

CHAPTER 1

HISTORICAL INTRODUCTION

1-1 Planck's theory of blackbody radiation. In 1901 Planck* introduced in physics a drastically new idea: he postulated that an oscillator can take on only a discrete set of energy values instead of all continuous values as tacitly assumed in classical mechanics. Originally, this assumption was made to explain the law of blackbody radiation. As history unfolded, it turned out that the introduction of this idea marked the beginning of a new age in the development of physics, the age of quantum theory.

Planck's argument is roundabout and abstruse; it will not be discussed in detail here. Nor shall we go through the lengthy thermodynamical reasoning leading to the law of blackbody radiation.† It will be sufficient here to say that the Rayleigh-Jeans law and the Wien law are valid respectively in the low- and the high-frequency regions of blackbody radiation; that Planck found a formula which not only included these two laws as its special cases, but also proved to be the correct formula for the entire frequency range; and that Planck tried to find a theory to explain his empirical formula. Let us write the Rayleigh-Jeans formula:

$$u(\nu) d\nu = \frac{8\pi\nu^2 kT}{c^3} d\nu; \quad (1-1)$$

the Wien formula (in convenient form):‡

$$u(\nu) d\nu \sim \nu^3 e^{-h\nu/kT} d\nu;$$

and the Planck formula:

$$u(\nu) d\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} d\nu, \quad (1-2)$$

where $u(\nu)$ is the energy per unit volume of the blackbody radiation in the frequency range from ν to $\nu + d\nu$, k is the Boltzmann constant, T is the absolute temperature, c is the velocity of light, and h is an empirical

* M. Planck, *Ann. d. Phys.* **4**, 553 (1901).

† A discussion of blackbody radiation may be found, for example, in Richtmyer, Kennard, and Lauritsen, *Introduction to Modern Physics* (McGraw-Hill Book Co.).

‡ For convenience, the empirical constant Wien introduced is written h/k .

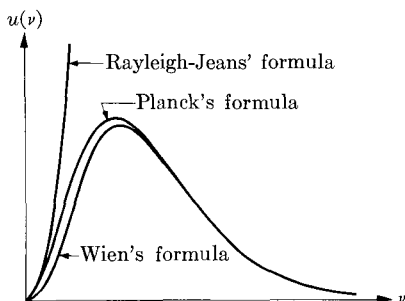


FIGURE 1-1

constant known as the Planck constant. The constant h may be determined by fitting Eq. (1-2) with the experimental data, but the following best value of h is obtained later by other methods:

$$h = 6.625 \times 10^{-27} \text{ erg} \cdot \text{sec.}$$

It is easily verified that Planck's formula includes the other two as its special cases.

All three formulas are represented graphically in Fig. 1-1. The Rayleigh-Jeans formula consists of a product of $(8\pi\nu^2/c^3) d\nu$ and kT , the former being the number of vibrational waves in the frequency range ν to $\nu + d\nu$ and the latter being the average energy of a mode of vibration at temperature T . Thus the Rayleigh-Jeans law is the result of a straightforward application of classical statistical mechanics. Its difficulty lies in the fact that it diverges at the high-frequency end. In Planck's formula, kT is replaced by $h\nu/(e^{h\nu/kT} - 1)$, which approaches zero sufficiently rapidly to make Eq. (1-2) converge at the high-frequency end. Thus the Planck law seems to imply a modification of the principle of equipartition of energy, which may be specified by the following substitution:

$$kT \rightarrow \frac{h\nu}{e^{h\nu/kT} - 1}. \quad (1-3)$$

Such a modification may be realized if, according to the Planck theory,* it is assumed that the energy of a mode of vibration of the radiation field

* We shall follow a simplified approach due to Debye (1910), according to which a mode of vibration may be treated as an oscillator. Planck considered that the energies given by Eq. (1-4) are those of the oscillators emitting black-body radiation, and not the energies of the modes of vibration themselves. He then derived his empirical formula by a consideration of the equilibrium between the oscillators and the radiation field.

can assume only the following values:

$$E_n = nh\nu, \quad n = 0, 1, 2, \dots; \quad (1-4)$$

in other words, the energy must be an integral multiple of a *quantum* of energy, $h\nu$. If the oscillator can take on any continuous value from 0 to ∞ , as the classical theory tacitly assumed, the average value of the energy will be

$$\bar{E} = \frac{\int_0^\infty E e^{-E/kT} dE}{\int_0^\infty e^{-E/kT} dE} = kT, \quad (1-5)$$

where $e^{-E/kT}$, according to the Boltzmann distribution law in statistical mechanics, is the relative probability of finding the energy value to be E . According to the Planck hypothesis, Eq. (1-4), the average value becomes

$$\bar{E} = \frac{\sum_{n=0}^\infty nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^\infty e^{-nh\nu/kT}}. \quad (1-6)$$

These summations may be evaluated by using the following identities:

$$\begin{aligned} \frac{1}{1-x} &= 1 + x + x^2 + \dots, \\ \frac{x}{(1-x)^2} &= x + 2x^2 + 3x^3 + \dots. \end{aligned} \quad (1-7)$$

As a result, Eq. (1-6) becomes

$$\bar{E} = \frac{h\nu e^{-h\nu/kT} / (1 - e^{-h\nu/kT})^2}{1 / (1 - e^{-h\nu/kT})} = \frac{h\nu}{e^{h\nu/kT} - 1}. \quad (1-8)$$

Thus the modification specified by Eq. (1-3) is realized by the introduction of the quantum hypothesis, Eq. (1-4). The above mathematical result may be illustrated graphically as follows. In Fig. 1-2 we plot the energy of an oscillator or a mode of vibration of the radiation field on the vertical axis. The relative probability distribution among these energy values is plotted to the left of the energy axis. In Fig. 1-2(a) the energy is assumed to be continuous. From the shape of the exponential distribution curve the average value of energy may be roughly estimated to be near $E = kT$, where the probability has reduced to $1/e$. In Fig. 1-2(b) the energy of the oscillator is assumed to take on only a set of discontinuous values, each represented by a horizontal line. If the lines are very close to one another they may be regarded as forming a continuous band, as in Fig. 1-2(a), and the average energy will be very close to that shown

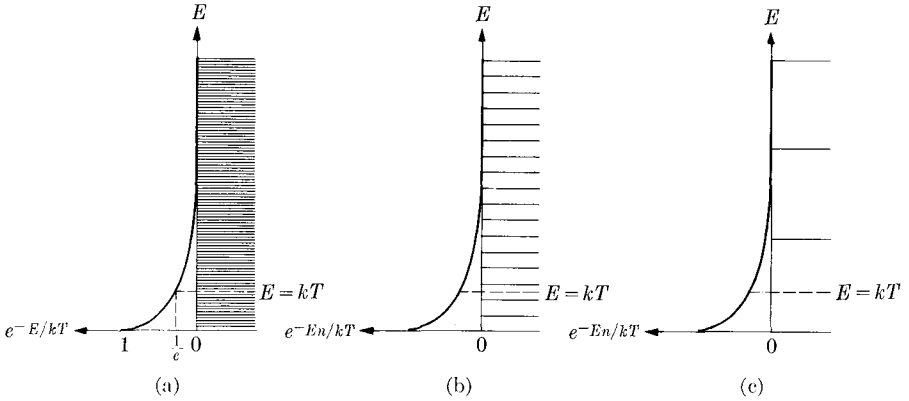


FIGURE 1-2

in Fig. 1-2(a). Therefore the continuous energy spectrum may be regarded as a limiting case of the discontinuous energy spectrum when the spacing between two adjacent energy values approaches zero. On the other hand, in Fig. 1-2(c), we have a situation where the discrete energy values are so widely separated that no allowed energy values are to be found near $E = kT$. In this case, all energy values except $E = 0$ have negligible probabilities, so that the average energy of the oscillator is near zero rather than kT . The average energy approaches zero when the spacing approaches infinity. According to Eq. (1-4), the energy spacing is proportional to frequency ν . Thus in the low-frequency region the situation will be like that in Fig. 1-2(b), while in the high-frequency region it will be like that in Fig. 1-2(c). The divergence difficulty of the Rayleigh-Jeans law is due to the fact that there are too many degrees of freedom (proportional to ν^2) at the high-frequency end, each being assumed to have a finite amount of energy kT . The introduction of the quantum hypothesis does not change the situation in the low-frequency region as demonstrated in Fig. 1-2(b). However, in the high-frequency region, Fig. 1-2(c) shows that each degree of freedom, i.e., each mode of oscillation, shares a negligibly small amount of energy instead of a finite amount kT , so that the total energy of all waves is finite instead of infinite. The introduction of the discontinuous energy values thus renders the many degrees of freedom at the high-frequency end ineffective so that the distribution function becomes convergent.

Although the formula of blackbody radiation may be “explained” by the quantum hypothesis, the problem is not solved; it is merely shifted from the radiation formula to the quantum hypothesis.

