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THE HELIUM ATOM

THE HELIUM ATOM WITHOUT ELECTRON-ELECTRON REPULSION

The helium atom consists of a nucleus of charge $Z = 2$ and two electrons, which we label 1 and 2. Each electron is attracted to the nucleus, and the two electrons repel each other. We assume, and this will turn out to be correct, that no forces, other than the electromagnetic ones (Coulomb to a very good approximation), are necessary to describe the dynamics of the helium atom with the help of quantum mechanics.

If the nucleus is placed at the origin, and if the electron coordinates are labeled \mathbf{r}_1 and \mathbf{r}_2 , then the Hamiltonian for the atom is (Fig. 18-1)

$$H = \frac{1}{2m} \mathbf{p}_1^2 + \frac{1}{2m} \mathbf{p}_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (18-1)$$

Here m is the electron mass. We shall ignore the small effects connected with the motion of the nucleus,¹ relativistic effects, spin-orbit effects, and the effect of the

¹The reduced mass effect takes a somewhat different form since one is trying to convert a three-particle problem into an effective two-particle problem. This is worked out in D. Park, *Introduction to the Quantum Theory*, McGraw-Hill, New York, Third Edition (1992).

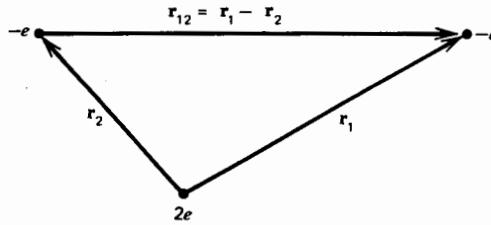


Figure 18-1. Coordinates used in the description of the helium atom.

current caused by the motion of one electron, upon the other electron. The Hamiltonian just given can be written as

$$H = H^{(1)} + H^{(2)} + V \quad (18-2)$$

with

$$H^{(i)} = \frac{1}{2m} \mathbf{p}_i^2 - \frac{Ze^2}{r_i} \quad (18-3)$$

and

$$V = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (18-4)$$

We shall work with the nuclear charge Z and set $Z = 2$ later. Our work on the hydrogen atom provides us with a complete set of eigenfunctions for $H^{(1)}$ and $H^{(2)}$. Thus, if we were to ignore V in the total Hamiltonian, we would have a solution to the eigenvalue problem for the two-electron system. The eigenfunctions would be

$$u(\mathbf{r}_1, \mathbf{r}_2) = \phi_{n_1 l_1 m_1}(\mathbf{r}_1) \phi_{n_2 l_2 m_2}(\mathbf{r}_2) \quad (18-5)$$

for the equation

$$[H^{(1)} + H^{(2)}] u(\mathbf{r}_1, \mathbf{r}_2) = E u(\mathbf{r}_1, \mathbf{r}_2) \quad (18-6)$$

and the energy would be given by (Fig. 18.2a)

$$E = E_{n_1} + E_{n_2} \quad (18-7)$$

where $E_n = -(mc^2/2)(Z\alpha)^2/n^2$. Thus in the idealized model in which the two electrons ignore each other, the lowest energy is

$$E = -2E_1 = -mc^2(2\alpha)^2 = -108.8 \text{ eV} \quad (18-8)$$

Note that this is $2 \times Z^2 = 8$ times the hydrogen energy of -13.6 eV .

The first excited state is one in which one electron is in its ground state, $n = 1$, and the second electron is raised to the first excited $n = 2$ state. Then

