

Chapter 4: Atomic Physics

“Nature resolves everything into its component atoms
and never reduces anything to nothing.”

Lucretius (95 BC - 55 BC)

4.1 The History of the Atom

The earliest attempt to find simplicity in matter occurred in the fifth century B.C., when the Greek philosophers Leucippus and Democritus stated that matter is composed of very small particles called atoms. The Greek word for *atom* means “that which is indivisible.” The concept of an atom of matter was to lie dormant for hundreds of years until 1803 when John Dalton, an English chemist, introduced his atomic theory of matter in which he proposed that to every known chemical element there corresponds an atom of matter. Today there are known to be 105 chemical elements. All other substances in the world are combinations of these elements.

The Greek philosophers’ statement about atoms was based on speculation, whereas Dalton’s theory was based on experimental evidence. Dalton’s world of the atom was a simple and orderly place until some new experimental results appeared on the scene. M. Faraday performed experiments in electrolysis by passing electrical charges through a chemical solution of sodium chloride, NaCl. His laws of electrolysis showed that one unit of electricity was associated with one atom of a substance. He assumed that this charge was carried by the atom. A study of the conduction of electricity through rarefied gases led the English physicist J. J. Thomson, in 1898, to the verification of an independent existence of very small negatively charged particles. Even before this, in 1891, the Irish physicist George Stoney had made the hypothesis that there is a natural unit of electricity and he called it an electron. In 1896, Henri Becquerel discovered radiation from the atoms of a uranium salt.

The results of these experiments led to some inevitable questions. Where did these negatively charged particles, the electrons, come from? Where did the radiations from the uranium atom come from? The only place they could conceivably come from was from inside the atom. But if they came from within the atom, the atom could no longer be considered indivisible. That is, the “indivisible” atom must have some internal structure. Also, because the atom is observed to be electrically neutral, there must be some positive charge within it in order to neutralize the effect of the negative electrons. It had also been determined experimentally that these negative electrons were thousands of times lighter than the entire atom. Therefore, whatever positive charges existed within the atom, they must contain most of the mass of the atom.

J. J. Thomson proposed the first picture of the atom in 1898. He assumed that atoms are uniform spheres of positively charged matter in which the negatively charged electrons are embedded, figure 4.1. This model of the atom was called the plum pudding model because it resembled the raisins embedded in a plum pudding.

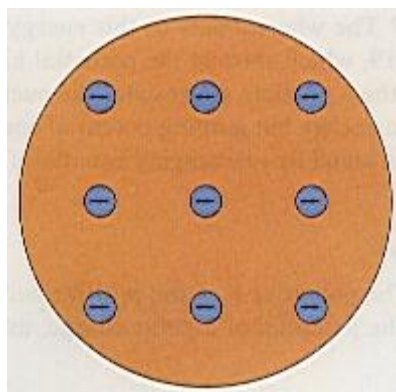


Figure 4.1 The plum pudding model of the atom.

That is, the electrons were like the raisins, and the pudding was the positively charged matter. But how are these electrons distributed within the atom? It became obvious that the only way to say exactly what is within the atom is to take a “look” inside the atom. But how do you “look” inside an atom?

In 1911, Hans Geiger (1882-1945) and Ernest Marsden, following a suggestion by Ernest Rutherford (1871-1937), bombarded atoms with alpha particles to “see” what was inside of the atom. The alpha particles, also written α particles, were high-energy particles emitted by radioactive substances that were discovered by Rutherford in 1899. These α particles were found to have a mass approximately four times the mass of a hydrogen atom and carried a positive charge of two units. (Today we know that the α particle is the nucleus of the helium atom.) Rutherford’s idea was that the direction of motion of the α particle should be changed or deflected by the electrical charges within the atom. In this way, we can “see” within the atom. The experimental arrangement is illustrated in figure 4.2.

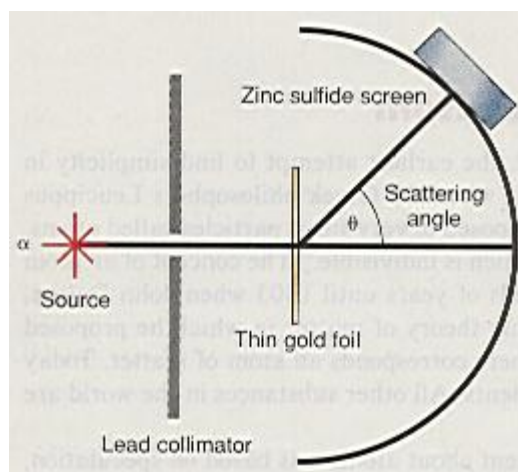


Figure 4.2 Rutherford scattering.

A polonium-214 source emits α particles of 7.68 MeV. A lead screen with a slit (the lead collimator) allows only those α particles that pass through the slit to

fall on a very thin gold foil. It is expected that most of these α particles should go straight through the gold atoms and arrive at the zinc sulfide (ZnS) screen. When the α particle hits the ZnS screen a small flash of light is given off (called a *scintillation*). It is expected that some of these α particles should be slightly deflected by some of the positive charge of the atomic pudding. The ZnS screen can be rotated through any angle around the gold foil and can therefore observe any deflected α particles. *This process of deflection of the α particle is called Rutherford scattering.* The expected scattering from the distributed positive charge should be quite small and this was what at first was observed. Then Rutherford suggested that Geiger and Marsden should look for some scattering through large angles. To everyone's surprise, some α particles were found to come straight backward ($\theta \cong 180^\circ$). This back-scattering was such a shock to Rutherford that as he described it, "It was almost as incredible as if you fired a 15-inch shell at a piece of paper and it bounced off and came right back to you."

The only way to explain this back-scattering is to assert that the positive charge is not distributed over the entire atom but instead it must be concentrated in a very small volume. Thus, the experimental results of large-angle scattering are not consistent with the plum pudding model of an atom. Rutherford, therefore, proposed a new model of the atom, the *nuclear atom*. In this model, the atom consists of a very small, dense, positively charged nucleus. Because the negatively charged electrons would be attracted to the positive nucleus and would crash into it if they were at rest, it was necessary to assume that the electrons were in motion orbiting around the nucleus somewhat in the manner of the planets orbiting about the sun in the solar system. In 1919, Rutherford found this positive particle of the nucleus and named it the *proton*. The proton has a positive charge equal in magnitude to the charge on the electron (i.e., 1.60×10^{-19} C). The atom must contain the same number of protons as electrons in order to account for the fact that the atom is electrically neutral. The mass of the proton is 1.67×10^{-27} kg, which is 1836 times more massive than the electron.

A simple analysis allows us to determine the approximate dimensions of the nucleus. Consider a head-on collision between the α particle and the nucleus, as shown in figure 4.3. Because both particles are positive, there is an electrostatic

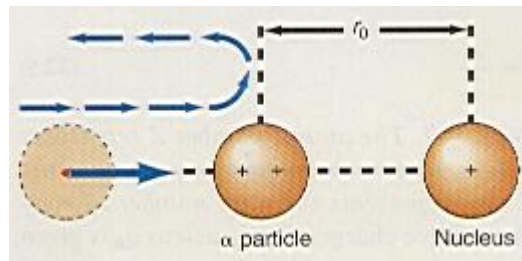


Figure 4.3 Approximate nuclear dimensions by a head-on collision.

force of repulsion between them. The α particle, as it approaches the nucleus, slows down because of the repulsion. Eventually it comes to a stop close to the nucleus, shown as the distance r_0 in the figure. The repulsive force now causes the α particle

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to accelerate away from the nucleus giving the back-scattering of 180° . When the α particle left the source, it had a kinetic energy of 7.68 MeV. When it momentarily came to rest at the position r_0 , its velocity was zero and hence its kinetic energy was also zero there. Where did all the energy go? The whereabouts of this energy can be determined by referring back to the potential hill of a positive point charge, such as a nucleus. As the α particle approaches the nucleus, it climbs up the potential hill, losing its kinetic energy but gaining potential energy. The potential energy that the α particle gains is found by

$$\text{PE} = q_{\alpha}V$$

where q_{α} is the charge on the α particle. The potential V of the positive nucleus is given by the equation for the potential of a point charge, that is,

$$V = \frac{kq_n}{r}$$

where q_n is the charge of the nucleus and k is the constant in Coulomb's law. Thus, the potential energy that the α particle gains as it climbs up the potential hill is

$$\text{PE} = \frac{kq_{\alpha}q_n}{r}$$

When the α particle momentarily comes to rest at the distance r_0 from the nucleus, all its kinetic energy has been converted to potential energy. Equating the kinetic energy of the α particle to its potential energy in the field of the nucleus, we get

$$\text{KE} = \text{PE} = \frac{kq_{\alpha}q_n}{r_0} \quad (4.1)$$

Because the kinetic energy of the α particle is known, equation 4.1 can be solved for r_0 , the approximate radius of the nucleus, to give

$$r_0 = \frac{kq_{\alpha}q_n}{\text{KE}} \quad (4.2)$$

It had previously been determined that the charge on the α particle was twice the charge of the electron, that is,

$$q_{\alpha} = 2e \quad (4.3)$$

To determine the charge of the nucleus, more detailed scattering experiments were performed with different foils, and it was found that the positive charge on the nucleus was approximately

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$$q_n = \frac{Ae}{2} \quad (4.4)$$

where A is the mass number of the foil material. *The mass number A is the nearest whole number to the atomic mass of an element.* For example, the atomic mass of nitrogen (N) is 14.0067, its mass number A is 14. A new number, *the atomic number Z is defined from equation 4.4 as¹*

$$Z = \frac{A}{2} \quad (4.5)$$

The atomic number of nitrogen is thus $14/2 = 7$. *The atomic number Z represents the number of positive charges in the nucleus, that is, the number of protons in the nucleus. Because an atom is neutral, Z also represents the total number of electrons in the atom.* Using this notation the positive charge of the nucleus q_n is given by

$$q_n = Ze \quad (4.6)$$

Substituting equations 4.3 and 4.6 into equation 4.2 gives, for the value of r_0 ,

$$r_0 = \frac{k(2e)(Ze)}{KE}$$

or

$$r_0 = \frac{2kZe^2}{KE} \quad (4.7)$$

Example 4.1

The radius of the gold nucleus found by scattering. Find the maximum radius of a gold nucleus that is bombarded by 7.68-MeV α particles.

Solution

The maximum radius of the gold nucleus is found from equation 4.7 with the atomic number Z for gold equal to 79,

$$r_0 = \frac{2kZe^2}{KE}$$

$$\begin{aligned} r_0 &= \left[\frac{2(9.00 \times 10^9 \text{ N m}^2/\text{C}^2)(79)(1.60 \times 10^{-19} \text{ C})^2}{7.68 \text{ MeV}} \right] \left(\frac{1 \text{ MeV}}{10^6 \text{ eV}} \right) \left(\frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} \right) \\ &= 2.96 \times 10^{-14} \text{ m} \end{aligned}$$

¹Equation 4.5 is only correct for the lighter elements. For the heavier elements, there are more neutrons in the nucleus raising the value of the atomic mass and hence its mass number. We will discuss the neutron shortly.

Thus, the approximate radius of a gold nucleus is 2.96×10^{-14} m. The actual radius is somewhat less than this value. Although this calculation is only an approximation, it gives us the order of magnitude of the radius of the nucleus.

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It was already known from experimental data, that the radius of the atom r_a is of the order

$$r_a = 10^{-10} \text{ m}$$

Comparing the relative size of the atom r_a to the size of the nucleus r_n , we get

$$\begin{aligned} \frac{r_a}{r_n} &= \frac{10^{-10} \text{ m}}{10^{-14} \text{ m}} \\ &= 10^4 \end{aligned}$$

or

$$r_a = 10^4 r_n = 10,000 r_n \quad (4.8)$$

That is, the radius of the atom is about 10,000 times greater than the radius of the nucleus.

More detailed scattering experiments have since led to the following approximate formula for the size of the nucleus

$$R = R_0 A^{1/3} \quad (4.9)$$

where A is again the mass number of the element and R_0 is a constant equal to 1.20×10^{-15} m.

Example 4.2

A more accurate value for the radius of a gold nucleus. Find the radius of the gold nucleus using equation 4.9.

Solution

The mass number A for gold is found by looking up the atomic mass of gold in the periodic table of the elements (appendix E). The atomic mass is 197.0. The mass number A for gold is the nearest whole number to the atomic mass, so $A = 197$. Now we find the radius of the gold nucleus from equation 4.9, as

$$R = R_0 A^{1/3}$$

$$\begin{aligned}
 &= (1.20 \times 10^{-15} \text{ m})(197)^{1/3} \\
 &= 0.698 \times 10^{-14} \text{ m}
 \end{aligned}$$

Notice that the radius obtained in this way is less than the value obtained by equation 4.7, which is, of course, to be expected.

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Because a nucleus contains Z protons, its mass should be Zm_p . Since the proton mass is so much greater than the electron mass, the mass of the atom should be very nearly equal to the mass of the nucleus. However, the atomic mass of an element was more than twice the mass of the Z protons. This led Rutherford in 1920 to predict the existence of another particle within the nucleus having about the same mass as the proton. Because this particle had no electric charge, Rutherford called it a neutron, for the neutral particle. In 1932, James Chadwick found this neutral particle, the neutron. The mass of the neutron was found to be $m_n = 1.6749 \times 10^{-27} \text{ kg}$, which is very close to the mass of the proton, $m_p = 1.6726 \times 10^{-27} \text{ kg}$.

With the finding of the neutron, the discrepancy in the mass of the nucleus was solved. *It can now be stated that an atom consists of Z electrons that orbit about a positive nucleus that contains Z protons and $(A - Z)$ neutrons.*

Example 4.3

The number of electrons, protons, and neutrons in a gold atom. How many electrons, protons, and neutrons are there in a gold atom?

Solution

From the table of the elements, we see that the atomic number Z for gold is 79. Hence, there are 79 protons in the nucleus of the gold atom surrounded by 79 orbiting electrons. The mass number A for gold is found from the table of the elements to be 197. Hence, the number of neutrons in the nucleus of a gold atom is

$$A - Z = 197 - 79 = 118 \text{ neutrons}$$

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A very interesting characteristic of nuclear material is that all nuclei have the same density. For example, to find the density of nuclear matter, we use the definition of density,

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$$\rho = \frac{m}{V}$$

Because the greatest portion of the matter of an atom resides in the nucleus, we can take for the mass of the nucleus

$$m = \frac{\text{Atomic mass}}{N_A} \quad (4.10)$$

where $N_A = 6.022 \times 10^{26}$ atoms/kmole $= 6.022 \times 10^{23}$ atoms/mole is Avogadro's number. Since the atomic mass, which has units of kg/kmole, is numerically very close to the mass number A , a dimensionless quantity, we can write the mass as

$$m = \frac{A(\text{kg/kmole})}{N_A} \quad (4.11)$$

We find the volume of the nucleus from the assumption that the atom is spherical, and hence

$$V = \frac{4}{3} \pi r^3 \quad (4.12)$$

Substituting the value for the radius of the nucleus found in equation 4.9 into equation 4.12, we get, for the volume of the nucleus,

$$V = \frac{4}{3} \pi (R_0 A^{1/3})^3$$

or

$$V = \frac{4}{3} \pi R_0^3 A \quad (4.13)$$

Substituting the mass from equation 4.11 and the volume from equation 4.13 back into the equation for the density, we get

$$\rho = \frac{m}{V} = \frac{A(\text{kg/kmole})/N_A}{(4/3)\pi R_0^3 A} \quad (4.14)$$

or

$$\begin{aligned} \rho &= \frac{3(\text{kg/kmole})}{4\pi N_A R_0^3} \\ &= \frac{3(\text{kg/kmole})}{4\pi(6.022 \times 10^{26} \text{ atoms/kmole})(1.2 \times 10^{-15} \text{ m})^3} \\ &= 2.29 \times 10^{17} \text{ kg/m}^3 \end{aligned} \quad (4.15)$$

Because the mass number A canceled out of equation 4.14, the density is the same for all nuclei. To get a “feel” for the magnitude of this nuclear density, note that a density of $2.29 \times 10^{17} \text{ kg/m}^3$ is roughly equivalent to a density of a billion tons of

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matter per cubic inch, an enormously large number in terms of our usual experiences.