The classical theory of physics is formulated on the basis that dynamical quantities, including energy, are all continuous. Restricting the energy

value of an oscillator to a selected set of numbers specified by Eq. (1-4) is a concept completely foreign to classical physics. Planck spent the rest of his life trying unsuccessfully to reconcile the quantum hypothesis with classical theory. With the advantage of retrospect, we now know that Planck's hypothesis is just a first step in a revolution in which many continuous physical quantities are to be replaced by discontinuous ones. In this revolution, the basic issue is discontinuity versus continuity, which is related to the issue of the finite versus the infinite. The divergence (infinity) of Eq. (1-1) originates from the fact that both the coordinates and the energy are continuous. The continuity of space makes it possible to conceive of waves of infinitely small wavelengths; the number of vibrational modes thus diverges to the square of ν . In Planck's theory the divergence is eliminated by making the energy variable discontinuous. Actually, the concepts of continuity and infinity are sophisticated mental products of mathematics. But we have become so accustomed to them by our training in mathematical analysis and its applications that we take for granted that all physical quantities are continuous without asking for experimental substantiation. In the following example we shall show that a theory based on the concept of continuity cannot always be continuous in every respect. Consider the specific heat of solids. Each atom in a solid is assumed to execute vibrational motion in three dimensions and thus is equivalent, in terms of energy, to three linear oscillators. If the energy variable is continuous, the average energy of one atom will be $3kT$. The average energy of one mole of material will be $3N_0kT$, where N_0 is the *Avogadro number*, and the molar specific heat will be $3N_0k$ or $3R$, where R is the *universal gas constant*. Now let the force constant of the oscillator increase. This will be accompanied by an increase in the frequency of vibration. Yet the specific heat remains $3R$ no matter how large the force constant may become. On the other hand, when the force constant reaches infinity, no vibration is possible and the specific heat should be zero. Therefore a discontinuous change of the specific heat from a constant value $3R$ to zero will take place when the force constant approaches infinity. This example shows that the assumption of continuity in energy leads to a result of discontinuity in specific heat. If we cannot avoid discontinuity in one physical quantity, there is no reason why we cannot accept discontinuity in another, say energy. In fact, if we accept Eq. (1-4) for the energy of an oscillator, the specific heat C of a solid will be given by

$$C = \frac{d}{dT} \left(N_0 \frac{3h\nu}{e^{h\nu/kT} - 1} \right). \quad (1-9)$$

When the force constant increases to infinity, this specific heat approaches zero gradually instead of discontinuously and there will be no discon-

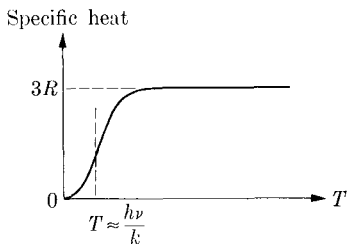


FIGURE 1-3

tinuity in specific heat. In a certain sense the theory based on discontinuous energy values, which may be reduced to the theory based on continuous values when the energy spacings are small, seems more flexible. It may well be that physical quantities are actually discontinuous and that the continuous theory of classical physics is but a macroscopic approximation.

The preceding discussion of specific heat serves to introduce another subject, namely, specific heat at low temperature, which provides further evidence that the energy of an oscillator is *quantized*, i.e., the oscillator can take on only a discrete set of energy values. The study of specific heat played an important part in the development of *quantum theory*, the theory dealing with quantized physical quantities. On the other hand, the quantum theory of specific heat is a straightforward extension of Planck's theory and no new idea is involved. It is thus appropriate to include a brief discussion of it in this section, disregarding that this work was done two years after another important step in the development of quantum theory, i.e., the theory of photoelectric effect which will be discussed in the next section.

As we have mentioned, classical theory sets forth that the molar specific heat of solids is a constant, $3R$, approximately 6 cal/mole/degree. This result has been verified for many solids at room temperature (Dulong-Petit's law). However, experimental evidence shows that when the temperature is reduced to near absolute zero, the specific heat decreases to zero, thus contradicting the prediction of classical theory (see Fig. 1-3). This deviation becomes noticeable at liquid air temperature, although a few materials such as the diamond reveal the beginning of this deviation even at room temperature. In attempting to explain this phenomenon, Einstein* in 1907 made the assumption that the oscillators in a solid behave just like the Planck oscillator. The specific heat of the solid, according to our discussion above, is then given by Eq. (1-9). It actually approaches zero when the temperature is reduced to zero. The reason is that in the low-temperature region kT is so small that the situation of

* A. Einstein, *Ann. d. Phys.* **22**, 180 (1907).

Fig. 1-2(c) prevails for all oscillators, and consequently the average energy of each oscillator becomes very small. In spite of the qualitative agreement, Einstein's theory is too simple to describe the complicated internal motion of a solid. Debye* in 1912 worked out a more complete theory which agreed well quantitatively with experimental results. Nevertheless, the basic idea involved is the same as Einstein's. The improvement lies in a more detailed analysis of the internal vibrational motion of a solid.

The specific heat of gases also furnishes evidence for the existence of quantized energy values. A diatomic molecule may execute oscillatory motion, the two atoms moving closer and farther apart alternately. The average energy of this oscillation, according to classical statistical mechanics, is again kT and thus contributes to the molar specific heat an amount equal to R . However, at room temperature experimental results do not show such a contribution in many diatomic gases. According to quantum theory, this may be explained by assuming that the frequency of oscillation is so high that even at room temperature the situation of Fig. 1-2(c) prevails and the average energy of this oscillation is nearly zero. However, at higher temperatures, when the situation of Fig. 1-2(b) prevails, the prediction of classical theory will be valid. This is also verified.

In Debye's theory the vibrational motion of a solid as a whole is analyzed. Such a theory is adequate for monatomic crystals. For polyatomic crystals, the vibrational motion of the molecule itself, like that of the diatomic molecule just mentioned, must also be considered. Accordingly, the vibrational frequencies may be divided into two parts: the *acoustical branch* for the vibration of the solid as a whole, and the *optical branch* for the vibration of the molecules. The first part may be treated by the Debye theory and the second by the Einstein theory. By such an analysis, which is rather complicated, the quantum theory of specific heat is able to account for many observed results.

1-2 Einstein's photon theory of light. In 1905 Einstein† took an important step in the development of quantum theory. Unlike Planck who, looking backward, tried to reconcile quantized energies with classical theory, Einstein, looking forward, tried to develop the new idea to its logical conclusion. His later application of quantum theory to specific heat (1907), discussed above, was another step in the same direction. If the quantization of energy in blackbody radiation is considered as a special instance indicating the existence of a general law of quantization, then the same situation may prevail for other types of oscillators, such

* P. Debye, *Ann. d. Phys.* **39**, 789 (1912).

† A. Einstein, *Ann. d. Phys.* **17**, 132 (1905).

as those contributing to the specific heat of solids and gases. The successful application of quantum theory to specific heat justifies Einstein's foresight. His work in 1905 on the photoelectric effect was carried out along the same line of thought. He assumed that the energy of the radiation field is quantized. Planck assumed that only the energy of an oscillator in equilibrium with blackbody radiation is quantized, and he derived the law of blackbody radiation by considering equilibrium between the radiation field and the oscillators. If the energy of an oscillator is assumed to take on only the values $nh\nu$, it can change only by an integral multiple of $h\nu$. In the emission and absorption processes, an oscillator thus can absorb or emit radiation energy only in units of $h\nu$. The logical conclusion seems to be that radiation energy itself exists only in units of $h\nu$, there being no fractions of one such unit. Since the frequency of an oscillator and that of the radiation it absorbs or emits are the same, the latter may also be denoted by ν , which was defined for the former. Thus the energy of a radiation field of frequency ν may be regarded as quantized to the unit of $h\nu$. This is what Einstein assumed. It may be noted parenthetically that Planck did not believe that the energy of a radiation field exists in discrete units.

By means of this assumption, Einstein was able to explain the photoelectric effect. This effect was first discovered by Hertz late in the nineteenth century in his experiments on electromagnetic waves to verify the Maxwell theory. It is found experimentally that light causes the emission of electrons from a metal surface. For a given metal there is a threshold frequency below which no electrons are ejected no matter what the strength of the light intensity. For a given frequency above the threshold, the electrons ejected, no matter how weak the light may be, have the same maximum energy, and the emission takes place within a short time interval, 10^{-8} to 10^{-9} sec. These facts are very difficult to understand from the point of view of the wave theory of light. According to the wave theory, the energy of a light wave is uniformly distributed over its wave front. Given enough intensity of light and enough time of exposure, the electron may absorb from the wave enough energy to break loose from the metal surface. Frequency has no role to play. Thus in wave theory there can be no threshold in frequency; the electron energy and the emission time are dependent on the light intensity. Experimental results contradict these predictions, and they indicate that frequency, rather than intensity, plays the dominant role. In some experiments in which light of very weak intensity is used, the time required to absorb the necessary amount of energy, according to the wave theory, is calculated to be many days, whereas actually the photoelectrons are ejected almost immediately. It seems that either the ejected electron is endowed with an unusual ability of collecting a large amount of light energy in a short

time at the expense of the other electrons, or the necessary amount of light energy is delivered in a package and the ejected electron happens to be the lucky recipient. By the tradition of the nineteenth-century physics and scientific method, the second alternative seems more reasonable; the photoelectric effect may be explained by assuming the existence of discontinuous units of light energy. Generalizing Planck's idea and applying it to the radiation field, Einstein introduced the concept of the *unidirectional quantum*, i.e., a quantum of radiation energy $h\nu$ propagated in one fixed direction without spreading. Such a quantum has the additional attribute that it has a linear momentum and thus has all the earmarks of a particle. Einstein essentially revived the corpuscular theory of light, the light particle being called the *photon*. According to the Maxwell theory, the energy-to-momentum ratio of a plane electromagnetic wave is c , the velocity of light. The amount of momentum p associated with the energy $h\nu$ is thus $h\nu/c$ or h/λ . Therefore the energy and momentum of a photon are $h\nu$ and h/λ , respectively.

$$E = h\nu, \quad p = \frac{h}{\lambda}. \quad (1-10)$$

These are known as the Einstein relations for a photon.

