

2

Atomic Structure and Atomic Radiation

2.1

The Atomic Nature of Matter (ca. 1900)

The work of John Dalton in the early nineteenth century laid the foundation for modern analytic chemistry. Dalton formulated and interpreted the laws of definite, multiple, and equivalent proportions, based on the existence of identical atoms as the smallest indivisible unit of a chemical element. The law of definite proportions states that in every sample of a chemical compound, the proportion by mass or weight of the constituent elements is always the same. When two elements combine to form more than one compound, the law of multiple proportions says that the proportions by mass of the different elements are always in simple ratios to one another. When two elements react completely with a third, then the ratio of the masses of the two is the same, regardless of what the third element is, a fact expressed by the law of equivalent proportions. Dalton also assumed a rule of greatest simplicity—that elements forming only a single compound do so by means of a simple one-to-one combination of atoms. This rule does not always hold.

These ideas were supported by the work of Dalton's contemporary, Gay-Lussac, on the law of combining volumes of gases. This law states that the volumes of gases that enter into chemical combination with one another are in the ratio of simple whole numbers when all volumes are measured under the same conditions of pressure and temperature. Avogadro hypothesized that equal volumes of any gases at the same pressure and temperature contain the same number of molecules. Avogadro also suggested that the molecules of some gaseous elements could be composed of two or more atoms of that element.

Today we recognize that a gram atomic weight of any element contains Avogadro's number, $N_0 = 6.022 \times 10^{23}$, of atoms.¹⁾ Furthermore, a gram molecular weight of any gas also contains N_0 molecules and occupies a volume of 22.41 L (liters) at standard temperature and pressure [STP, 0°C (=273 K on the absolute temperature scale) and 760 torr (1 torr = 1 mm Hg)]. The modern scale of atomic and molecular weights is set by stipulating that the gram atomic weight of the carbon isotope, ^{12}C , is exactly 12.000... g. A periodic chart, giving atomic numbers,

1 See Appendices A and B for physical constants, units, and conversion factors.

atomic weights, densities, and other information about the chemical elements, is shown in the back of this book.

Example

How many grams of oxygen combine with 2.3 g of carbon in the reaction $C + O_2 \rightarrow CO_2$? How many molecules of CO_2 are thus formed? How many liters of CO_2 are formed at $20^\circ C$ and 752 torr?

Solution

In the given reaction, 1 atom of carbon combines with one molecule (2 atoms) of oxygen. From the atomic weights given on the periodic chart in the back of the book, it follows that 12.011 g of carbon reacts with $2 \times 15.9994 = 31.9988$ g of oxygen. Rounding off to three significant figures, letting y represent the number of grams of oxygen asked for, and taking simple proportions, we have $y = (2.3/12.0) \times 32.0 = 6.13$ g. The number N of molecules of CO_2 formed is equal to the number of atoms in 2.3 g of C, which is $2.3/12.0$ times Avogadro's number: $N = (2.3/12.0) \times 6.02 \times 10^{23} = 1.15 \times 10^{23}$. Since Avogadro's number of molecules occupies 22.4 L at STP, the volume of CO_2 at STP is $(1.15 \times 10^{23}/6.02 \times 10^{23}) \times 22.4 = 4.28$ L. At the given higher temperature of $20^\circ C = 293$ K, the volume is larger by the ratio of the absolute temperatures, $293/273$; the volume is also increased by the ratio of the pressures, $760/752$. Therefore, the volume of CO_2 made from 2.3 g of C at $20^\circ C$ and 752 torr is $4.28 (293/273) (760/752) = 4.64$ L. This would also be the volume of oxygen consumed in the reaction under the same conditions of temperature and pressure, since 1 molecule of oxygen is used to form 1 molecule of carbon dioxide.

As mentioned in Chapter 1, mid-nineteenth century scientists could analyze light to identify the elements present in its source. Light entering an optical spectrometer is collimated by a lens and slit system, through which it is then directed toward an analyzer (e.g., a diffraction grating or prism). The analyzer disperses the light, changing its direction by an amount that depends on its wavelength. White light, for example, is spread out into the familiar rainbow of colors. Light that is dispersed at various angles with respect to the incident direction can be seen with the eye, photographed, or recorded electronically. Light from a single chemical element is observed as a series of discrete line images of the entrance slit that emerge at various angles from the analyzer. The spectrometer can be calibrated so that the angles at which the lines occur give the wavelengths of the light that appears there. Each chemical element produces its own unique, characteristic series of lines which identify it. The series is referred to as the optical, or line, spectrum of the element, or simply as the spectrum. When a number of elements are present in a light source, their spectra appear superimposed in the spectrometer, and the individual elemental spectra can be sorted out. Elements absorb light of the same wavelengths they emit.

Figure 2.1 shows the lines in the visible and near-ultraviolet spectrum of atomic hydrogen. [The wavelength of visible light is between about 4000 \AA (violet) and 7500 \AA (red).] In 1885 Balmer published an empirical formula that gives these

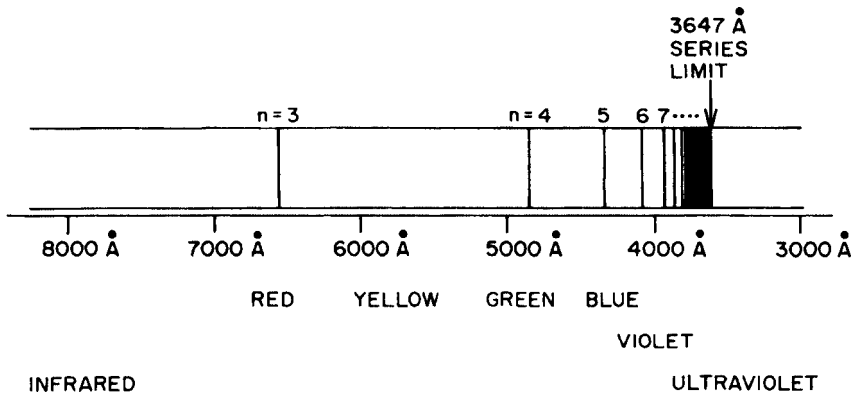


Fig. 2.1 Balmer series of lines in the spectrum of atomic hydrogen.

observed wavelengths, λ , in the hydrogen spectrum. His formula is equivalent to the following:

$$\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad (2.1)$$

where $R_{\infty} = 1.09737 \times 10^7 \text{ m}^{-1}$ is called the Rydberg constant and $n = 3, 4, 5, \dots$ represents any integer greater than 2. When $n = 3$, the formula gives $\lambda = 6562 \text{ \AA}$; when $n = 4$, $\lambda = 4861 \text{ \AA}$; and so on. The series of lines, which continue to get closer together as n increases, converges to the limit $\lambda = 3647 \text{ \AA}$ in the ultraviolet as $n \rightarrow \infty$. Balmer correctly speculated that other series might exist for hydrogen, which could be described by replacing the 2^2 in Eq. (2.1) by the square of other integers. These other series, however, lie entirely in the ultraviolet or infrared portions of the electromagnetic spectrum. We shall see in Section 2.3 how the Balmer formula (2.1) was derived theoretically by Bohr in 1913.

As mentioned in Section 1.3, J. J. Thomson in 1897 measured the charge-to-mass ratio of cathode rays, which marked the experimental “discovery” of the electron as a particle of matter. The value he found for the ratio was about 1700 times that associated with the hydrogen atom in electrolysis. One concluded that the electron was less massive than the hydrogen atom by this factor. Thomson pictured atoms as containing a large number of the negatively charged electrons in a positively charged matrix filling the volume of the electrically neutral atom. When a gas was ionized by radiation, some electrons were knocked out of the atoms in the gas molecules, leaving behind positive ions of much greater mass. Thomson’s concept of the structure of the atom is sometimes referred to as the “plum pudding” model.

2.2

The Rutherford Nuclear Atom

The existence of alpha, beta, and gamma rays was known by 1900. With the discovery of these different kinds of radiation came their use as probes to study the structure of matter itself.

Rutherford and his students, Geiger and Marsden, investigated the penetration of alpha particles through matter. Because the range of these particles is small, an energetic source and thin layers of material were employed. In one set of experiments, 7.69-MeV collimated alpha particles from ${}_{84}^{214}\text{Po}$ (RaC') were directed at a 6×10^{-5} cm thick gold foil. The relative number of particles leaving the foil at various angles with respect to the incident beam could be observed through a microscope on a scintillation screen. While most of the alpha particles passed through the foil with only slight deviation from their original direction, an occasional particle was scattered through a large angle, even backwards from the foil. About 1 in 8000 was deflected more than 90° . An enormously strong electric or magnetic field would be required to reverse the direction of the fast and relatively massive alpha particle. (In 1909 Rutherford conclusively established that alpha particles are doubly charged helium ions.) "It was about as credible as if you had fired a 15-in. shell at a piece of tissue paper and it came back and hit you," said Rutherford of this surprising discovery. He reasoned that the large-angle deflection of some alpha particles was evidence for the existence of a very small and massive nucleus, which was also the seat of the positive charge of an atom. The rare scattering of an alpha particle through a large angle could then be explained by the large repulsive force it experienced when it approached the tiny nucleus of a single atom almost head-on. Furthermore, the light electrons in an atom must move rapidly about the nucleus, filling the volume occupied by the atom. Indeed, atoms must be mostly empty space, allowing the majority of alpha particles to pass right through a foil with little or no scattering. Following these ideas, Rutherford calculated the distribution of scattering angles for the alpha particles and obtained quantitative agreement with the experimental data. In contrast to the plum pudding model, Rutherford's atom is sometimes called a planetary model, in analogy with the solar system.

Today we know that the radius of the nucleus of an atom of atomic mass number A is given approximately by the formula

$$R \cong 1.3A^{1/3} \times 10^{-15} \text{ m.} \quad (2.2)$$

The radius of the gold nucleus is $1.3(197)^{1/3} \times 10^{-15} = 7.56 \times 10^{-15}$ m. The atomic radius of gold is 1.79×10^{-10} m. The ratio of the two radii is $(7.56 \times 10^{-15} / 1.79 \times 10^{-10}) = 4.22 \times 10^{-5}$. In physical extent, the massive nucleus is only a tiny speck at the center of the atom.

Nuclear size increases with atomic mass number A . Equation (2.2) indicates that the nuclear volume is proportional to A . The so-called strong, or nuclear, forces²⁾ that hold nucleons (protons and neutrons) together in the nucleus have short ranges ($\sim 10^{-15}$ m). Nuclear forces saturate; that is, a given nucleon interacts with only a few others. As a result, nuclear size is increased in proportion as more and more nucleons are merged to form heavier atoms. The size of all atoms, in contrast, is more or less the same. All electrons in an atom, no matter how many, are attracted to the nucleus and repelled by each other. Electric forces do not saturate—all pairs of charges interact with one another.

2.3

Bohr's Theory of the Hydrogen Atom

An object that does not move uniformly in a straight line is accelerated, and an accelerated charge emits electromagnetic radiation. In view of these laws of classical physics, it was not understood how Rutherford's planetary atom could be stable. Electrons orbiting about the nucleus should lose energy by radiation and spiral into the nucleus.

In 1913 Bohr put forward a bold new hypothesis, at variance with classical laws, to explain atomic structure. His theory gave correct predictions for the observed spectra of the H atom and single-electron atomic ions, such as He^+ , but gave wrong answers for other systems, such as He and H_2^+ . The discovery of quantum mechanics in 1925 and its subsequent development has led to the modern mathematical theory of atomic and molecular structure. Although it proved to be inadequate, Bohr's theory gives useful insight into the quantum nature of matter. We shall see that a number of properties of atoms and radiation can be understood from its basic concepts and their logical extensions.

Bohr assumed that an atomic electron moves without radiating only in certain discrete orbits about the nucleus. He further assumed that the transition of the electron from one orbit to another must be accompanied by the emission or absorption of a photon of light, the photon energy being equal to the orbital energy lost or gained by the electron. In principle, Bohr's ideas thus account for the existence of discrete optical spectra that characterize an atom and for the fact that an element emits and absorbs photons of the same wavelengths.

Bohr discovered that the proper electronic energy levels, yielding the observed spectra, were obtained by requiring that the angular momentum of the electron about the nucleus be an integral multiple of Planck's constant h divided by 2π ($\hbar = h/2\pi$). (Classically, any value of angular momentum is permissible.) For an

2 The four fundamental forces in nature are (1) gravitational, (2) electromagnetic, (3) strong (nuclear), and (4) weak (responsible for beta decay). The attractive nuclear force is strong enough to overcome

the mutual Coulomb repulsion of protons in the nucleus (Section 3.1). The electromagnetic and weak forces are now recognized as a single, unified force.