$$E = E_1 + E_2 = -68.0 \text{ eV} \quad (18-9)$$

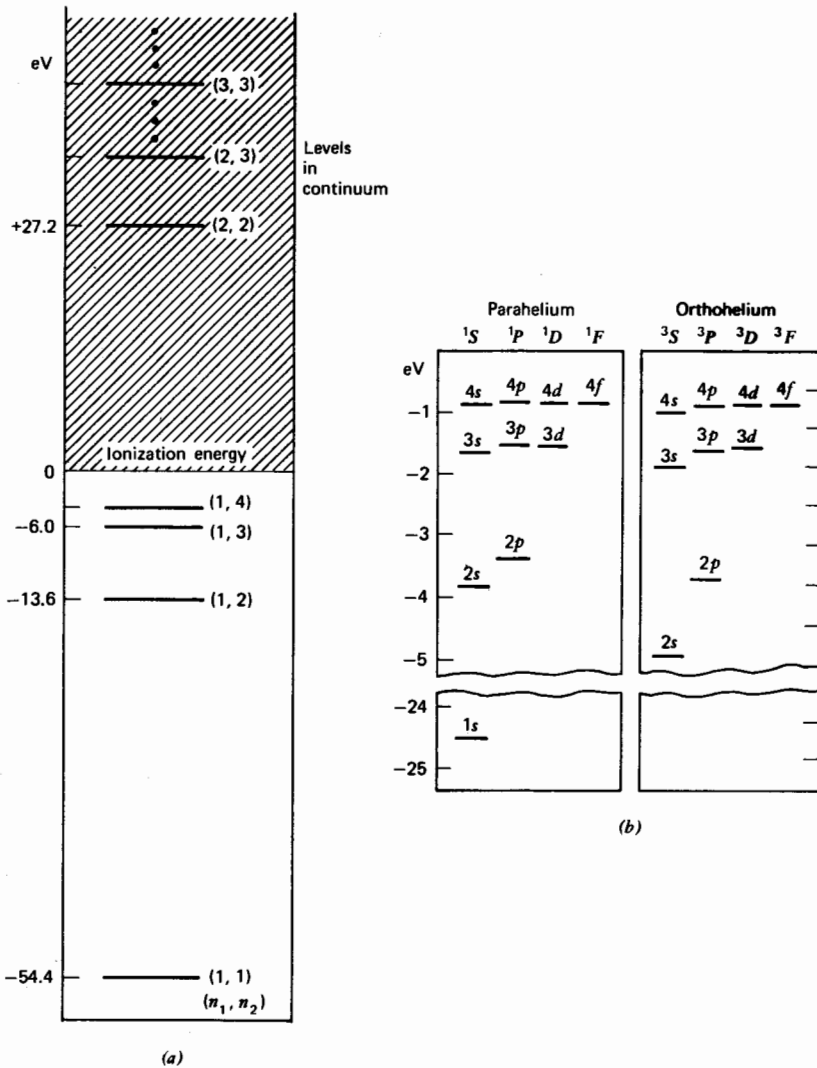


Figure 18-2. (a) The spectrum of helium as it would look in the absence of the electron-electron interaction. The zero energy point is chosen at the ionization energy. (b) The actual spectrum of helium for the singlet (parahelium) and triplet (orthohelium) states. The level labeling has a suppressed (1s), so that the level (2p) is approximately described by the (1s)(2p) orbital.

The ionization energy, that is, the energy required to remove one electron from the ground state to infinity is

$$E_{\text{ioniz}} = (E_1 + E_\infty) - 2E_1 = 54.4 \text{ eV} \tag{18-10}$$

and, interestingly enough, the onset of the continuum lies *lower* than the excited state for which both electrons are in the $n = 2$ state. The energy of the latter state is

$$E = 2E_2 = -27.2 \text{ eV} \tag{18-11}$$

and it brings up a new phenomenon: the existence of a discrete state in the continuum for the Hamiltonian $H^{(1)} + H^{(2)}$. We shall briefly discuss the implications of this at the end of the chapter.

Effects of the Exclusion Principle

Since the two electrons are *identical fermions* we must make the total wave function antisymmetric under the interchange of space and spin coordinates of the electrons. Thus a proper description of the ground state of this idealized model is

$$u_0(\mathbf{r}_1, \mathbf{r}_2) = \phi_{100}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2) \chi_{\text{singlet}} \quad (18-12)$$

The spatial part of the wave function is necessarily symmetric, and that is why the state must be a spin singlet state

$$\chi_{\text{singlet}} = \frac{1}{\sqrt{2}} (\chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)}) \quad (18-13)$$