Now that the **Rutherford model of the atom** has been developed, let us look at some of its dynamical aspects. Let us consider the dynamics of the hydrogen atom. Because this new model of the atom is very similar to the planetary system of our solar system, we would expect the dynamics of the atom to be very similar to the dynamics of the planetary system. Recall that we assumed that a planet moved in a circular orbit and the necessary centripetal force for that circular motion was supplied by the gravitational force. In a similar analysis, let us now assume that the negative electron moves in a circular orbit about the positive nucleus. The Coulomb attractive force between the electron and the proton supplies the necessary centripetal force to keep the electron in its orbit. Therefore, equating the centripetal force F_c to the electric force F_e , we obtain

$$F_c = F_e \quad (4.16)$$

$$\frac{mv^2}{r} = \frac{k(e)(e)}{r^2} \quad (4.17)$$

Solving for the speed of the electron in its circular orbit, we get

$$v = \sqrt{\frac{ke^2}{mr}} \quad (4.18)$$

Thus, for a particular orbital radius r , there corresponds a particular velocity of the electron. This is, of course, the same kind of a relation found for the planetary case.

The total energy of the electron is equal to the sum of its kinetic and potential energy. Thus,

$$E = KE + PE$$

$$E = \frac{1}{2}mv^2 + \left(-\frac{ke^2}{r}\right) \quad (4.19)$$

where the negative potential energy of the electron follows from the definition of potential energy. (The zero of potential energy is taken at infinity, and since the electron can do work, as it approaches the positive nucleus, it loses some of its electric potential energy. Because it started with zero potential energy at infinity, its potential energy becomes more negative as it approaches the nucleus.) Substituting the speed of the electron for the circular orbit found in equation 4.18 into equation 4.19, we have, for the total energy,

$$E = \frac{1}{2}m\left(\frac{ke^2}{mr}\right) + \left(-\frac{ke^2}{r}\right)$$

$$E = \frac{1}{2}\frac{ke^2}{r} - \frac{ke^2}{r}$$

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$$E = -\frac{ke^2}{2r} \quad (4.20)$$

The total energy of the electron is negative indicating that the electron is bound to the atom. Equation 4.20 says that the total energy of an electron in the Rutherford atom is not quantized — that is, the electron could be in any orbit of radius r and would have an energy consistent with that value of r .

From chemical analysis, it is known that it takes 13.6 eV of energy to ionize a hydrogen atom. This means that it takes 13.6 eV of energy to remove an electron from the hydrogen atom to infinity, where it would then have zero kinetic energy. Looking at this from the reverse process, it means that we need -13.6 eV of energy to bind the electron to the atom. This energy is called the *binding energy of the electron*. Knowing this binding energy permits us to calculate the orbital radius of the electron. Solving equation 4.20 for the orbital radius gives

$$\begin{aligned} r &= -\frac{ke^2}{2E} \\ &= -\left[\frac{(9.00 \times 10^9 \text{ N m}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{2(-13.6 \text{ eV})} \right] \left(\frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} \right) \\ &= 5.29 \times 10^{-11} \text{ m} \end{aligned} \quad (4.21)$$

which is certainly the right order of magnitude.

Because the electron is in a circular orbit, it is undergoing accelerated motion. From the laws of classical electromagnetic theory, an accelerated electric charge should radiate electromagnetic waves. The frequency of these electromagnetic waves should correspond to the frequency of the accelerating electron. The frequency ν of the moving electron is related to its angular velocity ω by

$$\nu = \frac{\omega}{2\pi}$$

But the linear velocity v of the electron is related to its angular velocity by

$$v = \omega r$$

or

$$\omega = \frac{v}{r}$$

The frequency becomes

$$\nu = \frac{\omega}{2\pi} = \frac{v}{2\pi r} \quad (4.22)$$

Substituting for the speed v from equation 4.18, we get

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$$\begin{aligned}\nu &= \frac{v}{2\pi r} = \frac{1}{2\pi r} \sqrt{\frac{ke^2}{mr}} \\ \nu &= \frac{1}{2\pi} \sqrt{\frac{ke^2}{mr^3}}\end{aligned}\tag{4.23}$$

The frequency of the orbiting electron, and hence the frequency of the electromagnetic wave radiated, should be given by equation 4.23. Assuming the value of r computed above, the frequency becomes

$$\begin{aligned}\nu &= \frac{1}{2\pi} \sqrt{\frac{ke^2}{mr^3}} \\ \nu &= \frac{1}{2\pi} \sqrt{\frac{(9.00 \times 10^9 \text{ N m}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{(9.11 \times 10^{-31} \text{ kg})(5.29 \times 10^{-10} \text{ m})^3}} \\ &= 6.56 \times 10^{15} \text{ Hz}\end{aligned}$$

This frequency corresponds to a wavelength of

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \frac{3.00 \times 10^8 \text{ m/s}}{6.56 \times 10^{15} \text{ 1/s}} \\ &= 4.57 \times 10^8 \text{ m} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) \\ &= 45.7 \text{ nm}\end{aligned}$$

The problem with this wavelength is that it is in the extreme ultraviolet portion of the electromagnetic spectrum, whereas some spectral lines of the hydrogen atom are known to be in the visible portion of the spectrum. An even greater discrepancy associated with Rutherford's model of the atom is that if the orbiting electron radiates electromagnetic waves, it must lose energy. If it loses energy by radiation, its orbital radius must decrease. For example, if the electron is initially in the state given by equation 4.20 as

$$E_i = \frac{ke^2}{2r_i}\tag{4.24}$$

After it radiates energy, it will have the smaller final energy E_f , given by

$$E_f = \frac{ke^2}{2r_f}$$

The energy lost by radiation is

$$E_f - E_i = \frac{ke^2}{2r_f} - \frac{ke^2}{2r_i}$$

$$= \frac{ke^2}{2} \left(\frac{1}{r_i} - \frac{1}{r_f} \right)$$

But since the final state has less energy than the initial state

$$E_f - E_i < 0$$

this implies that the quantity

$$= \frac{ke^2}{2} \left(\frac{1}{r_i} - \frac{1}{r_f} \right) < 0$$

The only way for this quantity to be less than zero is for

$$\left(\frac{1}{r_i} < \frac{1}{r_f} \right)$$

which requires that

$$r_f < r_i$$

That is, the final orbital radius is less than the initial radius. Hence, when the electron radiates energy, its orbital radius must decrease. But as the electron keeps orbiting, it keeps losing energy and its orbital radius keeps decreasing. As r decreases, the frequency of the electromagnetic waves increases according to equation 4.23 and its wavelength decreases continuously. Hence, the radiation from the atom should be continuous. Experimentally, however, it is found that the radiation from the atom is not continuous but is discrete. As the radius of the orbit keeps decreasing, the electron spirals into the nucleus and the atom should collapse. Because the entire world is made of atoms, it too should collapse. Since it does not, there is something very wrong with the dynamics of the Rutherford model of the atom.

4.2 The Bohr Theory of the Atom

The greatest difficulty with the Rutherford planetary model is that the accelerated electron should radiate a continuous spectrum of electromagnetic waves, thereby losing energy, and should thus, spiral into the nucleus. There is certainly merit in the planetary model, but it is not completely accurate. As we have seen, the search for truth in nature follows the path of successive approximations. Each approximation gets us closer to the truth, but we are still not there yet. How can this radiation problem of the atomic model be solved?

Niels Bohr (1885-1962), a young Danish physicist, who worked with J. J. Thomson, and then Rutherford, felt that the new success of the quantum theory by Planck and Einstein must be the direction to take in understanding the atom, that is, the atom must be quantized. But how?

In the **Bohr theory of the atom**, Bohr took the ingenious step of restricting the electron orbits to those for which the angular momentum is quantized. That is, *Bohr postulated that the electron could only be found in those orbits for which the angular momentum, L , is given by*

$$L = mvr = n\hbar \quad (4.25)$$

where n is called the principal quantum number and takes on the values 1, 2, 3, 4.... The value $\hbar = h/2\pi$ thus becomes a fundamental unit of angular momentum. *The consequence of this postulate is that the electron, which can now be looked on as a matter wave by the de Broglie hypothesis, can be represented in its orbit as a standing wave.* Consider the standing wave in figure 4.4(a). As you recall for a vibrating string, the nodes of a standing wave remain nodes for all time. The string cannot move up or down at that point, and, hence, cannot transmit any energy past that point. Thus, the standing wave does not move along the string, but is instead stationary or standing.

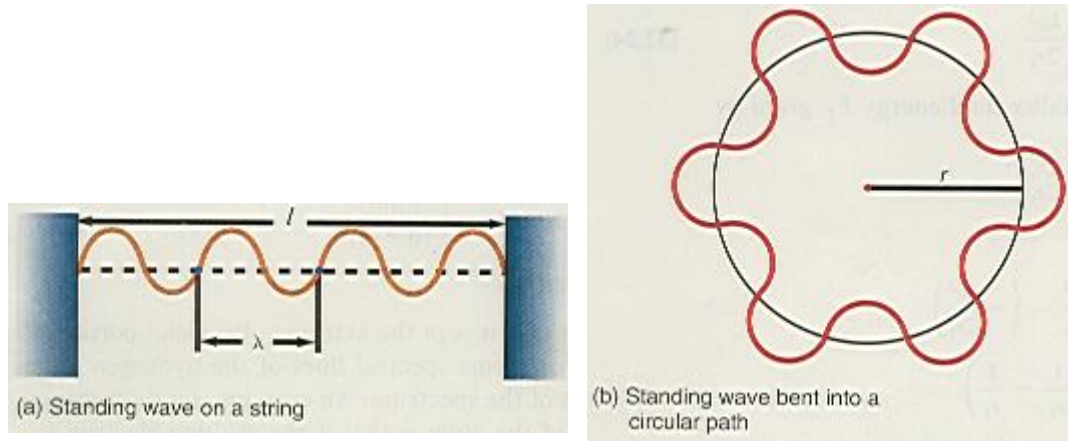


Figure 4.4 Standing wave of an electron in its orbit.

For the vibrating string fixed at both ends, the only waves that can stand for such a configuration are those for which the length of the string is equal to a multiple of a half wavelength, that is, for $l = n\lambda/2$. If the vibrating string is bent into a circle, figure 4.4(b), (perhaps this should be called a vibrating wire to justify bending it into a circle), the traveling waves are not reflected at a fixed boundary because there is now no fixed boundary. The waves keep passing around the circle. *The only waves that can stand in this circular configuration are those for which the length of the wire is a whole number of wavelengths.* Thus,

$$l = n\lambda \quad (4.26)$$

but the length of the wire is the circumference of the circle and is equal to $2\pi r$. Hence,

$$l = 2\pi r = n\lambda \quad (4.27)$$

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The wavelength of the matter wave is given by the de Broglie relation as

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad (4.28)$$

Substituting equation 4.28 into equation 4.27, gives

$$2\pi r = \frac{nh}{mv}$$

or

$$mvr = \frac{nh}{2\pi} = n\hbar \quad (4.29)$$

But this is precisely the Bohr postulate for the allowed electron orbits, previously defined in equation 4.25. *Hence, Bohr's postulate of the quantization of the orbital angular momentum is equivalent to a standing matter wave on the electron orbit. But because standing waves do not change with time and thus, do not transmit energy, these matter waves representing the electron should not radiate electromagnetic waves. Thus, an electron in this prescribed orbit does not radiate energy and hence it does not spiral into the nucleus.* This state wherein an electron does not radiate energy is called a *stationary state*. With electrons in stationary states the atom is now stable.

The quantization of the orbital angular momentum displays itself as a quantization of the orbital radius, the orbital velocity, and the total energy of the electron. As an example, let us consider the dynamics of the Bohr model of the atom. Because it is basically still a planetary model, equations 4.16 and 4.17 still apply. However, equation 4.18 for the orbital speed is no longer applicable. Instead, we use equation 4.29 to obtain the speed of the electron as

$$v = \frac{n\hbar}{mr} \quad (4.30)$$

Substituting this value of v into equation 4.17, we get

$$\begin{aligned} F_c &= F_e \\ \frac{mv^2}{r} &= \frac{m}{r} \left(\frac{n\hbar}{mr} \right)^2 = \frac{ke^2}{r^2} \\ \frac{mn^2\hbar^2}{rm^2r^2} &= \frac{ke^2}{r^2} \\ \frac{n^2\hbar^2}{rm} &= ke^2 \end{aligned}$$

Solving for r , we get

$$r_n = \frac{\hbar^2}{kme^2} n^2 \quad (4.31)$$

Because of the n on the right-hand side of equation 4.31, the electron orbits are quantized. The subscript n has been placed on r to remind us that there is one value of r corresponding to each value of n . From the derivation, we see that r must be quantized in order to have standing or stationary waves.

Example 4.4

The radius of a Bohr orbit. Find the radius of the first Bohr orbit.

Solution

The radius of the first Bohr orbit is found from equation 4.31 with $n = 1$. Thus,

$$\begin{aligned} r_1 &= \frac{\hbar^2}{kme^2} \\ &= \frac{(1.0546 \times 10^{-34} \text{ J s})^2}{(8.9878 \times 10^9 \text{ N m}^2/\text{C}^2)(9.1091 \times 10^{-31} \text{ kg})(1.6022 \times 10^{-19} \text{ C})^2} \\ &= 5.219 \times 10^{-11} \text{ m} \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}} \right) \\ &= 0.0529 \text{ nm} \end{aligned}$$

This is the radius of the electron orbit for the $n = 1$ state (called the *ground state*) and is called the *Bohr radius*.

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Now we can also write the radius of the n th orbit, equation 4.31, as

$$r_n = r_1 n^2 \quad (4.32)$$

Thus, the only allowed orbits are those for $r_n = r_1, 4r_1, 9r_1, 16r_1, \dots$

The speed of the electron in its orbit can be rewritten by substituting equation 4.31 back into equation 4.30, yielding

$$v_n = \frac{n\hbar}{mr_n} = \frac{n\hbar}{m((\hbar^2/kme^2)n^2)}$$

or

$$v_n = \frac{ke^2}{n\hbar} \quad (4.33)$$

Because of the n on the right-hand side of equation 4.33, the speed of the electron is also quantized.

Example 4.5

The speed of an electron in a Bohr orbit. Find the speed of the electron in the first Bohr orbit.

Solution

The speed, found from equation 4.33 with $n = 1$, is

$$\begin{aligned} v_1 &= \frac{ke^2}{\hbar} \\ &= \frac{(9.00 \times 10^9 \text{ N m}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{1.05 \times 10^{-34} \text{ J s}} \\ &= 2.19 \times 10^6 \text{ m/s} \end{aligned}$$

To go to this Interactive Example click on this sentence.

The speed of the electron in higher orbits is obtained from equation 4.33 as

$$v_n = \frac{v_1}{n} \quad (4.34)$$

We will now see that the quantizing of the orbital radius and speed leads to the quantizing of the electron's energy. The total energy of the electron still follows from equation 4.19, but now $v = v_n$ and $r = r_n$. Thus,

$$E = \frac{1}{2}mv_n^2 + \left(-\frac{ke^2}{r_n} \right)$$

Substituting for r_n and v_n from equations 4.31 and 4.33, respectively, leads to

$$E = \frac{m}{2} \left(\frac{ke^2}{n\hbar} \right)^2 - \frac{ke^2}{\hbar^2 n^2 / kme^2}$$

$$= \frac{mk^2e^4}{2n^2\hbar^2} - \frac{mk^2e^4}{n^2\hbar^2}$$

$$E_n = -\frac{mk^2e^4}{2n^2\hbar^2} \quad (4.35)$$

Because of the appearance of the quantum number n in equation 4.35, the electron's energy is seen to be quantized. To emphasize this fact, we have placed the subscript n on E .

