

and the overlap is negligible. This is quite gratifying. We never have to worry about the question of antisymmetrization with 10 billion electrons, nor is it necessary to take into account the antisymmetrization requirement between an electron in Los Angeles and an electron in Beijing.

6.4. THE HELIUM ATOM

A study of the helium atom is rewarding for several reasons. First of all, it is the simplest realistic problem where the question of identity—which we encountered in Section 6.3—plays an important role. Second, even though it is a simple system, the two-particle Schrödinger equation cannot be solved analytically; therefore, this is a nice place to illustrate the use of perturbation theory and also the use of the variational method.

The basic Hamiltonian is given by

$$H = \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}, \quad (6.4.1)$$

where $r_1 \equiv |\mathbf{x}_1|$, $r_2 \equiv |\mathbf{x}_2|$, and $r_{12} \equiv |\mathbf{x}_1 - \mathbf{x}_2|$; see Figure 6.3. Suppose the e^2/r_{12} -term were absent. Then, with the identity question ignored, the wave function would be just the product of two hydrogen atom wave functions with $Z=1$ changed into $Z=2$. The total spin is a constant of the motion, so the spin state is either singlet or triplet. The space part of the wave function for the important case where one of the electrons is in the ground state and the other in an excited state characterized by (nlm) is

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{x}_1)\psi_{nlm}(\mathbf{x}_2) \pm \psi_{100}(\mathbf{x}_2)\psi_{nlm}(\mathbf{x}_1)] \quad (6.4.2)$$

where the upper (lower) sign is for the spin singlet (triplet). We will come back to this general form for an excited state later.

For the ground state, we need a special treatment. Here the configuration is characterized by $(1s)^2$, that is, both electrons in $n=1$, $l=0$.

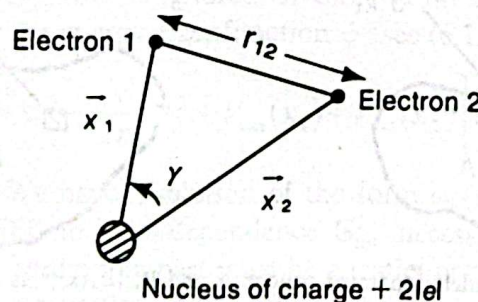


FIGURE 6.3. Schematic diagram of the helium atom.

The space function must then necessarily be symmetric and only the spin singlet function is allowed. So we have

$$\psi_{100}(\mathbf{x}_1)\psi_{100}(\mathbf{x}_2)\chi_{\text{singlet}} = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0} \chi \quad (6.4.3)$$

with $Z = 2$. Not surprisingly, this "unperturbed" wave function gives

$$E = 2 \times 4 \left(-\frac{e^2}{2a_0} \right) \quad (6.4.4)$$

for the ground-state energy, which is about 30% bigger than the experimental value.

This is just the starting point of our investigation because in obtaining the above form (6.4.3), we have completely ignored the last term in (6.4.1) that describes the interaction between the two electrons. One way to approach the problem of obtaining a better energy value is to apply first-order perturbation theory using (6.4.3) as the unperturbed wave function and e^2/r_{12} as the perturbation. We obtain

$$\Delta_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle_{(1s)^2} = \iint \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \frac{e^2}{r_{12}} d^3x_1 d^3x_2. \quad (6.4.5)$$

To carry out the indicated integration we first note

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\gamma}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos\gamma), \quad (6.4.6)$$

where $r_{>}$ ($r_{<}$) is the larger (smaller) of r_1 and r_2 and γ is the angle between \mathbf{x}_1 and \mathbf{x}_2 . The angular integration is easily performed by expressing $P_l(\cos\gamma)$ in terms of $Y_l^m(\theta_1, \phi_1)$ and $Y_l^m(\theta_2, \phi_2)$ using the addition theorem of spherical harmonics:

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2). \quad (6.4.7)$$

The angular integration is now trivial:

$$\int Y_l^m(\theta_i, \phi_i) d\Omega_i = \frac{1}{\sqrt{4\pi}} (4\pi) \delta_{l0} \delta_{m0}. \quad (6.4.8)$$

The radial integration is elementary (but involves tedious algebra!); it leads to

$$\begin{aligned} & \int_0^{\infty} \left[\int_0^{r_1} \frac{1}{r_1} e^{-(2Z/a_0)(r_1+r_2)} r_2^2 dr_2 + \int_{r_1}^{\infty} \frac{1}{r_2} e^{-(2Z/a_0)(r_1+r_2)} r_2^2 dr_2 \right] r_1^2 dr_1 \\ &= \frac{5}{128} \frac{a_0^5}{Z^5}. \end{aligned} \quad (6.4.9)$$

Combining everything, we have (for $Z = 2$)

$$\begin{aligned}\Delta_{(1s)^2} &= \left(\frac{Z^6 e^2}{\pi^2 a_0^6} \right) 4\pi (\sqrt{4\pi})^2 \left(\frac{5}{128} \right) \left(\frac{a_0^5}{Z^5} \right) \\ &= \left(\frac{5}{2} \right) \left(\frac{e^2}{2a_0} \right).\end{aligned}\tag{6.4.10}$$