The photoelectric effect, according to the photon theory, may be considered as due to the absorption of a light particle by an electron. The electron takes over the energy and momentum of the photon. Conservation of energy leads immediately to the Einstein equation of photoelectric effect,

$$\frac{1}{2}Mv^2 = h\nu - \phi, \quad (1-11)$$

where $\frac{1}{2}Mv^2$ is the kinetic energy of the ejected electron and ϕ , the *work function*, is the energy necessary to liberate an electron from the metal.* From Eq. (1-11) the threshold frequency ν_0 may be determined, the result being $h\nu_0 = \phi$. Equation (1-11) also expresses the frequency dependence of the kinetic energy of the photoelectrons. Thus, by the Einstein equation the experimental results of the photoelectric effects are easily explained.

In spite of this success, the photon theory revived the old controversy between the wave and corpuscular theories of light. However, the point at issue now is not which of the two theories is correct but how to reconcile them. Equations (1-10) define the property of a photon in terms of ν and λ , which are quantities meaningful only in the wave theory. Thus the photon theory cannot be stated without reference to the wave theory;

* Although mass is conventionally represented by the lower-case letter m , we use M to distinguish mass from the magnetic quantum number (to be introduced later) which is always designated by m .

the two theories are obviously related instead of contradictory. Einstein himself considered the photon theory as heuristic. The unification of the two theories, however, was not achieved until a generation later when a more general theory, *the quantum theory of radiation*, was established which includes both the Maxwell theory and the Einstein theory as special cases, and thus explains both the wave properties (interference and diffraction phenomena) and the corpuscular properties (photoelectric effects) within a single theoretical framework. Since this book deals primarily with *quantum mechanics of particles*, only a very brief discussion of the quantum theory of radiation will be given, in Chapter 12.

Although Eq. (1-11) was proposed in 1905, its conclusive, quantitative verification was not made until several years later, the most careful experiment being that of Millikan in 1916. In the meantime, the photoelectric effect induced by x-rays was studied. For this case, the Einstein equation may be written

$$\frac{1}{2}Mv^2 = h\nu, \quad (1-12)$$

because the work function, being several *electron volts** in magnitude, is negligible compared with the x-ray energy. Also the reverse reaction, producing x-rays by stopping high-energy electrons, has been studied. The maximum frequency of the x-rays emitted was found to be related to the kinetic energy of the electron by Eq. (1-12). The process may thus be regarded as one in which a photon is emitted with energy $h\nu$ equal to the energy loss of the electron, $E_2 - E_1$:

$$E_2 - E_1 = h\nu.$$

The photon concept is thus useful in studying the emission process as well as the absorption process of a free electron.

While considering the corpuscular properties of light we may depart from historical order to cite another experimentally determined fact, namely, the *Compton effect*, as further evidence. When hard x-rays are scattered by electrons, an increase in wavelength is observed which cannot be accounted for by the wave theory. In the wave theory no wavelength change is predicted (*Thomson scattering*). In the photon theory, however, this *Compton scattering* may be regarded as a collision process between a photon and an electron. The outcome of this collision is determined by the laws of conservation of energy and momentum. The energy and momentum of a photon are given by Eqs. (1-10). The theory of Compton scattering may thus be worked out by analogy to the collision

* The electron volt (ev) is a unit of energy defined as the amount gained by an electron in passing through a potential difference of one volt, its numerical value being 1.6021×10^{-12} erg.

of two billiard balls. Qualitatively, the photon loses energy after collision and therefore the frequency decreases because of the relation $E = h\nu$. This corresponds to an increase in wavelength. Quantitatively, it can be shown (Problem 1-1 at end of chapter) that

$$\lambda' - \lambda = \frac{h}{Mc} (1 - \cos \theta), \quad (1-13)$$

where $\lambda' - \lambda$ is the increase in wavelength, M is the electron mass, and θ is the angle of scattering. (The quantity h/Mc , numerically 2.42×10^{-10} cm, is called the *Compton wavelength of the electron*.) The agreement with experiment is another triumph of the photon theory. Another important feature of Compton scattering, determined experimentally, is that the scattered photon is *unidirectional*, contrary to the classical theory that the scattered x-ray forms a spherical wave.

1-3 Bohr's theory of the hydrogen atom. The next important step in the development of quantum theory was taken by Bohr* in 1913 when he proposed the quantum theory of the hydrogen atom and thus initiated the so-called *old quantum theory*. Our knowledge concerning the structure of the atom was fragmentary until 1911, when Rutherford performed his famous α -particle scattering experiments. This series of experiments established the atom as a planetary system with a small but heavy nucleus carrying a positive charge at the center of the atom and a number of electrons surrounding the nucleus. Once this is established, classical theory leads to a number of conclusions: First of all, according to electrostatics, the electrons cannot maintain a static equilibrium under the influence of the Coulomb forces (Earnshaw's theorem). Thus, they must be in motion like the planets revolving around the sun. Once granted that the electrons execute periodic motions, classical electrodynamics requires that the electrons radiate electromagnetic waves (just like the electrons in the antenna of a broadcasting station radiating radio waves), and thus lose their energy gradually. Eventually the energy will be dissipated and the electrons will collapse into the nucleus. Therefore, according to classical electrodynamics, the nuclear atom cannot be *stationary*. (A state is said to be stationary if it remains unchanged in the course of time.) Actually atoms usually do not radiate electromagnetic waves and they can be stationary. The theory of the nuclear atom thus faces a serious difficulty.

The origin of this difficulty seems to lie in the fact that we have presumed the continuity of energy and space so that the electron is given a chance to decrease its energy indefinitely and to curve in indefinitely. If the energy is assumed to be discontinuous, this process of losing energy

* N. Bohr, *Phil. Mag.* **26**, 1 (1913).

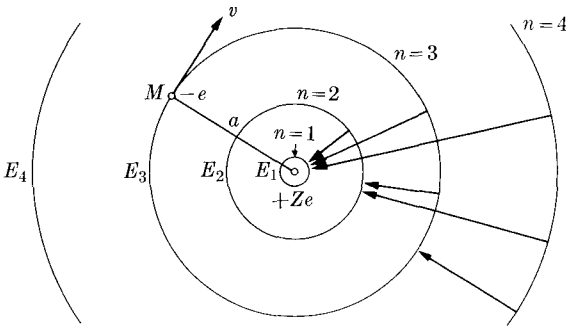


FIGURE 1-4

by radiation will come to an end when the lowest energy value is reached. We might have assumed the existence of things (such as the energy below the lowest energy value) which actually do not exist and thus have introduced a theoretical difficulty.

By 1913 a number of quantum phenomena were already known. The energy of the Planck oscillator was known to be quantized. Then energy in many other kinds of oscillators in solids and gases was known to be quantized. Not only mechanical systems but also the radiation field exhibited quantization. Photoelectric effects, the production of x-rays, and later the Compton effect provided ample evidence for the quantization of energy of the radiation field. Interactions between a mechanical system and a radiation field, i.e., the emission and absorption processes, also established the quantization of energy in these systems. Planck's oscillator absorbs and emits energy in the unit of $h\nu$. In photoelectric effects and production of x-rays, the electron (essentially a free electron) increases or decreases its energy from E_1 to E_2 upon the absorption or emission of light of frequency ν , the frequency being related to the energies by the relation $E_1 - E_2 = h\nu$. The interactions are such that the change of energy of a mechanical system is accompanied by the emission or absorption of a photon of the radiation field. With this background in mind it will be seen that the Bohr theory to be described presently is more or less a straightforward application of these ideas to the mechanics of the atom.

Bohr made two assumptions. The first is that the electron in the hydrogen atom can stay only on a series of selected circular orbits (see Fig. 1-4) specified by the condition that the angular momentum of the electron be an integral multiple of $h/2\pi$,

$$Mav = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \dots, \quad (1-14)$$

where M is the mass of the electron, a is the radius of the orbit, and v is the linear velocity of the electron. These orbits are *assumed* to be stationary against radiation. The state of motion corresponding to each orbit is called a *stationary state* or a *quantum state*. The second assumption is that the electron may "jump" from one orbit with energy E_1 to another with energy E_2 and cause the emission or absorption of radiation of frequency ν given by

$$E_2 - E_1 = h\nu. \quad (1-15)$$

Since each orbit has a definite energy, the selection of a set of discrete orbits implies the quantization of energy, the quantized energy values being determined by Eq. (1-14). Equation (1-14) may thus be called the *quantum condition*. The second assumption determines the frequency of the radiation and Eq. (1-15) may thus be called the *frequency rule*. Actually, in the first assumption Bohr extended the idea of energy quantization from an oscillator to the hydrogen atom, although he introduced a rule of quantization different from that of Eq. (1-4). Once the energy is quantized, it can change, in the course of emission and absorption of radiation, only in discontinuous steps among the quantized energy values; the frequency rule, Eq. (1-15), thus appears to be a natural generalization of Eq. (1-13) from the photoelectric effect to the atomic system. At first look, the quantum condition, Eq. (1-14), does not seem to be related to that of the oscillator, Eq. (1-4). In the next section, however, we shall see that they are related.