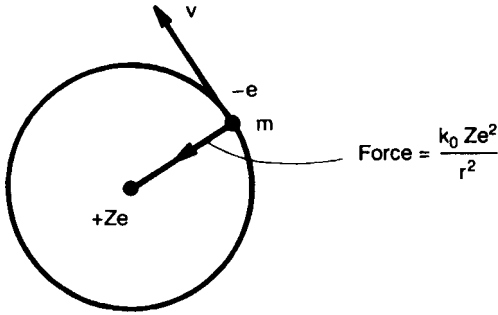


Fig. 2.2 Schematic representation of electron (mass m , charge $-e$) in uniform circular motion (speed v , orbital radius r) about nucleus of charge $+Ze$.

electron of mass m moving uniformly with speed v in a circular orbit of radius r (Fig. 2.2), we thus write

$$mvr = n\hbar, \quad (2.3)$$

where n is a positive integer, called a quantum number ($n = 1, 2, 3, \dots$). [Angular momentum, mvr , is defined in Appendix C; and $\hbar = 1.05457 \times 10^{-34}$ J s (Appendix A)]. If the electron changes from an initial orbit in which its energy is E_i to a final orbit of lower energy E_f , then a photon of energy

$$h\nu = E_i - E_f \quad (2.4)$$

is emitted, where ν is the frequency of the photon. ($E_f > E_i$ if a photon is absorbed.) Equations (2.3) and (2.4) are two succinct statements that embody Bohr's ideas quantitatively. We now use them to derive the properties of single-electron atomic systems.

When an object moves with constant speed v in a circle of radius r , it experiences an acceleration v^2/r , directed toward the center of the circle. By Newton's second law, the force on the object is mv^2/r , also directed toward the center (Problem 10). The force on the electron in Fig. 2.2 is supplied by the Coulomb attraction between the electronic and nuclear charges, $-e$ and $+Ze$. Therefore, we write for the equation of motion of the electron,

$$\frac{mv^2}{r} = \frac{k_0Ze^2}{r^2}, \quad (2.5)$$

where $k_0 = 8.98755 \times 10^9$ N m² C⁻² (Appendix C). Solving for the radius gives

$$r = \frac{k_0Ze^2}{mv^2}. \quad (2.6)$$

Solving Eq. (2.3) for v and substituting into (2.6), we find for the radii r_n of the allowed orbits

$$r_n = \frac{n^2\hbar^2}{k_0Ze^2m}. \quad (2.7)$$

Substituting values of the constants from Appendix A, we obtain

$$\begin{aligned} r_n &= \frac{n^2(1.05457 \times 10^{-34})^2}{(8.98755 \times 10^9 Z)(1.60218 \times 10^{-19})^2(9.10939 \times 10^{-31})} \\ &= 5.29 \times 10^{-11} \frac{n^2}{Z} \text{ m.} \end{aligned} \quad (2.8)$$

The innermost orbit ($n = 1$) in the hydrogen atom ($Z = 1$) thus has a radius of $5.29 \times 10^{-11} \text{ m} = 0.529 \text{ \AA}$, often referred to as the Bohr radius.

In similar fashion, eliminating r between Eqs. (2.3) and (2.6) yields the orbital velocities

$$v_n = \frac{k_0 Z e^2}{n \hbar} = 2.19 \times 10^6 \frac{Z}{n} \text{ m s}^{-1}. \quad (2.9)$$

The velocity of the electron in the first Bohr orbit ($n = 1$) of hydrogen ($Z = 1$) is $2.19 \times 10^6 \text{ m s}^{-1}$. In terms of the speed of light c , the quantity $v_1/c = k_0 e^2 / \hbar c \cong 1/137$ is called the fine-structure constant. Usually denoted by α , it determines the relativistic corrections to the Bohr energy levels, which give rise to a fine structure in the spectrum of hydrogen.

It follows that the kinetic and potential energies of the electron in the n th orbit are

$$\text{KE}_n = \frac{1}{2} m v_n^2 = \frac{k_0^2 Z^2 e^4 m}{2 n^2 \hbar^2} \quad (2.10)$$

and

$$\text{PE}_n = -\frac{k_0 Z e^2}{r_n} = -\frac{k_0^2 Z^2 e^4 m}{n^2 \hbar^2}, \quad (2.11)$$

showing that the potential energy is twice as large in magnitude as the kinetic energy (virial theorem). The total energy of the electron in the n th orbit is therefore

$$E_n = \text{KE}_n + \text{PE}_n = -\frac{k_0^2 Z^2 e^4 m}{2 n^2 \hbar^2} = -\frac{13.6 Z^2}{n^2} \text{ eV.} \quad (2.12)$$

[The energy unit, electron volt (eV), given in Appendix B, is defined as the energy acquired by an electron in moving freely through a potential difference of 1 V: $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$.] The lowest energy occurs when $n = 1$. For the H atom, this normal, or ground-state, energy is -13.6 eV ; for He^+ ($Z = 2$) it is $-13.6 \times 4 = -54.4 \text{ eV}$. The energy required to remove the electron from the ground state is called the ionization potential, which therefore is 13.6 eV for the H atom and 54.4 eV for the He^+ ion.

It remains to calculate the optical spectra for the single-electron systems based on Bohr's theory. Balmer's empirical formula (2.1) gives the wavelengths found in the visible spectrum of hydrogen. According to postulate (2.4), the energies of photons that can be emitted or absorbed are equal to the differences in the energy values given by Eq. (2.12). When the electron makes a transition from an initial orbit with

quantum number n_i to a final orbit of lower energy with quantum number n_f (i.e., $n_i > n_f$), then from Eqs. (2.4) and (2.12) the energy of the emitted photon is

$$h\nu = \frac{hc}{\lambda} = \frac{k_0^2 Z^2 e^4 m}{2\hbar^2} \left(-\frac{1}{n_i^2} + \frac{1}{n_f^2} \right), \quad (2.13)$$

where λ is the wavelength of the photon and c is the speed of light. Substituting the numerical values³ of the physical constants, one finds from Eq. (2.13) that

$$\frac{1}{\lambda} = 1.09737 \times 10^7 Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ m}^{-1}. \quad (2.14)$$

When $Z = 1$, the constant in front of the parentheses is equal to the Rydberg constant R_∞ in Balmer's empirical formula (2.1). The integer 2 in the Balmer formula is interpretable from Bohr's theory as the quantum number of the orbit into which the electron falls when it emits the photon. Derivation of the Balmer formula and calculation of the Rydberg constant from the known values of e , m , h , and c provided undeniable evidence for the validity of Bohr's postulates for single-electron atomic systems, although the postulates were totally foreign to classical physics.

Figure 2.3 shows a diagram of the energy levels of the hydrogen atom, calculated from Eq. (2.12), together with vertical lines that indicate the electron transitions that result in the emission of photons with the wavelengths shown. There are infinitely many orbits in which the electron has negative energy (bound states of the H atom). The orbital energies get closer together near the ionization threshold, 13.6 eV above the ground state. When an H atom becomes ionized, the electron is not bound and can have any positive energy. In addition to the Balmer series, Bohr's theory predicts other series, each corresponding to a different final-orbit quantum number n_f and having an infinite number of lines. The set that results from transitions of electrons to the innermost orbit ($n_f = 1$, $n_i = 2, 3, 4, \dots$) is called the Lyman series. The least energetic photon in this series has an energy

$$E = -13.6 \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = -13.6 \left(-\frac{3}{4} \right) = 10.2 \text{ eV}, \quad (2.15)$$

as follows from Eqs. (2.4) and (2.12) with $Z = 1$. Its wavelength is 1216 Å. As n_i increases, the Lyman lines get ever closer together, like those in the Balmer series, converging to the energy limit of 13.6 eV, the ionization potential of H. The photon wavelength at the Lyman series limit ($n_f = 1$, $n_i \rightarrow \infty$) is obtained from Eq. (2.14):

$$\frac{1}{\lambda} = 1.09737 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 1.09737 \times 10^7 \text{ m}^{-1}, \quad (2.16)$$

or $\lambda = 911 \text{ Å}$. The Lyman series lies entirely in the ultraviolet region of the electromagnetic spectrum. The series with $n_f \geq 3$ lie in the infrared. The shortest wavelength in the Paschen series ($n_f = 3$) is given by $1/\lambda = (1.09737 \times 10^7)/9 \text{ m}^{-1}$, or $\lambda = 8.20 \times 10^{-7} \text{ m} = 8200 \text{ Å}$.

3 For high accuracy, the *reduced* mass of the electron must be used. See last paragraph in this section.

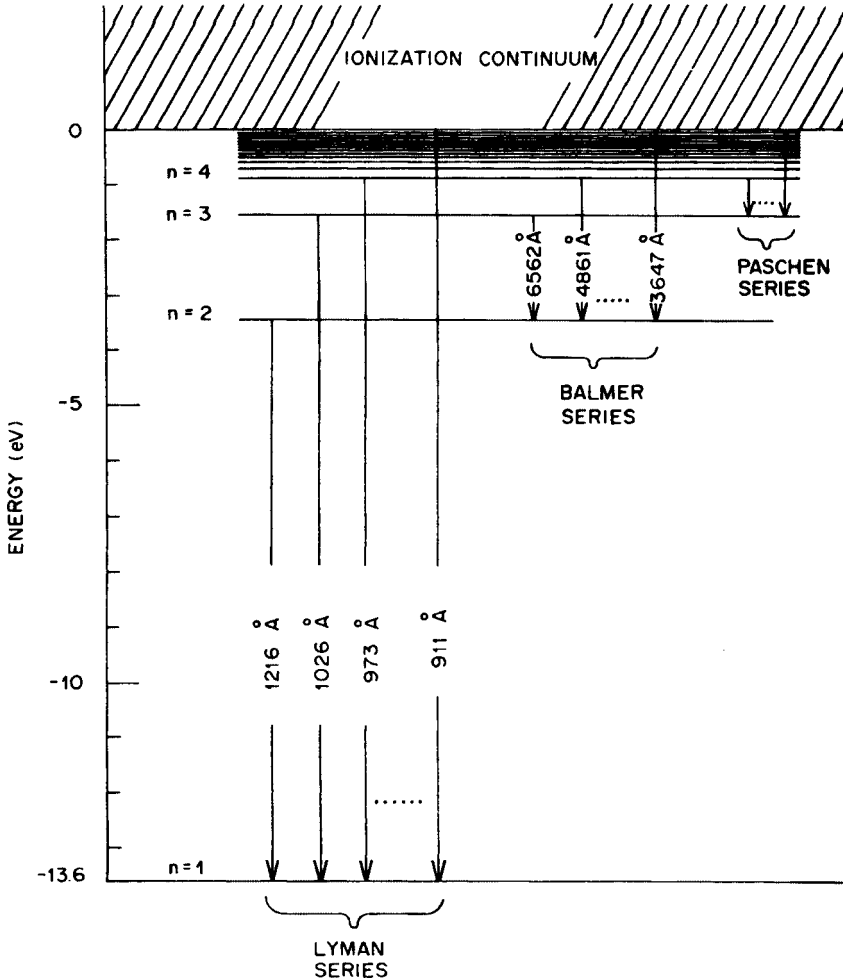


Fig. 2.3 Energy levels of the hydrogen atom. Vertical lines represent transitions that the electron can make between various levels with the associated emitted photon wavelengths shown.

Example

Calculate the wavelength of the third line in the Balmer series in Fig. 2.1. What is the photon energy in eV?

Solution

We use Eq. (2.14) with $Z = 1$, $n_f = 2$, and $n_i = 5$:

$$\frac{1}{\lambda} = 1.09737 \times 10^7 \left(\frac{1}{4} - \frac{1}{25} \right) = 2.30448 \times 10^6 \text{ m}^{-1}. \quad (2.17)$$

Thus $\lambda = 4.34 \times 10^{-7} \text{ m} = 4340 \text{ \AA}$. A photon of this wavelength has an energy

$$E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{4.34 \times 10^{-7}} = 4.58 \times 10^{-19} \text{ J}, \quad (2.18)$$

or 2.86 eV. Alternatively, we can obtain the photon energy from Eq. (2.12). The energy levels involved in the electronic transition are $13.6/4 = 3.40 \text{ eV}$ and $13.6/25 = 0.544 \text{ eV}$; their difference is 2.86 eV.

Example

What is the largest quantum number of a state of the Li^{2+} ion with an orbital radius less than 50 \AA ?

Solution

The radii of the orbits are described by Eq. (2.8) with $Z = 3$. Setting $r_n = 50 \text{ \AA} = 5 \times 10^{-9} \text{ m}$ and solving for n , we find that

$$n = \sqrt{\frac{r_n Z}{5.29 \times 10^{-11}}} = \sqrt{\frac{5 \times 10^{-9} \times 3}{5.29 \times 10^{-11}}} = 16.8. \quad (2.19)$$

A nonintegral quantum number is not defined in the Bohr theory. Equation (2.19) tells us, though, that $r_n > 50 \text{ \AA}$ when $n = 17$ and $r_n < 50 \text{ \AA}$ when $n = 16$. Therefore, $n = 16$ is the desired answer.

