1
The Failure of Classical Physics

Quantum mechanics (QM) emerged in the early twentieth century from attempts to explain some properties of blackbody radiation (BBR) and heat capacity of gases, as well as atomic spectra, light–matter interactions, and behavior of matter on the microscopic level. It soon became clear that classical physics was unable to account for these phenomena. Not only did classical predictions disagree with experiments, but even the mere existence of atoms seemed to be a miracle in the framework of classical physics. In this chapter, we briefly discuss some of the contradictions between classical concepts and observations.

1.1
Blackbody Radiation

First, we outline the failure of classical physics to describe some properties of radiation.

A macroscopic body with absolute temperature $T > 0$ emits radiation, which generally has a continuous spectrum. In the case of thermal equilibrium, in any frequency range the body absorbs as much radiation as it emits. We can envision such a body as the interior of an empty container whose walls are kept at a constant temperature [1,2]. Its volume is permeated with electromagnetic (EM) waves of all frequencies and directions, so there is no overall energy transfer and no change in energy density (random fluctuations neglected). Its spectrum is independent of the material of container's walls – be it mirrors or absorbing black soot. Hence, its name – the *blackbody radiation*. In an experiment, we can make a small hole in the container and record the radiation leaking out.

There is an alternative way [3] to think of BBR. Consider an atom in a medium. According to classical physics, its electrons orbit the atomic nucleus. Each orbital motion can be represented as a combination of two mutually perpendicular oscillations in the orbital plane. An oscillating electron radiates light. Through collisions with other atoms and radiation exchange, a thermal equilibrium can be

established. In equilibrium, the average kinetic energy per each degree of freedom is [1]

$$E_i = \frac{1}{2}kT, \tag{1.1}$$

where k is the *Boltzmann constant*. This is known as the *equipartition theorem*. The same formula holds for the average potential energy of the oscillator, so the total energy (average kinetic + average potential) per degree of freedom is kT. Thus, we end up with the average total energy kT per oscillation. In an open system, such equilibrium cannot be reached because the outgoing radiation is not balanced and the energy leaks out. This is why any heated body cools down when disconnected from the source of heat.

But if the medium is sufficiently extended or contained within a cavity whose walls emit radiation toward its *interior*, then essentially all radiation remains confined, and thermal equilibrium can be attained. Each oscillator radiates as before, but also absorbs radiation coming from other atoms. In equilibrium, both processes balance each other. In such a case, for each temperature T and each frequency ω there exists a certain characteristic energy density $\rho(\omega, T)$ of radiation such that the rate of energy loss by atoms through emission is exactly balanced by the rate of energy gain through absorption. The quantity $\rho(\omega, T)$ is called *spectral energy density* (the energy density per one unit of frequency range). In classical EM theory, it is determined by the corresponding field amplitudes $\mathcal{E}(\omega)$ and $\mathbf{B}(\omega)$ of mono-chromatic waves with frequency ω:

$$\rho(\omega, T) = \frac{1}{4}\left(\varepsilon_0|\mathcal{E}(\omega)|^2 + \frac{|\mathbf{B}(\omega)|^2}{\mu_0}\right) = \frac{1}{2}\varepsilon_0|\mathcal{E}(\omega)|^2 = \frac{|\mathbf{B}(\omega)|^2}{2\mu_0}. \tag{1.2}$$

The last two expressions in (1.2) are obtained in view of the relation $\mathbf{B} = \sqrt{\mu_0\varepsilon_0}(\hat{\mathbf{n}} \times \mathcal{E})$, where $\hat{\mathbf{n}}$ is the unit vector along the wave propagation. Note that ω is the angular frequency,[1] and all quantities involved are measured in the rest frame of the given medium.[2]

Under the described conditions, $\rho(\omega, T)$ is a *universal* function of ω and T. According to thermodynamics (Kirchhoff's law of thermal radiation), it must be the product of ω^3 and another universal function of ω/T [2,3]:

$$\rho(\omega, T) = \alpha\omega^3 f\left(\frac{\omega}{T}\right). \tag{1.3}$$

Using (1.3), one can show that the *total energy density* $\eta(T)$ of BBR is

$$\eta(T) = \int_0^\infty \rho(\omega, T)\mathrm{d}\omega = \sigma T^4, \tag{1.4}$$

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1) We will use throughout the book the angular frequency ω, which is ordinary frequency f (number of cycles/s) multiplied by 2π. In the physicists' jargon, the word "angular" is usually dropped.
2) Rest frame of an object is the frame of reference where the object's center of mass is at rest.

where

$$\sigma \equiv \alpha \int\limits_{0}^{\infty} \xi^3 f(\xi) d\xi, \quad \xi \equiv \frac{\omega}{T}. \tag{1.5}$$

The relation (1.4), known as the *Stefan–Boltzmann law*, is exact and has been experimentally confirmed. Figure 1.1 shows a few graphs of $\rho(\omega, T)$ obtained from experiments. But all attempts to derive the pivotal function $f(\omega/T)$ determining $\rho(\omega, T)$ and σ have failed.

By 1900 there were two half-successful attempts to derive $\rho(\omega, T)$. Their results were different due to the different models chosen to represent radiation.

The first model considered radiation as EM waves. In this model, the molecules interacting with radiation were represented as harmonic oscillators; similarly, each monochromatic component of radiation can also be considered as an oscillator with the corresponding frequency. Then, the total energy density could be evaluated as a product of the average energy $\langle E \rangle = kT$ per one EM oscillator and the number N of oscillators occupying all states with frequency ω [4]. Such an approach results in

$$\rho(\omega, T) = N(\omega)\langle E \rangle = \frac{\omega^2}{\pi^2 c^3} kT. \tag{1.6}$$