Let us consider the consequences of these two assumptions. Denote the nuclear charge by Ze for generality where Z is the atomic number and e is the numerical value of the electronic charge, i.e.,

$$e = +4.8029 \times 10^{-10} \text{ esu.} \quad (1-16)$$

For an electron in a circular orbit the centripetal force must equal the Coulomb force between the nucleus and the electron,

$$\frac{Mv^2}{a} = \frac{Ze^2}{a^2}. \quad (1-17)$$

Combining Eqs. (1-14) and (1-17) we have

$$v = \frac{2\pi Ze^2}{nh} \quad (1-18)$$

and

$$a = \frac{n^2 h^2}{4\pi^2 MZe^2}. \quad (1-19)$$

These equations give the velocity and radius of an orbit characterized by

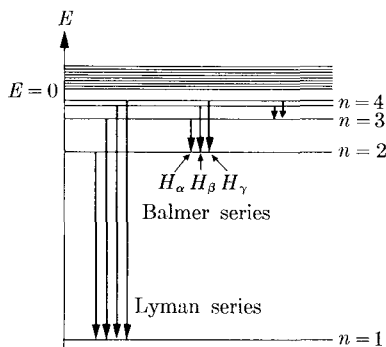


FIGURE 1-5

an integer n . The integer n is called the *quantum number*. The energy of this orbit is

$$\begin{aligned}
 E_n &= \frac{1}{2} Mv^2 - \frac{Ze^2}{a} \\
 &= \frac{1}{2} \frac{Ze^2}{a} - \frac{Ze^2}{a} \\
 &= -\frac{2\pi^2 MZ^2 e^4}{n^2 h^2}, \quad n = 1, 2, \dots
 \end{aligned} \tag{1-20}$$

These quantized energy values are plotted in Fig. 1-5. We note that the quantized energy values form a spectrum different from that of Eq. (1-4). The quantization of mechanical systems seems more complicated than that of the radiation field, which is always quantized to equal units $h\nu$. Each mechanical system has its own rule of quantization. The oscillator is quantized to equal intervals, whereas the hydrogen atom is quantized to a scheme shown in Fig. 1-5. For other mechanical systems, other rules of quantization are needed; and the task of finding the correct rule of quantization becomes the main concern of the old quantum theory.

After having obtained the quantized energy values, we now apply the second assumption to derive the frequencies of radiation that may be emitted or absorbed by the hydrogen atom. The frequency rule gives

$$\nu = \frac{2\pi^2 MZ^2 e^4}{h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

for emission: $n_f = 1, 2, \dots$

$$n_i = n_f + 1, n_f + 2, \dots \tag{1-21}$$

for absorption: $n_i = 1$

$$n_f = 2, 3, \dots,$$

where n_i and n_f are the initial and final values of n for a particular *quantum transition* (or "jump"). When $n_f = 1$, Eq. (1-21) reproduces the frequencies of the lines forming the Lyman series; $n_f = 2$ corresponds to the Balmer series; $n_f = 3$, the Paschen series, etc. The agreement between the predicted and observed values for the multitudes of spectral lines is so excellent that one feels the Bohr theory has made a breakthrough in the development of a theory of the atom. It is the first theory of line spectrum that agrees with experiments.

We shall not discuss other applications of the Bohr theory at this point. Some of the quantities derived here will be useful later, and we shall now express them in more convenient forms. From Eq. (1-20) we calculate the lowest of the quantized energy values by substituting $n = 1$ and $Z = 1$. The result is -13.6 ev (electron volt). The corresponding stationary state is called the *ground state*. Other states are called *excited states*. The energy values of the states may be represented by the *energy levels* in Fig. 1-5, which may be called the *energy level diagram* or the *level scheme*. Equation (1-20) may be more simply written as

$$E_n = -13.6 \frac{Z^2}{n^2} \text{ ev.} \quad (1-22)$$

From Eq. (1-19) we calculate the *first Bohr radius* a_0 , i.e., the radius of the first orbit, by substituting $n = 1$ and $Z = 1$,

$$a_0 = \frac{h^2}{4\pi^2 M e^2} = 0.529 \times 10^{-8} \text{ cm.} \quad (1-23)$$

This radius of about half an angstrom agrees in order of magnitude with the radius of the atom estimated by the kinetic theory of gases—an interesting byproduct of the Bohr theory. The radii of the excited states may be expressed by

$$a = \frac{n^2}{Z} a_0. \quad (1-24)$$

The velocity of the electron in the ground state may be calculated from Eq. (1-18), the result being $1/137$ of the velocity of light. We may make use of the so-called *Sommerfeld fine structure constant* α , defined by

$$\alpha = \frac{2\pi e^2}{hc} = \frac{1}{137}. \quad (1-25)$$

Equation (1-18) may thus be rewritten

$$v = \frac{Z}{n} \alpha c. \quad (1-26)$$

The electron moving in a circular orbit gives rise to a circular current which has a magnetic moment μ , the magnitude of which in emu is given by the product of the current and the area of the circuit loop:

$$\mu = \pi a^2 \frac{ev}{2\pi ac} = n \frac{eh}{4\pi Mc}. \quad (1-27)$$

The magnetic moment is thus an integral multiple of a unit $eh/4\pi Mc$, this unit being known as the *Bohr magneton*.

The Bohr theory applies only to circular orbits. Bohr assumed that the hyperbolic orbits corresponding to positive energy values are not quantized. Thus the energies of the hyperbolic orbits form a continuous band above the $E = 0$ line in Fig. 1-5. Transitions to and from this band correspond to absorption and emission lines forming a continuous spectrum beyond the series limit of the discrete spectrum. The continuous spectrum is also observed.

According to the Bohr theory, the energy of an atom cannot take on any arbitrary continuous values. After Bohr propounded his theory in 1913, Franck and Hertz* immediately started experiments on electron collisions with atoms; and their results verified the existence of discrete energy levels. The quantization of energy of the atomic systems is thus an experimentally established fact.

In spite of the success of the Bohr theory, it must be kept in mind that this theory consists of incoherent parts and cannot be considered as complete and satisfactory. It retained classical mechanics but arbitrarily restricted it by the quantum condition; it rejected classical electrodynamics and replaced it by the frequency rule. However, its many successes make one feel that if a coherent and satisfactory theory is to be developed, it will have to embrace the salient points of the Bohr theory. As the quantization of energy is a universal phenomenon, any physical theory must adapt itself to accommodate it. Two problems thus arise. First, how is a general mechanical system quantized? In other words, what is the general rule of quantization for a mechanical system? We have seen that the oscillator and the hydrogen atom are quantized according to different rules. We want to know if there is a general rule which may be applied for the quantization of any mechanical system. Such a rule may be sought on an empirical basis at first, but eventually it has to be made a coherent part of the whole theory. Once the energy is quantized, any change of energy can take place only in discontinuous steps. Therefore, all physical processes involving energy exchange assume a discontinuous character. Now classical theory is based on the concept that

* Franck and Hertz, *Verhandlungen der Deutschen Physikalische Gesellschaft*, 15, 613 (1913).

physical quantities and processes are all continuous, and this leads to the second problem: how to formulate a physical theory which describes physical processes in discontinuous steps. Furthermore, since classical theory is valid in macroscopic physics, the new theory, if it is a general theory, must include classical theory as a limiting case. The continuum of energy in classical theory most likely is an approximation of the quantized energy levels when the latter are so densely spaced that a continuous approximation may be valid. The classical theory may be just a continuous approximation of the quantized theory. In developing such a quantum theory, the rules of quantization for the oscillators and the hydrogen atom are important clues for the first problem. The frequency rule, which is essentially equivalent to the Einstein equation for the photoelectric effect, is important for the second problem. In the next section we shall discuss the work in this direction between 1913 and 1925 which constitutes the old quantum theory. The satisfactory solution of these problems, however, has to be found later in quantum mechanics.

1-4 Sommerfeld's generalization and the old quantum theory. Sommerfeld took the next important step after Bohr in developing quantum theory. He succeeded in introducing a general rule of quantization* which, in spite of its limitations, gave good results in a number of cases and thus partially solved the first problem mentioned at the end of the last section. For a multiply periodic system described by the generalized coordinates q_1, q_2, \dots, q_f and the generalized momenta p_1, p_2, \dots, p_f , Sommerfeld proposed the following quantum conditions that determine the stationary states and quantized energy levels,

$$\oint p_k dq_k = n_k h, \quad \begin{array}{l} n_k: \text{integers,} \\ k = 1, 2, \dots, f. \end{array} \quad (1-28)$$

In this equation the integral is to be performed over one cycle of the variable q_k , and f is the number of degrees of freedom. If we apply this condition to the circular orbit, the result obtained is the same as the Bohr quantum condition,

$$\oint p_\theta d\theta = \oint Mva d\theta = 2\pi Mva = n_\theta h; \quad (1-29)$$

$$\therefore Mva = \frac{n_\theta h}{2\pi}, \quad n_\theta = 1, 2, \dots \quad (1-30)$$

* A. Sommerfeld, *München Sitz.*, pp. 425, 459 (1915); *Ann. d. Phys.* **51**, 1 (1916). The rule was proposed independently and almost simultaneously by W. Wilson, *Phil. Mag.* **29**, 795 (1915); **31**, 156 (1916). It is thus known as the Wilson-Sommerfeld quantum condition.