Example 4.6

The energy of an electron in a Bohr orbit. Find the energy of the electron in the first Bohr orbit.

Solution

The energy is found from equation 4.35 with $n = 1$ as follows

$$E_1 = -\frac{mk^2e^4}{2\hbar^2} \quad (4.36)$$

$$= -\frac{(9.1092 \times 10^{-31} \text{ kg})(8.9878 \times 10^9 \text{ N m}^2/\text{C}^2)^2(1.6022 \times 10^{-19} \text{ C})^4}{2(1.054 \times 10^{-34} \text{ J s})^2} \left(\frac{1 \text{ eV}}{1.6022 \times 10^{-19} \text{ J}} \right)$$

$$= -13.6 \text{ eV}$$

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Thus, the energy of the electron in the first Bohr orbit is -13.6 eV . If this electron were to be removed from the atom, it would take 13.6 eV of energy. But the energy necessary to remove an electron from an atom is called the *ionization energy*, and it was previously known that the ionization energy of hydrogen was indeed 13.6 eV . Thus, the Bohr model of the atom seems to be on the right track in its attempt to represent the hydrogen atom.

When the electron is in the first Bohr orbit, it is said to be in the *ground state*. When it is in a higher orbit, it is said to be in an *excited state*. The energy of the electron in an excited state is given by equation 4.35, and in conjunction with equation 4.36, we can also write it as

$$E_n = -\frac{E_1}{n^2} \quad (4.37)$$

with $E_1 = 13.6$ eV. These different energy levels for the different states of the electron are drawn, in what is called an *energy-level diagram*, in figure 4.5. Note that as n gets larger the energy states get closer together until the difference between one energy state and another is so small that there are no longer any observable quantization effects. The energy spectrum is then considered continuous just as it is in classical physics. For positive values of energy ($E > 0$) the electron is no longer bound to the atom and is free to go anywhere.

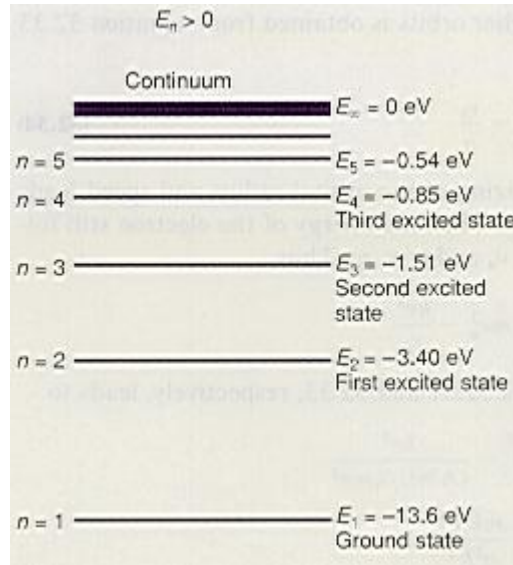


Figure 4.5 An energy-level diagram for the hydrogen atom.

4.3 The Bohr Theory and Atomic Spectra

Whenever sufficient energy is added to an electron it jumps to an excited state. The electron only stays in that excited state for a very short time (10^{-8} s). *Bohr next postulated that when the electron jumps from its initial higher energy state, E_i , to a final lower energy state, E_f , a photon of light is emitted in accordance with Einstein's relation*

$$h\nu = E_i - E_f \quad (4.38)$$

Using equation 4.37, we can write this as

$$h\nu = -\frac{E_1}{n_i^2} - \left(\frac{-E_1}{n_f^2} \right)$$

The frequency of the emitted photon is thus

$$\nu = \frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.39)$$

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The wavelength of the emitted photon, found from $\nu = c/\lambda$, is

$$\nu = \frac{c}{\lambda} = \frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

or

$$\frac{1}{\lambda} = \frac{E_1}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.40)$$

Computing the value of E_1/hc gives

$$\begin{aligned} \frac{E_1}{hc} &= \left[\frac{13.6 \text{ eV}}{(6.6262 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m/s})} \right] \left(\frac{1.6022 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) \\ &= (1.0969 \times 10^7 \frac{1}{\text{m}}) \left(\frac{10^{-9} \text{ m}}{1 \text{ nm}} \right) \\ &= 1.097 \times 10^{-2} (\text{nm})^{-1} \end{aligned}$$

We will come back to this shortly.

As seen in general physics, whenever white light is passed through a prism, it is broken up into a *continuous spectrum* of color from red through violet. On the other hand, if a gas such as hydrogen is placed in a tube under very low pressure and an electrical field is applied between two electrodes of the tube, the energy gained by the electrons from the field causes the electrons of the hydrogen atoms to jump to higher energy states. The gas glows with a characteristic color as the electrons fall back to the lower energy states. If the light from this spectral tube is passed through a prism or a diffraction grating, a line spectrum such as shown in figure 4.6 is found. That is, instead of the continuous spectrum of all the colors of

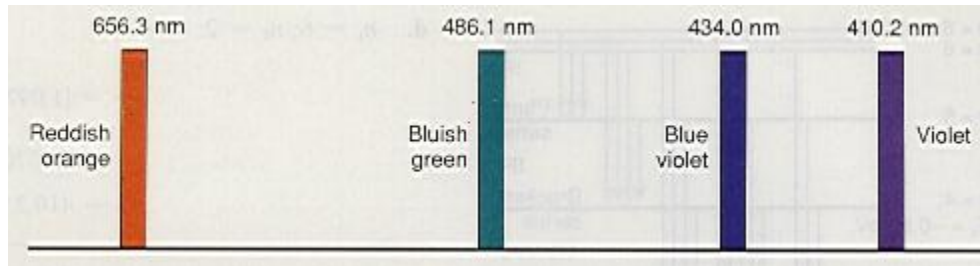


Figure 4.6 Line spectrum of hydrogen.

the rainbow, only a few discrete colors are found with the wavelengths indicated. The discrete spectra of hydrogen were known as far back as 1885 when Johann Jakob Balmer (1825-1898), a Swiss mathematician and physicist, devised the mathematical formula

$$\lambda = (364.56 \text{ nm}) \frac{n^2}{n^2 - 4}$$

to describe the wavelength of the hydrogen spectrum. In 1896, the Swedish spectroscopist J. R. Rydberg (1853-1919) found the empirical formula

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (4.41)$$

for $n = 3, 4, 5, \dots$, and where the constant R , now called the *Rydberg constant*, was given by $R = 1.097 \times 10^{-2} \text{ (nm)}^{-1}$. Comparing equation 4.41 with 4.40, we see that the Rydberg constant R is equal to the quantity E_1/hc and, if $n_f = 2$, the two equations are identical. Equation 4.41 was a purely empirical result from experiment with no indication as to why the spectral lines should be ordered in this way, whereas equation 4.40 is a direct result of the Bohr model of the hydrogen atom.

Example 4.7

Spectral lines with the Bohr model. Using the Bohr model of the hydrogen atom, determine the wavelength of the spectral lines associated with the transitions from the (a) $n_i = 3$ to $n_f = 2$ state, (b) $n_i = 4$ to $n_f = 2$ state, (c) $n_i = 5$ to $n_f = 2$ state, and (d) $n_i = 6$ to $n_f = 2$ state.

Solution

The wavelength of the spectral line is found from equation 4.40.

a. $n_i = 3$; $n_f = 2$:

$$\begin{aligned} \frac{1}{\lambda} &= \frac{E_1}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= [1.097 \times 10^{-2} \text{ (nm)}^{-1}] \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 1.5236 \times 10^{-3} \text{ (nm)}^{-1} \\ \lambda &= 656.3 \text{ nm} \end{aligned}$$

b. $n_i = 4$; $n_f = 2$:

$$\begin{aligned} \frac{1}{\lambda} &= [1.097 \times 10^{-2} \text{ (nm)}^{-1}] \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= 2.0569 \times 10^{-3} \text{ (nm)}^{-1} \\ \lambda &= 486.1 \text{ nm} \end{aligned}$$

c. $n_i = 5$; $n_f = 2$:

$$\begin{aligned} \frac{1}{\lambda} &= [1.097 \times 10^{-2} \text{ (nm)}^{-1}] \left(\frac{1}{2^2} - \frac{1}{5^2} \right) \\ &= 2.3037 \times 10^{-3} \text{ (nm)}^{-1} \\ \lambda &= 434.0 \text{ nm} \end{aligned}$$

d. $n_i = 6$; $n_f = 2$:

$$\begin{aligned}\frac{1}{\lambda} &= [1.097 \times 10^{-2} \text{ (nm)}^{-1}] \left(\frac{1}{2^2} - \frac{1}{6^2} \right) \\ &= 2.4370 \times 10^{-3} \text{ (nm)}^{-1} \\ \lambda &= 410.2 \text{ nm}\end{aligned}$$

To go to this Interactive Example click on this sentence.

Thus, the Bohr theory of the hydrogen atom agrees with the experimental values of the wavelengths of the spectral lines shown in figure 4.6. In fact, the Bohr formula is more complete than that given by the Rydberg formula. That is, the Rydberg series is associated with transitions to the $n = 2$ state. According to the Bohr formula, there should be spectral lines associated with transitions to the $n_f = 1, 2, 3, 4, \dots$, states. With such a prediction, it was not long before experimental physicists found these spectral lines. The reason they had not been observed before is because they were not in the visible portion of the spectrum. Lyman found the series associated with transitions to the ground state $n_f = 1$ in the ultraviolet portion of the spectrum. Paschen found the series associated with the transitions to the $n_f = 3$ state in the infrared portion of the spectrum. Brackett and Pfund found the series associated with the transitions to the $n_f = 4$ and $n_f = 5$ states, respectively, also in the infrared spectrum. The energy-level diagram and the associated spectral lines are shown in figure 4.7. Hence, the Bohr theory had great success in predicting the properties of the hydrogen atom.

Obviously, the Bohr theory of the atom was on the right track in explaining the nature and characteristics of the atom. However, as has been seen over and over again, physics arrives at a true picture of nature only through a series of successive approximations. The Bohr theory would be no different. As great as it was, it had its limitations. Why should the electron orbit be circular? The most general case would be elliptical. Arnold Sommerfeld (1868-1951) modified the Bohr theory to take into account elliptical orbits. The result increased the number of quantum numbers from one to two. With the advent of more refined spectroscopic equipment, it was found that some spectral lines actually consisted of two or more spectral lines. The Bohr theory could not account for this. Perhaps the greatest difficulty with the Bohr theory was its total inability to account for the spectrum of multielectron atoms. Also, some spectral lines were found to be more intense than others. Again, the Bohr theory could not explain why. Thus, the Bohr theory contains a great deal about the true nature of the atom, but it is not the complete picture. It is just a part of the successive approximations to a true picture of nature.

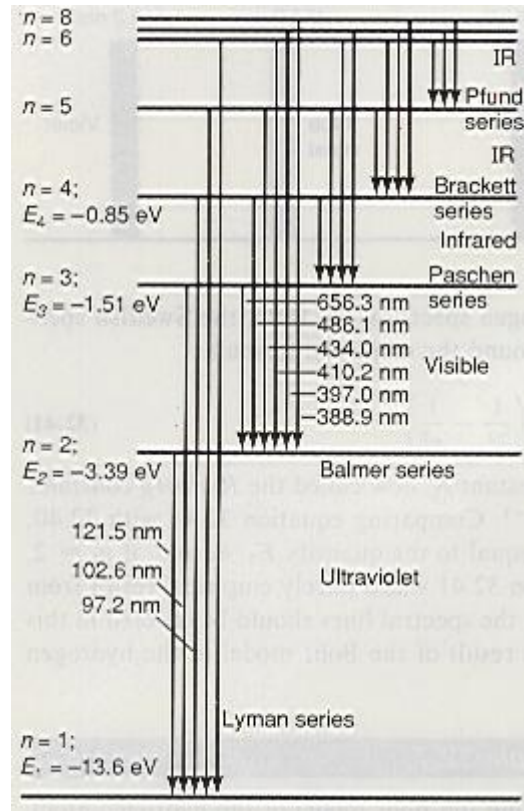


Figure 4.7 Associated spectrum for the energy-level diagram of hydrogen.

4.4 The Quantum Mechanical Model of the Hydrogen Atom

Obviously the Bohr theory of the hydrogen atom, although not wrong, was also not quite right. A new approach to the nature of the hydrogen atom was necessary. When de Broglie introduced his matter waves in 1924 to describe particles, it became necessary to develop a technique to find these matter waves mathematically. Erwin Schrödinger (1887-1961), an Austrian physicist, developed a new equation to describe these matter waves. This new equation is called the *Schrödinger wave equation*. (The Schrödinger wave equation is to quantum mechanics what Newton's second law is to classical mechanics. In fact, Newton's second law can be derived as a special case of the Schrödinger wave equation.) The solution of the wave equation is the wave function Ψ . For the **quantum mechanical model of the hydrogen atom**, the Schrödinger wave equation is applied to the hydrogen atom. It was found that it was necessary to have three quantum numbers to describe the electron in the hydrogen atom in this model,²

² Actually the quantum mechanical model of the hydrogen atom requires four quantum numbers for its description. The fourth quantum number m_s , called the spin magnetic quantum number, is associated with the spin of the electron. The concept of the spin of the electron is introduced in section 4.7 and its effects are described there.

whereas the Bohr theory had required only one. The three quantum numbers are (1) the principal quantum number n , which is the same as that used in the Bohr theory; (2) the orbital quantum number l ; and (3) the magnetic quantum number m_l . These quantum numbers are not completely independent; n can take on any value given by

$$n = 1, 2, 3, \dots \quad (4.42)$$

Whereas l , the orbital quantum number, can only take on the values

$$l = 0, 1, 2, \dots, (n - 1) \quad (4.43)$$

Thus, l is limited to values up to $n - 1$. The magnetic quantum number m_l can take on only the values given by

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (4.44)$$

Hence, m_l is limited to values up to $\pm l$. Let us now see a physical interpretation for each of these quantum numbers.

The Principal Quantum Number n

The principal quantum number n plays the same role in the quantum mechanical model of the hydrogen atom as it did in the Bohr theory in that it quantizes the possible energy of the electron in a particular orbit. The solution of the Schrödinger wave equation for the allowed energy values is

$$E_n = -\frac{k^2 e^4 m}{2\hbar^2} \frac{1}{n^2} \quad (4.45)$$

which we see has the same energy values as given by the Bohr theory in equation 4.35.

The Orbital Quantum Number l

In the Bohr theory, the angular momentum of the electron was quantized according to the relation $L = n\hbar$. The solution of the Schrödinger wave equation gives, for the angular momentum, the relation

$$L = \sqrt{l(l+1)} \hbar \quad (4.46)$$

where $l = 0, 1, 2, \dots, n - 1$.

Example 4.8

The angular momentum of an electron in a quantum mechanical model of the atom. Determine the angular momentum of an electron in the hydrogen atom for the orbital quantum numbers of (a) $l = 0$, (b) $l = 1$, (c) $l = 2$, and (d) $l = 3$.

Solution

The angular momentum of the electron is quantized according to equation 4.46 as

$$L = \sqrt{l(l+1)} \hbar$$

a. $l = 0$;

$$\begin{aligned} L &= \sqrt{0(0+1)} \hbar \\ &= 0 \end{aligned}$$

Thus for the $l = 0$ state, the angular momentum of the electron is zero. This is a very different case than anything found in classical physics. For an orbiting electron there must be some angular momentum, and yet for the $l = 0$ state, we get $L = 0$. Thus, the model of the atom with the electron orbiting the nucleus must now be considered questionable. We still speak of orbits, but they are apparently not the same simple concepts used in classical physics.

b. $l = 1$; $L = \sqrt{1(1+1)} \hbar = \sqrt{2} \hbar = 1.414\hbar$

c. $l = 2$; $L = \sqrt{2(2+1)} \hbar = \sqrt{6} \hbar = 2.449\hbar$

d. $l = 3$; $L = \sqrt{3(3+1)} \hbar = \sqrt{12} \hbar = 3.464\hbar$

Note that in the Bohr theory the angular momentum was a whole number times \hbar . Here in the quantum mechanical treatment the angular momentum is no longer a whole multiple of \hbar .