This expression is known as the *Rayleigh–Jeans formula*. Note that it does have the form (1.3). But, while matching the data at low frequencies, it diverges at high frequencies (Figure 1.2), predicting the infinite spectral density $\rho(\omega, T)$ and infinite total energy density $\eta(T)$ at $\omega \to \infty$, even at low temperatures! This conclusion of classical theory was dubbed "the UV catastrophe." Something was wrong with the classical notion of energy exchange between matter and radiation as a continuous process, especially when applied to the high-frequency range!
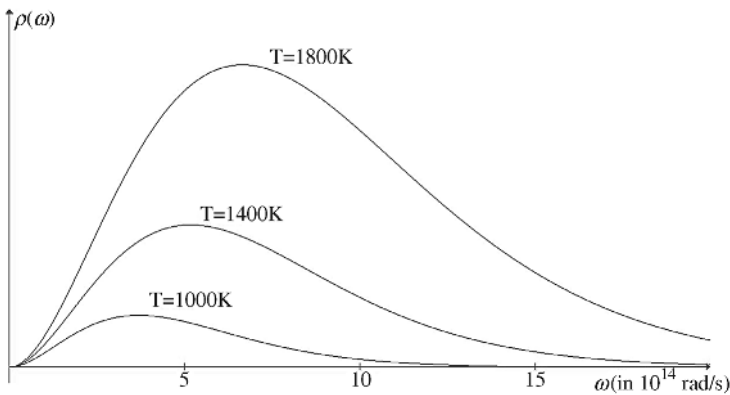

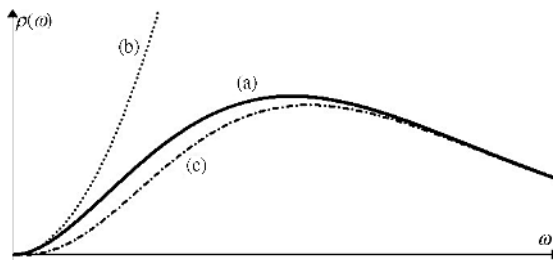**Figure 1.1** The BBR spectrum at various temperatures.

Figure 1.2 The BBR spectrum according to different approaches treating radiation as classical waves or particles, respectively. (a) BBR spectrum; (b) the Rayleigh–Jeans curve; (c) the Wien curve.

The second model suggested by W. Wien used the Newtonian view of radiation as a flux of particles. Applying to such particles Boltzmann's statistical treatment, he obtained the expression

$$\rho(\omega, T) = \text{const}\, \omega^3\, e^{-\gamma(\omega/T)}, \tag{1.7}$$

where γ is another constant. This expression also satisfies the requirement (1.3), and, in contrast with (1.6), it describes accurately the experimental data for high frequencies. However, it does not match the data at low frequencies (Figure 1.2). Something was wrong with the notion of radiation as classical particles, especially in the low-frequency range!

Thus, regardless of whether we view radiation as purely classical waves (Maxwell) or purely classical particles (Newton), either view only partially succeeds. The wave picture works well in describing low frequencies, and the particle picture works for high frequencies, but both fail to describe *all* available data. That was the first indication that the EM radiation is neither exactly waves nor exactly particles.

1.2
Heat Capacity

Heat capacity is the amount of heat dQ required to change a body's temperature T by 1 K: $C = dQ/dT$. We model the body as an *ideal gas* whose molecules do not interact with each other. The analysis for an ideal gas hinges on the number of degrees of freedom. For an atom considered as a point-like object, three mutually independent directions of its motion (or three components of its position vector) form three degrees of freedom. A diatomic molecule presents a more complex case. If it is a rigid pair of two point masses, then it has five degrees of freedom – three coordinates of its center of mass and two angular coordinates specifying the orientation of its axis. If the separation s between the two masses can change (e.g., two masses connected by a spring), then it becomes a variable s, and the total number j of degrees of freedom jumps from 5 to 6. This is the maximal number for a diatomic molecule formed from two point-like atoms. The number j here can also be determined as 3×2 (three degrees of freedom per particle times the number of particles).

But as stressed in comment to Eq. (1.1), the vibrational degree of freedom "absorbs" the energy kT, where the additional amount (1/2)kT is due to the average potential energy of vibration. This can be formally described by adding and extra degree of freedom for each vibration, so that for a classical diatomic molecule we can write $j' = j + 1 = 7$.

Suppose we have a system of particles (e.g., a container with gas) in a state of thermodynamic equilibrium. The gas in this case is described by the *ideal gas equation* $PV = NkT$ [3,5,6], where P and V are the gas pressure and volume, respectively, and N is the number of molecules. For one mole of gas, that is, $N = N_A$, where N_A is the Avogadro number, we have

$$PV = RT, \tag{1.8}$$

where $R = N_A k$ is the universal gas constant.

Let us now recall the relationship between pressure P and the internal energy U of the gas, $P = (2/j')(U/V)$. Combining this with (1.8) gives

$$U = \frac{j'}{2} RT. \tag{1.9}$$

There are two different types of heat capacity depending on two possible ways of transferring heat to a system. We can heat a gas keeping it either at fixed volume or at fixed pressure. The corresponding *molar heat capacities* will be denoted as c_P and c_V, respectively. To find them, recall the first law of thermodynamics [2,3], $dQ = dU + dW = dU + P\,dV$, where dW is an incremental work done by the system against external forces while changing its volume by an incremental amount dV. Applying the basic definition $C = dQ/dT$, we have for the case of fixed volume $dV = 0$:

$$C \rightarrow c_V = \frac{\partial U}{\partial T} = \frac{j'}{2} R. \tag{1.10}$$

When $P = $ const, we obtain

$$C \rightarrow c_P = \frac{\partial U}{\partial T} + P\frac{\partial V}{\partial T} = c_V + P\frac{\partial V}{\partial T}. \tag{1.11}$$

By virtue of (1.8) taken at $P = $ const, this gives

$$c_P = c_V + R = \left(\frac{j'}{2} + 1 \right) R. \tag{1.12}$$

The ratio

$$\gamma \equiv \frac{c_P}{c_V} = 1 + \frac{2}{j'} \tag{1.13}$$

gives us direct information about the number j'.

In the outlined classical picture, the number j' and thereby c_P, c_V, and γ are all independent of T. But this contradicts the experiments. Heat capacities of all substances at low temperatures turn out to be noticeably less than predicted and go to zero in the limit $T \rightarrow 0$. Shown in Table 1.1 are the classically predicted values of c_V, c_P, and γ for a few different substances and their experimental values at room temperature [6].