Applying this condition to an oscillator the coordinate of which is given by $x = A \sin \omega t$, with the period of oscillation denoted by T and energy by E , we obtain the Planck quantum condition,

$$\oint p_x dx = \oint MA^2 \omega^2 \cos^2 \omega t dt = MA^2 \omega^2 \frac{1}{2} T; \quad (1-31)$$

$$\therefore \oint p_x dx = ET = nh; \quad (1-32)$$

$$\therefore E = nh\nu, \quad n = 0, 1, 2, \dots \quad (1-33)^*$$

That the Wilson-Sommerfeld quantum condition includes the Planck and the Bohr quantum conditions as its special cases gives us some confidence in its general applicability. Sommerfeld applied his quantum conditions to the elliptical orbits of the hydrogen atom and thereby generalized the Bohr theory. For elliptical orbits there are two generalized momenta: the radial momentum p_r and the angular momentum p_θ . The two quantum conditions are

$$\oint p_r dr = n_r h, \quad n_r = 0, 1, 2, \dots, \quad (1-34)$$

$$\oint p_\theta d\theta = n_\theta h, \quad n_\theta = 1, 2, \dots \quad (1-35)$$

Here, n_θ starts from 1 instead of 0 because of the following consideration: $n_\theta = 0$ means no angular momentum; the elliptical orbit thus collapses into a line passing through the nucleus, which does not seem physically possible. Whereas the Bohr quantum condition is satisfied by a set of discrete circular orbits, the Sommerfeld quantum conditions are obeyed by a set of discrete elliptical orbits. We shall omit the mathematical derivation (Problem 1-2) and simply state the results. The energies of the elliptical orbits are

$$E = - \frac{2\pi^2 MZ^2 e^4}{(n_r + n_\theta)^2 h^2}. \quad (1-36)$$

Let

$$n = n_r + n_\theta, \quad n = 1, 2, \dots \quad (1-37)$$

Respectively, n_r , n_θ , and n are called the *radial*, *azimuthal*, and *principal quantum number*. Equation (1-36) may be rewritten as follows:

$$E = - \frac{2\pi^2 MZ^2 e^4}{n^2 h^2}, \quad n = 1, 2, \dots, \quad (1-38)$$

* There is some confusion as to where the integers start. In Eq. (1-30) they start at unity, while in Eq. (1-33) they start at zero. This point is not clearly settled in the Sommerfeld theory, and we shall see other examples of it later. This is an unsatisfactory feature of the old quantum theory.

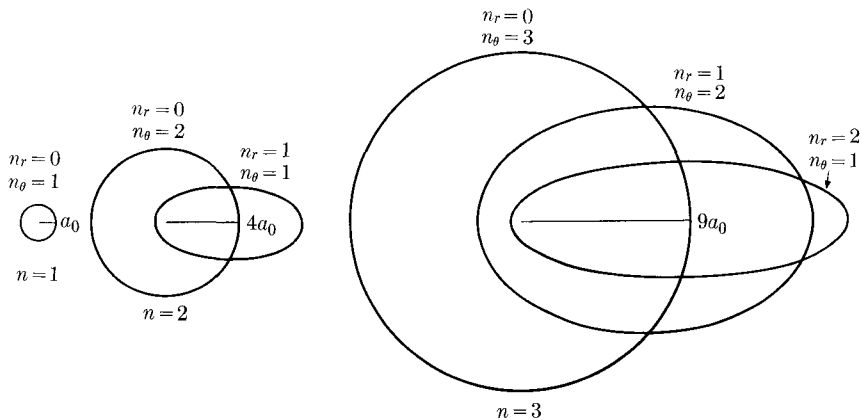


FIGURE 1-6

which is identical with Bohr's result, Eq. (1-20). Thus the success of the Bohr theory is retained. The elliptical motion has two degrees of freedom and thus has two constants of motion: one is the energy E and the other is the angular momentum p_θ . The energy is quantized according to Eq. (1-31). On the other hand, Eq. (1-35) gives rise to the equation

$$p_\theta = n_\theta \frac{\hbar}{2\pi}, \quad n_\theta = 1, 2, \dots, \quad (1-39)$$

so that the angular momentum is also quantized (a result also implied in Bohr's theory). According to the Wilson-Sommerfeld quantum conditions, a system of f degrees of freedom has f integral quantum numbers and therefore the f constants of motion are all quantized. Thus the concept of quantization is extended from energy to many other quantities. Having described the dynamical properties of the elliptical orbits, we now turn to their kinematical properties. The semimajor axis a and semiminor axis b may be shown to be given by the following expressions:

$$a = \frac{n^2}{Z} a_0, \quad (1-40)$$

$$b = \frac{nn_\theta}{Z} a_0, \quad (1-41)$$

where a_0 is the first Bohr radius. Both the energy and the semimajor axis depend on the principal quantum number n only. For a given n , n_θ can be any number from 1 to n corresponding to n ellipses having the same energy and semimajor axis, but differing in their angular momenta and semiminor axes. The ellipses may thus be classified according to the principal quantum number n as in Fig. 1-6. The energy level diagram is

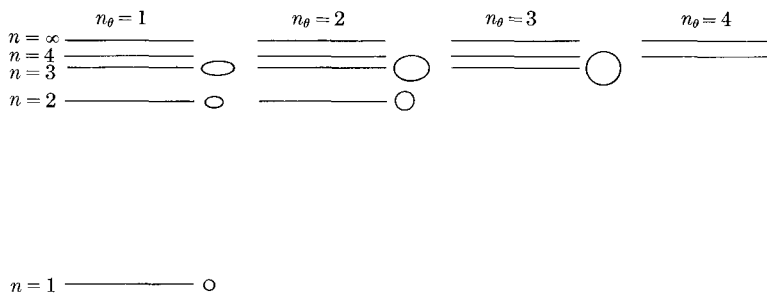


FIGURE 1-7

the same as in the Bohr theory. However, each level designated by n actually represents the energy of n elliptical orbits that happen to have the same energy. As these n orbits are different in other respects, it seems appropriate to show them separately in the energy level diagram. We adopt a scheme shown in Fig. 1-7 where the energy of each ellipse is represented by a line and energy levels of the same n_θ are grouped together in a column. In Fig. 1-7 we show some of the ellipses for easy identification. The vertical scale represents the energy and the columns specify the angular momentum.

Sommerfeld's next step was to introduce relativity into the quantum theory. According to the special theory of relativity, the mass of a particle increases with its velocity; the change becomes appreciable when the velocity approaches the velocity of light. The dependence of mass on velocity is given by

$$M = \frac{M_0}{\sqrt{1 - (v^2/c^2)}}. \quad (1-42)$$

The velocity of the electron in the first Bohr orbit is $c/137$. The corresponding change of mass is small but detectable. This change of mass gives rise to small changes of the orbit; a detailed mathematical analysis shows that the orbit is no longer a closed curve but may be approximated by a precessing ellipse, similar to the advance of perihelion of the planetary orbits. The relativistic effect also gives rise to small changes in energy. Sommerfeld carried out the calculation in detail and showed that the energies of the n "ellipses" with the same principal quantum number n are no longer the same. Thus each level in Fig. 1-5 splits into a number of closely spaced levels: the ground state does not split, the first excited state ($n = 2$) splits into two, the n th into n levels. As a result each line in the spectrum splits into a number of lines of nearly the same frequency. The splitting of a line into a number of components was actually observed in spectroscopy and this fact was known as the *fine structure* of spectral lines. The success of the Sommerfeld theory in deriving the correct fine

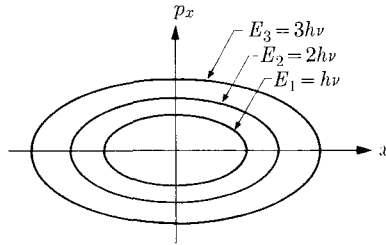


FIGURE 1-8

structure formula of the hydrogen atom is a major triumph of the old quantum theory. Although Sommerfeld's success, as we shall see later, is partly accidental, the formula bearing his name survived many changes of the theory until the discovery of the *Lamb shift* in 1947.

The meaning of the Wilson-Sommerfeld quantum condition may be brought out clearly by considering the motion in *phase space*. Let us take the oscillator as an example. The phase space for the oscillator is a two-dimensional space with x and p_x as its coordinates (see Fig. 1-8). As the oscillator moves, both x and p_x change with respect to time. Thus the representative point (x, p_x) moves in phase space. Because the motion of the oscillator is periodic, the representative point will return to the starting point after one period of oscillation, and its path will be a closed curve. For a linear harmonic oscillator, x and p_x are trigonometric functions with a phase difference of 90° , the closed curve being an ellipse. The integral appearing in the quantum condition is actually the *phase integral*, and its value represents the area inside the closed curve. The quantum condition thus means that the area inside the closed curve is an integral multiple of h . Figure 1-8 shows that the series of curves representing motions obeying the quantum condition cut the phase space into equal areas of h . In other words, each stationary state corresponds to an area of h in the phase space, and the quantum condition thus implies the quantization of the phase space. In classical statistical mechanics the phase space is assumed to be continuous, capable of being subdivided into parts as small as we wish without limit. The quantum theory thus requires a modification of classical statistical mechanics. In fact the failure of the latter in the theory of blackbody radiation is rooted on the presumption that phase space may be indefinitely subdivided. Planck was led to his theory by considering the energy distribution from the point of view of phase space. He noted that Eq. (1-3) requires that at low temperature the average energy of an oscillator be much lower than kT . This may be the case only if we forbid the energy values immediately above zero to appear, i.e., the energy must be discontinuous from zero up.