Example

Calculate the angular velocity of the electron in the ground state of He^+ .

Solution

With quantum number n , the angular velocity ω_n in radians s^{-1} is equal to $2\pi f_n$, where f_n is the frequency, or number of orbital revolutions of the electron about the nucleus per second. In general, $f_n = v_n/(2\pi r_n)$; and so $\omega_n = v_n/r_n$. With $n = 1$ and $Z = 2$, Eqs. (2.8) and (2.9) give $\omega_1 = v_1/r_1 = 1.66 \times 10^{17} \text{ s}^{-1}$, where the dimensionless angular unit, radian, is understood.

In deriving Eq. (2.14) it was tacitly assumed that an electron of mass m orbits about a stationary nucleus. In reality, the electron and nucleus (mass M) orbit about their common center of mass. The energy levels are determined by the relative motion of the two, in which the effective mass is the reduced mass of the system (electron plus nucleus), given by

$$m_r = \frac{mM}{m + M}. \quad (2.20)$$

For the hydrogen atom, $M = 1836m$, and so the reduced mass $m_r = 1836m/1837 = 0.9995m$ is nearly the same as the electron mass. The heavier the nucleus, the closer the reduced mass is to the electron mass. The symbol R_∞ is used to denote the

Rydberg constant for a stationary (infinitely heavy) nucleus, with $m_r = m$. Then the Rydberg constant for ions with different nuclear masses M is given by

$$R_M = \frac{R_\infty}{1 + m/M}. \quad (2.21)$$

Problem 29 shows an example in which the reduced mass plays a significant role. Problem 31 indicates how Eq. (2.20) can be derived for motion in one dimension.

2.4

Semiclassical Mechanics, 1913–1925

The success of Bohr's theory for hydrogen and single-electron ions showed that atoms are "quantized" systems. They radiate photons with the properties described earlier by Planck and by Einstein. At the same time, the failure of the Bohr theory to give correct predictions for other systems led investigators to search for a more fundamental expression of the quantum nature of atoms and radiation.

Between Bohr's 1913 theory and Heisenberg's 1925 discovery of quantum mechanics, methods of semiclassical mechanics were explored in physics. A general quantization procedure was sought that would incorporate Bohr's rules for single-electron systems and would also be applicable to many-electron atoms and to molecules. Basically, as we did above with Eq. (2.5), one used classical equations of motion to describe an atomic system and then superimposed a quantum condition, such as Eq. (2.3).

A principle of "adiabatic invariance" was used to determine which variables of a system should be quantized. It was recognized that quantum transitions occur as a result of *sudden* perturbations on an atomic system, not as a result of gradual changes. For example, the rapidly varying electric field of a passing photon can result in an electronic transition with photon absorption by a hydrogen atom. On the other hand, the electron is unlikely to make a transition if the atom is simply placed in an external electric field that is slowly increased in strength. The principle thus asserted that those variables in a system that were invariant under slow, "adiabatic" changes were the ones that should be quantized.

A generalization of Bohr's original quantum rule (2.3) was also worked out (by Wilson and Sommerfeld, independently) that could be applied to pairs of variables, such as momentum and position. So-called phase integrals were used to quantize systems after the classical laws of motion were applied.

These semiclassical procedures had some successes. For example, elliptical orbits were introduced into Bohr's picture and relativistic equations were used in place of the nonrelativistic Eq. (2.5). The relativistic theory predicted a split in some atomic energy levels with the same quantum number, the magnitude of the energy difference depending on the fine-structure constant. The existence of the split gives rise to a fine structure in the spectrum of most elements in which some "lines" are observed under high resolution to be two closely separated lines. The well-known doublet in the sodium spectrum, consisting of two yellow lines at 5890 Å

and 5896 Å, is due to transitions from two closely spaced energy levels, degenerate in nonrelativistic theory. In spite of its successes in some areas, semiclassical atomic theory did not work for many-electron atoms and for such simple systems as some diatomic molecules, for which it gave unambiguous but incorrect spectra.

As a guide for discovering quantum laws, Bohr in 1923 introduced his correspondence principle. This principle states that the predictions of quantum physics must be the same as those of classical physics in the limit of very large quantum number n . In addition, any relationships between states that are needed to obtain the classical results for large n also hold for all n . The diagram of energy levels in Fig. 2.3 illustrates the approach of a quantum system to a classical one when the quantum numbers become very large. Classically, the electron in a bound state has continuous, rather than discrete, values of the energy. As $n \rightarrow \infty$, the bound-state energies of the H atom get arbitrarily close together.

Advances toward the discovery of quantum mechanics were also being made along other lines. The classical Maxwellian wave theory of electromagnetic radiation seemed to be at odds with the existence of Einstein's corpuscular photons of light. How could light act like waves in some experiments and like particles in others? The diffraction and interference of X rays was demonstrated in 1912 by von Laue, thus establishing their wave nature. The Braggs used X-ray diffraction from crystal layers of known separation to measure the wavelength of X rays. In 1922, discovery of the Compton effect (Section 8.4)—the scattering of X-ray photons from atoms with a decrease in photon energy—demonstrated their nonwave, or corpuscular, nature in still another way. The experimental results were explained by assuming that a photon of energy E has a momentum $p = E/c = h\nu/c$, where ν is the photon frequency and c is the speed of light. In 1924, de Broglie proposed that the wave/particle dualism recognized for photons was a characteristic of all fundamental particles of nature. An electron, for example, hitherto regarded as a particle, also might have wave properties associated with it. The universal formula that links the property of wavelength, λ , with the particle property of momentum, p , is that which applies to photons: $p = h\nu/c = h/\lambda$. Therefore, de Broglie proposed that the wavelength associated with a particle be given by the relation

$$\lambda = \frac{h}{p} = \frac{h}{\gamma mv}, \quad (2.22)$$

where m and v are rest mass and speed of the particle and γ is the relativistic factor defined in Appendix C.

Davisson and Germer in 1927 published the results of their experiments, which demonstrated that a beam of electrons incident on a single crystal of nickel is diffracted by the regularly spaced crystal layers of atoms. Just as the Braggs measured the wavelength of X rays from crystal diffraction, Davisson and Germer measured the wavelength for electrons. They found excellent agreement with Eq. (2.22). The year before this experimental confirmation of the existence of electron waves, Schroedinger had extended de Broglie's ideas and developed his wave equation for the new quantum mechanics, as described in the next section.

A convenient formula can be used to obtain the wavelength λ of a non-relativistic electron in terms of its kinetic energy T . (An electron is nonrelativistic as long as T is small compared with its rest energy, $mc^2 = 0.511$ MeV.) The nonrelativistic formula relating momentum p and kinetic energy T is $p = \sqrt{2mT}$ (Appendix C). It follows from Eq. (2.22) that

$$\lambda = \frac{h}{\sqrt{2mT}}. \quad (2.23)$$

It is often convenient to express the wavelength in \AA and the energy in eV. Using these units for λ and T in Eq. (2.23), we write

$$\lambda_{\text{\AA}} \times 10^{-10} = \frac{6.6261 \times 10^{-34}}{\sqrt{2 \times 9.1094 \times 10^{-31} \times T_{\text{eV}} \times 1.6022 \times 10^{-19}}}, \quad (2.24)$$

or

$$\lambda_{\text{\AA}} = \frac{12.264}{\sqrt{T_{\text{eV}}}} = \frac{12.3}{\sqrt{T_{\text{eV}}}}. \quad (\text{Nonrelativistic electrons}) \quad (2.25)$$

The subscripts indicate the units for λ and T when this formula is used.

An analogous expression can be derived for photons. Since the photon energy is given by $E = h\nu$, the wavelength is $\lambda = c/\nu = hc/E$. Analogously to Eq. (2.25), we find

$$\lambda_{\text{\AA}} = \frac{12398}{E_{\text{eV}}} = \frac{12400}{E_{\text{eV}}}. \quad (\text{Photons}) \quad (2.26)$$

Example

In some of their experiments, Davisson and Germer used electrons accelerated through a potential difference of 54 V. What is the de Broglie wavelength of these electrons?

Solution

The nonrelativistic formula (2.25) gives, with $T_{\text{eV}} = 54$ eV, $\lambda_{\text{\AA}} = 12.3/\sqrt{54} = 1.67$ \AA . Electron wavelengths much smaller than optical ones are readily obtainable. This is the basis for the vastly greater resolving power that electron microscopes have over optical microscopes (wavelengths $\gtrsim 4000$ \AA).

Example

Calculate the de Broglie wavelength of a 10-MeV electron.

Solution

We must treat the problem relativistically. We thus use Eq. (2.22) after determining γ and v . From Appendix C, with $T = 10$ MeV and $mc^2 = 0.511$ MeV, we have

$$10 = 0.511(\gamma - 1), \quad (2.27)$$

giving $\gamma = 20.6$. We can compute ν directly from γ . In this example, however, we know that ν is very nearly equal to c . Using $\nu = c$ in Eq. (2.22), we therefore write

$$\lambda = \frac{h}{\gamma mc} = \frac{6.63 \times 10^{-34}}{20.6 \times 9.11 \times 10^{-31} \times 3 \times 10^8} = 1.18 \times 10^{-13} \text{ m.} \quad (2.28)$$

For the last example one can, alternatively, derive the relativistic form of Eq. (2.25) for electrons. The result is (Problem 42)

$$\lambda_{\text{\AA}} = \frac{12.264}{\sqrt{T_{\text{eV}} \left(1 + \frac{T_{\text{eV}}}{1.022 \times 10^6} \right)}}. \quad (\text{Relativistic electrons}) \quad (2.29)$$

The last term in the denominator is $T_{\text{eV}}/(2mc^2)$ and is, therefore, not important when the electron's kinetic energy can be neglected compared with its rest energy. Equation (2.29) then becomes identical with Eq. (2.25).

Also, in the period just before the discovery of quantum mechanics, Pauli formulated his famous exclusion principle. This rule can be expressed by stating that no two electrons in an atom can have the same set of four quantum numbers. We shall discuss the Pauli principle in connection with the periodic system of the elements in Section 2.6.

2.5

Quantum Mechanics

Quantum mechanics was discovered by Heisenberg in 1925 and, from a completely different point of view, independently by Schroedinger at about the same time. Heisenberg's formulation is termed matrix mechanics and Schroedinger's is called wave mechanics. Although they are entirely different in their mathematical formulation, Schroedinger showed in 1926 that the two systems are completely equivalent and lead to the same results. We shall discuss each in turn.

Heisenberg associated the failure of the Bohr theory with the fact that it was based on quantities that are not directly observable, like the classical position and speed of an electron in orbit about the nucleus. He proposed a system of mechanics based on observable quantities, notably the frequencies and intensities of the lines in the emission spectrum of atoms and molecules. He then represented dynamical variables (e.g., the position x of an electron) in terms of observables and worked out rules for representing x^2 when the representation for x is given. In so doing, Heisenberg found that certain pairs of variables did not commute multiplicatively (i.e., $xp \neq px$ when x and p represent position and momentum in the direction of x), a mathematical property of matrices recognized by others after Heisenberg's original formulation. Heisenberg's matrix mechanics was applied to various systems and gave results that agreed with those predicted by Bohr's theory where the latter was consistent with experiment. In other instances it gave new theoretical predictions that also agreed with observations. For example, Heisenberg explained the

pattern of alternating strong and weak lines in the spectra of diatomic molecules, a problem in which Bohr's theory had failed. He showed that two forms of molecular hydrogen should exist, depending on the relative directions of the proton spin, and that the form with spins aligned (ortho-hydrogen) should be three times as abundant as the other with spins opposed (para-hydrogen). This discovery was cited in the award of the 1932 Nobel Prize in physics to Heisenberg.

The concept of building an atomic theory on observables and its astounding successes led to a revolution in physics. In classical physics, objects move with certain endowed properties, such as position and velocity at every moment in time. If one knows these two quantities at any one instant and also the total force that an object experiences, then its motion is determined completely for all times by Newton's second law. Such concepts are applied in celestial mechanics, where the positions of the planets can be computed backwards and forwards in time for centuries. The same determinism holds for the motion of familiar objects in everyday life. However, on the atomic scale, things are inherently different. In an experiment that would measure the position and velocity of an electron in orbit about a nucleus, the act of measurement itself introduces uncontrollable perturbations that prevent one's obtaining all the data precisely. For example, photons of very short wavelength would be required to localize the position of an electron within an atomic dimension. Such photons impart high momentum in scattering from an electron, thereby making simultaneous knowledge of the electron's position and momentum imprecise.