Table 1.1 Predicted versus observed heat capacities at $T = 293$ K (in J/(mol K))

Gas	j	c_V		c_P		γ	
		Theory	Exp	Theory	Exp	Theory	Exp
Helium (He)	3	12.47	12.46	20.79	20.90	1.67	1.67
Hydrogen (H_2)	6	24.42	20.36	32.73	28.72	1.33	1.41
Water vapor (H_2O)	9	37.41	27.80	45.73	36.16	1.22	1.31
Methane (CH_4)	15	62.36	27.21	70.67	35.57	1.13	1.30

The table shows a very interesting (and mixed) picture. The measurement results almost exactly confirm theoretical predictions for monatomic gases such as helium. The calculated and measured values of c and γ are in excellent agreement for $j = 3$.

For diatomic gases ($j = 6$, $j' = 7$), however, the results are more complicated. Consider, for instance, hydrogen. Its measured value of $c_V = 20.36$ is significantly lower than the expected value 24.42. A similar discrepancy is observed for γ: the measured value is 1.41 instead of predicted 1.33. A closer look at these numbers reveals something very strange: they are still in excellent agreement with Equations 1.10–1.13, but for $j' = 5$ instead of 7. Thus, the agreement can be recovered, but only at the cost of decreasing the number j' ascribed to a diatomic molecule. It looks like two "effective" degrees of freedom "freezes" when the particles get bound to one another. Which kind of motion could possibly undergo "freezing"? Certainly not 2 out of 3 translational motions: there is nothing in the isotropic space that could single out one remaining motion. It could be either 2 rotational motions, or 1 vibrational motion. Running ahead of ourselves, we will say here that it is vibrational motion that freezes first as the gas is cooled down. Already at room temperatures, we cannot pump energy into molecular vibrations. At these temperatures, the connection between the two atoms in an H_2 molecule is effectively absolutely rigid.

Thus, already the experimental results for different gases at room temperature show that something is wrong with the classical picture. But the situation becomes even worse if we carry out experiments for the same gas at widely different temperatures. As an example, consider the data for molecular hydrogen (Table 1.2).

At sufficiently low temperatures, experimental values become lower than the classical prediction even after we ascribe to the diatomic molecules only five degrees of freedom instead of effective seven. For instance, the experimental

Table 1.2 Constant-volume heat capacity of hydrogen as a function of temperature (in degrees Kelvin)

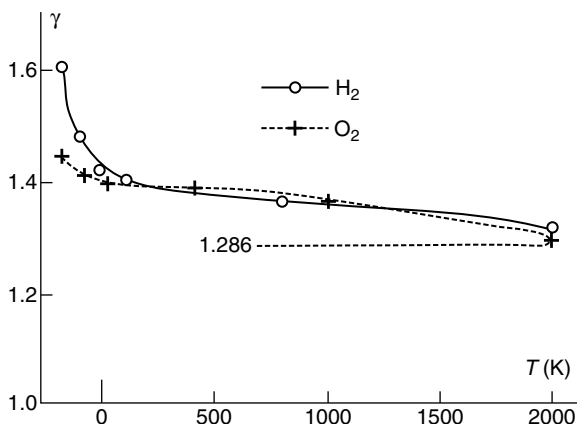| T	c_V
197	18.32
90	13.60
40	12.46

Figure 1.3 Experimental values of γ as functions of T for H_2 and O_2. The dashed horizontal line is the classical prediction for a diatomic molecule with vibrational degree of freedom ($j' = 7$). (Reproduced from Refs [3,6].)

value $c_V = 12.46$ at 40 K is significantly less than $c_V = 20.36$ measured at room temperature. It could still fall within the classical prediction, but only at the cost of reducing the number of degrees of freedom from 5 to 3. It looks as if more and more degrees of freedom become frozen as the substance is cooled down. This time we can, by the same argument as before, assume the freezing of two rotational degrees of freedom associated with the spatial orientation of the molecule.

The same tendency is observed in the measurements of γ (Figure 1.3). Contrary to the classical predictions, experiments show that γ increases with T, and this behavior, in view of Equation 1.13, can be attributed to the same mysterious mechanism of "freezing." We can thus say that decrease of c_V and increase of γ at low temperatures represent two sides of the same coin.

The general feature can be illustrated by Figure 1.4. It shows that heat capacities fall off with temperature in a step-like fashion. Each step is associated with the freezing of one or two degrees of freedom. At the end of this road, all of the initial degrees of freedom are frozen and accordingly heat capacities approach zero.

If we now increase the temperature, starting from the absolute zero, we observe the same phenomenon in reverse. As we heat a body, it effectively regains its degrees of freedom all the way back to their normal number at sufficiently high temperatures.

What causes these strange effects? And what is the "normal" number for γ to begin with? Classical physics cannot answer these questions even in the simplest case of a monatomic gas. Let us, for instance, get back to helium. We started with the apparently innocuous statement that a helium atom at room temperature has $j = 3$. But after a second thought we can ask: "Why is j equal to 3, in the first place?" After all, the helium atom consists of the nucleus and two electrons, so there are three particles in it, and therefore there must be $j = 3 \times 3 = 9$. Further, the He nucleus consists of two protons and two neutrons, so altogether we have six particles in a
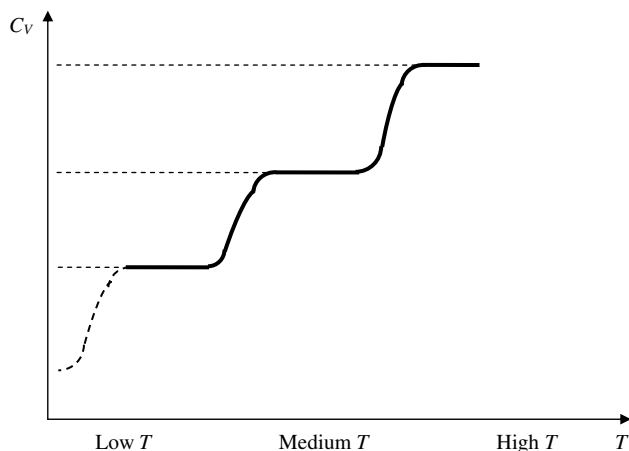
Figure 1.4 Graph of the heat capacity versus temperature for a diatomic ideal gas.

helium atom and accordingly the number j must be $j = 6 \times 3 = 18$ instead of 3. And if we also realize that each nucleon, in turn, consists of three quarks, which makes the total number of particles in the helium atom equal to 14, then the number j must be $j = 14 \times 3 = 42$. Accordingly, the theoretical prediction for the molar heat capacities for He must be $c_V = 174.6$ and $c_P = 182.9$ instead of 12.46 and 20.8, respectively. In other words, already at room temperature and in the simplest case of a monatomic gas, there is a wide (by about one order of magnitude!) discrepancy between theory and experiment. Experiment shows that *nearly all* degrees of freedom of the subatomic particles are frozen so fundamentally that they are as good as nonexisting, at least at room temperatures, and only the remaining three degrees determining the motion of the atom as a whole survive. Why is this so?