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The different angular momentum quantum states are usually designated in terms of the spectroscopic notation shown in table 4.1. The different states of the electron in the hydrogen atom are now described in terms of this spectroscopic notation in table 4.2. For the ground state, $n = 1$. However, because l can only take on values up to $n - 1$, l must be zero. Thus, the only state for $n = 1$ is the $1s$ or ground state of the electron. When $n = 2$, l can take on the values 0 and 1. Hence, there can be only a $2s$ and $2p$ state associated with $n = 2$. For $n = 3$, l can take on the values $l = 0, 1, 2$, and hence the electron can take on the states $3s$, $3p$, and $3d$. In this way, for various values of n , the states in table 4.2 are obtained.

Table 4.1 Spectroscopic Notation for Angular Momentum			
Orbital Quantum Number l	Angular Momentum	State	Spectroscopic Name
0	0	s	Sharp
1	$\sqrt{2} \hbar$	p	Principal
2	$\sqrt{6} \hbar$	d	Diffuse
3	$2\sqrt{3} \hbar$	f	Fundamental
4	$\sqrt{20} \hbar$	g	
5	$\sqrt{30} \hbar$	h	

Table 4.2 Atomic States in the Hydrogen Atom						
	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

The Magnetic Quantum Number m_l

Recall that angular momentum is a vector quantity and thus has a direction as well as a magnitude. We have just seen that the magnitude of the angular momentum is quantized. The result of the Schrödinger equation applied to the hydrogen atom shows that the direction of the angular momentum vector must also be quantized. The magnetic quantum number m_l specifies the direction of \mathbf{L} by requiring the z -component of \mathbf{L} to be quantized according to the relation

$$L_z = m_l \hbar \quad (4.47)$$

Quantization of the z -component of angular momentum specifies the direction of the angular momentum vector. As an example, let \mathbf{L} be the angular momentum vector of the electron shown in figure 4.8. The z -component of \mathbf{L} is found from the diagram to be

$$L_z = L \cos \theta \quad (4.48)$$

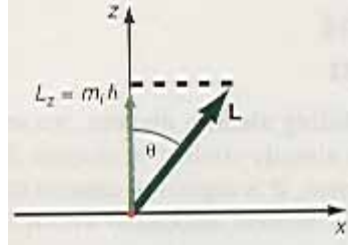


Figure 4.8 Direction of the angular momentum vector.

Substituting the value of L_z from equation 4.48 and the value of L from equation 4.46, gives

$$m_l \hbar = \sqrt{l(l+1)} \hbar \cos \theta$$

Solving for the angle θ that determines the direction of \mathbf{L} , we get

$$\theta = \cos^{-1} \frac{m_l}{\sqrt{l(l+1)}} \quad (4.49)$$

Thus, for particular values of the quantum numbers l and m_l , the angle θ specifying the direction of \mathbf{L} is determined.

Example 4.9

The direction of the angular momentum vector. For an electron in the state determined by $n = 4$ and $l = 3$, determine the magnitude and the direction of the possible angular momentum vectors.

Solution

For $n = 4$ and $l = 3$, the electron is in the $4f$ state. The magnitude of the angular momentum vector, found from equation 4.46, is

$$\begin{aligned} L &= \sqrt{l(l+1)} \hbar \\ &= \sqrt{3(3+1)} \hbar \\ &= 2\sqrt{3} \hbar \end{aligned}$$

The possible values of m_l , found from equation 4.44, are

$$m_l = 0, \pm 1, \pm 2, \pm 3$$

The angle θ , that the angular momentum vector makes with the z -axis, found from equation 4.49, is

$$\theta = \cos^{-1} \frac{m_l}{\sqrt{l(l+1)}}$$

$$m_l = 0;$$

$$\theta_0 = \cos^{-1} 0 = 90^\circ$$

$$m_l = \pm 1;$$

$$\theta_1 = \cos^{-1} \frac{+1}{2\sqrt{3}} = \pm 73.2^\circ$$

$$m_l = \pm 2;$$

$$\theta_2 = \cos^{-1} \frac{+2}{2\sqrt{3}} = \pm 54.7^\circ$$

$$m_l = \pm 3;$$

$$\theta_3 = \cos^{-1} \frac{+3}{2\sqrt{3}} = \pm 30.0^\circ$$

The various orientations of the angular momentum vector are shown in figure 4.9.

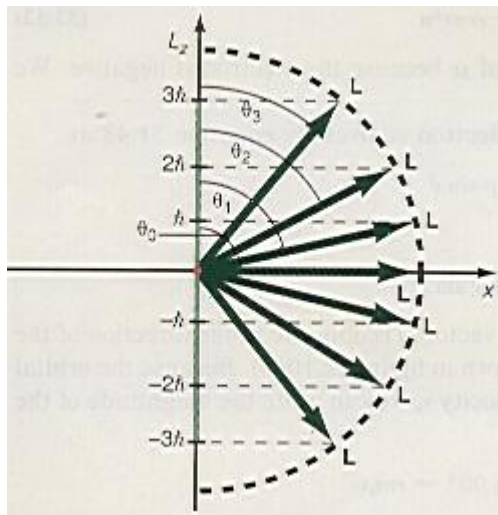


Figure 4.9 Quantization of the angular momentum vector.

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4.5 The Magnetic Moment of the Hydrogen Atom

Using the picture of an atom as an electron orbiting about a nucleus, we see that the orbiting electron looks like the current loop already studied in magnetism. Because a current loop has a magnetic dipole moment, it is logical to assume that the orbiting electron must also have a magnetic dipole moment associated with it.

Figure 4.10(a) shows a current loop, while figure 4.10(b) shows the electron in its orbit. The usual notation for a magnetic dipole moment in atomic physics is the

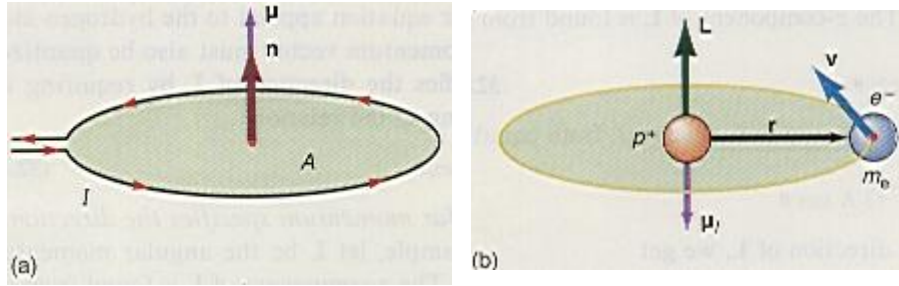


Figure 4.10 Orbital magnetic dipole moment.

Greek letter μ (mu). The magnetic dipole moment for the current loop in figure 4.10(a), becomes

$$\mu = IAn$$

Recall that I is the current in the loop, A is the area of the loop, and \mathbf{n} is a unit vector that is normal to the current loop. The orbiting electron of figure 4.10(b) constitutes a current given by

$$I = \frac{-e}{T} \quad (4.50)$$

where $-e$ is the negative electronic charge and T is the time it takes for the electron to go once around its orbit. But the time to go once around its orbit is its period and, as seen previously, the period T is equal to the reciprocal of its frequency ν . That is, $T = 1/\nu$. Hence, equation 4.50 becomes

$$I = -e\nu \quad (4.51)$$

where ν is the number of times the electron circles its orbit in one second.

Thus, the orbiting electron looks like a current loop, with a current given by equation 4.51. We attribute to this current loop a magnetic dipole moment and call it the *orbital magnetic dipole moment*, designated by μ_l , and now given by

$$\mu_l = IAn = -e\nu An$$

Assuming the orbit to be circular, $A = \pi r^2$ and hence,

$$\mu_l = -e\nu\pi r^2 \mathbf{n} \quad (4.52)$$

Note that μ_l is in the opposite direction of \mathbf{n} because the electron is negative. We will return to this equation shortly.

The angular momentum of the electron is given by equation 3.47 as

$$L = rp \sin \theta$$

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Since $p = m_e v$ we can write

$$L = r m_e v \sin \theta$$

where m_e is the mass of the electron. The vector \mathbf{L} is opposite to the direction of the orbital magnetic dipole moment $\boldsymbol{\mu}_l$, as shown in figure 4.10(b). Because the orbital radius r is perpendicular to the orbital velocity \mathbf{v} , we can write the magnitude of the angular momentum of the electron as

$$L = r m_e v \sin 90^\circ = r m_e v$$

Using the same unit vector \mathbf{n} to show the direction perpendicular to the orbit in figure 4.10(a), we can express the angular momentum of the orbiting electron as

$$\mathbf{L} = m_e r v \mathbf{n} \quad (4.53)$$

The speed of the electron in its orbit is just the distance s it travels along its arc divided by the time, that is,

$$v = \frac{s}{T} = \frac{2\pi r}{T} = 2\pi v r$$

Substituting this into equation 4.53, yields

$$\mathbf{L} = m_e r (2\pi v r) \mathbf{n} = 2\pi m_e v r^2 \mathbf{n} \quad (4.54)$$

Dividing equation 4.54 by $2m_e$, we get

$$\frac{\mathbf{L}}{2m_e} = \pi v r^2 \mathbf{n} \quad (4.55)$$

Returning to equation 4.52 and dividing by e , we get

$$-\frac{\boldsymbol{\mu}_l}{e} = \pi v r^2 \mathbf{n} \quad (4.56)$$

Comparing the right-hand sides of equations 4.55 and 4.56, we see that they are identical and can therefore be equated to each other giving

$$-\frac{\boldsymbol{\mu}_l}{e} = \frac{\mathbf{L}}{2m_e}$$

Solving for $\boldsymbol{\mu}_l$, we have

$$\boldsymbol{\mu}_l = -\frac{e}{2m_e} \mathbf{L} \quad (4.57)$$

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Equation 4.57 is the orbital magnetic dipole moment of the electron in the hydrogen atom. That is, the orbiting electron has a magnetic dipole associated with it, and, as seen from equation 4.57, it is related to the angular momentum \mathbf{L} of the electron. The quantity $e/2m_e$ is sometimes called the *gyromagnetic ratio*.

The magnitude of the orbital magnetic dipole moment is found from equation 4.57, with the value of L determined from equation 4.46. Hence,

$$\begin{aligned}\mu_l &= \frac{eL}{2m_e} = \frac{e}{2m_e} \sqrt{l(l+1)} \hbar \\ \mu_l &= \frac{e\hbar}{2m_e} \sqrt{l(l+1)}\end{aligned}\tag{4.58}$$

The quantity $e/2m_e$ is considered to be the smallest unit of magnetism, that is, an atomic magnet, and is called the *Bohr magneton*. Its value is

$$\begin{aligned}\frac{e\hbar}{2m_e} &= \frac{(1.6021 \times 10^{-19} \text{ C})(1.054 \times 10^{-34} \text{ J s})}{2(9.1091 \times 10^{-31} \text{ kg})} \\ &= 9.274 \times 10^{-24} \text{ A m}^2 = 9.274 \times 10^{-24} \text{ J/T}\end{aligned}$$

Example 4.10

The orbital magnetic dipole moment. Find the orbital magnetic dipole moment of an electron in the hydrogen atom when it is in (a) an s state, (b) a p state, and (c) a d state.

Solution

The magnitude of μ_l , found from equation 4.58, is

$$\mu_l = \frac{e\hbar}{2m_e} \sqrt{l(l+1)}$$

a. For an s state, $l = 0$,

$$\mu_l = 0$$

b. For a p state, $l = 1$,

$$\begin{aligned}\mu_l &= \frac{e\hbar}{2m_e} \sqrt{1(1+1)} \\ &= (9.274 \times 10^{-24} \text{ J/T})\sqrt{2} \\ &= 1.31 \times 10^{-23} \text{ J/T}\end{aligned}$$

c. For a d state, $l = 2$,

$$\mu_l = \frac{e\hbar}{2m_e} \sqrt{2(2+1)}$$

$$\begin{aligned}
 &= (9.274 \times 10^{-24} \text{ J/T})\sqrt{6} \\
 &= 2.26 \times 10^{-23} \text{ J/T}
 \end{aligned}$$

To go to this Interactive Example click on this sentence.

The Potential Energy of a Magnetic Dipole in an External Magnetic Field

In general physics we saw that when a magnetic dipole μ is placed in an external magnetic field \mathbf{B} , it experiences a torque given by

$$\tau = \mu B \sin \theta$$

This torque acts to rotate the dipole until it is aligned with the external magnetic field. Because the orbiting electron constitutes a magnetic dipole, if the hydrogen atom is placed in an external magnetic field, the orbital magnetic dipole of the atom rotates in the external field until it is aligned with it. Of course, since μ_l is 180° opposite to \mathbf{L} , the angular momentum of the atom, aligning the dipole in the field is equivalent to aligning the angular momentum vector of the atom. (Actually \mathbf{L} is antiparallel to \mathbf{B} .)

Because the natural position of μ_l is parallel to the field, as shown in figure 4.11(a), work must be done to rotate μ_l in the external magnetic field. When work was done in lifting a rock in a gravitational field, the rock then possessed potential

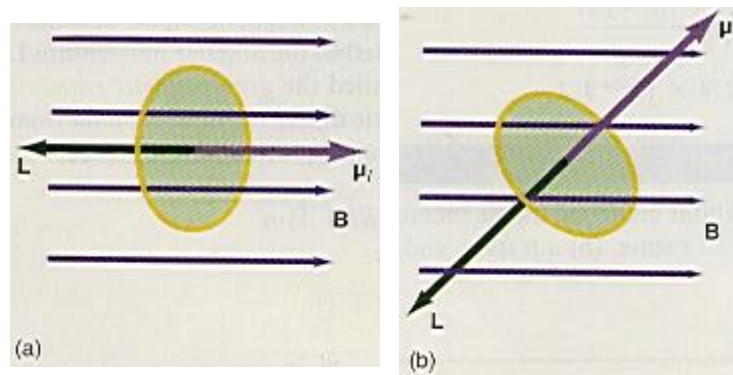


Figure 4.11 Orbital magnetic dipole in an external magnetic field \mathbf{B} .

energy. In the same way, work done in rotating the dipole in the magnetic field shows up as potential energy of the dipole figure 4.11(b). That is, the electron now possesses an additional potential energy associated with the work done in rotating μ_l . It was shown in general physics, that the potential energy of a dipole in an external magnetic field \mathbf{B} is given by

$$\text{PE} = -\mu_l B \cos \theta \quad (4.59)$$

Example 4.11

The potential energy of an orbital magnetic dipole moment. Find the potential energy of the orbital magnetic dipole in an external field when (a) it is antiparallel to \mathbf{B} (i.e., $\theta = 180^\circ$), (b) it is perpendicular to \mathbf{B} (i.e., $\theta = 90^\circ$), and (c) it is aligned with \mathbf{B} (i.e., $\theta = 0^\circ$).

Solution

The potential energy of the dipole, found from equation 4.59, is

a.

$$\begin{aligned} \text{PE} &= -\mu_l B \cos 180^\circ \\ \text{PE} &= +\mu_l B \end{aligned}$$

b.

$$\begin{aligned} \text{PE} &= -\mu_l B \cos 90^\circ \\ \text{PE} &= 0 \end{aligned}$$

c.

$$\begin{aligned} \text{PE} &= -\mu_l B \cos 0^\circ \\ \text{PE} &= -\mu_l B \end{aligned}$$

Thus, the dipole has its highest potential energy when it is antiparallel (180°), decreases to zero when it is perpendicular (90°), and decreases to its lowest potential energy, a negative value, when it is aligned with the magnetic field, $\theta = 0^\circ$. This is shown in figure 4.12. So, just as the rock falls from a position of high potential energy to the ground where it has its lowest potential energy, the dipole, if given a slight push to get it started, rotates from its highest potential energy (antiparallel) to its lowest potential energy (parallel).