In 1927 Heisenberg enunciated the uncertainty principle, which sets the limits within which certain pairs of quantities can be known simultaneously. For momentum p and position x (in the direction of the momentum) the uncertainty relation states that

$$\Delta p \Delta x \geq \hbar. \quad (2.30)$$

Here Δp and Δx are the uncertainties (probable errors) in these quantities, determined simultaneously; the product of the two can never be smaller than \hbar , which it can approach under optimum conditions. Another pair of variables consists of energy E and time t , for which

$$\Delta E \Delta t \geq \hbar. \quad (2.31)$$

The energy of a system cannot be measured with arbitrary precision in a very short time interval. These uncertainties are not due to any shortcomings in our measuring ability. They are a result of the recognition that only observable quantities have an objective meaning in physics and that there are limits to making measurements on an atomic scale. The question of whether an electron "really" has a position and velocity simultaneously—whether or not we try to look—is metaphysical. Schools of philosophy differ on the fundamental nature of our universe and the role of the observer.

Whereas observation is immaterial to the future course of a system in classical physics, the observer's role is a basic feature of quantum mechanics, a formalism based on observables. The uncertainty relations rule out classical determinism

for atomic systems. Knowledge obtained from one measurement, say, of an electron's orbital position, will not enable one to predict with certainty the result of a second measurement of the orbital position. Instead of this determinism, quantum mechanics enables one to predict only the *probabilities* of finding the electron in various positions when the second measurement is made. Operationally, such a probability distribution can be measured by performing an experiment a large number of times under identical conditions and compiling the frequency distribution of the different results. The laws of quantum mechanics are definite, but they are statistical, rather than deterministic, in nature. As an example of this distinction, consider a sample of 10^{16} atoms of a radioactive isotope that is decaying at an average rate of 10^4 atoms per second. We cannot predict which particular atoms will decay during any given second nor can we say exactly how many will do so. However, we can predict with assurance the probability of obtaining any given number of counts (e.g., 10,132) in a given second, as can be checked by observation.

Example

What is the minimum uncertainty in the momentum of an electron that is localized within a distance $\Delta x = 1 \text{ \AA}$, approximately the diameter of the hydrogen atom? How large can the kinetic energy of the electron be, consistent with this uncertainty?

Solution

The relation (2.30) requires that the uncertainty in the momentum be at least as large as the amount

$$\Delta p \cong \frac{\hbar}{\Delta x} = \frac{1.05 \times 10^{-34} \text{ J s}}{10^{-10} \text{ m}} \sim 10^{-24} \text{ kg m s}^{-1}. \quad (2.32)$$

To estimate how large the kinetic energy of the electron can be, we note that its momentum p can be as large as Δp . With $p \sim \Delta p$, the kinetic energy T of the electron (mass m) is

$$T = \frac{p^2}{2m} \sim \frac{(10^{-24})^2}{2 \times 9.11 \times 10^{-31}} \sim 5 \times 10^{-19} \text{ J}, \quad (2.33)$$

or about 3 eV. This analysis indicates that an electron confined within a distance $\Delta x \sim 1 \text{ \AA}$ will have a kinetic energy in the eV range. In the case of the H atom we saw that the electron's kinetic energy is 13.6 eV. The uncertainty principle implies that electrons confined to even smaller regions become more energetic, as the next example illustrates.

Example

If an electron is localized to within the dimensions of an atomic nucleus, $\Delta x \sim 10^{-15} \text{ m}$, estimate its kinetic energy.

Solution

In this case, we have $p \sim \Delta p \sim \hbar/\Delta x \sim 10^{-34}/10^{-15} \sim 10^{-19} \text{ kg m s}^{-1}$. Comparison with the last example ($p \sim 10^{-24} \text{ kg m s}^{-1}$) indicates that we must use the relativistic

formula to find the kinetic energy from the momentum in this problem (Appendix C). The total energy E_T of the electron is given by

$$E_T^2 = p^2 c^2 + m^2 c^4 \quad (2.34)$$

$$= (10^{-19})^2 (3 \times 10^8)^2 + (9 \times 10^{-31})^2 (3 \times 10^8)^4 \quad (2.35)$$

$$= 9 \times 10^{-22} \text{ J}^2, \quad (2.36)$$

from which we obtain $E_T \sim 200$ MeV. It follows that electrons in atomic nuclei would have energies of hundreds of MeV. Before the discovery of the neutron in 1932 it was speculated that a nucleus of atomic number Z and atomic mass number A consists of A protons and $A - Z$ electrons. The uncertainty principle argued against such a picture, since maximum beta-particle energies of only a few MeV are found. (In addition, some nuclear spins would be different from those observed if electrons existed in the nucleus.) The beta particle is created in the nucleus at the time of decay.

We turn now to Schroedinger's wave mechanics. Schroedinger began with de Broglie's hypothesis (Eq. 2.22) relating the momentum and wavelength of a particle. He introduced an associated oscillating quantity, ψ , and constructed a differential equation for it to satisfy. The coefficients in the equation involve the constants h and the mass and charge of the particle. Equations describing waves are well known in physics. Schroedinger's wave equation is a linear differential equation, second order in the spatial coordinates and first order in time. It is linear, so that the sum of two or more solutions is also a solution. Linearity thus permits the superposition of solutions to produce interference effects and the construction of wave packets to represent particles. The wave-function solution ψ must satisfy certain boundary conditions, which lead to discrete values, called eigenvalues, for the energies of bound atomic states. Applied to the hydrogen atom, Schroedinger's wave equation gave exactly the Bohr energy levels. It also gave correct results for the other systems to which it was applied. Today it is widely used to calculate the properties of many-electron atomic and molecular systems, usually by numerical solution on a computer.

A rough idea can be given of how wave mechanics replaces Bohr's picture of the H atom. Instead of the concept of the electron moving in discrete orbits about the nucleus, we envision the electron as being represented by an oscillating cloud. Furthermore, the electron cloud oscillates in such a way that it sets up a standing wave about the nucleus. A familiar example of standing waves is provided by a vibrating string of length L stretched between two fixed points P_1 and P_2 , as illustrated in Fig. 2.4. Standing waves are possible only with wavelengths λ given by

$$L = n \frac{\lambda}{2}, \quad n = 1, 2, 3, \dots \quad (2.37)$$

This relation describes a discrete set of wavelengths λ . In an analogous way, an electron standing-wave cloud in the H atom can be envisioned by requiring that an integral number of wavelengths $n\lambda$ fit exactly into a circumferential distance $2\pi r$ about the nucleus: $2\pi r = n\lambda$. Using the de Broglie relation (2.22) then implies

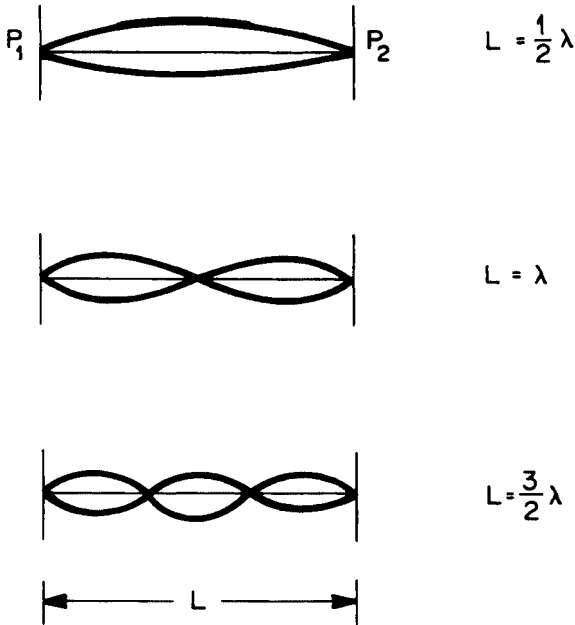


Fig. 2.4 Examples of standing waves in string of length L stretched between two fixed points P_1 and P_2 . Such waves exist only with discrete wavelengths given by $\lambda = 2L/n$, where $n = 1, 2, 3, \dots$

nonrelativistically ($\gamma = 1$) that $2\pi r = nh/mv$, or $mvr = n\hbar$. One thus arrives at Bohr's original quantization law, Eq. (2.3).

Schroedinger's wave equation is nonrelativistic, and he proposed a modification of it in 1926 to meet the relativistic requirement for symmetry between space and time. As mentioned earlier, the Schroedinger differential equation is second order in space and first order in time variables. His relativistic equation, which contained the second derivative with respect to time, led to a fine structure in the hydrogen spectrum, but the detailed results were wrong. Taking a novel approach, Dirac proposed a wave equation that was first order in both the space and time variables. In 1928 Dirac showed that the new equation automatically contained the property of intrinsic angular momentum for the electron, rotating about its own axis. The predicted value of the electron's spin angular momentum was $\hbar/2$, the value ascribed experimentally in 1925 by Uhlenbeck and Goudsmit to account for the structure of the spectra of the alkali metals. Furthermore, the fine structure of the hydrogen-atom spectrum came out correctly from the Dirac equation. Dirac's equation also implied the existence of a positive electron, found later by Anderson, who discovered the positron in cosmic radiation in 1932. In 1927 Dirac also laid the foundation for quantum electrodynamics—the modern theory of the emission and absorption of electromagnetic radiation by atoms. The reader is referred to the historical outline in Section 1.3 for a chronology of events that occurred with the discovery of quantum mechanics.

2.6

The Pauli Exclusion Principle

Originally based on the older, semiclassical quantum theory, the Pauli exclusion principle plays a vital role in modern quantum mechanics. The principle was developed for electrons in orbital states in atoms. It holds that no two electrons in an atom can be in the same state, characterized by four quantum numbers which we now define. The Pauli principle enables one to use atomic theory to account for the periodic system of the chemical elements.

In the Bohr theory with circular orbits, described in Section 2.3, only a single quantum number, n , was used. This is the first of the four quantum numbers, and we designate it as the principal quantum number. In Bohr's theory each value of n gives an orbit at a given distance from the nucleus. For an atom with many electrons, we say that different values of n correspond to different electron shells. Each shell can accommodate only a limited number of electrons. In developing the periodic system, we postulate that, as more and more electrons are present in atoms of increasing atomic number, they fill the innermost shells. The outer-shell electrons determine the gross chemical properties of an element; these properties are thus repeated successively after each shell is filled. When $n = 1$, the shell is called the K shell; $n = 2$ denotes the L shell; $n = 3$, the M shell; and so on.

The second quantum number arises in the following way. As mentioned in Section 2.4, elliptical orbits and relativistic mechanics were also considered in the older quantum theory of the hydrogen atom. In nonrelativistic mechanics, the mean energy of an electron is the same for all elliptical orbits having the same major axis. Furthermore, the mean energy is the same as that for a circular orbit with a diameter equal to the major axis. (The circle is the limiting case of an ellipse with equal major and minor axes.) Relativistically, the situation is different because of the increase in velocity and hence mass that an electron experiences in an elliptical orbit when it comes closest to the nucleus. In 1916 Sommerfeld extended Bohr's theory to include elliptical orbits with the nucleus at one focus. The formerly degenerate energies of different ellipses with the same major axis are slightly different relativistically, giving rise to the fine structure in the spectra of elements. The observed fine structure in the hydrogen spectrum was obtained by quantizing the ratio of the major and minor axes of the elliptical orbits, thus providing a second quantum number, called the azimuthal quantum number. In modern theory it amounts to the same thing as the orbital angular-momentum quantum number, l , with values $l = 0, 1, 2, \dots, n-1$. Thus, for a given shell, the second quantum number can be any non-negative integer smaller than the principal quantum number. When $n = 1$, $l = 0$ is the only possible azimuthal quantum number; when $n = 2$, $l = 0$ and $l = 1$ are both possible.

The magnetic quantum number m is the third. It was introduced to account for the splitting of spectral lines in a magnetic field (Zeeman effect). An electron orbiting a nucleus constitutes an electric current, which produces a magnetic field. When an atom is placed in an external magnetic field, its own orbital magnetic

field lines up only in certain discrete directions with respect to the external field. The magnetic quantum number gives the component of the orbital angular momentum in the direction of the external field. Accordingly, m can have any integral value between $+l$ and $-l$; viz., $m = 0, \pm 1, \pm 2, \dots, \pm l$. With $l = 1$, for example, $m = -1, 0, 1$.