One could try to explain this by the fact that the binding forces between the electrons and the atomic nucleus are so strong that they practically stop any relative motion within an atom; this is true even more so for the protons and neutrons within a nucleus, and so on. As we go farther down the subatomic scale, the interaction forces increase enormously, thus "turning off" the corresponding degrees of freedom. But this argument does not hold. The notion about the forces is true, but the conclusion that it must "turn off" the corresponding motions is wrong.

The equipartition theorem is a very general statement that applies to *any* conservative (i.e., described by potential) forces, regardless of their physical nature or magnitude. As a simple example, consider two different types of diatomic molecules in thermodynamic equilibrium. Let each molecule be represented by a system of two masses connected by a spring, but the spring constant is much higher for one molecule than for the other. Equilibrium is established in the process of collisions between the molecules, in which they can exchange their energy. Eventually, molecules of both types will have, on average, an equal amount of vibration energy. The total mechanical energy of vibration for a spring described by

Hooke's law is $E = kA^2/2$, where k is the spring constant (not to be confused with the Boltzmann constant!) and A is the amplitude of vibration. In thermal equilibrium, we will have $E_1 = E_2$, that is, $k_1 A_1^2 = k_2 A_2^2$.

The fact that one spring is much stronger than the other will only result in the smaller amplitude of vibration for this type of molecules, that is, $A_2 = \sqrt{k_1/k_2}A_1$, and $A_2 \ll A_1$ if $k_2 \gg k_1$, but it *will not affect the energy* of vibration. Applying this to our system, we can say that the constituents of an atomic nucleus, according to the classical theory, must jitter with a very small amplitude, but with the same energy as twice the average energy of the atom's translational motion in a state of thermal equilibrium. And this energy must contribute to the observed heat capacity on the same footing as the energy of translational motion, even in the limit of arbitrarily high k. But no such contributions are evident in the observed capacities. It turns out that the word "freezing" is not strong enough and must be understood as *total elimination* of any contributions from the corresponding degrees of freedom.

It is only because the physicists did not know much and accordingly did not think much about the subatomic structure of matter 100 years ago that they could mislead themselves into believing that the existing theory at least partially accounted for the experimental observations. Strictly speaking, there was not even a partial match between the two.

What could have caused such a miserable failure of the classical picture? As we try to figure it out and go to the origins of the equipartition theorem, we realize that it was the assumption that energy exchange between the systems is a continuous process and the energy of a bound system of particles is a continuous variable. The resulting discrepancy with observations shows that there was something wrong with these classical notions of energy.

1.3
The Photoelectric Effect

The *photoelectric effect* (PEE) is the ejection of electrons from the surface of an illuminated conducting material (mostly metals). Such an effect is by itself easy to understand in the framework of classical physics. The conducting electrons in a metallic plate are bound to it by the electric forces in such a way that, while being free to move within the plate, they are not free to leave it. This can be modeled by a simple picture of an electron trapped within a potential well of macroscopic dimensions (Figure 1.5). The electron within such a well has a negative potential energy, and if its kinetic energy is not sufficiently high, it can only move within the well by bouncing off its walls, but it cannot go beyond the wall, and thus finds itself trapped.

However, when the plate is illuminated, those electrons that are sufficiently close to the surface get exposed to the EM field, which starts "shaking" them with an oscillating force. The resulting motion of the electron under such a force is well known [7,8]. For instance, if the light is monochromatic and linearly polarized, it will cause the electron to oscillate along the direction of the electric field with the frequency ω of the incident wave. In addition, the electron will start drifting along
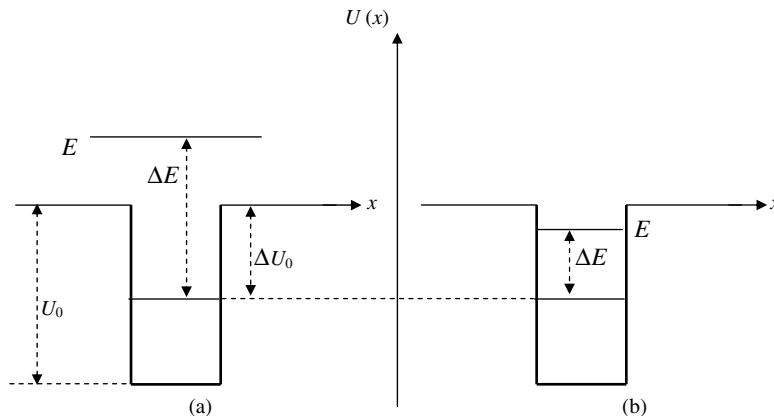
Figure 1.5 An electron in a valence band in a conducting plate can be represented as trapped within a potential well U_0. The electron can break loose of the plate only if it obtains from the environment the minimal energy equal to ΔU_0 (the work function). (a) The electron obtains the energy $K > \Delta U_0$ and becomes free. (b) The electron obtains the energy $K < \Delta U_0$. In this case, it remains trapped within the plate.

the direction of wave propagation. The kinetic energy associated with both kinds of motion stands in proportion to the light intensity I. Therefore, one can expect that at a sufficiently bright illumination the electron eventually will accumulate enough energy to quit the plate.[3] Thus, the effect itself could be easily explained. However, its specific details were in flat contradiction with theoretical predictions.

First, according to the simple picture outlined above, a sufficiently intense light beam, regardless of its frequency, must cause electron emission from the illuminated surface and should produce free electrons with accordingly high kinetic energy. On the other hand, if I is less than a certain critical value depending on the kind of material involved, no electrons will be emitted since they cannot collect enough energy to break loose from the trap (Figure 1.5b).