For the first excited state, we have two possibilities, which, for $V = 0$, are degenerate in energy. These are

$$u_1^{(s)} = \frac{1}{\sqrt{2}} [\phi_{100}(\mathbf{r}_1) \phi_{2lm}(\mathbf{r}_2) + \phi_{2lm}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2)] \chi_{\text{singlet}} \quad (18-14)$$

and the space-antisymmetric, spin symmetric

$$u_1^{(t)} = \frac{1}{\sqrt{2}} [\phi_{100}(\mathbf{r}_1) \phi_{2lm}(\mathbf{r}_2) - \phi_{2lm}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2)] \chi_{\text{triplet}} \quad (18-15)$$

where

$$\chi_{\text{triplet}} = \begin{cases} \chi_+^{(1)} \chi_+^{(2)} \\ \frac{1}{\sqrt{2}} (\chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)}) \\ \chi_-^{(1)} \chi_-^{(2)} \end{cases} \quad (18-16)$$

is orthogonal to χ_{singlet} .

EFFECT OF ELECTRON-ELECTRON REPULSION

The presence of V , the electron-electron Coulomb interaction may, in first approximation, be treated as a perturbation. Let us first compute the energy shift of the ground state to first order in V . We have

$$\Delta E = \int d^3r_1 d^3r_2 u_0^*(\mathbf{r}_1, \mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} u_0(\mathbf{r}_1, \mathbf{r}_2) \quad (18-17)$$

Since the perturbation does not involve the spin, we need only consider

$$\Delta E = \int d^3r_1 d^3r_2 |\phi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\phi_{100}(\mathbf{r}_2)|^2 \quad (18-18)$$

The integral has a simple physical interpretation. Since $|\phi_{100}(\mathbf{r}_1)|^2$ is the probability density of finding electron 1 at \mathbf{r}_1 , we may interpret $e|\phi_{100}(\mathbf{r}_1)|^2$ as the charge density due to electron 1. Hence

$$U(\mathbf{r}_2) = - \int d^3r_1 \frac{e|\phi_{100}(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (18-19)$$

is the potential at \mathbf{r}_2 due to the charge distribution of electron 1, and

$$\Delta E = - \int d^3r_2 e|\phi_{100}(\mathbf{r}_2)|^2 U(\mathbf{r}_2) \quad (18-20)$$

is therefore the electrostatic energy of interaction of electron 2 with that potential. The integral can be carried out. With $\phi_{100} = (2/\sqrt{4\pi})(Z/a_0)^{3/2} e^{-Zr/a_0}$ we have

$$\begin{aligned} \Delta E = & \left[\frac{1}{\pi} (Z/a_0)^3 \right]^2 e^2 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0} \\ & \int d\Omega_1 \int d\Omega_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \end{aligned} \quad (18-21)$$

In writing this, we used the separation

$$\int d^3r = \int_0^\infty r^2 dr d\Omega$$

and isolated the only term that depends on the angles between \mathbf{r}_1 and \mathbf{r}_2 . We have

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2 \cos \theta)^{1/2}} \quad (18-22)$$

where θ is the angle between \mathbf{r}_1 and \mathbf{r}_2 . We may proceed in one of two ways.

(a) Most directly, we choose the direction of \mathbf{r}_1 as z-axis for the $d\Omega_2$ integration, and get

$$\begin{aligned} \int d\Omega_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2 \cos \theta)^{1/2}} \\ &= -2\pi \frac{1}{r_1r_2} \left[(r_1^2 + r_2^2 - 2r_1r_2 \cos \theta)^{1/2} \right]_{\cos \theta = -1}^{\cos \theta = +1} \\ &= \frac{2\pi}{r_1r_2} (r_1 + r_2 - |r_1 - r_2|) \end{aligned} \quad (18-23)$$

The integration over $d\Omega_1$ is trivial, since nothing depends on that angle, so that

$$\int d\Omega_1 = 4\pi \quad (18-24)$$

and we are left with

$$8e^2 \left(\frac{Z}{a_0}\right)^6 \int_0^\infty r_1 dr_1 e^{-2Zr_1/a_0} \int_0^\infty r_2 dr_2 e^{-2Zr_2/a_0} \times (r_1 + r_2 - |r_1 - r_2|) \quad (18-25)$$