Although the Bohr–Sommerfeld theory explained a number of features of atomic spectra, problems still persisted. Unexplained was the fact that the alkali-metal spectra (e.g., Na) show a doublet structure even though these atoms have only a single valence electron in their outer shell (as we show in the next section). In addition, spectral lines do not split into a normal pattern in a weak magnetic field (anomalous Zeeman effect). These problems were cleared up when Pauli introduced a fourth quantum number of “two-valuedness,” having no classical analogue. Then, in 1925, Uhlenbeck and Goudsmit proposed that the electron has an intrinsic angular momentum $\frac{1}{2}\hbar$ due to rotation about its own axis; thus the physical significance of Pauli’s fourth quantum number was evident. The electron’s intrinsic spin endows it with magnetic properties. The spin quantum number, s , has two values, $s = \pm\frac{1}{2}$. In an external magnetic field, the electron aligns itself either with “spin up” or “spin down” with respect to the field direction.

The Pauli exclusion principle states that no two electrons in an atom can occupy a state with the same set of four quantum numbers n, l, m , and s . The principle can also be expressed equivalently, but more generally, by saying that no two electrons in a system can have the same complete set of quantum numbers. Beyond atomic physics, the Pauli exclusion principle applies to all types of identical particles of half-integral spin (called fermions and having intrinsic angular momentum $\frac{1}{2}\hbar$, $\frac{3}{2}\hbar$, etc.). Such particles include positrons, protons, neutrons, muons, and others. Integral-spin particles (called bosons) do not obey the exclusion principle. These include photons, alpha particles, pions, and others.

We next apply the Pauli principle as a basis for understanding the periodic system of the elements.

2.7

Atomic Theory of the Periodic System

The K shell, with $n = 1$, can contain at most two electrons, since $l = 0$, $m = 0$, and $s = \pm\frac{1}{2}$ are the only possible values of the other three quantum numbers. The two electrons in the K shell differ only in their spin directions. The element with atomic number $Z = 2$ is the noble gas helium. Like the other noble-gas atoms it has a completed outer shell and is chemically inert. The electron configurations of H and He are designated, respectively, as $1s^1$ and $1s^2$. The symbols in the configurations give the principal quantum number, a letter designating the azimuthal quantum number (s denotes $l = 0$; p denotes $l = 1$; d , $l = 2$; and f , $l = 3$), and a superscript giving the total number of electrons in the states with the given values of n and l . The electron configurations of each element are shown in the periodic table in the

back of this book, to which the reader is referred in this discussion. The first period contains only hydrogen and helium.

The next element, Li, has three electrons. Two occupy the full K shell and the third occupies a state in the L shell ($n = 2$). Electrons in this shell can have $l = 0$ (s states) or $l = 1$ (p states). The 2s state has lower energy than the 2p, and so the electron configuration of Li is $1s^2 2s^1$. With $Z = 4$ (Be), the other 2s state is occupied, and the configuration is $1s^2 2s^2$. No additional s electrons ($l = 0$) can be added in these two shells. However, the L shell can now accommodate electrons with $l = 1$ (p electrons) and with three values of m : $-1, 0, +1$. Since two electrons with opposite spins (spin quantum numbers $\pm \frac{1}{2}$) can occupy each state of given n, l , and m , there can be a total of six electrons in the 2p states. The configurations for the next six elements involve the successive filling of these states, from $Z = 5$ (B), $1s^2 2s^2 p^1$, to $Z = 10$ (Ne), $1s^2 2s^2 p^6$. The noble gas neon has the completed L shell. To save repeating the writing of the identical inner-shell configurations for other elements, one denotes the neon configuration by [Ne]. The second period of the table begins with Li and ends with Ne.

With the next element, sodium, the filling of the M shell begins. Sodium has a 3s electron and its configuration is $[\text{Ne}]3s^1$. Its single outer-shell electron gives it properties akin to those of lithium. One sees that the other alkali metals in the group IA of the periodic table are all characterized by having a single s electron in their outer shell. The third period ends with the filling of the $3s^2 p^6$ levels in the noble gas, Ar ($Z = 18$). The chemical and physical properties of the eight elements in the third period are similar to those of the eight elements in the second period with the same outer-shell electron configurations.

The configuration of Ar ($Z = 18$), which is $[\text{Ne}]3s^2 p^6$, is also designated as [Ar]. All of the states with $n = 1, l = 0$; $n = 2, l = 0, 1$; and $n = 3, l = 0, 1$ are occupied in Ar. However, the M shell is not yet filled, because d states ($l = 2$) are possible when $n = 3$. Because there are five values of m when $l = 2$, there are five d states, which can accommodate a total of ten electrons (five pairs with opposite spin), which is the number needed to complete the M shell. It turns out that the 4s energy levels are lower than the 3d. Therefore, the next two elements, K and Ca, that follow Ar have the configurations $[\text{Ar}]4s^1$ and $[\text{Ar}]4s^2$. The next ten elements, from Sc ($Z = 21$) through Zn ($Z = 30$), are known as the transition metals. This series fills the 3d levels, sometimes in combination with $4s^1$ and sometimes with $4s^2$ electrons. The configuration of Zn is $[\text{Ar}]3d^{10} 4s^2$, at which point the M shell ($n = 3$) is complete. The next six elements after Zn fill the six 4p states, ending with the noble gas, Kr, having the configuration $[\text{Ar}]3d^{10} 4s^2 p^6$.

After Ar, the shells with a given principal quantum number do not get filled in order. Nevertheless, one can speak of the filling of certain subshells in order, such as the 4s subshell and then the 3d in the transition metals. The lanthanide series of rare-earth elements, from $Z = 58$ (Ce) to $Z = 71$ (Lu), occurs when the 4f subshell is being filled. For these states $l = 3$, and since $-3 \leq m \leq 3$, a total of $7 \times 2 = 14$ elements compose the series. Since it is an inner subshell that is being filled, these elements all have very nearly the same chemical properties. The situation is

repeated with the actinide elements from $Z = 90$ (Th) to $Z = 103$ (Lr), in which the 5f subshell is being filled.

The picture given here is that of an independent-electron model of the atom, in which each electron independently occupies a given state. In reality, the atomic electrons are indistinguishable from one another and an atomic wave function is one in which any electron can occupy any state with the same probability as any other electron. Moreover, hybrid atomic states of mixed configurations are used to explain still other phenomena (e.g., the tetrahedral bonds in CH_4).

2.8

Molecules

Quantum mechanics has also been very successful in areas other than atomic structure and spectroscopy. It has also explained the physics of molecules and condensed matter (liquids and solids). Indeed, the nature of the chemical bond between two atoms, of either the same or different elements, is itself quantum mechanical in nature, as we now describe.

Consider the formation of the H_2 molecule from two H atoms. Experimentally, it is known from the vibrational spectrum of H_2 that the two protons' separation oscillates about an equilibrium distance of 0.74 \AA and the dissociation energy of the molecule is 4.7 eV . The two electrons move very rapidly about the two nuclei, which, by comparison, move slowly back and forth along the direction between their centers. When the nuclei approach each other, their Coulomb repulsion causes them to reverse their directions and move apart. The electrons more than keep pace and move so that the separating nuclei again reverse directions and approach one another. Since the electrons move so quickly, they make many passes about the nuclei during any time in which the latter move appreciably. Therefore, one can gain considerable insight into the structure of H_2 and other molecules by considering the electronic motion at different fixed separations of the nuclei (Born-Oppenheimer approximation).

To analyze H_2 , we begin with the two protons separated by a large distance R , as indicated in Fig. 2.5(a). The lowest energy of the system will then occur when each electron is bound to one of the protons. Thus the ground state of the H_2 system at large nuclear separations is that in which the two hydrogen atoms, H_A and H_B , are present in their ground states. We denote this structure by writing $(\text{H}_A 1, \text{H}_B 2)$, indicating that electron number one is bound in the hydrogen atom H_A and electron number two in H_B . Another stable structure at large R is an ionic one, $(\text{H}_A 12^-, \text{H}_B^+)$, in which both electrons orbit one of the protons. This structure is shown in Fig. 2.5(b). Since 13.6 eV is required to remove an electron from H and its binding energy in the H^- ion is only 0.80 eV , the ionic structure in Fig. 2.5(b) has less binding energy than the natural one in (a). In addition to the states shown in the figure, one can consider the same two structures in which the two electrons are interchanged, $(\text{H}_A 2, \text{H}_B 1)$ and $(\text{H}_A 21^-, \text{H}_B^+)$.

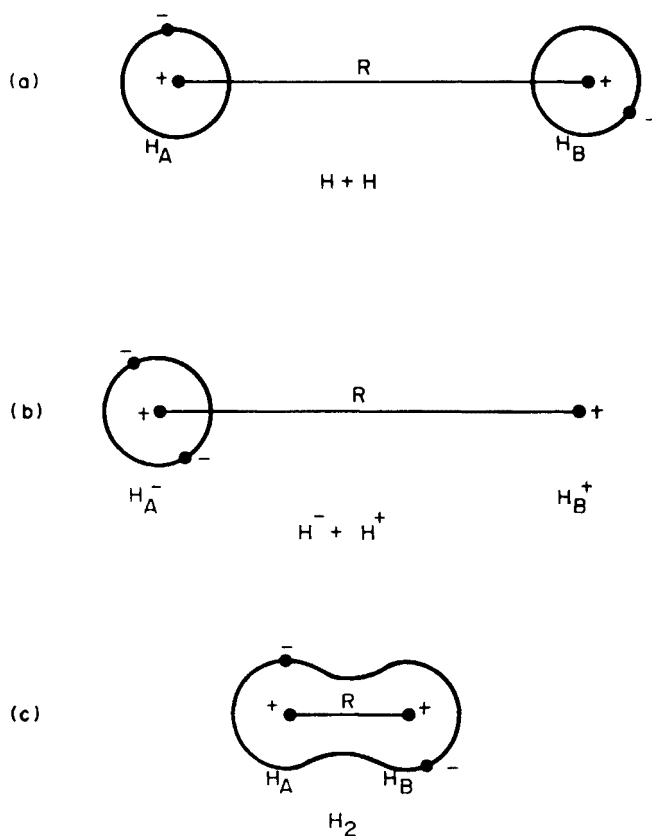


Fig. 2.5 At large internuclear separation R , the structure of the H_2 molecule can approach (a) that of two neutral H atoms, $H + H$, or (b) that of two ions, $H^- + H^+$. These structures merge at close separations in (c). The indistinguishability of the two electrons gives stability to the bond formed through the quantum-mechanical phenomenon of resonance.

Next, we consider what happens when R becomes smaller. When the nuclei move close together, as in Fig. 2.5(c), the electron wave functions associated with each nucleus overlap. Detailed calculations show that neither of the structures shown in Fig. 2.5(a) or (b) nor a combination of the two leads to the formation of a stable molecule. Instead, stability arises from the indistinguishable participation of both electrons. The neutral structure alone will bind the two atoms when, in place of either (H_{A1}, H_{B2}) or (H_{A2}, H_{B1}) alone, one uses the superposed structure $(H_{A1}, H_{B2}) + (H_{A2}, H_{B1})$. The need for the superposed structure is a purely quantum-mechanical concept, and is due to the fact that the two electrons are indistinguishable and their roles must be exchangeable without affecting observable quantities. The energy contributed to the molecular binding by the electron exchange is called the resonance energy, and its existence with the neutral structure in Fig. 2.5(c) accounts for $\sim 80\%$ of the binding energy of H_2 . The type of electron-pair bond that

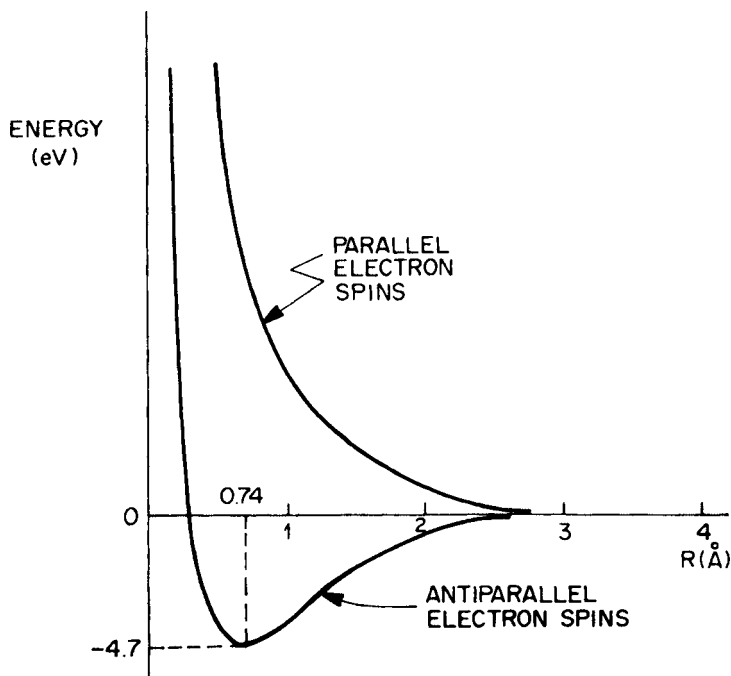


Fig. 2.6 Total energy of the H_2 molecule as a function of internuclear separation R . A stable molecule is formed when the spins of the two electrons are antiparallel. A nonbonding energy level is formed when the spins are parallel. The two energies coincide at large R .

is thus formed by the exchange is called covalent. Resonance also occurs between the ionic structures ($H_A 12^-, H_B^+$) and ($H_A 21^-, H_B^+$) from Fig. 2.5(b) and contributes $\sim 5\%$ of the binding energy, giving the H_2 bond a small ionic character. The remaining 15% of the binding energy comes from other effects, such as deformation of the electron wave functions from the simple structures discussed here and from partial shielding of the nuclear charges by each electron from the other. In general, for covalent bonding to occur, the two atoms involved must have the same number of unpaired electrons, as is the case with hydrogen. However, the atoms need not be identical.