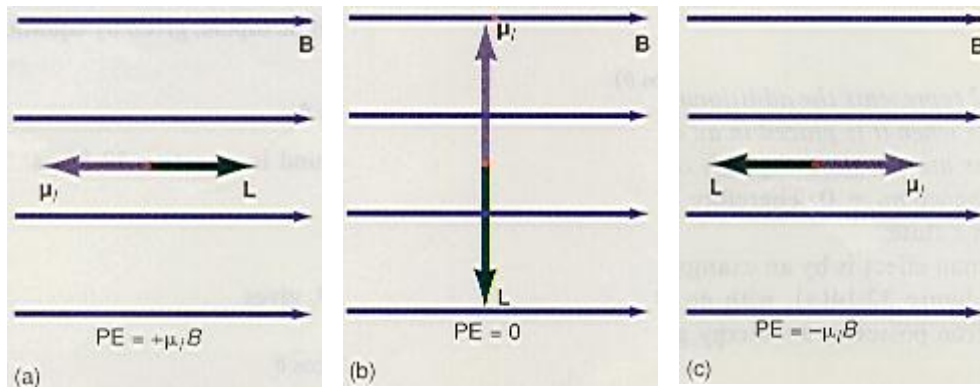


Figure 4.12 Potential energy of a dipole in an external magnetic field.

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4.6 The Zeeman Effect

The fact that there is a potential energy associated with a magnetic dipole placed in an external magnetic field has an important consequence on the energy of a particular atomic state, because the energy of a particular quantum state can change because of the acquired potential energy of the dipole. This acquired potential energy manifests itself as a splitting of a single energy state into multiple energy states, with a consequent splitting of the spectral lines associated with the transitions from these multiple energy states to lower energy states. The entire process is called the **Zeeman effect** after the Dutch physicist Pieter Zeeman (1865-1943) who first observed the splitting of spectral lines into several components when the atom was placed in an external magnetic field. Let us now analyze the phenomenon.

Let us begin by orienting an ordinary magnetic dipole, as shown in figure 4.13(a). A uniform magnetic field \mathbf{B} is then turned on, as shown in figure 4.13(b). A torque acts on the dipole and the dipole becomes aligned with the field as expected. If the orbital magnetic dipole is oriented in the same way, figure 4.13(c),

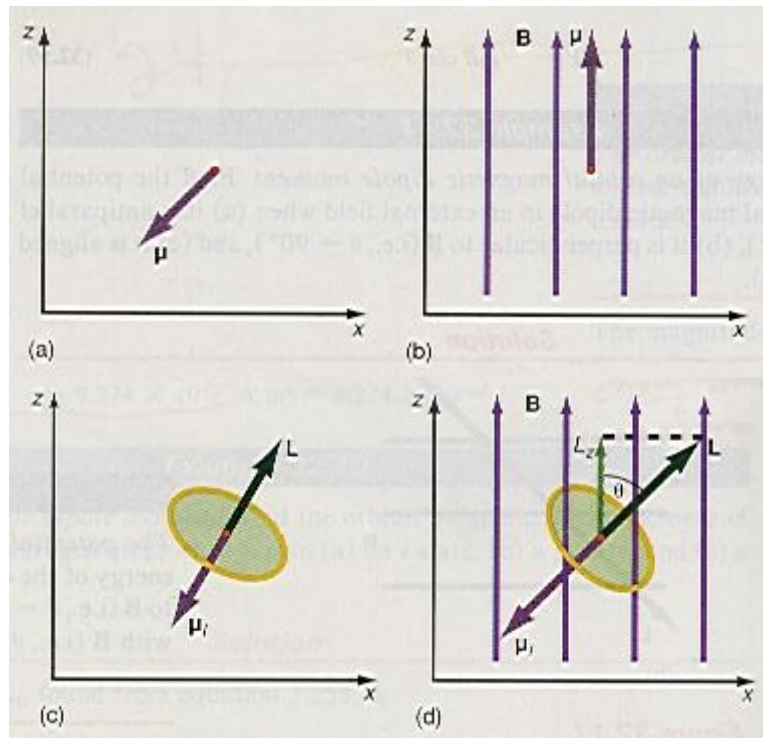


Figure 4.13 Orientation of the magnetic dipole in an external magnetic field.

and then the magnetic field \mathbf{B} is turned on, a torque acts to align μ_l . But the quantum conditions say that the angular momentum vector \mathbf{L} can only be oriented such that its z -component L_z must be equal to $m_l\hbar$, equation 4.47. Hence, the dipole cannot rotate completely to align itself with \mathbf{B} , but stops rotating at a position, such

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as in figure 4.13(d), where $L_z = m_l \hbar$. The orbital magnetic dipole has the potential energy given by equation 4.59 when stopped in this position.

This is strictly a quantum mechanical phenomenon, not found in classical physics. Its analogue in classical physics would be dropping a rock in the gravitational field, where the rock falls a certain distance and then comes to a stop some distance above the surface of the earth. This is an effect never observed classically.

The potential energy of the orbital magnetic dipole, given by equation 4.59, is

$$\text{PE} = - \mu_l B \cos \theta$$

But the orbital magnetic dipole moment was found in equation 4.57 as

$$\mu_l = - \frac{e}{2m_e} \mathbf{L}$$

Substituting equation 4.57 into equation 4.59, gives

$$\text{PE} = + \frac{e}{2m_e} LB \cos \theta \quad (4.60)$$

But,

$$LB \cos \theta = B(L \cos \theta) \quad (4.61)$$

And, as seen from figure 4.13(d),

$$L \cos \theta = L_z$$

Substituting this into equation 4.60, gives

$$\text{PE} = \frac{e}{2m_e} L_z B$$

Finally, substituting for $L_z = m_l \hbar$ we get

$$\text{PE} = m_l \frac{e\hbar}{2m_e} B \quad (4.62)$$

where $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. Equation 4.62 represents the additional energy that an electron in the hydrogen atom can possess when it is placed in an external magnetic field. Hence, the energy of a particular atomic state depends on m_l as well as n . Also, note that for s states, $l = 0$, and hence $m_l = 0$. Therefore, there is no potential energy for the dipole when it is in an s state.

Perhaps the best way to explain the Zeeman effect is by an example. Suppose an electron is in the $2p$ state, as shown in figure 4.14(a), with no applied external

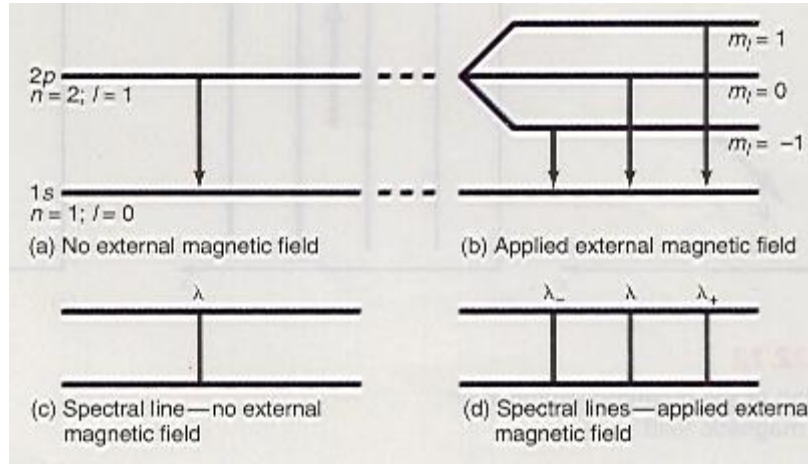


Figure 4.14 The Zeeman effect.

magnetic field. In the $2p$ state, the electron possesses an energy given by equation 4.45 as

$$E_2 = -\frac{k^2 e^4 m}{2\hbar^2} \frac{1}{2^2} = \frac{E_1}{4} \quad (4.63)$$

When the electron drops to the $1s$ state it has the energy

$$E_1 = -\frac{k^2 e^4 m}{2\hbar^2} = -13.6 \text{ eV}$$

and has emitted a photon of energy

$$h\nu = E_2 - E_1 = \frac{E_1}{4} - E_1 = -\frac{3E_1}{4}$$

with a frequency of

$$\nu_0 = -\frac{3E_1}{4h} \quad (4.64)$$

and a wavelength of

$$\lambda = \frac{c}{\nu_0} = \frac{ch}{\frac{3}{4}E_1} \quad (4.65)$$

Example 4.12

An electron drops from the $2p$ state to the $1s$ state. Find (a) the energy of an electron in the $2p$ state, (b) the energy lost by the electron as it drops from the $2p$ state to the $1s$ state, (c) the frequency of the emitted photon, and (d) the wavelength of the emitted photon.

Solution

a. The energy of the electron in the $2p$ state, given by equation 4.63, is

$$E_2 = \frac{E_1}{4} = -\frac{13.6 \text{ eV}}{4} = -3.40 \text{ eV}$$

b. The energy lost by the electron when it drops from the $2p$ state to the $1s$ state is found from

$$\Delta E = E_2 - E_1 = -3.40 \text{ eV} - (-13.6 \text{ eV}) = 10.2 \text{ eV}$$

c. The frequency of the emitted photon, found from equation 4.64, is

$$\begin{aligned} \nu_0 &= \frac{-3E_1}{4h} \\ &= \left[\frac{-3(-13.6 \text{ eV})}{4(6.63 \times 10^{-34} \text{ J s})} \right] \left(\frac{1.60 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) \\ &= 2.46 \times 10^{15} \text{ Hz} \end{aligned}$$

d. The wavelength of the emitted photon, found from equation 4.65, is

$$\begin{aligned} \lambda &= \frac{c}{\nu_0} = \frac{ch}{\frac{3}{4}E_1} \\ \lambda_0 &= \frac{c}{\nu_0} = \frac{3.00 \times 10^8 \text{ m/s}}{2.46 \times 10^{15} \text{ 1/s}} = 1.22 \times 10^{-7} \text{ m} \end{aligned}$$

To go to this Interactive Example click on this sentence.

When the magnetic field is turned on, the electron in the $2p$ state acquires the potential energy of the dipole and now has the energy

$$E'_2 = E_2 + \text{PE} = E_2 + m_l \frac{(e\hbar)B}{2m_e} \quad (4.66)$$

But for a p state, $l = 1$ and m_l then becomes equal to 1, 0, and -1 . Thus, there are now three energy levels associated with E'_2 because there are now three values of m_l . Therefore,

$$E'_2 = E_2 + \frac{(e\hbar)B}{2m_e} \quad (4.67)$$

$$E'_2 = E_2 \quad (4.68)$$

$$E'_2 = E_2 - \frac{(e\hbar)B}{2m_e} \quad (4.69)$$

These energy states are shown in figure 4.14(b). Thus, the application of the magnetic field has split the single $2p$ state into 3 states. Since there are now three energy states, an electron can be in any one of them and hence, there are now three possible transitions to the ground state, where before there was only one. Corresponding to each of these three transitions are three spectral lines, as shown in figure 4.14(d). *Thus, the application of the magnetic field splits the single spectral line of figure 4.14(c) into the three spectral lines of figure 4.14(d).* The emitted photon associated with the transition from the $m_l = +1$ state is

$$\begin{aligned} h\nu_+ &= E'_{2+} - E_1 = E_2 + \frac{e\hbar B}{2m_e} - E_1 \\ &= \frac{E_1}{4} - E_1 + \frac{e\hbar B}{2m_e} = -\frac{3E_1}{4} + \frac{e\hbar B}{2m_e} \end{aligned}$$

Using equation 4.64 the frequency of this spectral line becomes

$$\nu_+ = \nu_0 + \frac{e\hbar B}{2m_e h}$$

The wavelength of the spectral line is given by

$$\lambda_+ = \frac{c}{\nu_+} = \frac{c}{\nu_0 + e\hbar B / 2m_e h} \quad (4.70)$$

Comparing equation 4.70 with equation 4.65, we see that λ_+ is slightly smaller than the original wavelength λ_0 .

The transition from the $m_l = 0$ state is the same as the original transition from the $2p$ state because the electron has no potential energy associated with the magnetic dipole for $m_l = 0$. Thus, the spectral line is of the same wavelength λ_0 observed in the nonsplit spectral line.

The transition from the $m_l = -1$ state to the $1s$ state emits a photon of energy,

$$\begin{aligned} h\nu_- &= E'_{2-} - E_1 = E_2 - \frac{e\hbar B}{2m_e} - E_1 \\ &= \frac{E_1}{4} - E_1 - \frac{e\hbar B}{2m_e} = -\frac{3E_1}{4} - \frac{e\hbar B}{2m_e} \end{aligned}$$

Using equation 4.64, the frequency of this spectral line becomes

$$\nu_- = \nu_0 - \frac{e\hbar B}{2m_e h}$$

The wavelength of the spectral line is

$$\lambda_- = \frac{c}{\nu_-} = \frac{c}{\nu_0 - e\hbar B / 2m_e h} \quad (4.71)$$

Comparing equation 4.71 with equation 4.65, we see that the wavelength λ_- is slightly larger than the original wavelength λ_0 .

It turns out that all transitions from split states are not necessarily observed. Certain transitions are forbidden, and the allowed transitions are given by a set of selection rules on the allowed values of the quantum numbers. *Allowed transitions are possible only for changes in states where*

Selection Rules	$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m_l &= 0, \pm 1 \end{aligned} \quad (4.72)$
-----------------	--

Note that these selection rules were obeyed in the preceding example.

The selection rule requiring l to change by ± 1 means that the emitted photon must carry away angular momentum equal to the difference between the angular momentum of the atom's initial and final states.

4.7 Electron Spin

The final correction to the model of the atom assumes that the electron is not quite a point charge, but its charge is distributed over a sphere. As early as 1921 A. H. Compton suggested that the electron might be a spinning particle. The Dutch-American physicists, Samuel Goudsmit and George Uhlenbeck inferred, in 1925, that the electron did spin about its own axis and because of this spin had an additional angular momentum, \mathbf{S} , associated with this spin. Thus, this semiclassical model of the atom has an electron orbiting the nucleus, just as the earth orbits the sun, and the electron spinning on its own axis, just as the earth does about its axis. The model of the electron as a rotating charged sphere gives rise to an equivalent current loop and hence a magnetic dipole moment $\boldsymbol{\mu}_s$ associated with this spinning electron.

Associated with the orbital angular momentum \mathbf{L} was the orbital quantum number l . Similarly, associated with the spin angular momentum \mathbf{S} is the spin quantum number s . Whereas l could take on the values $l = 0, 1, 2, \dots, n - 1$, s can only take on the value

$$s = \frac{1}{2} \quad (4.73)$$

Similar to the magnitude of the orbital angular momentum given in equation 4.46, the magnitude of the spin angular momentum is given by

$$S = \sqrt{s(s+1)} \hbar \quad (4.74)$$

Because s can only take on the value $1/2$, the magnitude of the spin angular momentum S can only be

$$S = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \hbar = \frac{1}{2} \sqrt{3} \hbar \quad (4.75)$$

Just as the direction of the orbital angular momentum vector was quantized according to equation 4.47, the z -component of the spin angular momentum is quantized to

$$S_z = m_s \hbar \quad (4.76)$$

where m_s is called the spin magnetic quantum number. Just as the angular momentum vector \mathbf{L} could have $2l + 1$ directions, that is, $m_l = 0, \pm 1, \pm l$, the spin angular momentum vector \mathbf{S} can have $2s + 1$ directions, that is, $2s + 1 = 2(1/2) + 1 = 2$ directions specified by $m_s = 1/2$ and $m_s = -1/2$. Thus, the z -component of the spin angular momentum can only be

$$S_z = \pm \frac{\hbar}{2} \quad (4.77)$$

The only two possible spin angular momentum orientations are shown in figure 4.15. When $m_s = +1/2$, the electron is usually designated as spin-up, while $m_s = -1/2$ is referred to as spin-down. The state of any electron in an atom is now specified by the four quantum numbers n, l, m_l , and m_s .

