spin dependent eigenstates of $\hat{H}_0(1, 2)$. This immediately implies a coupling between the electron spins. Three states emerge with $s = 1$ (the triplet series) and one state emerges with $s = 0$ (the singlet series). When the electrostatic interaction e^2/r_{12} is brought into play, it is found that the triplet states all lie lower in energy than the singlet states. In this

manner we will find that symmetry requirements couple the electron spins and electrostatic interaction separates the resulting singlet and triplet states.

Insofar as $\hat{H}_0(1, 2)$ does not contain the spin, spin-dependent eigenstates of $\hat{H}_0(1, 2)$ are quite simple to construct. If $\varphi(\mathbf{r}_1, \mathbf{r}_2)$ is a space-dependent eigenstate (12.37) of $H_0(1, 2)$, then following the procedure described in Section 12.3 for two free electrons, we find that the properly antisymmetrized wavefunctions are given by

$$
\begin{aligned}
{}^1\chi &= \varphi_S(\mathbf{r}_1, \mathbf{r}_2)\xi_A(1, 2) && (s = 0) \\
{}^3\chi &= \varphi_A(\mathbf{r}_1, \mathbf{r}_2)\begin{Bmatrix} \xi_S^{(1)}(1, 2) \\ \xi_S^{(0)}(1, 2) \\ \xi_S^{(-1)}(1, 2) \end{Bmatrix} && (s = 1)
\end{aligned}
\tag{12.39}
$$

The ξ-spin functions are listed in Table 11.3. We see how symmetrization requirements, together with the Pauli principle, effect a coupling between the spins of the two electrons in helium. In the triplet state ($s = 1$) the spins are aligned, whereas in the singlet state ($s = 0$) the spins are antialigned.

Electrostatic Interaction

To understand how the coupling augments the energies of helium, we recall the following property of symmetrized states (see Problem 8.32): namely, two particles in a symmetric state attract one another (in a statistical sense). It follows that the two electrons in the singlet ${}^1\chi$ state, which contains the symmetric φ_S state, are closer to each other than they are in the triplet ${}^3\chi$ state, which contains the antisymmetric φ_A state. Thus, owing to the positive repulsive energy of the electrostatic interaction, e^2/r_{12}, the triplet states lie lower in energy than do the singlet states (Fig. 12.12).

This is the mechanism behind Hund's first rule (see Problem 12.25)—that the total spin assumes the maximum value consistent with the Pauli principle. In this symmetric spin state, the space component of the wavefunction must be antisymmetric so that electrons are further removed from each other than in the corresponding symmetric space state.

Exchange and Coulomb Interaction Energies

Let us consider the space component eigenstates (12.37) of helium in more detail. As it turns out, the only states of helium that are of practical significance are those for which one of the two electrons is in its own ground state, with $n = 1, l = m_l = 0$. The reason for this is that it takes less energy to ionize a helium atom from the ground state than it does to raise both electrons to excited levels (Fig. 12.13). This means that one is more likely to find an He^+ ion (hydrogenic ion with $Z = 2$) than a helium atom

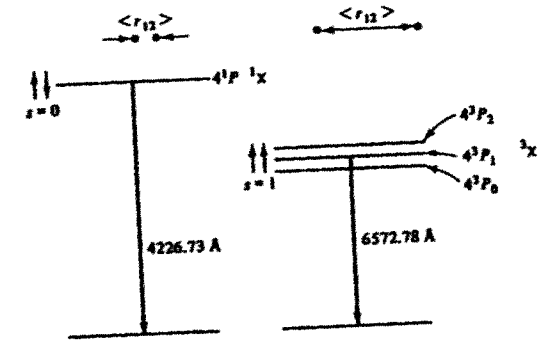

FIGURE 12.12 The $4P$ states of calcium, illustrating the fact that in two-electron atoms, triplet states lie lower than the corresponding singlet state. This is due to the fact that the average interelectron distance is smaller in the symmetric space state, φ_S, than in the antisymmetric space state, φ_A, thereby increasing the singlet electrostatic contribution to the total energy compared to the corresponding triplet contribution.

$$\langle {}^1\chi | H_{ES} | {}^1\chi \rangle > \langle {}^3\chi | H_{ES} | {}^3\chi \rangle$$

$$H_{ES} = +\frac{e^2}{r_{12}}$$

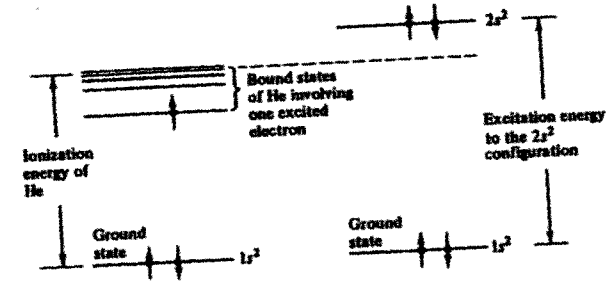

FIGURE 12.13 The ionization energy of He is smaller than the energy of the lowest energy state of He with both electrons excited. It is possible for He in this excited state to decay to He^+ and a free electron.

with both electrons in excited states. It follows that the space-dependent states of helium atoms that exist under natural conditions are mostly of the form

$$\varphi_{S,A}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\varphi_{100}(\mathbf{r}_1)\varphi_{nlm}(\mathbf{r}_2) \pm \varphi_{100}(\mathbf{r}_2)\varphi_{nlm}(\mathbf{r}_1)\right] \tag{12.40}$$

One may use these eigenstates to calculate the corrections to the eigenenergies of $\hat{H}_0$ due to the electrostatic interaction, e^2/r_{12}. As described above, we expect the triplet states to lie lower in energy than the singlet states.