The character of the bond in HF and HCl, for example, is more ionic than in the homonuclear H_2 or N_2 . The charge distribution in a heteronuclear diatomic molecule is not symmetric, and so the molecule has a permanent electric dipole moment. (The two types of bonds are called homopolar and heteropolar.)

Figure 2.6 shows the total energy of the H_2 molecule as a function of the internuclear separation R . (The total energy of the two H atoms at large R is taken as the reference level of zero energy.) The bound state has a minimum energy of -4.7 eV at the equilibrium separation of 0.74 Å, in agreement with the data given earlier in this section. In this state the spins of the bonding electron pair are antiparallel.

A second, nonbonding state is formed with parallel spins. These two energy levels are degenerate at large R , where the wave functions of the two atomic electrons do not overlap appreciably.

Molecular spectra are very complicated. Changes in the rotational motion of molecules accompany the emission or absorption of photons in the far infrared. Vibrational changes together with rotational ones usually produce spectra in the near infrared. Electronic transitions are associated with the visible and ultraviolet part of molecular spectra. Electronic molecular spectra have a fine structure due to the vibrational and rotational motions of the molecule. Molecular spectra also show isotopic structure. The presence of the naturally occurring ^{35}Cl and ^{37}Cl isotopes in chlorine, for example, gives rise to two sets of vibrational and rotational energy-level differences in the spectrum of HCl.

2.9

Solids and Energy Bands

We briefly discuss the properties of solids and the origin of energy bands, which are essential for understanding how semiconductor materials can be used as radiation detectors (Chapter 10).

Solids can be crystalline or noncrystalline (e.g., plastics). Crystalline solids, of which semiconductors are an example, can be put into four groups according to the type of binding that exists between atoms. Crystals are characterized by regular, repeated atomic arrangements in a lattice.

In a *molecular* solid the bonds between molecules are formed by the weak, attractive van der Waals forces. Examples are the noble gases, H_2 , N_2 , and O_2 , which are solids only at very low temperatures and can be easily deformed and compressed. All electrons are paired and hence molecular solids are poor electrical conductors.

In an *ionic* solid all electrons are also paired. A crystal of NaCl, for example, exists as alternating charged ions, Na^+ and Cl^- , in which all atomic shells are filled. These solids are also poor conductors. The electrostatic forces between the ions are very strong, and hence ionic solids are hard and have high melting points. They are generally transparent to visible light, because their electronic absorption frequencies are in the ultraviolet region and lattice vibration frequencies are in the infrared.

A *covalent* solid is one in which adjacent atoms are covalently bound by shared valence electrons. Such bonding is possible only with elements in Group IVB of the periodic system; diamond, silicon, and germanium are examples. In diamond, a carbon atom (electronic configuration $1s^2 2s^2 2p^2$) shares one of its four L-shell electrons with each of four neighbors, which, in turn, donates one of its L electrons for sharing. Each carbon atom thus has its full complement of eight L-shell electrons through tight binding with its neighbors. Covalent solids are very hard and have high melting points. They have no free electrons, and are therefore poor conductors. Whereas diamond is an insulator, Si and Ge are semiconductors, as will be discussed in Chapter 10.

In a *metallic* solid (e.g., Cu, Au) the valence electrons in the outermost shells are weakly bound and shared by all of the atoms in the crystal. Vacancies in these shells permit electrons to move with ease through the crystal in response to the presence of an electric field. Metallic solids are good conductors of electricity and heat. Many of their properties can be understood by regarding some of the electrons in the solid as forming an “electron gas” moving about in a stationary lattice of positively charged ions. The electrons satisfy the Pauli exclusion principle and occupy a range of energies consistent with their temperature. This continuous range of energies is called a conduction band.

To describe the origin of energy bands in a solid, we refer to Fig. 2.6. We saw that the twofold exchange degeneracy between the electronic states of two widely separated hydrogen atoms was broken when their separation was reduced enough for their electron wave functions to overlap appreciably. The same twofold splitting occurs whenever any two identical atoms bind together. Moreover, the excited energy levels of isolated atoms also undergo a similar twofold splitting when the two atoms unite. Such splitting of exchange-degenerate energy levels is a general quantum-mechanical phenomenon. If three identical atoms are present, then the energy levels at large separations are triply degenerate and split into three different levels when the atoms are brought close together. In this case, the three levels all lie in about the same energy range as the first two if the interatomic distances are comparable. If N atoms are brought together in a regular arrangement, such as a crystal solid, then there are N levels in the energy interval.

Figure 2.7 illustrates the splitting of electronic levels for $N = 2, 4,$ and 8 and the onset of band formation. Here the bound-state energies E are plotted schematically as functions of the atomic separations R , with R_0 being the normal atomic spacing in the solid. When N becomes very large, as in a crystal, the separate levels are “compressed together” into a band, within which an electron can have any energy. At a given separation, the band structure is most pronounced in the weakly bound states, in which the electron cloud extends over large distances. The low-lying levels, with tightly bound electrons, remain discrete and unperturbed by the presence of neighboring atoms. Just as for the discrete levels, electrons cannot exist in the solid with energies between the allowed bands. (The existence of energy bands also arises directly out of the quantum-mechanical treatment of the motion of electrons in a periodic lattice.)

While the above properties are those of “ideal” crystalline solids, the presence of impurities—even in trace amounts—often changes the properties markedly. We shall see in Chapter 10 how doping alters the behavior of intrinsic semiconductors and the scintillation characteristics of crystals.

2.10

Continuous and Characteristic X Rays

Roentgen discovered that X rays are produced when a beam of electrons strikes a target. The electrons lose most of their energy in collisions with atomic electrons

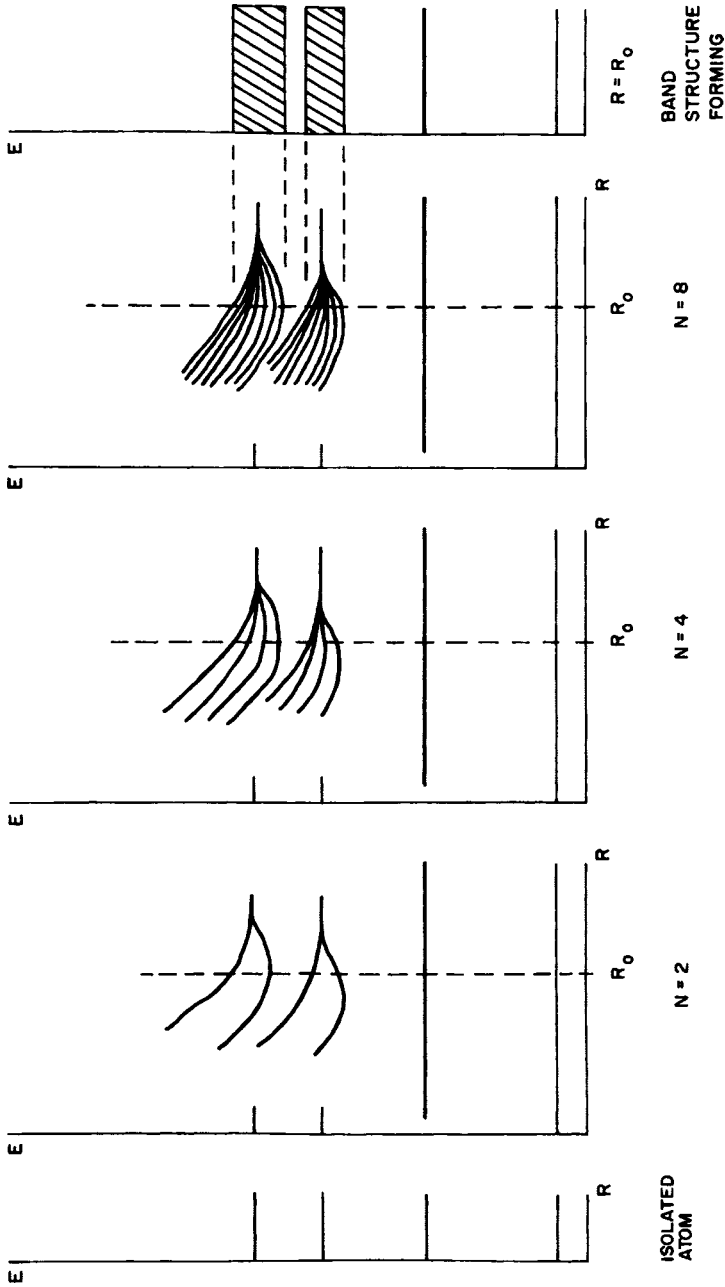


Fig. 2.7 Energy-level diagram schematically showing the splitting of discrete atomic energy levels when $N = 2, 4,$ and 8 atoms are brought together in a regular array. When N is very large, continuous energy bands result, as indicated at the right of the figure.

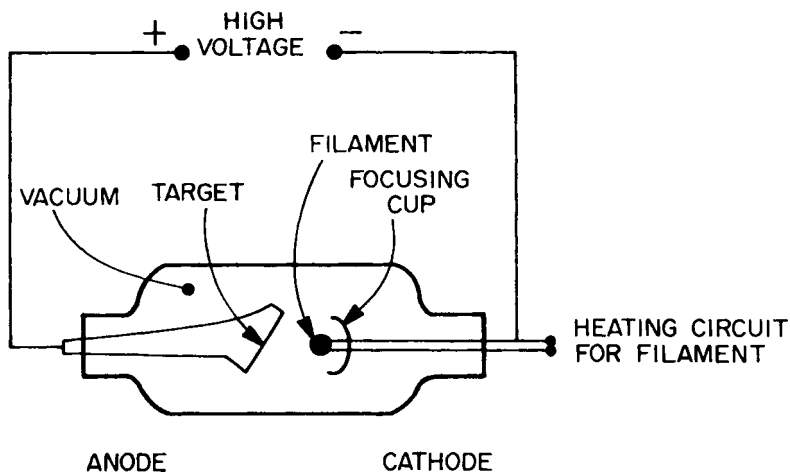


Fig. 2.8 Schematic diagram of modern X-ray tube with fixed target anode.

in the target, causing the ionization and excitation of atoms. In addition, they can be sharply deflected in the vicinity of the atomic nuclei, thereby losing energy by irradiating X-ray photons. Heavy nuclei are much more efficient than light nuclei in producing the radiation because the deflections are stronger. A single electron can emit an X-ray photon having any energy up to its own kinetic energy. As a result, a monoenergetic beam of electrons produces a continuous spectrum of X rays with photon energies up to the value of the beam energy. The continuous X rays are also called bremsstrahlung, or “braking radiation.”

A schematic diagram, showing the basic elements of a modern X-ray tube, is shown in Fig. 2.8. The tube has a cathode and anode sealed inside under high vacuum. The cathode assembly consists of a heated tungsten filament contained in a focusing cup. When the tube operates, the filament, heated white hot, “boils off” electrons, which are accelerated toward the anode in a strong electric field produced by a large potential difference (high voltage) between the cathode and anode. The focusing cup concentrates the electrons onto a focal spot on the anode, usually made of tungsten. There the electrons are abruptly brought to rest, emitting continuous X rays in all directions. Typically, less than 1% of the electrons’ energy is converted into useful X rays that emerge through a window in the tube. The other 99+ % of the energy, lost in electronic collisions, is converted into heat, which must be removed from the anode. Anodes can be cooled by circulating oil or water. Rotating anodes are also used in X-ray tubes to keep the temperature lower.