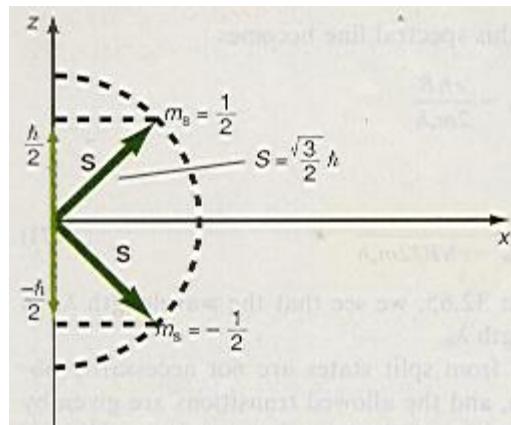


Figure 4.15 Orientations of the spin angular momentum vector.

We should note that the semiclassical picture of the spinning electron is not quite correct. Using the picture of a spinning sphere, we can find its angular momentum about its own axis from the study of rotational motion as

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$$\begin{aligned} L = I\omega &= \left(\frac{2}{5} mr^2\right)\left(\frac{v}{r}\right) \\ &= \frac{2}{5} mrv \end{aligned}$$

where r is the radius of the electron, which is of the order of 10^{-15} m. Because the spin angular momentum has only the one value given by equation 4.75, for these angular momenta to be equal, $\mathbf{L} = \mathbf{S}$, or

$$\frac{2}{5} mrv = \frac{1}{2} \sqrt{3} \hbar$$

The speed of a point on the surface of the spinning electron would have to be

$$\begin{aligned} v &= \frac{5\sqrt{3} \hbar}{4mr} \\ &= \frac{5\sqrt{3} (1.0546 \times 10^{-34} \text{ J s})}{4(9.11 \times 10^{-31} \text{ kg})(1.00 \times 10^{-15} \text{ m})} \\ &= 2.5 \times 10^{11} \text{ m/s} \end{aligned}$$

But this is a velocity greater than the velocity of light, which cannot be. Hence, the classical picture of the charged rotating sphere cannot be correct. However, in 1928, Paul A. M. Dirac (1902-1984) joined together the special theory of relativity and quantum mechanics, and from this merger of the two theories found that the electron must indeed have an intrinsic angular momentum that is the same as that given by the semiclassical spin angular momentum. This angular momentum is purely a quantum mechanical effect and although of the same magnitude as the spin angular momentum, it has no classical analogue. However, because the value of the angular momentum is the same, it is still customary to speak of the spin of the electron.

Just as the orbital angular momentum has an orbital magnetic dipole moment μ_l given by equation 4.57, the spin angular momentum has a spin magnetic dipole moment given by

$$\mu_s = -2.0024 \left(\frac{e}{2m_e} \right) S \quad (4.78)$$

and the spin magnetic dipole moment is shown in figure 4.16. In what follows, we will round off the value 2.0024 in equation 4.78 to the value 2.

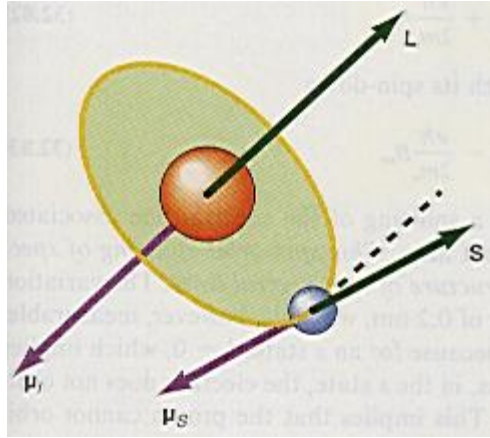


Figure 4.16 Orbital and spin angular momentum vectors and their associated dipole moments.

When the orbital magnetic dipole μ_l was placed in a magnetic field, a torque acted on μ_l trying to align it with the magnetic field. The space quantization of \mathbf{L} made it impossible for \mathbf{L} to become aligned, and hence, the electron had the potential energy given by equation 4.62. In the same way, the spin magnetic dipole moment μ_s should try to align itself in any magnetic field and because of the space quantization of the spin angular momentum, the electron should have the potential energy

$$PE = -\mu_s B \cos \theta \quad (4.79)$$

Substituting equation 4.78 into equation 4.79, gives

$$PE = +2 \left(\frac{e}{2m_e} \right) S B \cos \theta \quad (4.80)$$

If there is an applied magnetic field \mathbf{B} , the electron acquires the additional potential energy given by equation 4.80. However, if there is no applied magnetic field, this potential energy term is still present, because from the frame of reference of the electron, the proton is in orbit about the electron, figures 4.17(a) and 4.17(b). The revolving proton constitutes a current loop and produces a magnetic field \mathbf{B}_{so} at the location of the electron. This magnetic field interacts with the spin magnetic dipole moment μ_s as given by equation 4.80. *The interaction of the spin magnetic dipole with the magnetic field \mathbf{B}_{so} produced by the orbiting proton is called the spin-orbit interaction.*

We can now write equation 4.80 as

$$PE = +2 \left(\frac{e}{2m_e} \right) S B_{so} \cos \theta$$

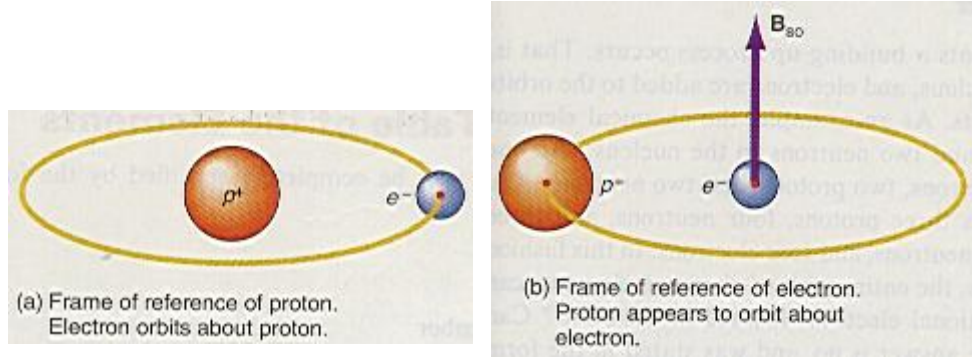


Figure 4.17 The spin-orbit interaction.

But $S \cos \theta = S_z$, the z -component of the spin angular momentum vector. Hence,

$$PE = +2 \left(\frac{e}{2m_e} \right) S_z B_{so}$$

But $S_z = \pm \hbar/2$ from equation 4.77, thus

$$PE = +2 \left(\frac{e}{2m_e} \right) \frac{\pm \hbar}{2} B_{so}$$

or the acquired potential energy of an electron caused by the spin-orbit interaction is

$$PE = \pm \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.81)$$

Hence, every quantum state, except s states, splits into two energy states, one corresponding to the electron with its spin-up

$$E_1 = E_0 + \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.82)$$

and one corresponding to the electron with its spin-down

$$E_1 = E_0 - \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.83)$$

The splitting of the energy state causes a splitting of the spectral line associated with each energy state into two component lines. *This spin-orbit splitting of spectral*

lines is sometimes called the fine structure of the spectral lines. The variation in wavelength is quite small, of the order of 0.2 nm, which is, however, measurable.

There is no splitting of s states because for an s state, $l = 0$, which implies that there is no angular momentum. Thus, in the s state, the electron does not orbit about the proton in any classical sense. This implies that the proton cannot orbit about the electron and hence, cannot create the magnetic field, B_{so} , at the location of the electron. Therefore, if $B_{so} = 0$ in equation 4.81, then the potential energy term must also equal zero, and there can be no splitting of such a state.

4.8 The Pauli Exclusion Principle and the Periodic Table of the Elements

An electron in the hydrogen atom can now be completely specified by the four quantum members:

n = the principal quantum number

l = the orbital quantum number

m_l = the orbital magnetic quantum number

m_s = the spin magnetic quantum number

To obtain the remaining chemical elements a building up process occurs. That is, protons and neutrons are added to the nucleus, and electrons are added to the orbits to form the rest of the chemical elements. As an example, the chemical element helium is formed by adding one proton and two neutrons to the nucleus, and one orbital electron to give a total of two electrons, two protons, and two neutrons. The next chemical element, lithium, contains three protons, four neutrons, and three electrons. Beryllium has four protons, five neutrons, and four electrons. In this fashion of adding electrons, protons, and neutrons, the entire table of chemical elements can be generated. But where are these additional electrons located in the atom? Can they all be found in the same orbit? The answer is no, and was stated in the form of the Pauli exclusion principle by the Austrian physicist Wolfgang Pauli (1900-1958) in 1925. *The Pauli exclusion principle states that no two electrons in an atom can exist in the same quantum state.* Because the state of any electron is specified by the quantum numbers n , l , m_l , and m_s , *the exclusion principle states that no two electrons can have the same set of the four quantum numbers.*

Electrons with the same value of n are said to be in the same orbital shell, and the shell designation is shown in table 4.3. Electrons that have the same value of l in a shell are said to occupy the same subshell. Electrons fill up a shell by starting at the lowest energy.

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Table 4.3 Atomic Shells					
Quantum number n	1	2	3	4	5
Shell	K	L	M	N	O

The building up of the chemical elements is shown in table 4.4. Thus, the first electron is found in the K shell with quantum numbers (1001/2) and this is the

Table 4.4 Electron States in Terms of the Quantum Numbers								
		n	l	m_l	m_s		Numbers of States for Value of l	Total # of States for Value of n
$n = 1$	$l = 0$	1	0	0	-1/2	$1s\uparrow$	2	2
		1	0	0	-1/2	$1s\downarrow$		
$n = 2$	$l = 0$	2	0	0	1/2	$2s\uparrow$	2	8
		2	0	0	-1/2	$2s\downarrow$		
	$l = 1$	2	1	1	1/2		6	
		2	1	1	-1/2			
		2	1	0	1/2			
		2	1	0	-1/2			
		2	1	-1	1/2			
		2	1	-1	-1/2			
$n = 3$	$l = 0$	3	0	0	1/2	$3s\uparrow$	2	18
		3	0	0	-1/2	$3s\downarrow$		
	$l = 1$	3	1	1	1/2		6	
		3	1	1	-1/2			
		3	1	0	1/2			
		3	1	0	-1/2			
		3	1	-1	1/2			
		3	1	-1	-1/2			
	$l = 2$	3	2	2	1/2		10	
		3	2	2	-1/2			
		3	2	1	1/2			
		3	2	1	-1/2			
		3	2	0	1/2			
		3	2	0	-1/2			
		3	2	-1	1/2			
		3	2	-1	-1/2			
		3	2	-2	1/2			
		3	2	-2	-1/2			

configuration of the hydrogen atom. When the next electron is placed in the atom, it cannot have the quantum numbers of the first electron, so it must now be the electron given by the quantum numbers (100 -1/2), that is, this second electron must have its spin-down. The atom with two electrons is the helium atom, and, as we now see, its two electrons are found in the K shell, one with spin-up the other with spin-down. The addition of the third electron cannot go into the K shell because all of the quantum numbers associated with $n = 1$ are already used up.

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Hence, a third electron must go into the $n = 2$ state or L shell. The rest of the table shows how the process of building up the set of quantum numbers continues. The notation $1s\uparrow$ means that the electron is in the $1s$ state with its spin-up. The notation $1s\downarrow$ means that the electron is in the $1s$ state with its spin-down.

The electron configuration is stated symbolically in the form

$$n(l)^{\#}$$

where n is the principal quantum number, l is the orbital quantum number expressed in the spectroscopic notation, and $\#$ stands for the number of electrons in that subshell. Hence, the electron configuration for the hydrogen atom would be $1s^1$, and for the helium atom, $1s^2$. The electron configuration for the first few chemical elements is shown in table 4.5. Note that the difference between one chemical element and the next is the addition of one more proton and electron.

Table 4.5				
Electron Configuration for the First Few Chemical Elements				
Chemical Element	Electron Configuration			
H	$1s^1$			
He	$1s^2$			
Li	$1s^2 2s^1$			
Be	$1s^2 2s^2$			
B	$1s^2 2s^2$	$2p^1$		
C	$1s^2 2s^2$	$2p^2$		
N	$1s^2 2s^2$	$2p^3$		
O	$1s^2 2s^2$	$2p^4$		
F	$1s^2 2s^2$	$2p^5$		
Ne	$1s^2 2s^2$	$2p^6$		
Na	$1s^2 2s^2$	$2p^6$	$3s^1$	
Mg	$1s^2 2s^2$	$2p^6$	$3s^2$	
Al			$3s^2$	$3p^1$
Si			$3s^2$	$3p^2$
P			$3s^2$	$3p^3$
S			$3s^2$	$3p^4$
Cl			$3s^2$	$3p^5$
Ar			$3s^2$	$3p^6$

The complete electron configurations for the ground states of all the chemical elements is shown somewhat differently in table 4.6. Thus, the entire set of chemical elements can be built-up in this way.

The way that an element reacts chemically depends on the number of electrons in the outer shell. Hence, all the chemical elements can be grouped into a table that shows how these elements react. Such a table, called the Periodic Table of the Elements and first formulated by the Russian chemist, Dmitri Mendeleev (1834-1907) around 1869, is shown in figure 4.18.

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Table 4.6 Electron Configurations for the Ground States of the Elements																			
		K		L		M		N				O			P		Q		
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7f
1	H	1																	
2	He	2																	
3	Li	2	1																
4	Be	2	2																
5	B	2	2	1															
6	C	2	2	2															
7	N	2	2	3															
8	O	2	2	4															
9	F	2	2	5															
10	Ne	2	2	6															
11	Na	2	2	6	1														
12	Mg	2	2	6	2														
13	Al	2	2	6	2	1													
14	Si	2	2	6	2	2													
15	P	2	2	6	2	3													
16	S	2	2	6	2	4													
17	Cl	2	2	6	2	5													
18	Ar	2	2	6	2	6													
19	K	2	2	6	2	6		1											
20	Ca	2	2	6	2	6		2											
21	Sc	2	2	6	2	6	1	2											
22	Ti	2	2	6	2	6	2	2											
23	V	2	2	6	2	6	3	2											
24	Cr	2	2	6	2	6	5	1											
25	Mn	2	2	6	2	6	5	2											
26	Fe	2	2	6	2	6	6	2											
27	Co	2	2	6	2	6	7	2											
28	Ni	2	2	6	2	6	8	2											
29	Cu	2	2	6	2	6	10	1											
30	Zn	2	2	6	2	6	10	2											
31	Ga	2	2	6	2	6	10	2	1										
32	Ge	2	2	6	2	6	10	2	2										
33	As	2	2	6	2	6	10	2	3										
34	Se	2	2	6	2	6	10	2	4										
35	Br	2	2	6	2	6	10	2	5										
36	Kr	2	2	6	2	6	10	2	6										
37	Rb	2	2	6	2	6	10	2	6			1							
38	Sr	2	2	6	2	6	10	2	6			2							
39	Y	2	2	6	2	6	10	2	6	1		2							
40	Zr	2	2	6	2	6	10	2	6	2		2							
41	Nb	2	2	6	2	6	10	2	6	4		1							
42	Mo	2	2	6	2	6	10	2	6	5		1							
43	Tc	2	2	6	2	6	10	2	6	5		2							
44	Ru	2	2	6	2	6	10	2	6	7		1							
45	Rh	2	2	6	2	6	10	2	6	8		1							
46	Pd	2	2	6	2	6	10	2	6	10									
47	Ag	2	2	6	2	6	10	2	6	10		1							
48	Cd	2	2	6	2	6	10	2	6	10		2							

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Table 4.6 (Continued)																			
		K		L		M		N				O			P			Q	
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7f
49	In	2	2	6	2	6	10	2	6	10		2	1						
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	I	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99	Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100	Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101	Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2

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Table 4.6 (Continued)																			
		K		L		M			N				O			P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7f
102	No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
103	Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2
104	Rf																		
105	Ha																		

Period	Group I	Group II											Group III	Group IV	Group V	Group VI	Group VII	Group VIII
1	1 H 1.00																	2 He 4.00
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.00	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.98	16 S 32.06	17 Cl 35.46	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.8
5	37 Rb 85.47	38 Sr 87.66	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98.91)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
6	55 Cs 132.91	56 Ba 137.34	57-71 * Rare earths	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (218)	86 Rn 222
7	87 Fr (223)	88 Ra 226.05	89-103 ** Actinides															
			57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.92	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
			89 Ac 227	90 Th 232.04	91 Pa 231	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)	

Figure 4.18 Periodic table of the elements.