(b) A very useful expansion, necessary when there is additional angular dependence in the numerator, is the following. For $r_1 > r_2$,

$$\begin{aligned} (r_1^2 + r_2^2 - 2r_1r_2 \cos \theta)^{-1/2} &= r_1^{-1} \left(1 + \frac{r_2^2}{r_1^2} - 2\frac{r_2}{r_1} \cos \theta\right)^{-1/2} \\ &= \frac{1}{r_1} \sum_{L=0}^{\infty} \left(\frac{r_2}{r_1}\right)^L P_L(\cos \theta) \end{aligned} \quad (18-26)$$

with the roles of r_1 and r_2 reversed when $r_2 > r_1$. Thus

$$\int d\Omega_1 \int d\Omega_2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int d\Omega_1 \int d\Omega_2 \sum_{L=0}^{\infty} \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos \theta) \quad (18-27)$$

where $r_>$ ($r_<$) is the larger (smaller) of r_1 and r_2 . We can now proceed as before, using the fact that

$$\frac{1}{2} \int_{-1}^1 d(\cos \theta) P_L(\cos \theta) = \delta_{L0} \quad (18-28)$$

as a special case of

$$\frac{1}{2} \int_{-1}^1 d(\cos \theta) P_L(\cos \theta) P_{L'}(\cos \theta) = \frac{\delta_{LL'}}{2L+1} \quad (18-29)$$

In any case, (18-25) becomes

$$\begin{aligned} \Delta E &= 8e^2(Z/a_0)^6 \int_0^\infty r_1 dr_1 e^{-2Zr_1/a_0} \left\{ 2 \int_0^{r_1} r_2^2 dr_2 e^{-2Zr_2/a_0} \right. \\ &\quad \left. + 2r_1 \int_{r_1}^\infty r_2 dr_2 e^{-2Zr_2/a_0} \right\} \end{aligned} \quad (18-30)$$

The integrals are straightforward and yield the answer

$$\Delta E = \frac{5}{8} \frac{Ze^2}{a_0} = \frac{5}{4} Z \left(\frac{1}{2} mc^2 \alpha^2\right) \quad (18-31)$$

This is a positive contribution, since it arises from a repulsive force, and its magnitude, for $Z = 2$ is 34 eV. When this is added to the zero-order result of -108.8 eV we obtain, to first order

$$E \approx -74.8 \text{ eV} \quad (18-32)$$

When this is compared with

$$E_{\text{exp}} = -78.975 \text{ eV} \quad (18-33)$$

a sizable discrepancy is seen. Physically, we can attribute this discrepancy to the fact that in our calculation we took no account of "screening," that is, the effect that the presence of one electron tends to decrease the net charge "seen" by the other electron. Very roughly, if one argues that, for example, electron 1 is half the time "between" electron 2 and the nucleus, then half the time electron 2 sees a charge Z and half the time it sees a charge $Z - 1$, that is, effectively, in the expression

$$E + \Delta E = -\frac{1}{2} mc^2 \alpha^2 \left(2Z^2 - \frac{5}{4} Z \right) \quad (18-34)$$

$(Z - 1/2)$ should be substituted for Z . This does improve agreement, but the crude argument advanced is not sufficient justification for the choice of 50 percent for the probability of effective screening. We will return to this subject later in this chapter, when we discuss the Rayleigh-Ritz variational principle for the ground state energy.