Figure 2.9 shows typical continuous X-ray spectra generated from a tube operated at different voltages with the same current. The efficiency of bremsstrahlung production increases rapidly when the electron energy is raised. Therefore, the X-ray intensity increases considerably with tube voltage, even at constant current. The wavelength of an X-ray photon with maximum energy can be computed from Eq. (2.26). For the top curve in Fig. 2.9, we find $\lambda_{\min} = 12400/50000 = 0.248 \text{ \AA}$, where

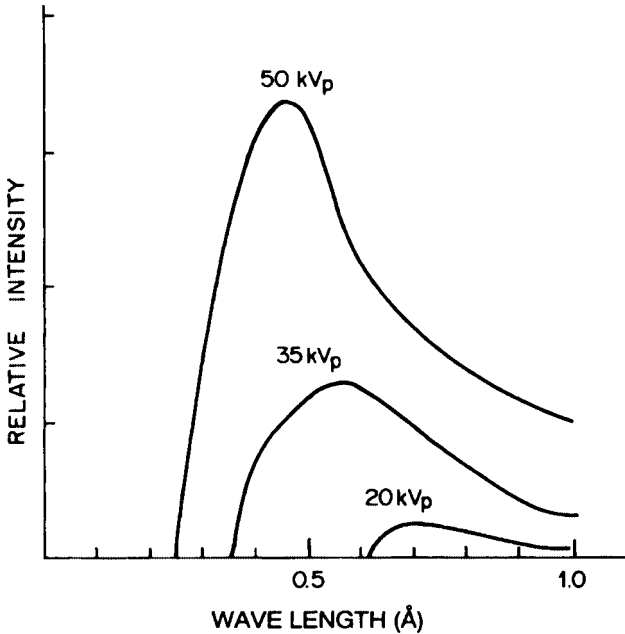


Fig. 2.9 Typical continuous X-ray spectra from tube operating at three different peak voltages with the same current.

this curve intersects the abscissa. The X-ray energies are commonly referred to in terms of their peak voltages in kilovolts, denoted by kVp.

If the tube voltage is sufficient, electrons striking the target can eject electrons from the target atoms. (The K-shell binding energy is $E_K = 69.525$ keV for tungsten.) Discrete X rays are then also produced. These are emitted when electrons from higher shells fill the inner-shell vacancies. The photon energies are characteristic of the element of which the target is made, just as the optical spectra are in the visible range. Characteristic X rays appear superimposed on the continuous spectrum, as illustrated for tungsten in Fig. 2.10. They are designated K_α , K_β , and so forth, when the K-shell vacancy is filled by an electron from the L shell, M shell, and so on. (In addition, when L-shell vacancies are filled, characteristic L_α , L_β , and so forth, X rays are emitted. These have low energy and are usually absorbed in the tube housing.)

Because the electron energies in the other shells are not degenerate, the K X rays have a fine structure, not shown in Fig. 2.10. The L shell, for example, consists of three subshells, in which for tungsten the electron binding energies in keV are $E_{LI} = 12.098$, $E_{LII} = 11.541$, and $E_{LIII} = 10.204$. The transition $LIII \rightarrow K$ gives a $K_{\alpha 1}$ photon with energy $E_K - E_{LIII} = 69.525 - 10.204 = 59.321$ keV; the transition $LII \rightarrow K$ gives a $K_{\alpha 2}$ photon with energy 57.984 keV. The optical transition $LI \rightarrow K$ is quantum mechanically forbidden and does not occur.

The first systematic study of characteristic X rays was carried out in 1913 by the young British physicist, H. G. J. Moseley, working in Rutherford's laboratory.

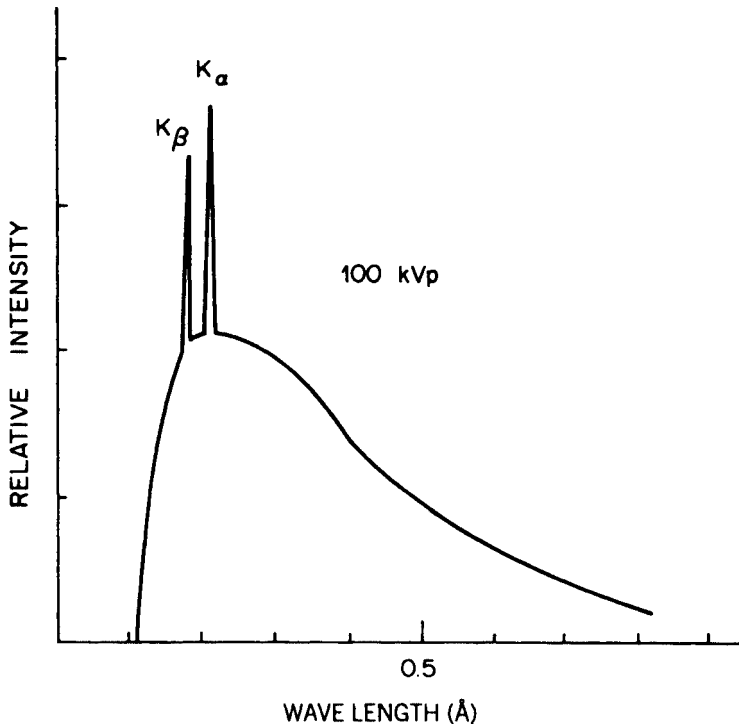


Fig. 2.10 Spectrum showing characteristic K_{α} and K_{β} discrete X rays in addition to the continuous X rays. Characteristic K X rays are present only when the tube operating voltage is high enough to give the incident electrons sufficient energy to eject an electron from the K shell in the target atoms. Potential difference across the tube in volts is then practically \geq K-shell binding energy in eV.

The diffraction of X rays by crystals had been discovered by von Laue in 1912, and Moseley used this process to compare characteristic X-ray wavelengths. He found that the square root of the frequencies of corresponding lines (e.g., $K_{\alpha 1}$) in the characteristic X-ray spectra increases by an almost constant amount from element to element in the periodic system. Alpha-particle scattering indicated that the number of charge units on the nucleus is about half the atomic weight. Moseley concluded that the number of positive nuclear charges and the number of electrons both increase by one from element to element. Starting with $Z = 1$ for hydrogen, the number of charge units Z determines the atomic number of an element, which gives its place in the periodic system.

The linear relationship between $\sqrt{\nu}$ and Z would be predicted if the electrons in many-electron atoms occupied orbits like those predicted by Bohr's theory for single-electron systems. As seen from Eq. (2.13), the frequencies of the photons for a given transition $i \rightarrow f$ in different elements are proportional to Z^2 .

In view of Moseley's findings, the positions of cobalt and nickel had to be reversed in the periodic system. Although Co has the larger atomic weight, 58.93 compared with 58.70, its atomic number is 27, while that of Ni is 28. Moseley also predicted the existence of a new element with $Z = 43$. Technetium, which has no stable form, was discovered after nuclear fission.

2.11

Auger Electrons

An atom in which an L electron makes a transition to fill a vacancy in the K shell does not always emit a photon, particularly if it is an element of low Z . A different, nonoptical transition can occur in which an L electron is ejected from the atom, thereby leaving two vacancies in the L shell. The electron thus ejected from the atom is called an Auger electron.

The emission of an Auger electron is illustrated in Fig. 2.11. The downward arrow indicates the transition of an electron from the L_I level into the K-shell vacancy,

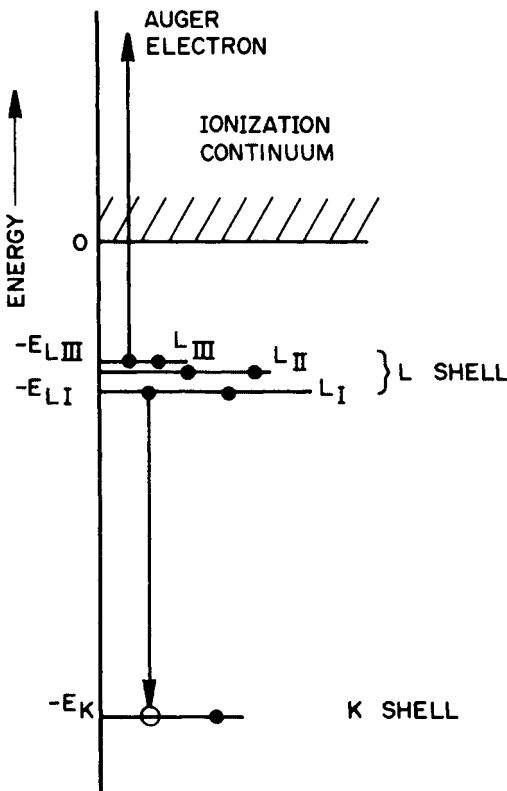


Fig. 2.11 Schematic representation of an atomic transition that results in Auger-electron emission.

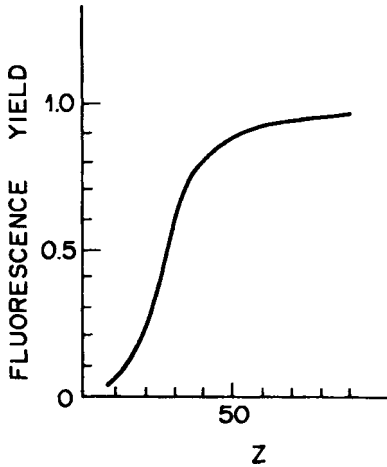


Fig. 2.12 K fluorescence yield as a function of atomic number Z .

thus releasing an energy equal to the difference in binding energies, $E_K - E_{L_I}$. As the alternative to photon emission, this energy can be transferred to an L_{III} electron, ejecting it from the atom with a kinetic energy

$$T = E_K - E_{L_I} - E_{L_{III}}. \quad (2.38)$$

Two L-shell vacancies are thus produced. The Auger effect can occur with other combinations of the three L-shell levels. Equations analogous to (2.38) provide the possible Auger-electron energies.

The Auger process is not one in which a photon is emitted by one atomic electron and absorbed by another. In fact, the $L_I \rightarrow K$ transition shown in Fig. 2.11 is optically forbidden.

The K fluorescence yield of an element is defined as the number of K X-ray photons emitted per vacancy in the K shell. Figure 2.12 shows how the K fluorescence yield varies from essentially zero for the low- Z elements to almost unity for high Z . Auger-electron emission is thus favored over photon emission for elements of low atomic number.

The original inner-shell vacancy in an Auger-electron emitter can be created by orbital electron capture, internal conversion, or photoelectric absorption of a photon from outside the atom. (These processes are described in Chapter 3.) As pointed out previously, emission of an Auger electron increases the number of vacancies in the atomic shells by one unit. Auger cascades can occur in relatively heavy atoms, as inner-shell vacancies are successively filled by the Auger process, with simultaneous ejections of the more loosely bound atomic electrons. An original, singly charged ion with one inner-shell vacancy can thus be converted into a highly charged ion by an Auger cascade. This phenomenon is being studied in radiation research and therapy. Auger emitters can be incorporated into DNA and other biological molecules. For example, ^{125}I decays by electron capture. The ensuing cascade can release some 20 electrons, depositing a large amount of energy (~ 1 keV)

within a few nanometers. A highly charged ^{125}Te ion is left behind. A number of biological effects can be produced, such as DNA strand breaks, chromatid aberrations, mutations, bacteriophage inactivation, and cell killing.

2.12

Suggested Reading

- 1 Alvarez, L. W., *Adventures of a Physicist*, Basic Books, New York, NY (1987). [Alvarez received the 1968 Nobel Prize for pioneering contributions in the field of high-energy physics and subatomic particles. This volume is part of the Alfred P. Sloan Foundation to encourage outstanding scientists to write personal accounts of their experiences for the general reader.]
- 2 Born, Max, *The Mechanics of the Atom*, Frederick Ungar Publ., New York, NY (1960). [An advanced text on semi-classical atomic theory. A number of atomic and molecular systems are solved explicitly using Hamilton–Jacobi theory and applying the older quantization procedures.]
- 3 Fano, U., and Fano, L., *Physics of Atoms and Molecules*, University of Chicago Press, Chicago, IL (1972). [An intermediate text on much of the material of this chapter and other subjects.]
- 4 Gamow, George, *Thirty Years that Shook Physics*, Dover Publications, New York, NY (1985). [The nonmathematical story of quantum mechanics as interestingly related by a participant.]
- 5 Halliday, David; Resnick, Robert; and Walker, Jearl, *Fundamentals of Physics*, 7th ed., John Wiley, New York, NY (2004). [This excellent, time-tested text covers many of the subjects in this chapter.]
- 6 Hawking, Stephen, *A Brief History of Time*, Bantam Books, New York, NY (1988). [Describes the uncertainty principle, elementary particles, nature’s forces, and cosmology. A readable, nontechnical book with only the single equation, $E = mc^2$.]
- 7 Hawking, Stephen, *A Brief History of Time: The Updated and Expanded Tenth Anniversary Edition*, Bantam Books, New York, NY (1998).
- 8 Heisenberg, Werner, *The Physical Principles of the Quantum Theory*, Dover Publications, New York, NY (1930). [A reprint of Heisenberg’s 1929 lectures at the University of Chicago.]
- 9 Johns, H. E., and Cunningham, J. R., *The Physics of Radiology*, 4th ed., Charles C Thomas, Springfield, IL (1983). [A classic treatise. Chapter 2 is devoted to the fundamentals of diagnostic and therapeutic X-ray production.]
- 10 Pauling, Linus, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY (1960). [The author received the Nobel Prize in Chemistry for his research into the nature of the chemical bond and its application to understanding the structure of complex substances.]
- 11 Pauling, L., and Haywood, R., *The Architecture of Molecules*, W. H. Freeman, San Francisco, CA (1964). [An introductory look at 57 pictured molecules. Chemical bonds are discussed.]
- 12 Ponomarev, L. I., *The Quantum Dice*, Institute of Physics Publ., Bristol, England (1993). [“A ray of sunlight over the cradle of a baby has always been a symbol of peace. But the ray carries not just caressing heat, it brings us rich information about the fiery storms and flares on the Sun, and about the elements it is composed of—you need only know how to read this information” (p. 25).]