In fact, however, it was found that for a sufficiently high ω, no matter how dim the incident light, at least one emitted electron can be observed, and the number of emissions increases with I, but no matter how intense the light, the maximum kinetic energy of ejected electrons is the same. So instead of kinetic energy, it is the *number* of the ejected electrons that increases in proportion to I. This statement is known as the *first law of PEE* (or Stoletow's law).

3) The explanation seems straightforward to us, as we are looking at it retrospectively, but in fact the discovery of the PEE by Hertz, in 1887, preceded the discovery of the electron (the latter would only be discovered in 1897 by J.J. Thomson). For this reason, the nature of the phenomenon was not quite as obvious to nineteenth-century physicists as it is to us. Actually, Thomson *used* the photoeffect in his cathode ray tube experiments, which led him to identify the electron as a charged subatomic particle.

Second, the classical picture predicts that electron emission will occur regardless of the value of ω. At any ω, an electron could eventually accumulate enough energy to overcome the potential barrier if I is sufficiently high and the exposure is long enough. Moreover, according to the classical picture, low-frequency waves pump energy into electrons *more* efficiently than high-frequency ones since in each cycle the former provide more time for an electron to accelerate in one direction and thereby to attain higher speed and kinetic energy [8]. But experiments performed by Lenard in 1902 demonstrated that no matter how intense the incident light, there were no electrons emitted when ω was below a certain critical value (the *threshold frequency*), depending on the kind of material, and above the threshold frequency there was an emission, with the maximum kinetic energy of the emitted electrons increasing linearly with ω (Figure 1.6). This is the *second law of photoeffect*.

Third, classical physics predicts the existence of a certain time interval (the transition period) between the beginning of exposure and the beginning of the resulting emission. This seems natural, since according to the classical view any energy exchange is a continuous process, and it always takes a certain time for a system's energy to change. However, in experiments, electron emission started practically instantly (within less than 10^{-9} s) after the illumination. There was no
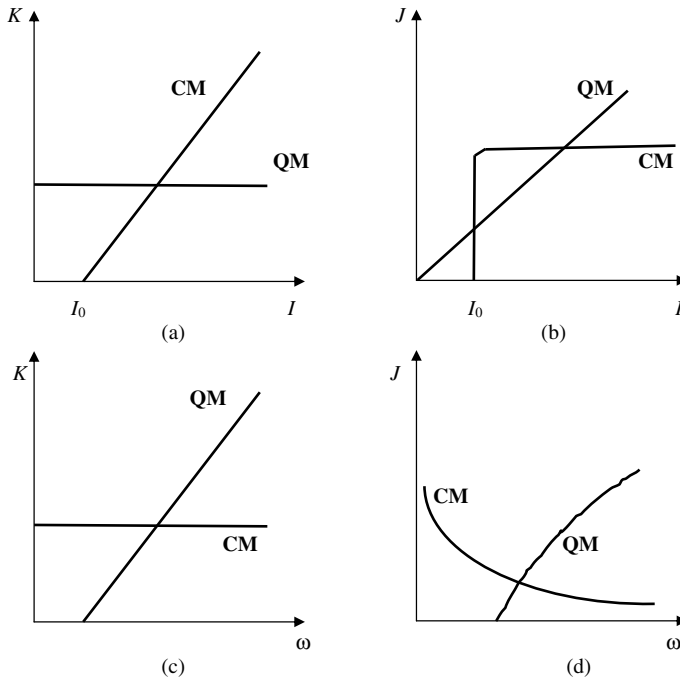

Figure 1.6 Comparison of CM and QM predictions for the basic characteristics of the photoeffect. (a) Dependence of the electrons' kinetic energy $K = K(I)$ on the intensity I of the incident light; (b) dependence of photocurrent $J(I)$ on I; (c) dependence of K on the light frequency ω; (d) dependence of J on ω.

way to reconcile this observation with the notion of interaction as a continuous process.

Summary. In the example considered here (as well as examples in the previous two sections), the notion of continuity of certain physical characteristics such as energy, intensity of monochromatic light, and so on leads to the wrong description of a real process.

1.4
Atoms and Their Spectra

According to the classical picture (the "planetary" model) based on Rutherford's experiments, an atom is a system of electrons orbiting around the nucleus like planets around the sun (hence the name of the model). This model looked simple and very compelling, all the more so that the interaction law (attraction $F \sim r^{-2}$) is mathematically the same in both cases. And some could find it philosophically attractive as well: the big is just an upscale of the small, and vice versa!

However, according to the same classical physics, such an atom cannot exist. The reason is very simple. The electrons in a Rutherford's atom seem to be in far more favorable conditions than, say, Earth's artificial satellites, which eventually spiral downward due to a small drag force in the upper atmosphere. In contrast, the electrons appear totally free of any dissipative forces: there is nothing else in the space around the nucleus. They should be ideal "planets" – no energy losses on the way!

This argument overlooks the fundamental fact that each electron carries an electric charge, and accordingly, its own electromagnetic field. Due to this field, electrons become down-spiraling artificial satellites rather than ideal planets. According to the EM theory, if an electron is moving with constant velocity, then its field just follows this motion, remaining "rigidly" attached to its "master" [7,8]. If, however, the electron accelerates, its field is getting partially detached. This is precisely what happens with an orbiting electron – orbiting involves acceleration! Accordingly, the electron must be losing its energy, which is radiated away together with the "detached" part of its field. The classical atomic electron must, in a way, move in an "atmosphere" of its own radiation field, and it must lose energy due to the "radiative friction" in this atmosphere [3,7]. As a result, very soon (in about 10^{-8} s) all electrons, having emitted a blend of electromagnetic waves of different frequencies, must fall onto the nucleus, and Rutherford's atom will cease to exist.

It seems that classical physics has come to a dead end. On the one hand, the Rutherford's experiments have shown that his planetary model is the only one possible. On the other hand, according to the ongoing experiment carried out by *Nature*, atoms are stable. And in cases when they do radiate (say, in collisions or after an optical excitation), the corresponding spectrum is discrete: one sees on a dark screen or a photographic film a set of distinct spectral lines (Figure 1.7). An atom of each chemical element has its own unique discrete spectrum.