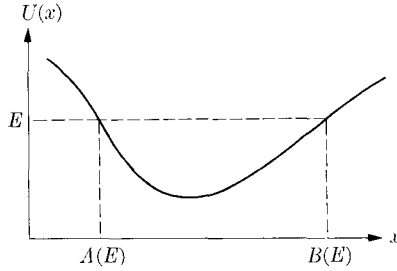


FIGURE 1-9

The significance of the phase integral may be demonstrated by a theorem in classical mechanics described below. Consider a particle of mass M moving in a potential $U(x)$ shown in Fig. 1-9. Given energy E , the particle is confined in a region $A < x < B$, where A and B are two points dependent on E . Let the phase integral be I . Then

$$\begin{aligned}
 I &= \oint p_x dx \\
 &= 2 \int_{A(E)}^{B(E)} M \sqrt{(2/M)[E - U(x)]} dx.
 \end{aligned} \tag{1-43}$$

Differentiation with respect to E leads to the following result (remember that the integrand vanishes at both limits):

$$\begin{aligned}
 \frac{dI}{dE} &= M \sqrt{\frac{2}{M}} \int_{A(E)}^{B(E)} \frac{dx}{\sqrt{E - U(x)}} + 0 + 0 \\
 &= 2 \int_{A(E)}^{B(E)} \frac{dx}{v} \\
 &= T,
 \end{aligned}$$

where T is the period. In terms of frequency ν , we have

$$\frac{dE}{dI} = \nu. \tag{1-44}$$

We now consider this relation in connection with the quantum theory, taking the Bohr orbits of the hydrogen atom as an example. When the quantum number n is large, say 1,000,000, a small change of n , say 1 or 2 units, will not change the energy and radius of the orbit much and we may consider the two orbits of $n = 1,000,000$ and $n = 1,000,001$ as approximately the same. In other words, in the high quantum number region, the quantized energies and orbits are so close that they may be

treated as being continuous. As a result, classical mechanics may be valid, and we may invoke Eq. (1-44),

$$\nu = \frac{dE}{dI} = \frac{E_{n'} - E_n}{I_{n'} - I_n}. \quad (1-45)$$

Since I is an integral multiple of h , the value of $I_{n'} - I_n$ will be h if $n' - n = 1$. Therefore

$$E_{n+1} - E_n = h\nu. \quad (1-46)$$

Note that the quantity ν here is the frequency of the mechanical oscillation of the n th orbit (or the $(n + 1)$ th, as these two are nearly indistinguishable). Comparing Eq. (1-46) with the Bohr frequency condition, we conclude that the frequency of the radiation emitted when transition $(n + 1) \rightarrow n$ takes place is the same as the instantaneous frequency of the mechanical oscillation. This is exactly what the classical electrodynamics asserts.* In other words, Bohr's frequency rule agrees with classical electrodynamics in the high quantum number region. This is a very important result. When we first stated the frequency rule, it appeared to have no connection of any kind with classical electrodynamics. This result is a strong suggestion that classical theory, mechanical as well as electrical, is a continuous approximation of a discontinuous theory and is valid in the high quantum number region where the discrimination of an orbit of $n = 1,000,001$ from that of $n = 1,000,000$ is unnecessary. From this point of view, the classical and quantum laws must be the same in a region where n is large enough to be regarded as a continuous variable. There then exists a correspondence between these two, and the quantum laws in the high quantum number region may be guessed at from the classical laws. This is the essence of the so-called *correspondence principle* of Bohr (1923). Once the quantum laws in the high quantum number region are obtained in this way, they are assumed to apply equally well in the low quantum number region; a complete quantum theory may thus be established. The correspondence principle is thus the answer by the old quantum theory to the second problem stated at the end of the last section: the formulation of a theory for discontinuous physical processes. As an illustration of the application of the correspondence principle we discuss the *selection rules* of optical transitions which have some bearing in later discussions.

* Classical electrodynamics also predicts the emission of the harmonics 2ν , 3ν , \dots , $n\nu$, in addition to the fundamental frequency ν . These correspond to quantum transitions in which $I_{n'} - I_n$ equals $2h$, $3h$, \dots , nh , respectively, since the Bohr frequencies of these transitions are 2ν , 3ν , \dots , $n\nu$ by virtue of Eq. (1-45).

In spectroscopy it was found that not all transitions among the levels in Fig. 1-7 are possible. The correspondence principle leads to the result that in a transition the quantum number n_r may change by any units, whereas n_θ may change only by one unit,* i.e.,

$$\Delta n_\theta = \pm 1. \quad (1-47)$$

This means that transitions can take place only between levels which belong to adjacent columns in Fig. 1-7. Selection rules of this kind have been derived for a number of cases and they agree with experimental results.

The old quantum theory has been extensively developed, based on the Wilson-Sommerfeld quantum condition and the Bohr correspondence principle. By generalization and elaboration it was made applicable to a number of atomic systems and physical processes. It succeeded in explaining a large body of experimental data in spectroscopy. Most importantly, it explains not only the *Zeeman effect* (changes in spectra due to a magnetic field) but also the *Stark effect* (changes in spectra due to an electric field). While the Zeeman effect can be explained by classical theory, the Stark effect cannot. The success in explaining the Stark effect was considered a major triumph of the old quantum theory. It may be mentioned parenthetically that the Zeeman effect is accounted for by introducing space quantization, i.e., the orientation of an elliptical orbit in space is quantized and can take on only a finite number of specified orientations with respect to an external field. In spite of many successes, the old quantum theory is unable to account for the half-integer quantum numbers, the existence of which is forced on us empirically. It is unable to give even a qualitative account of the spectra of the helium atom and the hydrogen molecule. It soon becomes evident that the difficulties of the old quantum theory cannot be removed by minor modifications. A new theory is required. We add here in passing that some of the results of the Sommerfeld theory, such as the assignment of the angular momentum to the states represented in Fig. 1-7, are not correct and have to be revised according to quantum mechanics.

* The orbital motion of a charged particle when the orbit is not a closed curve may be considered as a closed-curve motion with angular frequency ω_r superimposed with a precessional motion of angular frequency $\omega_\theta - \omega_r$. The coordinates x, y, z expressed in Fourier series thus contain all harmonics of ω_r but only the fundamental of ω_θ . These are the frequencies, according to classical electrodynamics, that appear in the radiation emitted by the particle. In the high quantum number region these frequencies correspond to quantum transitions with arbitrary Δn_r and $\Delta n_\theta = \pm 1$ by virtue of Eq. (1-45). According to the correspondence principle, we conclude that Δn_r may be arbitrary and Δn_θ must be ± 1 . Once these rules are established in the high quantum number region, they are assumed to hold for all quantum numbers.

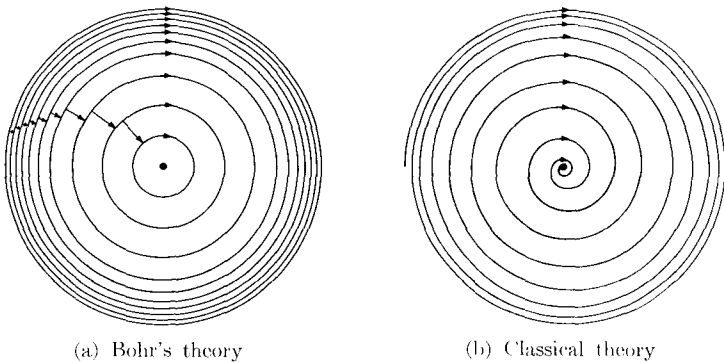


FIG. 1-10. Schematic diagram of transition of states.

The first appearance of quantum effects puzzled and shocked physicists. It seemed as if nature had unexpectedly betrayed us. After the first impact is over, we come to realize that the discontinuous nature of physical quantities and natural processes is a fact of universal occurrence, ignored previously because of the inadequacy of experimental observation. Our physical theory must then be generalized in such a way that dynamical quantities are allowed to be discontinuous and natural processes are described in terms of discrete transitions rather than continuous evolution. Such a theory is called a *quantized theory*.