- 13 Rozenental, S., ed., *Niels Bohr*, North-Holland, Amsterdam, Netherlands (1967). [A collection of essays and personal accounts of the life and work of Bohr by his colleagues and contemporaries.]
- 14 Selman, Joseph, *The Fundamentals of Imaging Physics and Radiobiology*, 9th ed., Charles C Thomas, Springfield, IL (2000). [Previous (8th) edition, *The Fundamentals of X-Ray and Radium Physics*. An outstanding text for technicians that explains X-ray generation and utilization in radiology.]
- 15 Weisskopf, Victor, *The Privilege of Being a Physicist*, W. H. Freeman, New York, NY (1988). [The author knew most and worked with many of the leading physicists during the development of quantum mechanics and made many important contributions himself. This autobiography is another in the Alfred P. Sloan Foundation series (see Alvarez, above) to convey the excitement of science and discovery to general readers. This delightful book will also speak to those who are fond of classical music.]
- 16 Whittaker, E. T., *A History of the Theories of the Aether and Electricity*, Thomas Nelson and Sons, London, England (1953). [Volume 2, subtitled *The Modern Theories. 1900–1926*, begins with “The Age of Rutherford” (Chapter 1) and ends with “The Discovery of Wave Mechanics” (Chapter IX). Interesting, informative, and personal accounts of the discoveries of the time.]

2.13

Problems

- How many atoms are there in 3 L of N_2 at STP?
- What is the volume occupied by 1 kg of methane (CH_4) at $23^\circ C$ and 756 torr?
- How many hydrogen atoms are there in the last problem?
- What is the mass of a single atom of aluminum?
- Estimate the number of atoms/cm² in an aluminum foil that is 1 mm thick.
- Estimate the radius of a uranium nucleus. What is its cross-sectional area?
- What is the density of the nucleus in a gold atom?
- What was the minimum distance to which the 7.69-MeV alpha particles could approach the center of the gold nuclei in Rutherford's experiments?
- How much energy would an alpha particle need in order to “just touch” the nuclear surface in a gold foil?
- Figure 2.13 represents a particle moving with constant speed v ($= |\mathbf{v}_1| = |\mathbf{v}_2|$) in a circular orbit of radius r . When the particle advances through a small angle $\Delta\theta$ about the center of the circle, the change in velocity $\Delta\mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1$ is indicated. Denoting the elapsed time by Δt , one has $\Delta\theta = \omega\Delta t$, where $\omega = v/r$ is the angular velocity expressed in radians per unit time.
 - For small Δt , show that the acceleration of the particle is given by $a \cong \Delta v/\Delta t \cong v\Delta\theta/\Delta t$.

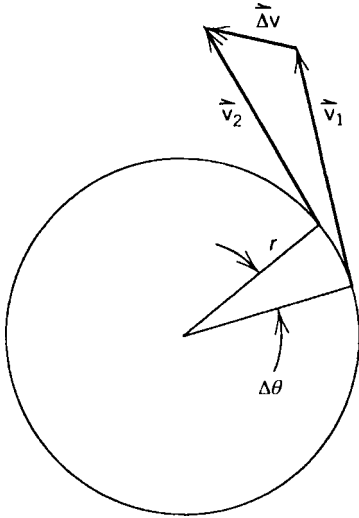


Fig. 2.13 See Problem 10.

- (b) In the limit $\Delta t \rightarrow 0$, show that the acceleration of the particle is directed toward the center of the circle and has a magnitude $a = \omega v = v^2/r$, as used in writing Eq. (2.5).
11. How much force acts on the electron in the ground state of the hydrogen atom?
 12. What is the angular momentum of the electron in the $n = 5$ state of the H atom?
 13. How does the angular momentum of the electron in the $n = 3$ state of H compare with that in the $n = 3$ state of He^+ ?
 14. Calculate the ionization potential of Li^{2+} .
 15. Calculate the radius of the $n = 2$ electron orbit in the Bohr hydrogen atom.
 16. Calculate the orbital radius for the $n = 2$ state of Li^{2+} .
 17. Do H and He^+ have any states with the same orbital radius?
 18. What is the principal quantum number n of the state of the H atom with an orbital radius closest to that of the $n = 3$ state of He^+ ?
 19. What are the energies of the photons with the two longest wavelengths in the Paschen series (Fig. 2.3)?
 20. Calculate the wavelengths in the visible spectrum of the He^+ ion in which the electron makes transitions from higher states to states with quantum number $n = 1, 2, 3$, or 4.
 21. How many energy levels of the He^+ ion lie below -1 eV?
 22. Calculate the current of the electron in the ground state of the hydrogen atom.

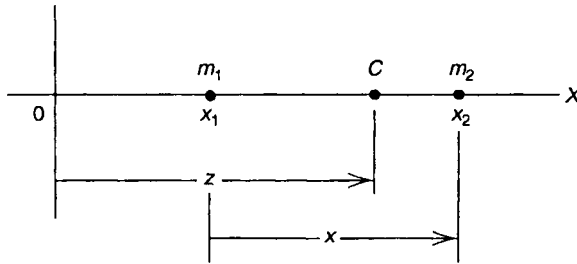


Fig. 2.14 See Problem 31.

23. What is the lowest quantum number of an H-atom electron orbit with a radius of at least 1 cm?
24. According to Bohr theory, how many bound states of He^+ have energies equal to bound-state energies in H?
25. How much energy is needed to remove an electron from the $n = 5$ state of He^+ ?
26. (a) In the Balmer series of the hydrogen atom, what is the smallest value of the principal quantum number of the initial state for emission of a photon of wavelength less than 4200 \AA ?
(b) What is the change in the angular momentum of the electron for this transition?
27. Calculate the reduced mass for the He^+ system.
28. What percentage error is made in the Rydberg constant for hydrogen if the electron mass is used instead of the reduced mass?
29. The negative muon is an elementary particle with a charge equal to that of the electron and a mass 207 times as large. A proton can capture a negative muon to form a hydrogen-like "mesic" atom. (The muon was formerly called the mu meson.) For such a system, calculate
(a) the radius of the first Bohr orbit
(b) the ionization potential.
Do not assume a stationary nucleus.
30. What is the reduced mass for a system of two particles of equal mass, such as an electron and positron, orbiting about their center of mass?
31. Figure 2.14 shows two interacting particles, having masses m_1 and m_2 and positions x_1 and x_2 . The particles are free to move only along the X-axis. Their total energy is $E = \frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_2 \dot{x}_2^2 + V(x)$, where $\dot{x}_1 = dx_1/dt$ and $\dot{x}_2 = dx_2/dt$ are the velocities, and the potential energy $V(x)$ depends only on the separation $x = x_2 - x_1$ of the particles. Let z be the coordinate of the center of mass C : $m_1(z - x_1) = m_2(x_2 - z)$.

Show that $E = \frac{1}{2}(m_1 + m_2)\dot{z}^2 + \frac{1}{2}m_r\dot{x}^2 + V(x)$, where m_r is the reduced mass, given by Eq. (2.20), and $\dot{x} = dx/dt$. The total energy is thus the sum of the translational kinetic energy of the motion of the total mass along the X-axis and the total energy associated with the relative motion (coordinate x and mass m_r).

32. What is meant by the fine structure in the spectrum of hydrogen and what is its physical origin?
33. Calculate the momentum of an ultraviolet photon of wavelength 1000 Å.
34. What is the momentum of a photon of lowest energy in the Balmer series of hydrogen?
35. Calculate the de Broglie wavelength of the 7.69-MeV alpha particles used in Rutherford's experiment. Use nonrelativistic mechanics.
36. What is the energy of a proton that has the same momentum as a 1-MeV photon?
37. What is the energy of an electron having a wavelength of 0.123 Å?
38. Calculate the de Broglie wavelength of a 245-keV electron.
39. (a) What is the momentum of an electron with a de Broglie wavelength of 0.02 Å?
(b) What is the momentum of a photon with a wavelength of 0.02 Å?
40. Calculate the kinetic energy of the electron and the energy of the photon in the last problem.
41. A microscope can resolve as distinct two objects or features that are no closer than the wavelength of the light or electrons used for the observation.
(a) With an electron microscope, what energy is needed for a resolution of 0.4 Å?
(b) What photon energy would be required of an optical microscope for the same resolution?
42. Show that Eq. (2.29) follows from Eq. (2.22) for relativistic electrons.
43. Estimate the uncertainty in the momentum of an electron whose location is uncertain by a distance of 2 Å. What is the uncertainty in the momentum of a proton under the same conditions?
44. What can one conclude about the relative velocities and energies of the electron and proton in the last problem? Are wave phenomena apt to be more apparent for light particles than for heavy ones?
45. The result given after Eq. (2.36) shows that an electron confined to nuclear dimensions, $\Delta x \sim 10^{-15}$ m, could be

expected to have a kinetic energy $T \sim 200$ MeV. What would be the value of Δx for $T \sim 100$ eV?

46. (a) Write the electron configuration of carbon.
(b) How many s electrons does the C atom have?
(c) How many p electrons?
47. The configuration of boron is $1s^2 2s^2 p^1$.
(a) How many electrons are in the L shell?
(b) How many electrons have orbital angular-momentum quantum number $l = 0$?
48. How many electrons does the nickel atom have with azimuthal quantum number $l = 2$?
49. What is the electron configuration of the magnesium ion, Mg^{2+} ?
50. What is incorrect in the electron configuration $1s^2 2s^2 p^6 3s^2 p^8 d^{10}$?
51. (a) What are the largest and the smallest values that the magnetic quantum number m has in the Zn atom?
(b) How many electrons have $m = 0$ in Zn?
52. Show that the total number of states available in a shell with principal quantum number n is $2n^2$.
53. What is the wavelength of a photon of maximum energy from an X-ray tube operating at a peak voltage of 80 kV?
54. If the operating voltage of an X-ray tube is doubled, by what factor does the wavelength of a photon of maximum energy change?
55. (a) How many electrons per second strike the target in an X-ray tube operating at a current of 50 mA?
(b) If the potential difference between the anode and cathode is 100 kV, how much power is expended?
56. If the binding energies for electrons in the K, L, and M shells of an element are, respectively, 8979 eV, 951 eV, and 74 eV, what are the energies of the K_α and K_β characteristic X rays? (These values are representative of Cu without the fine structure.)
57. Given that the $K_{\alpha 1}$ characteristic X ray of copper has an energy of 8.05 keV, estimate the energy of the $K_{\alpha 1}$ X ray of tin.
58. The oxygen atom has a K-shell binding energy of 532 eV and L-shell binding energies of 23.7 eV and 7.1 eV. What are the possible energies of its Auger electrons?

2.14

Answers

1. 1.61×10^{23}
2. 1530 L
7. $1.81 \times 10^{17} \text{ kg m}^{-3}$
9. 23.6 MeV
11. $8.23 \times 10^{-8} \text{ N}$
12. $5.27 \times 10^{-34} \text{ J s}$
14. 122 eV
16. 0.705 \AA
18. 2
19. 0.661 eV; 0.967 eV
20. 4030, 4100, 4200, 4340, 4540, 4690, 4860, 5420, and 6560 \AA
21. 7
22. 1.05 mA
26. (a) 6
(b) $4\hbar$
27. $0.99986m$
29. (a) $2.84 \times 10^{-13} \text{ m}$
(b) 2.53 keV
33. $6.63 \times 10^{-27} \text{ kg m s}^{-1}$
35. $5.19 \times 10^{-5} \text{ \AA}$
36. 533 eV
38. 0.0222 \AA
40. 0.294 MeV;
0.621 MeV
41. (a) 946 eV
(b) 31.0 keV
43. $5.27 \times 10^{-25} \text{ kg m s}^{-1}$;
same
45. 0.2 \AA
47. (a) 3
(b) 4
51. (a) ± 2
(b) 14
53. 0.155 \AA
55. (a) $3.12 \times 10^{17} \text{ s}^{-1}$
(b) 5000 W
57. 24 keV