Moreover, the features of this spectrum defied all classical notions about its possible origin. In principle, one could try to explain the discrete spectrum
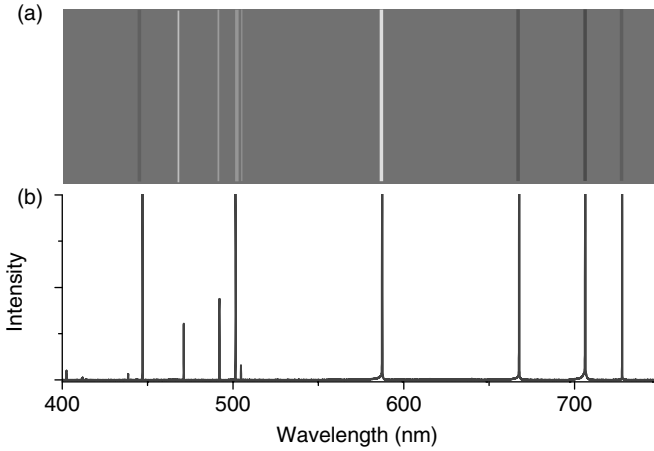
Figure 1.7 (a) Visible spectrum of a He lamp. (b) Schematic of the corresponding optical transitions of a He atom. (Courtesy Andrei Sirenko, Department of Physics, NJIT.)

classically by neglecting the continuous spiraling of the electron toward its nucleus. Suppose that spiraling is very slow as compared with the orbital frequency (it takes much longer than one complete cycle). Then the electron's motion can be approximated as periodic. In this case, its coordinates in the orbital plane can be expanded into a Fourier series [9]

$$x(t) = \sum_{n=-\infty}^{\infty} x_n \, e^{in\omega_1 t}, \qquad y(t) = \sum_{n=-\infty}^{\infty} y_n \, e^{in\omega_1 t}, \tag{1.14}$$

where ω_1 is the fundamental frequency and $|n| > 1$. According to EM theory, the amplitudes x_n and y_n determine the intensity I_n of radiation with frequency $\omega_n = n\omega_1$. The possible frequencies thus form a discrete linear set $\omega = \omega_1, \omega_2, \ldots, \omega_n, \ldots$. In the same way, one can arrange the corresponding intensities I_n. However, this classical picture was also in contradiction with experiment, and even in two different ways. First, the *observed* frequencies are determined by *two* numbers m and n from the linear array of *auxiliary* frequencies $\Omega = \Omega_1, \Omega_2, \ldots, \Omega_n, \ldots$ in such a way that each ω comes as the difference of two Ω_i, that is,

$$\omega_n \to \omega_{mn} \equiv \Omega_m - \Omega_n \tag{1.15}$$

(*Ritz's combination principle*) [9]. In other words, instead of forming a linear array, the observed frequencies form a matrix

$$\omega = \begin{pmatrix} 0 & \omega_{12} & \omega_{13} & \cdots & \omega_{1n} & \cdots \\ \omega_{21} & 0 & \omega_{23} & \cdots & \omega_{2n} & \cdots \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ \omega_{m1} & \omega_{m2} & \omega_{m3} & 0 & \omega_{mn} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{1.16}$$

A similar matrix is formed by the corresponding intensities or the oscillation amplitudes: $I_n \to I_{mn}$; $x_n \to x_{mn}$. Second, the auxiliary frequencies Ω_n do not form multiple harmonics of a certain fundamental frequency, that is, $\Omega_n \neq n\Omega_1$.

One could try to resolve these contradictions by assuming that each of the frequencies (1.16) is an independent *fundamental* frequency of periodic motion corresponding to its own degree of freedom. But then there follows an implication that even the simplest atom is a system with a huge, in principle, infinite, number of degrees of freedom, and accordingly, any substance must have an infinite heat capacity, which flatly contradicts reality. In addition, each of the fundamental frequencies must be accompanied by a set of its respective harmonics, which are absent in the observed spectra. This clash between the classical predictions and the experiment shows that something is wrong in the classical picture of electrons moving along their paths within an atom.

1.5
The Double-Slit Experiment

When Newton published his "Opticks" in 1704, he argued that light is made up of small particles – corpuscles. Although Newton's theory had some initial success, it was relatively short-lived. In 1801, Thomas Young conducted his famous double-slit experiment, which caused the whole scientific community to completely abandon Newton's corpuscular model. The experimental results bore an unambiguous signature of wave diffraction. Accordingly, we will first focus on the predictions of the classical *wave theory*.

In the simplest case, a monochromatic wave of amplitude $\mathcal{E}_0$ and frequency ω is incident at the right angle on an opaque screen with two narrow slits separated by distance d (Figure 1.8). Due to diffraction (or, if you wish, according to the *Huygens principle* [10,11]), each slit acts as an effective source of light, radiating uniformly in all directions on the other side of the slit, so we have two over-lapping diverging waves from two sources. The sources are coherent since they act as "transformers" of *one* incident plane wave into two diverging ones (the so-called *wavefront-splitting* interference [10]). Denoting the wavelength as λ, we can determine the directions θ along which the waves from the two sources interfere constructively:

$$d \sin\theta = m\lambda, \quad |m| = 0, 1, 2, \ldots, \quad \lambda = 2\pi\frac{c}{\omega}. \tag{1.17}$$