One obtains

$$\left\langle \frac{e^2}{r_{12}} \right\rangle_{\text{singlet}} = \langle {}^1\chi | \left(\frac{e^2}{r_{12}}\right) | {}^1\chi \rangle = A + B \tag{12.41}$$

where

$$\begin{aligned} A &= \langle \varphi_{100}(1)\varphi_{nlm}(2) | \frac{e^2}{r_{12}} | \varphi_{100}(1)\varphi_{nlm}(2) \rangle \\ &= \int d\mathbf{r}_1\, d\mathbf{r}_2 |\varphi_{100}(1)|^2 |\varphi_{nlm}(2)|^2 \frac{e^2}{r_{12}} \end{aligned} \tag{12.42}$$

$$\begin{aligned} B &= \langle \varphi_{100}(1)\varphi_{nlm}(2) | \frac{e^2}{r_{12}} | \varphi_{100}(2)\varphi_{nlm}(1) \rangle \\ &= \int d\mathbf{r}_1\, d\mathbf{r}_2\, \varphi^*_{100}(1)\varphi_{nlm}(1)\varphi_{100}(2)\varphi^*_{nlm}(2) \frac{e^2}{r_{12}} \end{aligned}$$

The energy A is called the *Coulomb interaction energy*. It is akin to the classical interaction potential of two electron clouds with respective charge densities $e|\varphi_{100}(1)|^2$ and $e|\varphi_{nlm}(2)|^2$. The second term, B, has no counterpart in classical physics. It is called the *exchange interaction energy*.

In the triplet state the Coulomb interaction energy becomes

$$\left\langle \frac{e^2}{r_{12}} \right\rangle_{\text{triplet}} = \langle {}^3\chi | \left(\frac{e^2}{r_{12}}\right) | {}^3\chi \rangle = A - B \tag{12.43}$$

For A and B positive this correction energy is smaller than the corresponding singlet correction energy, $A + B$ (see Problem 12.31).

Thus we find that the electrostatic interaction separates the singlet and triplet states of helium. Furthermore, when spin-orbit interaction is brought into play, different j values have slightly different energies in the triplet states. For a given value of l, the total angular momentum j number has the three values

$$j = l - 1, l, l + 1$$

which in turn give three distinct values for the spin-orbit coefficient $\langle \mathbf{L} \cdot \mathbf{S} \rangle$, thereby splitting l-levels into triplets.

Helium in antisymmetric spin states (singlet series) is called *parahelium*. Helium in symmetric spin states is called *orthohelium*. The distinct spectra associated with these different atomic configurations are shown in Fig. 12.14.

Similar descriptions apply to the heavier two-electron atoms. Their spectra also are observed to separate into singlet and triplet series. The corresponding energy-level diagram for Ca^{20} is shown in Fig. 12.15.

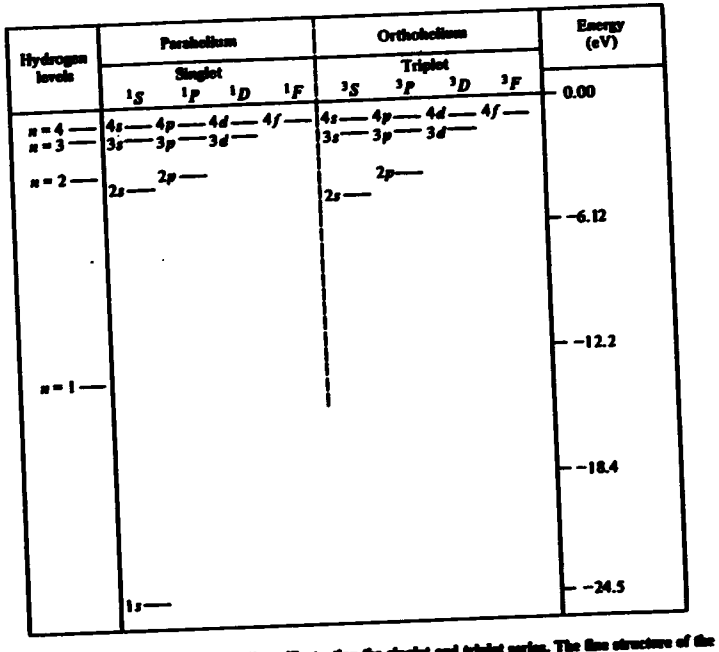

FIGURE 12.14 Energy levels of helium, illustrating the singlet and triplet series. The fine structure of the triplet levels is not shown. The energies of hydrogen appear at the left.