Notice that there are vertical columns called groups and the chemical elements within each group have very similar properties. As an example, Group I contains elements that have only one electron in their outermost shell and these chemicals react very strongly. The horizontal rows are called periods, and progressing from one column to another in a particular row, the chemical element contains one more electron. Thus in column I, there is one outer electron; in column II, there are two; in column III, there are three; and so on until we get to column VIII, where there are eight electrons in a closed shell. The chemical properties within a period change gradually as the additional electron is added. However, the first element of the period is very active chemically, whereas the last element of a period contains the inert gases. These gases are inert because the outer electron shell is closed and there is no affinity to either gain or lose electrons, and, hence, these elements do not react chemically with any of the other elements. Thus, there is a drastic chemical difference between the elements in Group I and Group VIII. The chemical properties of any element is a function of the number of electrons in the outer shell.

As mentioned earlier, an electron always falls into the state of lowest energy, and this can be seen in table 4.6. For the early elements, each lower quantum state is filled before a higher one starts. However, starting with the element potassium (K), a change occurs in the sequence of quantum numbers. Instead of the 19th electron going into a $3d$ state, it goes into the $4s$ state, as shown in table 4.6. The reason for this is that these elements of higher atomic number start to have an energy dependence on the quantum number l , because the higher orbits are partially shielded from the nuclear charge by the inner electrons of low values of l . Thus, as l increases, the energy of the state also increases. Hence, a $4s$ state is actually at a lower energy than a $3d$ state. Therefore, the 19th electron goes into the $4s^1$ state; the 20th electron goes into the $4s^2$ state; and the 21st electron goes into the $3d$ state, which is lower than the $4p$ state. This is seen in both table 4.6 and figure 4.18. Additional electrons now start to fill up the $3d$ shell as shown. The order in which electron subshells are filled in atoms is given by $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d$. Table 4.7 is a reproduction of table 4.2 and it can be used to generate the sequence in which electrons fill the orbital subshells by following the diagonal lines traced on the table.

Table 32.7
Sequence of Atomic States in the Hydrogen Atom

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

Table 4.7 Sequence of Atomic States in the Hydrogen Atom

One of the characteristics of a closed shell is that the total orbital angular momentum \mathbf{L} is zero and the total spin angular momentum \mathbf{S} is also zero. To see this, let us consider the electrons in a closed $2p$ subshell. The angular momentum vectors associated with the (211) , (210) , and $(21-1)$ quantum numbers are shown in figure 4.19(a). The angular momentum vector associated with the state (211) should be fixed in its direction in space by the requirement that $L_z = \hbar$, as shown in the figure. However, by the *Heisenberg uncertainty principle*, the direction of \mathbf{L} cannot be so precisely stated. Hence, the angular momentum vector can precess around the

z -axis as shown. Thus, the value of θ is fixed, but \mathbf{L} precesses around z , always at the same angle θ . Sometimes, \mathbf{L} is toward the right, sometimes toward the left, sometimes toward the back, and sometimes toward the front. Its mean position is, therefore, in the positive z -direction. The angular momentum vector

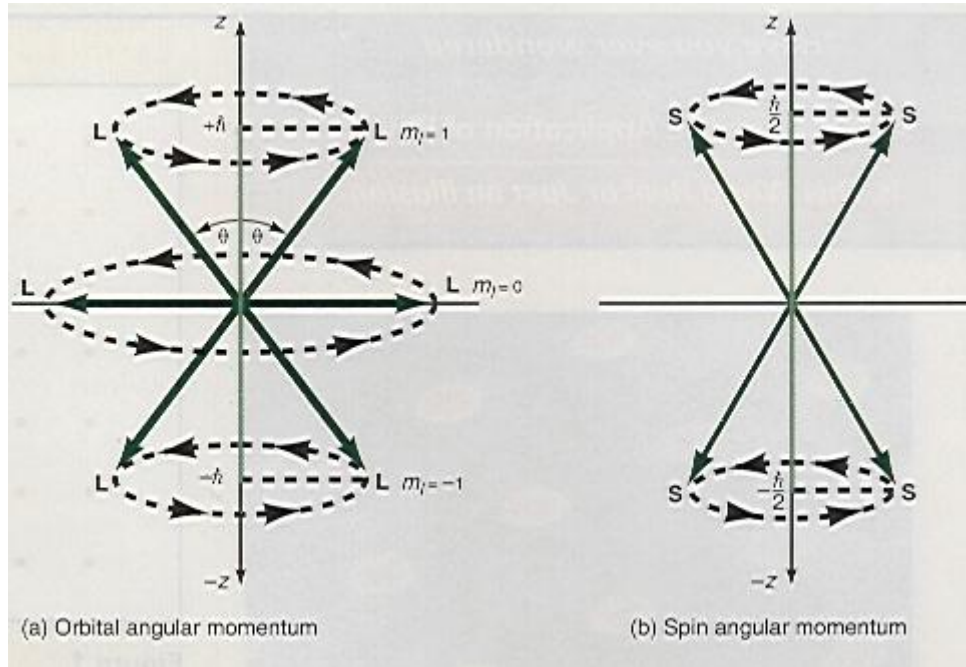


Figure 4.19 The total angular momentum of a closed shell is zero.

associated with (21-1) precesses in the same way about the negative z -axis and its mean position is in the negative z -direction. Since the magnitude of \mathbf{L} is the same for both vectors, the average or mean value of L for the two states adds up to zero. The mean value of \mathbf{L} for the (210) state is zero, because sometimes it is toward the right and sometimes toward the left, and so on. Hence, for any closed subshell the total angular momentum \mathbf{L} is zero. Because the angular momentum vector for the s state is already equal to zero, because $l = 0$, the orbital angular momentum of a completely filled shell is zero.

In the same way, the spin angular momentum \mathbf{S} also adds up to zero when there are the same number of electrons with spin-up as with spin-down, figure 4.19(b). But this is exactly the case of a closed shell, so the total spin angular momentum of a closed shell is also zero. An atom with a closed shell also has a zero dipole moment because \mathbf{L} and \mathbf{S} are both zero.

For the magnetic elements iron (Fe), cobalt (Co), and nickel (Ni), the electrons in the $3d$ shell are not paired off according to spin. Iron has five electrons with spin-up, cobalt has four, and nickel has three. Thus, the spin angular momentum vectors add up very easily to give a rather large spin magnetic dipole moment. Hence, when a piece of iron is placed in an external magnetic field, all these very strong magnetic dipoles align themselves with the field, thereby producing the ordinary bar magnet.

Have you ever wondered ...? An Essay on the Application of Physics Is This World Real or Just an Illusion?

Have you ever wondered if this solid world that we see around us is really an illusion? Philosophers have argued this question for centuries. To see for ourselves all we have to do is slam our fist down on the table. Ouch! That table is real, I can tell because my hand hurts where I hit the table. That table is solid and is no illusion.

Let us look a little bit more carefully at the solid table. It certainly looks solid. If we were to take a very powerful microscope and look at the smooth table we would see that the table is made up of a lattice structure, the simplest lattice structure is shown in figure 1. Each one of those dots represents an atom of the

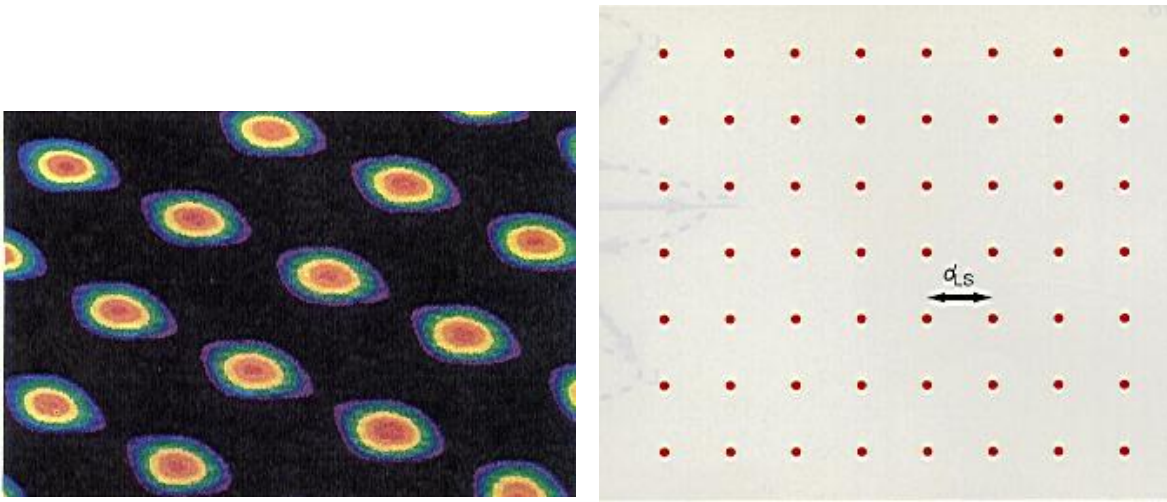


Figure 1 The lattice structure.

material. They are arranged in a symmetric net. The distance separating each atom in the lattice structure is actually quite small, a typical distance is about 5.6×10^{-10} m. The diameter of an atom is about 1.1×10^{-10} m. Hence, the ratio of the separation between atoms in the lattice structure d_{LS} to the diameter of the atom d_A is

$$\frac{d_{LS}}{d_A} = \frac{5.6 \times 10^{-10} \text{ m}}{1.1 \times 10^{-10} \text{ m}} = 5.09 \quad (4H.1)$$

or the distance separating the atoms in the lattice structure is

$$d_{LS} = 5.09 d_A \quad (4H.2)$$

Equation 4H.2 says that each nearest atom is about 5.09 atomic diameters distant.

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If we now look at the problem in three dimensions, the lattice structure looks like a box with the atom at each corner of the box, each separated by the distance d_{LS} . The box is called a *unit cell*, and is shown in figure 2. The volume of the box is given by

$$V_{\text{box}} = (d_{LS})^3 = (5.6 \times 10^{-10} \text{ m})^3 = 1.76 \times 10^{-28} \text{ m}^3 \quad (4H.3)$$

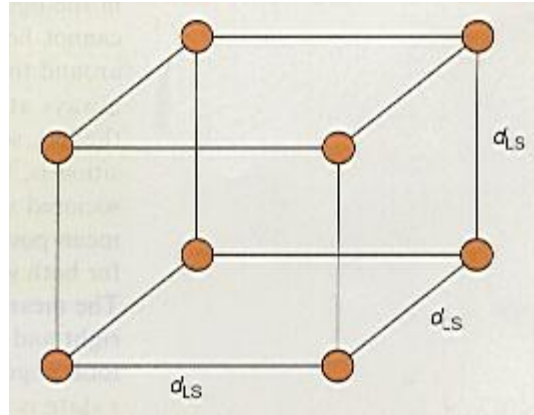


Figure 2 The unit cell.

But part of the volume of each atom is shared with the surrounding boxes. Figure 3 shows four of these boxes where they join. Consider the atom as the sphere located

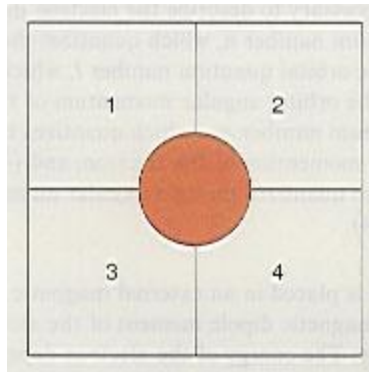


Figure 3 Determining the number of atoms in a unit cell.

at the bottom corner of box 1 and protruding into boxes 2, 3, and 4. Each box shown contains $\frac{1}{4}$ of the volume of the sphere. There are four more boxes in front of the four boxes shown here. Hence, each box contains $\frac{1}{8}$ of the volume of the sphere. Therefore, each box contains the atomic volume of

$$\left(\frac{8 \text{ atoms}}{\text{box}}\right)\left(\frac{1}{8}\right)\left(\frac{\text{atomic volume}}{\text{atom}}\right) = \frac{1 \text{ atomic volume}}{\text{box}} \quad (4H.4)$$

That is, the unit cell or box contains the equivalent of one atom. The volume occupied by the atom in the box is

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$$\begin{aligned}
 V_{\text{atomic}} &= \frac{4}{3} \pi r^3 \\
 &= \frac{4}{3} \pi (0.55 \times 10^{-10} \text{ m})^3 \\
 &= 6.95 \times 10^{-31} \text{ m}^3
 \end{aligned} \tag{4H.5}$$

The ratio of the volume of the box to the volume of the atom contained in the box is

$$\frac{V_{\text{box}}}{V_{\text{atomic}}} = \frac{1.76 \times 10^{-28} \text{ m}^3}{6.95 \times 10^{-31} \text{ m}^3} = 2.53 \times 10^2$$

Hence, the volume of the box is

$$V_{\text{box}} = 253 V_{\text{atomic}} \tag{4H.6}$$

That is, the volume of one unit cell of the lattice structure is 253 times the volume occupied by the atom. Hence, the solid table that you see before you, constructed from that lattice structure, is made up of a great deal of empty space.

The atoms making up the lattice structure are also composed of almost all empty space. For example, the simplest atom, hydrogen, shown in figure 4, has a diameter d_A of about $1.1 \times 10^{-10} \text{ m}$. The diameter of the nucleus is about $1 \times 10^{-14} \text{ m}$.

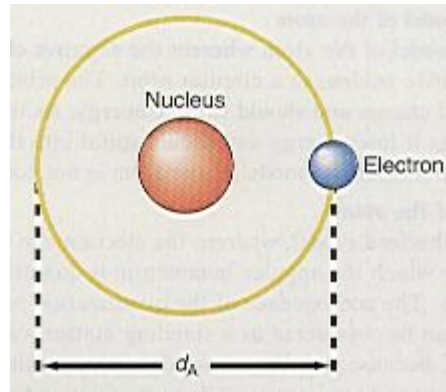


Figure 4 The size of an atom.

Because the mass of the electron is so small compared to the mass of the proton and neutron, the nucleus contains about 99.9% of the mass of the atom. The size of the electron is so small that its volume can be neglected compared to the volume of the nucleus and the atom. The ratio of the volume of the atom to the volume of the nucleus is about

$$\begin{aligned}
 \frac{V_A}{V_N} &= \frac{\frac{4}{3} \pi r_A^3}{\frac{4}{3} \pi r_N^3} = \frac{r_A^3}{r_N^3} \\
 &= \frac{(0.55 \times 10^{-10} \text{ m})^3}{(0.5 \times 10^{-14} \text{ m})^3} = 1.1 \times 10^{12}
 \end{aligned} \tag{4H.7}$$

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Hence, the volume of the atom is

$$V_A = 1.1 \times 10^{12} V_N = 1,100,000,000,000 V_N \quad (4H.8)$$

That is, the volume of the atom is over one trillion times the volume of the nucleus. Hence, the atoms that make up that lattice structure are also composed of almost all empty space. When we combine the volume of the box (unit cell) with respect to the volume of each atom in the box, equation 4H.6, with the volume of the atom with respect to the nucleus, equation 4H.8, we get

$$V_{\text{box}} = 253 V_{\text{atomic}} = 253(1.1 \times 10^{12} V_N) = 278 \times 10^{12} V_N$$

or the volume of the box (unit cell) is 278 trillion times the volume of the nucleus. Therefore, the solid is made up almost entirely of empty space.