More generally, we can write the expression for the sum of two diverging waves as

$$\mathcal{E}(\mathbf{r}, t) = \alpha\mathcal{E}_0\left(\frac{e^{ik\cdot r_1}}{r_1} + \frac{e^{ik\cdot r_2}}{r_2}\right)e^{-i\omega t} \approx \alpha\frac{\mathcal{E}_0}{r}\left(e^{ik(r_1-r)} + e^{ik\cdot(r_2-r)}\right)e^{i(k\cdot r-\omega t)}$$

$$= 2\alpha\frac{\mathcal{E}_0}{r}\cos\left(\frac{kd\sin\theta}{2}\right)e^{i(k\cdot r-\omega t)}. \tag{1.18}$$
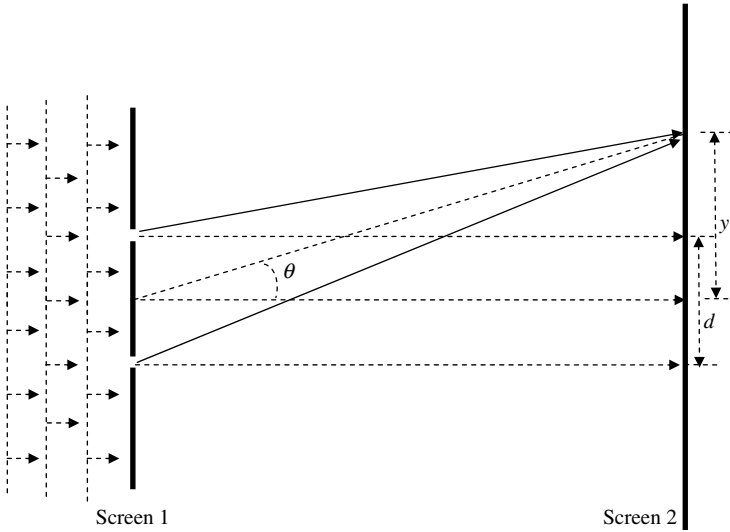
Figure 1.8 The double-slit experiment. The distance *d* between the slits is exaggerated for better clarity. In the actual experiment, the separation between the slits is so small that directions from them to a landing point *y* make practically the same angle θ with the symmetry axis.

This expression is a mathematical formulation of the Huygens principle for the case of two narrow slits. Here $\alpha \equiv 2\pi i/k$ [7], $\mathcal{E}_0$ is the amplitude of incident light (polarization ignored), r_1 and r_2 are the distances between the observation point **r** and slits 1 and 2, respectively, and the factors $\exp(ikr_j)/r_j$ describe secondary spherical wavelets coming to this point from the elements of the wavefront passing through the slits.[4] The maximal intensity will be observed along the directions θ satisfying the condition $kd \sin \theta = 2m\pi$. Since $k = 2\pi/\lambda$, this condition is identical to (1.17).

Introducing the second (observational) screen a distance $L \gg d$ away from the first one (Figure 1.8), we can write $\sin \theta \cong y/L$, where y is the distance between the observation point and the center of the screen. The resulting intensity distribution on the secondary screen is

$$I(y) \sim \mathcal{E}^2(y) \cong 4\alpha^2 \frac{I_0}{r^2} \cos^2\left(\pi \frac{d}{L\lambda} y\right), \quad r^2 = L^2 + y^2, \quad I_0 \equiv \mathcal{E}_0^2. \tag{1.19}$$

It produces alternating bright and dark fringes with the spatial period

$$\Delta y = \frac{L}{d} \lambda. \tag{1.20}$$

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4) Strictly speaking, two narrow slits would produce two *cylindrical* waves, and we would accordingly have $\sqrt{r}$ rather than just r in the denominators of the above expressions. But this will not, for the given conditions, change the main results.

Figure 1.9 The diffraction pattern in the double-slit experiment.

This expression explains why at all we can observe spatial undulations on the screen due to the periodic undulations in the light wave, even though a typical wavelength λ in the visible region of spectrum is $\sim 0.6\,\mu k$. This is far below the minimal size we can see with the naked eye. And yet, we can see the diffraction pattern in Young's experiment! This is because of the coefficient $(L/d) \gg 1$ in Equation 1.20. In this respect, the setup with two close narrow slits and a large distance between the two screens acts as an effective magnifying glass for the wavelength, magnifying its "image" (undulation period) on the screen by the factor L/d.

The intensity distribution (1.19) for $\gamma \ll L$ is shown in Figure 1.9. This is a typical interference picture, *regardless of the physical nature of interfering waves*. The same intensity distribution would be obtained with an acoustic wave in air or a surface wave in a pond if such a wave were incident on a large plate with a pair of narrow slits separated by a distance $d \geq \lambda$.

Now, what happens if we gradually dim the incident light? According to Equation 1.19, this will only decrease the brightness of the interference pattern. If light is truly a wave, then – no matter how faint it is – the observation screen will remain continuously, albeit less and less brightly, illuminated, and exhibit the same pattern. In other words, decrease in intensity will only result in decrease of the coefficient I_0 in (1.19). This was indeed the conclusion of Young and it was well supported by his observations. Thus, the double-slit experiment caused physicists to accept the view of light as waves in a hypothetical medium (ether).

Ironically, under a different scenario Young's experiment could have done exactly the opposite. If Young had taken high-frequency, low-intensity light sources and used short exposures and sufficiently sensitive light detectors, his work would have provided compelling evidence of the *corpuscular* nature of light. Indeed, the diffraction experiments under these conditions show gradual disintegration of the continuous pattern into granular spots. When the brightness falls beyond the visibility threshold, one can use special detectors or a scintillating screen. In the limit of nearly zero intensity, nothing will remain of the continuous undulation (1.19). Instead, one will only observe discrete and apparently random flashes on the otherwise dark screen (Figure 1.10). Remarkably, all flashes have the same brightness, or, if one uses photodetectors, their "clicks" sound equally loud (an actual
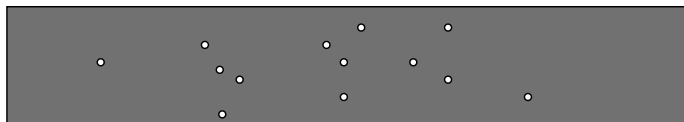

Figure 1.10 The granular pattern in the double-slit experiment at low intensities.

photodetector converts light into electric pulses, so in a real experiment one will see identical peaks on the oscilloscope screen). One must conclude then that light comes in identical portions: either one portion or nothing. This behavior has nothing to do with periodic undulations of a monochromatic wave. It looks exactly as if the screen were bombarded by identical *particles* that passed through the slits. If such measurement techniques were available to Young, then all proponents of the wave nature of light might immediately (at least, until new data were collected from experiments with high intensities or long exposures) flock toward Newton's corpuscular camp. Accordingly, the word "photon" could have become a part of scientific vocabulary about two centuries ago!