In the region of high quantum numbers (corresponding to macroscopic phenomena) the discreteness of the dynamical quantities and natural processes are so inconspicuous that a continuous approximation may be valid. The classical theory of physics may be just such an approximation of the quantized theory. On the other hand, in the low quantum number region (corresponding to atomic phenomena) the difference between the classical theory and the quantized theory becomes apparent. The quantized theory thus appears to be a natural extension of classical theory into a region where classical theory, verified only by macroscopic observation, has no right to claim validity. This observation may be illustrated with the Bohr theory as an example. The Bohr theory provides a series of discrete orbits over which the radiating electron jumps down in cascades to the lowest energy level. Having reached the lowest level it stops jumping; there is no other level to jump into [see Fig. 1-10(a)]. In the region of high quantum numbers the orbits are so close together that the cascading process through a number of orbits may be approximated by a continuous spiral [see Fig. 1-10(b)]. Actually, according to classical electrodynamics the electron should follow such a spiral path. The frequencies of radiation emitted during the cascading transitions are represented by the slopes $(E_2 - E_1)/h$ of the broken line in Fig. 1-11. Again,

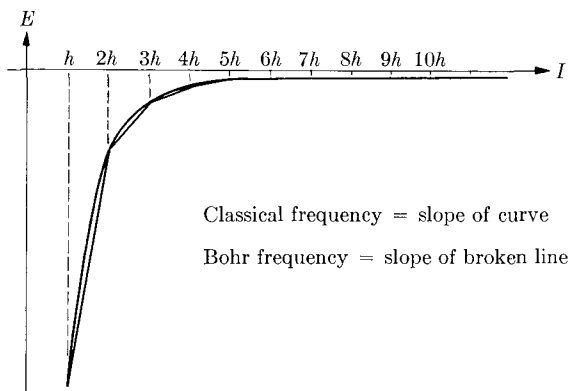


FIGURE 1-11

in the high quantum number region a continuous approximation may be valid which takes the form of the curve in Fig. 1-11. In fact the slope of this curve gives the classical frequency dE/dI . Both continuous approximations agree with the classical theory in the high quantum number region. On the other hand, both cease to be valid in the low quantum number region. There the curve of Fig. 1-11 is no longer a good approximation of the broken line and the spiral in Fig. 1-10(b) curves into the nucleus instead of terminating at the innermost quantized orbit.

Although the general features of the quantized theory are borne out in the old quantum theory, the latter is not a coherent theory. Efforts to formulate a satisfactory quantized theory culminated in 1925 in the establishment of *quantum mechanics*, which will be the main concern of this book. The remainder of this chapter will be devoted to the historical development of this theory.

1-5 De Broglie's wave theory of matter. A new page was turned in 1923-1924 when de Broglie* introduced the wave theory of matter. Inasmuch as many elements of his theory will be discussed mathematically in detail in Chapter 2, we shall not present it here as fully as we did the Bohr theory. We shall concern ourselves only with the historical aspect.

The similarity of the equations of motion in corpuscular mechanics and wave propagation (the principle of least action and the Fermat principle) strongly suggested to de Broglie that there exists a close relation between the concepts of particle and wave. Since radiation is known to have a dual property in that it behaves like a wave in interference and

* L. de Broglie, Thèse, Paris (1924); *Phil. Mag.* **47**, 446 (1924); *Ann. d. Phys.* **3**, 22 (1925).

diffraction phenomena and like a particle in photoelectric and Compton effects, de Broglie reasoned that matter might also have a dual property. A wave of frequency ν and wavelength λ might be assumed to be associated with a moving particle of energy E and momentum p . In strict analogy to the Einstein relations, Eqs. (1-10), he assumed the relations between ν , λ and E , p to be

$$E = h\nu, \quad p = \frac{h}{\lambda}. \quad (1-48)$$

These are known as the *de Broglie relations*. In arriving at these, he was guided by a consideration based on the special theory of relativity. The phase of a wave, $2\pi(\sigma_x x + \sigma_y y + \sigma_z z - \nu t)$, where σ_x , σ_y , σ_z are the three components of the wave number vector, is a relativistic invariant. As a result the four quantities σ_x , σ_y , σ_z , ν transform like a four-vector when a space-time transformation (Lorentz transformation) is carried out. On the other hand, the four quantities p_x , p_y , p_z , E transform in exactly the same way. It seems reasonable to assume that the two sets of quantities are proportional to each other. If the proportionality constant is identified with the Planck constant, we have the Einstein or de Broglie relations.

Once the frequency and wavelength are given, the phase velocity V follows immediately. Thus

$$\begin{aligned} V &= \lambda\nu \\ &= \frac{E}{p} \\ &= \frac{M_0 c^2}{\sqrt{1 - (v^2/c^2)}} \div \frac{M_0 v}{\sqrt{1 - (v^2/c^2)}} \\ &= \frac{c^2}{v}, \end{aligned} \quad (1-49)$$

where v is the velocity of the moving particle. Although the phase velocity is greater than the velocity of light, no contradiction to relativity will ensue, for the phase velocity is not the velocity of energy propagation. In wave motion, it is usually the *group velocity* (to be discussed more in detail in Section 2-1) that represents the velocity of energy propagation. The group velocity v_g of the *de Broglie waves* may be calculated according to a formula to be derived in Chapter 2 (Eq. 2-14),

$$v_g = \frac{dv}{d(1/\lambda)} = \frac{dE}{dp} = v. \quad (1-50)$$

The group velocity thus turns out to be the same as the velocity of the particle. Therefore a moving particle may be represented by a *wave*

packet (to be discussed in detail in Section 2-1) of de Broglie waves. The propagation of a wave packet is determined by the Fermat principle which, by the substitution of the de Broglie relation $p = h/\lambda$, leads to the principle of least action (also see Section 2-1). Thus the equation of motion of the particle is implied in the wave theory. The kinematical and dynamical attributes of a particle may therefore be regarded as manifestations of de Broglie waves and the wave theory may include the corpuscular mechanics as a special case. Furthermore, the wave properties so introduced may be invoked in an attempt to explain quantum phenomena. In fact, de Broglie succeeded in *deriving* the quantum condition from such a consideration. In a circular orbit of the hydrogen atom, the length of the circle, according to the wave theory, must be an integral multiple of the wavelength. Otherwise the wave, after having traveled once around, will be out of phase with the original wave; the waves, having traveled 1, 2, 3, . . . , times around, will have random phase relations to one another at any point so that the resultant wave will be zero (due to interference). The condition that a nonvanishing wave may be established along a circular orbit of length s is thus

$$\oint \frac{ds}{\lambda} = n, \quad n = 1, 2, \dots \quad (1-51)$$

The de Broglie relation then leads to the following equation:

$$\oint p_s ds = nh, \quad n = 1, 2, \dots, \quad (1-52)$$

which is the quantum condition. In the old quantum theory, the quantum condition is introduced without any explanation. In the de Broglie theory the origin of the quantum condition is traced to an assumed wave property of matter. Incidentally, another pleasing point is that light may be regarded as a special kind of de Broglie wave and the dual property of light may thus be accounted for.

While the dual property of light had been well established by 1924, the dual property of matter was merely speculation by de Broglie at that time. This speculation was experimentally verified by Davisson and Germer* in 1927 and later by many others. Diffraction of electron beams was achieved by using crystals as the grating, and the de Broglie relation $p = h/\lambda$ was verified for electrons of various energies. Not only electron beams but also atomic beams of helium and molecular beams of hydrogen were diffracted on a crystal surface. The wave property of matter is thus an experimentally established fact.

* Davisson and Germer, *Phys. Rev.* **30**, 705 (1927); *Proceedings of the National Academy*, **14**, 317, (1928).

The success of de Broglie's theory only leads to a more intriguing problem concerning the dual property of matter and radiation. However, we shall not concern ourselves with the question: Is the electron a particle or a wave? Electron diffraction experiments tell us merely that under certain conditions an electron beam behaves like a wave. They do not identify it as a wave. At best we may say that the electron has a wave-like property. Similarly in view of the photoelectric effect we may merely say that light has a particle-like property. Experimental evidence tells us only that both matter and radiation have some particle-like properties and some wavelike properties. The task before us is to construct a logically consistent and coherent theory, not merely a collection of *ad hoc* assumptions, which accounts for all the observed properties. Classical corpuscular theory explains the particle-like properties but not the wavelike properties. Classical wave theory does just the opposite. Both are incomplete. Quantum mechanics, as we shall see in later chapters, accounts for both kinds of properties. Once such a theory is established, the dual nature of matter and radiation is no longer a mystery and the question of whether the electron is a particle or a wave disappears.

We have discussed two classes of quantum phenomena, namely, the quantization of energy and the wave property of matter. The latter cannot be accounted for in the old quantum theory, a serious defect of this theory. Both may be accounted for in the de Broglie theory without introducing any *ad hoc* assumption regarding quantization. This important achievement is retained in quantum mechanics, as will be seen in later chapters.

To emphasize that a wavelike property does not necessarily guarantee the existence of a physical wave, we shall discuss here a quantum theory of diffraction by Duane* (1923). The diffraction of light was considered as evidence proving that light is a wave. Nevertheless, we shall see in this theory that the diffraction phenomena may be explained by a quantum theory of the light particle. Consider that a photon impinges on a grating of spacing d with an incident angle i and emerges with an angle r (see Fig. 1-12). The momentum transferred to the grating along the surface of the grating is

$$p_y = \frac{h}{\lambda} (\sin i - \sin r), \quad (1-53)$$

according to the law of conservation of momentum. On the other hand, an infinite grating may be considered as a periodic system, and a vertical motion over a distance d

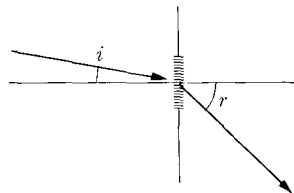


FIGURE 1-12

* W. Duane, *Proc. Nat. Acad. Sci.* **9**, 158 (1923).

completes one cycle of a periodic motion. The Wilson-Sommerfeld quantum condition thus gives rise to the following equation:

$$\oint p_y dy = p_y d = nh \quad (1-54)$$

or

$$p_y = \frac{nh}{d}. \quad (1-55)$$

The quantum condition thus requires that the momentum transferred to the grating be quantized to the unit of h/d . Combining Eqs. (1-53) and (1-55), we obtain

$$n\lambda = d(\sin i - \sin r). \quad (1-56)$$

This is identical with the equation derived in the wave theory specifying the directions of the diffracted rays caused by a grating. Thus the same result may be derived by either the wave theory or the corpuscular theory. This example shows that the observation of a diffraction phenomenon does not necessarily prove that light is a wave. The wave theory is but one of the theories that explain the diffraction phenomenon. From such an experiment we can say no more than that light has a wavelike property.