EXCLUSION PRINCIPLE AND EXCHANGE INTERACTION

We next consider the first excited state of helium. It will be sufficient to calculate the energy shift with the singlet and triplet $m = 0$ states listed in (18-14) and (18-15), since the shift is caused by a perturbation that commutes with L_z . For such a perturbation, the shift must be independent of the m -value. Again, because of the spin-independence of the perturbing potential, V , we have

$$\begin{aligned} \Delta E_1^{(s,t)} &= \frac{1}{2} e^2 \int d^3r_1 \int d^3r_2 [\phi_{100}(\mathbf{r}_1) \phi_{210}(\mathbf{r}_2) \pm \phi_{210}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2)]^* \\ &\quad \times \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} [\phi_{100}(\mathbf{r}_1) \phi_{210}(\mathbf{r}_2) \pm \phi_{210}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2)] \\ &= e^2 \int d^3r_1 \int d^3r_2 |\phi_{100}(\mathbf{r}_1)|^2 |\phi_{210}(\mathbf{r}_2)|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &\quad \pm e^2 \int d^3r_1 \int d^3r_2 \phi_{100}^*(\mathbf{r}_1) \phi_{210}^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{210}(\mathbf{r}_1) \phi_{100}(\mathbf{r}_2) \end{aligned} \quad (18-35)$$

In obtaining this simplified form, we made use of the symmetry of V under $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$.

The energy shift is seen to consist of two terms: the first has the familiar form

of an electrostatic interaction between two "electron clouds" distributed according to the wave functions of the two electrons. This term is just a simple generalization of the term that we found for the ground-state energy shift. The second term has no classical interpretation. Its origin lies in the Pauli principle, and its sign depends on whether the state has spin 0 or 1. Thus, because of this *exchange* contribution, the singlet and triplet terms are no longer degenerate. Although we considered $n = 2$ here, we have quite generally

$$\begin{aligned}\Delta E_{n,l}^{(t)} &= J_{nl} - K_{nl} \\ \Delta E_{n,l}^{(s)} &= J_{nl} + K_{nl}\end{aligned}\quad (18-36)$$

The integrals can be evaluated in closed form [it is here that (18-27) becomes useful], but we shall not do this here. The integral J_{nl} is manifestly positive, and it turns out that this is also the case for K_{nl} . For $l = n - 1$ this is obvious: the wave functions appearing in (18-35) have no nodes in that case. That the triplet state should have a lower energy than the singlet state, that is, that

$$J_{nl} - K_{nl} < J_{nl} + K_{nl}$$

or equivalently

$$K_{nl} > 0 \quad (18-37)$$

can be argued on qualitative grounds. For the triplet state the spatial wave function is antisymmetric, so that the electrons are somewhat constrained to stay away from each other. This tends to reduce the screening effect, so that each electron "sees" more of the nuclear charge, and it also tends to make the repulsion between the electrons less effective than for the spatially symmetric singlet state. An interesting aspect of this result is that, although the perturbing potential $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ does not depend on the spins of the electrons, the symmetry of the wave function does make the potential act as if it were spin-dependent. We may write (18-36) in a form that exhibits this. Let the spins of the two electrons be \mathbf{s}_1 and \mathbf{s}_2 . Then the total spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$, and

$$\mathbf{S}^2 = \mathbf{s}_1^2 + \mathbf{s}_2^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2 \quad (18-38)$$

If we act with this on triplet and singlet states (18-16) and (18-13) that are also eigenstates of \mathbf{s}_1^2 and \mathbf{s}_2^2 , we get

$$S(S + 1)\hbar^2 = \frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2\mathbf{s}_1 \cdot \mathbf{s}_2$$

that is,

$$2\mathbf{s}_1 \cdot \mathbf{s}_2/\hbar^2 = S(S + 1) - \frac{3}{2} = \begin{cases} \frac{1}{2} & \text{triplet} \\ -\frac{3}{2} & \text{singlet} \end{cases} \quad (18-39)$$

We may thus write, in terms of the σ 's related to the spins by $\mathbf{s}_i = (1/2) \hbar \boldsymbol{\sigma}_i$,

$$\Delta E_{n,l} = J_{n,l} - \frac{1}{2} (1 + \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2) K_{nl} \quad (18-40)$$

We shall see this phenomenon again when we discuss the H_2 molecule. Usually spin-dependent forces between atoms are quite weak. As illustrated in the example of spin-orbit coupling, the spin-dependent forces tend to arise from relativistic corrections to the static forces. In the spin-orbit example, these forces are down by a factor of α^2 , which is just $(v/c)^2$. Such forces could not be strong enough to keep the electron spins aligned in a ferromagnet, except at unrealistically low temperatures. The spin dependence due to exchange is much stronger than that: the force is of the same order of magnitude as the electrostatic force, and, as first observed by Heisenberg, it is responsible for the phenomenon of ferromagnetism.