Suppose for a moment that history indeed took such a turn, forcing scientists to accept the *corpuscular* view based on the low-intensity version of Young's experiment. And, if the particle picture were accepted as the final truth for light, it would be considered equally true for electrons. So, assume that electrons are *pure particles* and consider the same double-slit experiment, but with electrons instead of light [3]. We will replace the incident wave in Figure 1.8 with a flux of electrons from a source (the "electron gun"), all having the same kinetic energy. Distance d between the slits must be much smaller in the case of electrons, so the described setup is merely a thought experiment. Real experiments with electrons have been carried out with a specially carved single crystal and used reflection from the crystal lattice rather than transmission [9,12,13], but the basic features are still the same. So we can try to visualize the electrons from the electron gun as bullets from a machine gun directed toward two slits in a steel plate. Each bullet has a chance to pass through one of the slits and hit the second screen, leaving a mark on it. In the end, we can record the resulting distribution of bullet marks on the screen. The result will be the sum of two independent contributions: one from the bullets that passed through slit 1, and the other from the bullets that chose slit 2. These predictions can be confirmed by two additional trials – one with only slit 1 open and the other with only slit 2 open (Figure 1.11). In either case, the outcome can be represented by a curve describing
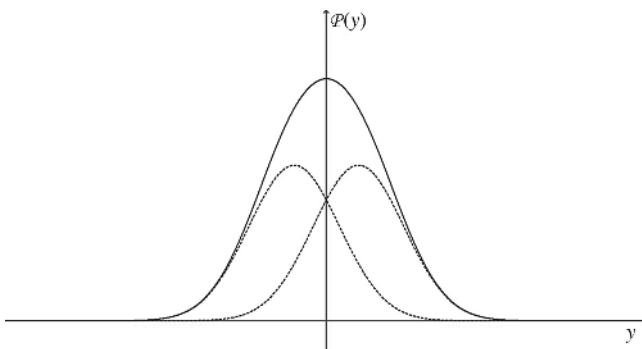

Figure 1.11 The double-slit experiment with classical particles. Each dashed curve represents statistical distribution of particle landings through the corresponding slit. The maximum of each curve is directly opposite the respective slit. The solid curve shows the net distribution with both slits open.

the density of marks on the screen. In the first case, the curve peaks right opposite the slit 1 since this is the place most likely to be hit by a bullet passing through this slit. In the second case, the corresponding curve will have its peak at the point opposite the slit 2. Then, in the case with both slits open the outcome will be just the sum of both curves: since the presence of one slit has no bearing on the probability for a bullet to pass through the other slit, the net probability (more accurately, probability density $\rho(y)$) for a bullet to hit a point y will be

$$\rho(y) = \rho_1(y) + \rho_2(y). \tag{1.21}$$

Let us now turn to the Supreme Judge – the Experiment. When carried out within the full range of parameters, it shows a very strange thing. If the flux intensity is so low that we have only one particle at a time passing through the slits, then each arrival is recorded as a point hit on the second screen (Figure 1.10), so that nothing reminds us of the diluted but still continuous pattern in Figure 1.9, characteristic of a wave. This part of the Experiment suggests that electrons are pure particles.

But there is another part that contradicts this conclusion: The *distribution* of the apparently random arrivals emerging after a long exposure is illustrated by Figure 1.12, not Figure 1.11. It describes the diffraction pattern in Figure 1.9 and is an unambiguous and indisputable signature of waves, not particles! It can only be explained as the result of *interference of waves* passing through two separate slits. In particular, it shows that there are points on the screen where particles never land, even though each particle has high probability of landing there with either slit acting separately. With both slits open, the net probability of landing at such points is *less* than that with only one slit open! The actual probability distribution is *not* the sum of the individual probabilities.

An attempt to combine both pictures on a higher level that includes all the described results leaves us with a puzzle on that level as well. We said the results obtained for low-intensity beams evidence the corpuscular aspect of matter and the ones for high intensity show its wave nature. This could produce an impression that the wave features are necessarily associated with a bunch of particles. But now we see that the
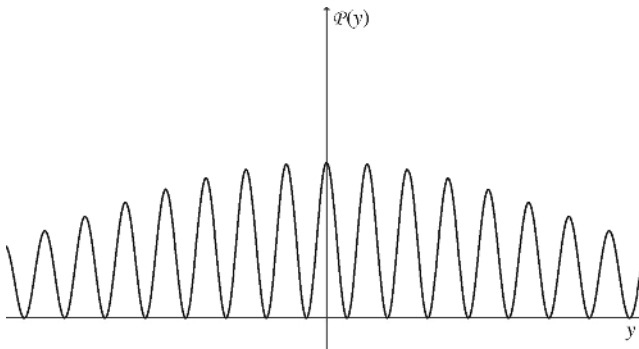

Figure 1.12 The double-slit experiment with QM particles. The diffraction pattern is the same as shown in Figure 1.9 for waves.

results are much more subtle. The *statistics* learned at long exposures shows both corpuscular and the wave aspects already at low intensities. Even if we were tempted to think that a diffraction pattern results from particles interacting with one another, this notion is immediately discarded when we turn to experiments with only one particle at a time passing through the device. It seems that under such conditions there is no room left for wave behavior! And yet, in no trial do we find a particle landing in the middle between the bright fringes. We cannot avoid the conclusion that even a single particle passing through the device has complete information telling it where it cannot land and where it can – even being encouraged to land there. Such information can exist only in a wave, in the form of instructions about directions of constructive and destructive interference impinged on it *by the geometry of both slits*. Following these instructions constitutes a wave behavior. *Each particle in these experiments interferes with itself, not with other particles*. So already a single particle shows some features of the wave behavior. And yet it crashes into the screen as a discrete unit, having nothing to do with a continuous wave. Our classical intuition is insufficient to handle the whole phenomenon.

Summary: We see a complete failure of classical physics when we attempt to apply it to the phenomena described in this chapter. In particular, we see inadequacy of the notion that an entity can be either a pure wave or a pure particle. Real objects of Nature turned out to be neither exactly waves nor exactly particles. Rather, they are something much more subtle, exhibiting sometimes one aspect, sometimes the other, depending on experimental conditions.

What is then their true nature?

The rest of the book is an attempt to describe the answer to these questions as we know it today.

Problem

1.1 Derive the Stefan–Boltzmann law using universal form (1.3) of the radiation energy density in thermal equilibrium.

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