1-6 The development of quantum mechanics. In 1925 Heisenberg* introduced a system of mechanics, later known as *matrix mechanics*, in which classical concepts of mechanics were drastically revised. He considered that the atomic theory should emphasize the observable quantities, namely, the frequencies and intensities of the spectral lines, rather than those not directly observable, such as the shape of the electronic orbit. This theory was rapidly developed by Heisenberg, Born, and Jordan, making use of matrix algebra. We shall not discuss it in detail. It may be considered as a calculus of the observable quantities. If the mathematical problem involved can be solved completely, this theory can predict the frequencies and intensities of the spectral lines.

Parallel to the development of matrix mechanics, Schrödinger† in 1926 initiated a new line of study, inspired by de Broglie's wave theory of matter, which was then developed into a system of *wave mechanics*. He introduced an equation, now bearing his name, as the "equation of motion" of the de Broglie waves. From this equation, quantization follows automatically; wave mechanics thus becomes a powerful tool for the study of quantization. Its mathematical apparatus, involving the solution of a partial differential equation, is more convenient to handle than that of matrix mechanics and thus it is more widely used in practical applications.

* W. Heisenberg, *Zeits. f. Phys.* **33**, 879 (1925).

† E. Schrödinger, *Ann. d. Phys.* **79**, 361, 489; **80**, 437; **81**, 109 (1926).

Not long after, Schrödinger proved that wave mechanics was mathematically equivalent to matrix mechanics. On the other hand, the physical meaning of the new theory was not clear at first. Schrödinger first considered the de Broglie wave as a physical entity, i.e., the electron is actually a wave. But this soon led to difficulty. A wave may be partially reflected and partially transmitted at a boundary, but an electron cannot be split into two parts for transmission and reflection. The difficulty was removed by Born,* who proposed a statistical interpretation of de Broglie waves which is now generally accepted. The introduction of the statistical interpretation results in a drastic change in scientific thought, for it replaces the deterministic classical theory by a probabilistic theory. De Broglie, conceding that kinematics may be probabilistic because of the wave property, once tried to retain a deterministic dynamics (the pilot wave theory) but was not successful. The new theory based on the statistical interpretation was very rapidly developed into a general, coherent system of mechanics which now bears the name *quantum mechanics*. To this, Dirac, Jordan, Heisenberg, and Pauli made important contributions. Applications of the theory, made in many branches of physics, met with remarkable success.

So far we have confined ourselves to the development of quantum mechanics as applied to atomic systems. This subdivision may be called *quantum mechanics of particles*. However, atomic systems interact with the radiation field, and a complete theory cannot leave out the latter. Furthermore, the quantum theory originated from a study of the quantum effects of the radiation field (the blackbody radiation, the photoelectric effects); and to account for these effects, a quantum theory of radiation is necessary. On the other hand, the development of the general theory of quantum mechanics leads to the establishment of a general technique of quantization which may be applied to many other physical systems. The application of the general methods of quantization to the radiation field resulted in the development of the *quantum theory of radiation*.† In spite of many difficulties encountered, the quantum theory of radiation is able to make successful predictions for many observable processes. It is able to account for both the particle-like properties and wavelike properties of radiation. No previous theory was able to explain all of these properties at the same time.

The application of the general methods of quantization to the radiation field is just one of many. Extensive work has been done in extending

* M. Born, *Zeits. f. Phys.* **37**, 863; **38**, 803 (1926).

† P. A. M. Dirac, *Proc. Roy. Soc.* **114**, 243, 710 (1927); P. Jordan and W. Pauli, *Zeits. f. Phys.* **47**, 151 (1928); E. Fermi, *Rev. Mod. Phys.* **4**, 131 (1932); W. Heisenberg and W. Pauli, *Zeits. f. Phys.* **56**, 1 (1929); **59**, 169 (1930).

quantum theory to many other fields. In this introductory volume we shall limit ourselves to an introduction of quantum mechanics of particles, primarily quantum mechanics of one particle without spin. Nevertheless, general methods of quantum mechanics and its various applications will be discussed briefly in the last chapter.

Let us summarize the difficulties of the classical theories which quantum mechanics is supposed to resolve. We know as fact that physical quantities of mechanical systems and radiation fields are quantized and, as a result, physical processes take place by discontinuous transitions. We also know that both the radiation field and the material particle have the particle-wave dual property. Classical theories consider the physical quantities of both material particles and radiation fields as continuous, and the two pictures of wave and particle are mutually exclusive.

Quantum mechanics will have to be formulated on the basis of discrete physical quantities, and its equation of motion must deal with discrete transitions in physical processes. Under certain circumstances, it should include classical theories as special cases. At the same time, quantum mechanics should be such that the wave and the particle pictures become compatible. In the next chapter we shall formulate a theory which allows discontinuous physical quantities and reduces to classical mechanics of a particle as a special case. Although this theory is based on the particle picture, it nevertheless accounts for the wavelike properties. In the following chapters this theory will be applied to study the quantization of physical quantities in various problems and to describe the physical processes in terms of discrete transitions.

From classical theory to quantum theory a basic change is that the concept of continuity is given up and replaced by discontinuity. This change necessitates the abandonment of *determinism* in classical theory and the adoption of *indeterminism*. Scientific thought since the Greek times has been dominated by determinism (the *law of causality*). But a quantized theory may be shown to be necessarily probabilistic. In classical theory all physical quantities are continuous and thus all rates of change are continuous. Once the equation of motion specifies the rate of change, the initial condition determines completely and uniquely the future development of the system. On the other hand, when physical quantities are quantized, a precise specification of the rate of change and the initial condition does not necessarily dictate a unique course of development of the system. To illustrate this we consider the radiating electron in the hydrogen atom. In classical theory the electron circles the nucleus in a uniquely determined spiral path, since the rate of energy loss is precisely specified by the theory of radiation. Once the energy is quantized, energy loss takes place by quantum transitions. The specified rate of energy loss may be realized in a number of alternative courses of

transitions (an electron in the state $n = 3$ may go to the state $n = 1$ directly or first to the state $n = 2$ and then to the state $n = 1$), and the electron is given a chance to choose its future course among a number of alternatives without violating the equation of motion. The future course of the electron is thus not uniquely determined by the equation of motion and the initial condition. Therefore, only probabilistic predictions of its future, not deterministic predictions, may be made. We thus see that the introduction of probability in quantum mechanics, which has profound consequences in many respects, is forced on us because of the experimental fact of quantization. This important point will be elaborated later on a number of occasions.

PROBLEMS

1-1. Derive Eq. (1-13), the equation giving the wavelength change in Compton scattering, the process being considered as a collision of a photon with an electron. [*Hint*: Set up three equations by considering conservation of energy and momentum in the collision process. There are four variables involved: the scattering angle θ of the photon, the recoil angle φ of the electron, the wavelength after scattering λ' , and the velocity of recoil of the electron v . One of the four, say θ , is to be left undetermined.]

1-2. Derive Eq. (1-36) of the Sommerfeld theory. [*Hint*: In applying Eq. (1-34) remember that

$$p_r = \sqrt{2M[E + (ze^2/r)] - (p_\theta^2/r^2)}$$

and carry out the integration over one cycle of the elliptical orbit.]

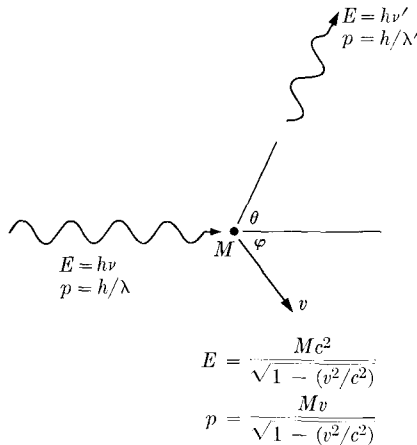


FIGURE 1-13

*1-3. By the method of the old quantum theory, determine the quantized energy levels of a three-dimensional harmonic oscillator the potential function of which is specified by

$$U(r, \theta, \varphi) = \frac{1}{2}kr^2. \quad (1-57)$$

Note that in classical mechanics any central force problem is two-dimensional and angular momentum is a constant of motion. The problem may thus be conveniently solved by using the plane polar coordinates. As an orientation the student may determine the quantized energy values of the circular orbits first.

*1-4. Solve Problem 1-3 by using rectangular coordinates. The method of separation of variables may be used (the treatment of the Stark effect by the old quantum theory, to be given in Section 10-4, may be consulted for this purpose).

* Indicates more difficult problems.