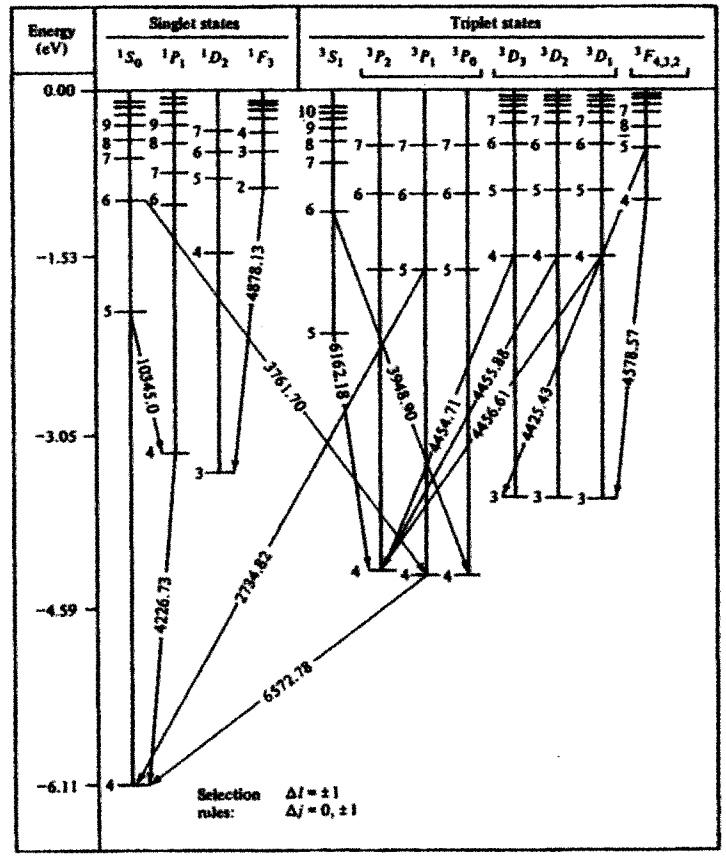

FIGURE 12.15 Energy levels of calcium, exhibiting the fine structure of the triplet states. A few typical transitions are also shown. Transition wavelengths are in angstroms. Principal quantum numbers appear at the left of levels.

PROBLEMS

12.28 (a) What is the ground-state wavefunction for helium in the approximation $\hat{H}_{ES} = \hat{H}_{SO} = 0$ in (12.34)?

(b) What is the ground-state energy in this approximation?

(c) What is the correction to this ground-state energy due to the electrostatic interaction, e^2/r_{12}? What is the total ground-state energy obtained in this manner?

(d) In view of your answer to part (c), is the ground state of $\hat{H}_0(1, 2)$ a good guess for the ground state of $\hat{H}_0(1, 2) + \hat{H}_{ES}$?

Answers

(a) The ground state is $\varphi_S(r_1, r_2)$, with $n_1 = n_2 = 1$ and $l_1 = l_2 = 0$. This gives

$$\varphi_S = \frac{8}{\pi a_0^3} \exp\left(-\frac{r_1 + r_2}{a_0/2}\right)$$

(b) $$E_{11}^{(0)} = -4R(1 + 1) = -4mc^2\alpha^2 = -108.8 \text{ eV}$$

(c) $$\Delta E = \langle \varphi_S | \frac{e^2}{r_{12}} | \varphi_S \rangle$$

$$= \iint |\varphi_S|^2 \frac{e^2}{r_{12}} \, d\tau_1 \, d\tau_2 = \frac{5e^2}{4a_0} = 34 \text{ eV}$$

$$d\tau_1 = r_1^2 \, dr_1 \, d\Omega_1, \qquad d\tau_2 = r_2^2 \, dr_2 \, d\Omega_2$$

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\beta$$

(See Figs. 9.9 and 12.11, and recall the generating function for Legendre polynomials given in Table 9.2.) This gives the corrected ground-state energy

$$E = E_{11}^{(0)} + \Delta E = -74.8 \text{ eV}$$

(d) The fact that ΔE is not small compared to $E_{11}^{(0)}$ means that φ_S is not a good guess for the ground state of $\hat{H}_0 + \hat{H}_{ES}$. (*Note*: $E_{obs} = -78.98$ eV.)

12.29 Which of the following operators are diagonalized by the states $^1\chi$ and $^3\chi$ (12.39) relevant to helium?

$$\hat{L}^2, \hat{L}_z, \hat{J}^2, \hat{J}_z, \hat{S}^2, \hat{S}_z, \hat{H}_0, \hat{\Sigma}_{12}$$

12.30 The spin-orbit interaction in two-electron atoms gives three distinct energies in the triplet series. What are the values of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ if one electron is an s electron and the other is a d electron.

12.31 Show that the integrals A and B in (12.41) are both positive. [*Hint*: Recall the Fourier transform of the Coulomb potential,

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \exp(i\mathbf{k} \cdot \mathbf{r}_{12}) \frac{d\mathbf{k}}{k^2}.]$$

12.32 A positron is the antiparticle of an electron. When in the presence of an electron, it may bind to the electron, forming a *positronium atom* that is unstable to positron–electron annihilation.