But if a solid consists almost entirely of empty space, then why can't you put your hand through the solid? You can't place your hand through the solid because there are electrical and atomic forces that hold the atom and lattice structure together, and your hand cannot penetrate that force field.

You can't put your hand through a block of ice either, but by heating the ice you give energy to the water molecules that make up the ice, and that energy is enough to pull the molecules away from the lattice structure, thereby melting the ice. You can now put your hand in the water, even though you could not put it through the ice. If you heat the water further, the water evaporates into the air and becomes invisible. You can walk through the air containing the water vapor as though it weren't even there.

So, is the world real or only an illusion? The world is certainly real because it is made up of all those atoms and molecules. But is it an illusion? In the sense described here, yes it is. But it is truly a magnificent illusion. For this solid world that we live in is composed almost entirely of empty space. It is a beautiful stage on which we all act out our lives.

The Language of Physics

Rutherford model of the atom

A planetary model of the atom wherein the negative electron orbits about the positive nucleus in a circular orbit. The orbiting electron is an accelerated charge and should radiate energy. As the electron radiates energy it loses energy and should spiral into the nucleus. Therefore, the Rutherford model of the atom is not correct (p.).

Bohr theory of the atom

A revised Rutherford model, wherein the electron can be found only in an orbit for which the angular momentum is quantized in multiples of \hbar . The consequence of the quantization postulate is that the electron can be considered as a standing matter wave in the electron orbit. Because standing waves do not transmit energy, the electron does not radiate energy while in its orbit and does not spiral into the nucleus. The Bohr model is thus stable. Bohr then postulated that when the electron jumps from a higher energy orbit to a lower energy orbit, a photon of light is emitted. Thus, the spectral lines of the hydrogen atom should be discrete, agreeing with experimental results. However, the Bohr theory could not explain the spectra from multielectron atoms and it is not, therefore, a completely accurate model of the atom (p.).

Quantum mechanical model of the atom

This model arises from the application of the Schrödinger equation to the atom. The model says that the following four quantum numbers are necessary to describe the electron in the atom: (1) the principal quantum number n , which quantizes the energy of the electron; (2) the orbital quantum number l , which quantizes the magnitude of the orbital angular momentum of the electron; (3) the magnetic quantum number m_l , which quantizes the direction of the orbital angular momentum of the electron; and (4) the spin quantum number s , which quantizes the spin angular momentum of the electron (p.).

Zeeman effect

When an atom is placed in an external magnetic field a torque acts on the orbital magnetic dipole moment of the atom giving it a potential energy. The energy of the electron depends on the magnetic quantum number as well as the principal quantum number. For a particular value of n , there are multiple values of the energy. Hence, instead of a single spectral line associated with a transition from the n^{th} state to the ground state, there are many spectral lines depending on the value of m_l . Thus, a single spectral line has been split into several spectral lines (p.).

Pauli exclusion principle

No two electrons in an atom can exist in the same quantum state. Hence, no two electrons can have the same quantum numbers (p.).

Summary of Important Equations

Distance of closest approach to nucleus	$r_0 = \frac{2kZe^2}{\text{KE}}$	(4.7)
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Relative size of atom	$r_a = 10,000 r_n$	(4.8)
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Radius of nucleus	$R = R_0 A^{1/3}$	(4.9)
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Bohr Theory of the Hydrogen Atom

Angular momentum is quantized $L = mvr = n\hbar$ (4.25)

Orbital radius $r_n = \frac{\hbar^2}{kme^2} n^2$ (4.31)

$r_n = r_1 n^2$ (4.32)

Orbital velocity $v_n = \frac{ke^2}{n\hbar}$ (4.33)

$v_n = \frac{v_1}{n}$ (4.34)

Electron energy $E_n = -\frac{mk^2e^4}{2n^2\hbar^2}$ (4.35)

$E_n = -\frac{E_1}{n^2}$ (4.37)

Einstein's relation $h\nu = E_i - E_f$ (4.38)

Frequency of emitted photon $\nu = \frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ (4.39)

Wavelength of emitted photon $\frac{1}{\lambda} = \frac{E_1}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ (4.40)

Quantum Mechanical Theory of the Hydrogen Atom

Principal quantum number $n = 1, 2, 3, \dots$ (4.42)

Orbital quantum number $l = 0, 1, 2, \dots, (n-1)$ (4.43)

Magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ (4.44)

Electron energy $E_n = -\frac{k^2e^4m}{2\hbar^2} \frac{1}{n^2}$ (4.45)

Angular momentum $L = \sqrt{l(l+1)} \hbar$ (4.46)

z-component of angular momentum $L_z = m_l \hbar$ (4.47)

Direction of **L** $\theta = \cos^{-1} \frac{m_l}{\sqrt{l(l+1)}}$ (4.49)

Orbital magnetic dipole moment

$\mu_l = -\frac{e}{2m_e} \mathbf{L}$ (4.57)

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$$\mu_l = \frac{e\hbar}{2m_e} \sqrt{l(l+1)} \quad (4.58)$$

Potential energy of a dipole in an external magnetic field

$$\text{PE} = \mu_l B \cos \theta \quad (4.59)$$

$$\text{PE} = m_l \frac{e\hbar}{2m_e} B \quad (4.62)$$

Zeeman Effect

Splitting of energy state

$$E' = E + m_l \frac{(e\hbar)B}{2m_e} \quad (4.66)$$

Splitting of spectral lines in an external magnetic field

$$\lambda_+ = \frac{c}{\nu_+}$$

$$\lambda_+ = \frac{c}{\nu_0 + e\hbar B / 2m_e h} \quad (4.70)$$

$$\lambda = \frac{c}{\nu_0} = \frac{ch}{\frac{3}{4}E_1} \quad (4.65)$$

$$\lambda_- = \frac{c}{\nu_-}$$

$$\lambda_- = \frac{c}{\nu_0 - e\hbar B / 2m_e h} \quad (4.71)$$

Selection rules for transitions

$$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m_l &= 0, \pm 1 \end{aligned} \quad (4.72)$$

Spin quantum number

$$s = \frac{1}{2} \quad (4.73)$$

Spin angular momentum

$$S = \sqrt{s(s+1)} \hbar \quad (4.74)$$

$$S = \frac{1}{2} \sqrt{3} \hbar \quad (4.75)$$

z-component of spin

$$S_z = m_s \hbar \quad (4.76)$$

$$S_z = \pm \hbar/2 \quad (4.77)$$

Spin magnetic dipole moment

$$\mu_s = -2.0024 \left(\frac{e}{2m_e} \right) S \quad (4.78)$$

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Potential energy of electron due to spin

$$PE = -\mu_s B \cos \theta \quad (4.79)$$

$$PE = +2 \left(\frac{e}{2m_e} \right) SB \cos \theta \quad (4.80)$$

$$PE = \pm \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.81)$$

Spin-orbit splitting of energy state

$$E_1 = E_0 + \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.82)$$

$$E_1 = E_0 - \left(\frac{e\hbar}{2m_e} \right) B_{so} \quad (4.83)$$

Questions for Chapter 4

1. Discuss the differences among (a) the plum pudding model of the atom, (b) the Rutherford model of the atom, (c) the Bohr theory of the atom, and (d) the quantum mechanical theory of the atom.

*2. Discuss the effect of the uncertainty principle and the Bohr theory of electron orbits.

*3. How can you use spectral lines to determine the chemical composition of a substance?

4. If you send white light through a prism and then send it through a tube of hot hydrogen gas, what would you expect the spectrum to look like when it emerges from the hydrogen gas?

*5. In most chemical reactions, why are the outer electrons the ones that get involved in the reaction? Is it possible to get the inner electrons of an atom involved?

6. When an atom emits a photon of light what does this do to the angular momentum of the atom?

7. Explain how the Bohr theory can be used to explain the spectra from singly ionized atoms.

*8. Discuss the process of absorption of light by matter in terms of the atomic structure of the absorbing medium.

*9. Rutherford used the principle of scattering to “see” inside the atom. Is it possible to use the principle of scattering to “see” inside a proton and a neutron?

*10. How can you determine the chemical composition of a star?

*11. How can you determine if a star is approaching or receding from you? How can you determine if it is a small star or a very massive star?

Problems for Chapter 4

Section 4.1 The History of the Atom

1. Find the potential energy of two α particles when they are brought together to a distance of 1.20×10^{-15} m, the approximate size of a nucleus.
2. Find the potential energy of an electron and a proton when they are brought together to a distance of 5.29×10^{-11} m to form a hydrogen atom.
3. A silver nucleus is bombarded with 8-MeV α particles. Find (a) the maximum radius of the silver nucleus and (b) the more probable radius of the silver nucleus.
4. Estimate the radius of a nucleus of ${}^{238}_{92}\text{U}$.
5. How many electrons, protons, and neutrons are there in a silver atom?
6. How many electrons, protons, and neutrons are there in a uranium atom?
7. Find the difference in the orbital radius of an electron in the Rutherford atom if the electron is initially in an orbit of 5.29×10^{-11} m radius and the atom radiates 2.00 eV of energy.

Section 4.2 The Bohr Theory of the Atom

- *8. An electron is in the third Bohr orbit. Find (a) the radius, (b) the speed, (c) the energy, and (d) the angular momentum of the electron in this orbit.
9. The orbital electron of a hydrogen atom moves with a speed of 5.459×10^5 m/s. (a) Determine the value of the quantum number n associated with this electron. (b) Find the radius of this orbit. (c) Find the energy of the electron in this orbit.
- *10. An electron in the third Bohr orbit drops to the ground state. Find the angular momentum of the electron in (a) the third Bohr orbit, and (b) the ground state. (c) Find the change in the angular momentum of the electron. (d) Where did the angular momentum go?
11. At what temperature will the average thermal speed of a free electron equal the speed of an electron in its second Bohr orbit?
12. The lifetime of an electron in an excited state of an atom is about 10^{-8} s. How many orbits will an electron in the $2p$ state execute before falling back to the ground state?
13. Show that the ratio of the speed of an electron in the first Bohr orbit to the speed of light is equal to $1/137$. This ratio is called the *fine-structure constant*.
14. Find the radius of the first Bohr orbit of an electron in a singly ionized helium atom.
15. Find the angular momentum of an electron in the third Bohr orbit and the second Bohr orbit. How much angular momentum is lost when the electron drops from the third orbit to the second orbit?

Section 4.3 The Bohr Theory and Atomic Spectra

16. An electron in the third Bohr orbit drops to the second Bohr orbit. Find (a) the energy of the photon emitted, (b) its frequency, and (c) its wavelength.

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17. An electron in the third Bohr orbit drops to the ground state. Find (a) the energy of the photon emitted, (b) its frequency, and (c) its wavelength.
18. Calculate the wavelength of the first two lines of the Paschen series.

Section 4.4 The Quantum Mechanical Model of the Hydrogen Atom

19. Find the angular momentum of the electron in the quantum mechanical model of the hydrogen atom when it is in the $2p$ state. How much angular momentum is lost when the electron drops to the $1s$ state?

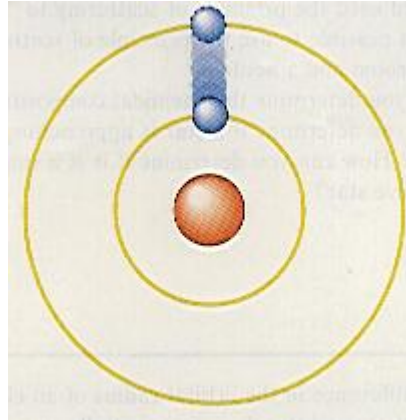


Diagram for problem 19.

20. Find the angular momentum of the electron in the quantum mechanical model of the hydrogen atom when it is in the $3d$ state. (a) How much angular momentum is lost when the electron drops to the $1s$ state? (b) How much energy is lost when the electron drops to the $1s$ state?
21. An orbital electron is in the $5d$ state. (a) Find the energy of the electron in this state. (b) Find the orbital angular momentum of the electron. (c) Compute all possible values of the z -component of the orbital angular momentum of the electron. (d) Determine the largest value of θ , the angle between the orbital angular momentum vector and the z -axis.
22. Find the angle θ that the angular momentum vector makes with the z -axis when the electron is in the $3d$ state.
23. Find (a) the z -component of the angular momentum of an electron when it is in the $2p$ state and (b) the angle that \mathbf{L} makes with the z -axis.

Section 4.5 The Magnetic Moment of the Hydrogen Atom

24. Find the orbital magnetic dipole moment of an electron in the hydrogen atom when it is in the $4f$ state.
25. Find the torque acting on the magnetic dipole of an electron in the hydrogen atom when it is in the $3d$ state and is in an external magnetic field of $2.50 \times 10^{-3} \text{ T}$.
26. Find the additional potential energy of an electron in a $2p$ state when the atom is placed in an external magnetic field of 2.00 T .

Section 4.6 The Zeeman Effect

*27. Find (a) the total energy of an electron in the three $2p$ states when it is placed in an external magnetic field of 2.00 T, (b) the energy of the photons emitted when the electrons fall to the ground state, (c) the frequencies of the spectral lines associated with these transitions, and (d) the wavelengths of their spectral lines.

Section 4.7 Electron Spin

28. Calculate the magnitude of the spin magnetic dipole moment of the electron in a hydrogen atom.

29. Find the potential energy associated with the spin magnetic dipole moment of the electron in a hydrogen atom when it is placed in an external magnetic field of 2.50×10^{-3} T.

Section 4.8 The Pauli Exclusion Principle and the Periodic Table of the Elements

30. How many electrons are necessary to fill the N shell of an atom?

31. Write the electron configuration for the chemical element potassium.

32. Write the electron configuration for the chemical element iron.

33. Enumerate the quantum states (n , l , m_l , m_s) of each of the orbital electrons in the element $^{40}_{20}\text{Ca}$.

Additional Problems

34. Find the velocity of an electron in a 5.29×10^{-11} m radius orbit by (a) the Rutherford model and (b) the Bohr model of the hydrogen atom.

35. In what quantum state must an orbital electron be such that its orbital angular momentum is 4.719×10^{-34} J s (i.e., find l , the orbital angular momentum quantum number).

*4. Determine the angular momentum of the moon about the earth. (a) Use Bohr's postulate of quantization of angular momentum and determine the quantum number associated with this orbit. (b) If the quantum number n increases by 1, what is the new angular momentum of the moon? (c) What is the change in the orbital radius of the moon for this change in the quantum number? (d) Is it reasonable to neglect quantization of angular momentum for classical orbits?

37. From the frame of reference of the electron in the hydrogen atom, the proton is in an orbit about the electron and constitutes a current loop. Determine the magnitude of the magnetic field produced by the proton when the electron is in the $2p$ state.

*38. Using the results of problem 37, (a) determine the additional potential energy of an electron caused by the spin-orbit interaction. (b) Find the change in energy when electrons drop from the $2p$ state back to the ground state. (c) Find the frequencies of the emitted photons. (d) Find the wavelengths of the emitted photons.

Interactive Tutorials

39. *Bohr theory of the atom.* An electron is in a Bohr orbit with a principal quantum number $n_i = 3$, and then jumps to a final orbit for the final value $n_f = 1$, find (a) the radius of the n^{th} orbit, (b) the speed of the electron in the n^{th} orbit, (c) the energy of the electron in the initial n_i orbit, (d) the energy of the electron in the final n_f orbit, (e) the energy given up by the electron as it jumps to the lower orbit, (f) the frequency, and (g) the wavelength of the spectral line associated with the transition from the initial $n_i = 3$ state to the final $n_f = 1$ state.

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