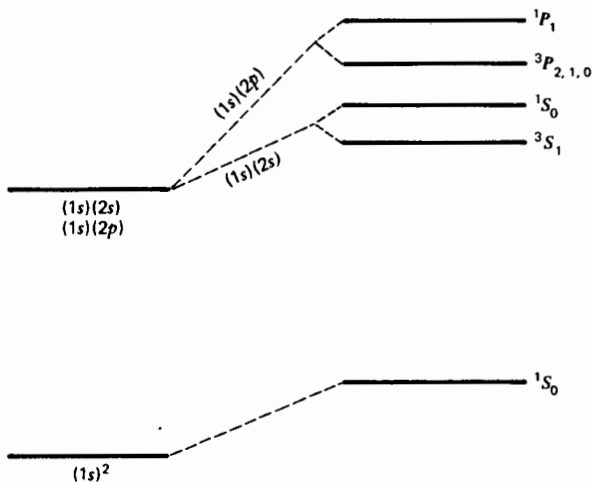


Figure 18-3. Schematic sketch of splitting of the first excited states of helium.

The spectrum of the first few excited states of helium is shown in Fig. 18-3. The notation used for the unperturbed states is that of *orbitals*, that is, the quantum numbers of the unperturbed electrons. Thus both electrons in the ground state are in $n = 1, l = 0$ states, and we write this as $(1s, 1s)$, or more briefly $(1s)^2$. It should be understood that when we write $(1s)(2p)$, as for the first excited state, this does not mean that one electron is in one state, and the other electron in the other, since we must write totally antisymmetric wave functions for the electrons. Another way of labeling the state is by the $^{2S+1}L_J$ notation, which we use for the perturbed states in the figure. We see that the singlet states lie above the triplet states in a given multiplet. This follows from the symmetry (cf. our argument that $K_{nl} > 0$) and is a special example of one of *Hund's Rules*: *Other things being equal, the states of highest spin will have the lowest energy.*²

If we excite helium from the ground state by shining ultraviolet light on it, we find that the *selection rule* $\Delta L = 1$, which we will derive later, implies an excitation

²Hund's rules are discussed in more detail in Chapter 19.

to the **P states**. Furthermore, there is a selection rule $\Delta S = 0$, that is, only transitions **singlet** \rightarrow singlet and triplet \rightarrow triplet dominate.³ Hence the state most strongly **excited** from the ground state is the 1P_1 state. The other levels may also become **occupied** through other mechanisms, for example, collisional excitation. Once **occupied**, the radiative transitions to the ground state are very improbable. The 3P state, which may be populated when atoms in the 1P_1 state undergo collisions with other atoms in the gas, can only decay to the 3S_1 state, and that state is *metastable*, since it cannot decay to the ground state easily. The fact that there are no transitions, to good approximation, between triplet states and singlet states, led, at one time, to the belief that there existed two kinds of helium, ortho-helium (triplet) and para-helium (singlet).

The spectrum of helium that we saw in Fig. 18-2b shows that the excited states $(1s)(nl)$ have energies that do not differ very much from those of the hydrogen atom levels. Thus the binding energy of one electron in the atom is 24.6 eV (total binding energy minus binding energy of singly ionized helium = $79.0 - 54.4 = 24.6$ eV), whereas the energy that would be liberated if one electron were to be removed from the $2s$ state is of the order of 4 – 5 eV, which is comparable to the energy 3.4 eV ($= 13.6/n^2$ eV) for hydrogen. The reason for this effect is that the "outer" electron sees only a unit positive charge, since the "inner" electron in the $(1s)$ orbital tends to shield the nucleus, leaving a net effective charge $\approx Z - 1$. This is not the case for the ground state, since both electrons have access to the nucleus. Thus the ground state lies quite a bit deeper than the hydrogen ground state.