Adding this energy shift to (6.4.4), we have

$$E_{\text{cal}} = \left(-8 + \frac{5}{2} \right) \left(\frac{e^2}{2a_0} \right) \approx -74.8 \text{ eV}.\tag{6.4.11}$$

Compare this with the experimental value,

$$E_{\text{exp}} = -78.8 \text{ eV}.\tag{6.4.12}$$

This is not bad, but we can do better! We propose to use the variational method with Z , which we call Z_{eff} , as a variational parameter. The physical reason for this choice is that the effective Z seen by one of the electrons is smaller than 2 because the positive charge of 2 units at the origin (see Figure 6.3) is “screened” by the negatively charged cloud of the other electron; in other words, the other electron tends to neutralize the positive charge due to the helium nucleus at the center. For the normalized trial function we use

$$\langle \mathbf{x}_1, \mathbf{x}_2 | \tilde{0} \rangle = \left(\frac{Z_{\text{eff}}^3}{\pi a_0^3} \right) e^{-Z_{\text{eff}}(r_1 + r_2)/a_0}.\tag{6.4.13}$$

From this we obtain

$$\begin{aligned}\bar{H} &= \left\langle \tilde{0} \left| \frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} \right| \tilde{0} \right\rangle - \left\langle \tilde{0} \left| \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \right| \tilde{0} \right\rangle + \left\langle \tilde{0} \left| \frac{e^2}{r_{12}} \right| \tilde{0} \right\rangle \\ &= \left(2 \frac{Z_{\text{eff}}^2}{2} - 2ZZ_{\text{eff}} + \frac{5}{8} Z_{\text{eff}} \right) \left(\frac{e^2}{a_0} \right).\end{aligned}\tag{6.4.14}$$

We easily see that the minimization of \bar{H} is at

$$Z_{\text{eff}} = 2 - \frac{5}{16} = 1.6875.\tag{6.4.15}$$

This is smaller than 2, as anticipated. Using this value for Z_{eff} we get

$$E_{\text{cal}} = -77.5 \text{ eV},\tag{6.4.16}$$

which is already very close considering the crudeness of the trial wave function.

Historically, this achievement was considered to be one of the earliest signs that Schrödinger's wave mechanics was on the right track. We

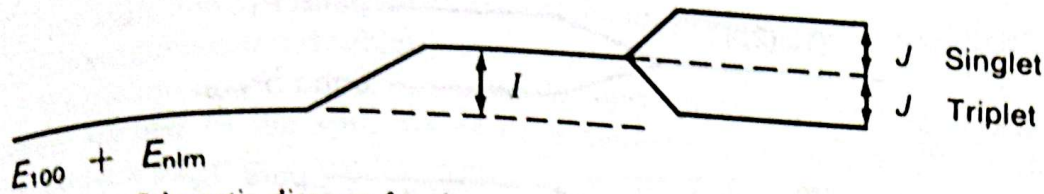


FIGURE 6.4. Schematic diagram for the energy-level splittings of $(1s)(nl)$ for the helium atom.

cannot get this kind of number by the purely algebraic (operator) method. The helium calculation was first done by A. Unsöld in 1927.*

Let us briefly consider excited states. This is more interesting from the point of view of illustrating quantum-mechanical effects due to identity. We consider just $(1s)(nl)$. We write the energy of this state as

$$E = E_{100} + E_{nlm} + \Delta E. \quad (6.4.17)$$

In first-order perturbation theory, ΔE is obtained by evaluating the expectation value of e^2/r_{12} . We can write

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = I \pm J, \quad (6.4.18)$$

where I and J , known respectively as the direct integral and the exchange integral, are given by

$$I = \int d^3x_1 \int d^3x_2 |\psi_{100}(\mathbf{x}_1)|^2 |\psi_{nlm}(\mathbf{x}_2)|^2 \frac{e^2}{r_{12}}, \quad (6.4.19a)$$

$$J = \int d^3x_1 \int d^3x_2 \psi_{100}(\mathbf{x}_1) \psi_{nlm}(\mathbf{x}_2) \frac{e^2}{r_{12}} \psi_{100}^*(\mathbf{x}_2) \psi_{nlm}^*(\mathbf{x}_1). \quad (6.4.19b)$$

The upper (lower) sign goes with the spin singlet (triplet) state. Obviously, I is positive; we can also show that J is positive. So the net result is such that for the same configuration, the spin singlet state lies higher, as shown in Figure 6.4.

The physical interpretation for this is as follows: In the singlet case the space function is symmetric and the electrons have a tendency to come close to each other. Therefore, the effect of the electrostatic repulsion is more serious; hence, a higher energy results. In the triplet case, the space function is antisymmetric and the electrons tend to avoid each other. Helium in spin-singlet states is known as **parahelium**, while helium in spin-triplet states is known as **orthohelium**. Each configuration splits into

*A. Unsöld, Ann. Phys. 82 (1927) 355.

