

statement that the emission and absorption of radiation by atoms are "fully directed events" and not spherically symmetric ones.

We recall that Planck derived his radiation formula by introducing harmonic oscillators (the Planck resonators) as the constituents of matter in equilibrium with the radiation. Bohr later used the quantum theory to explain the line spectrum of the elements by introducing his postulates about the absorption and emission of photons by individual atoms. However, up to that time (1913) nobody had shown that Planck's radiation law is independent of the type of resonators that one assumes and that the law can be derived without making any assumptions about the specific nature of the atomic systems. This Einstein did in the paper we are here discussing, by means of general statistical arguments in which the only assumptions are that the atoms (or molecules, as Einstein calls them) are in dynamic equilibrium with the radiation field and that each atom can be in only one of a set of discrete atomic states. The atom is then pictured as interacting with the radiation field by absorbing photons from and emitting photons into the field.

To make the analysis as simple as possible Einstein considers only two of the possible quantum states of the atom and investigates the condition for statistical equilibrium between these two states and the radiation field surrounding the atoms. He then considers three possible processes involving the emission and absorption of radiation by the atoms and assumes that these processes proceed at such rate that the total number of atoms in each of the two quantum states does not change with time (the condition of statistical equilibrium). Two of the processes involve the emission of photons by the atoms and one involves absorption, and we already find in the mere enumeration of these processes a departure from previous ideas. For in considering the emission of radiation, Einstein assumes not only that an atom can radiate a photon spontaneously, and thus pass from a higher to a lower state of energy, but also that the atom in the higher state can be induced or stimulated to emit a photon more readily than it would spontaneously. This can be achieved in the presence of electromagnetic radiation or photons of the same frequency as that of the emitted photons. Einstein called this "induced emission of radiation."

Einstein now introduces probability coefficients (the famous Einstein A and B coefficients) for each of these three processes, spontaneous emission, stimulated emission, and absorption. He assumes that the number of each of these processes occurring per unit time is proportional to the appropriate Einstein coefficient times the number of atoms in the given state. The spontaneous emission process is proportional only to the probability coefficient times this number of atoms, but the process of stimulated emission and the process of absorption are proportional to this number of atoms multiplied by the product of the appropriate co-

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QUANTUM THEORY OF RADIATION AND ATOMIC PROCESSES



Albert Einstein (1879-1955)

Although the Bohr theory of atomic spectra and Moseley's work on the X-ray spectra of heavy atoms had placed the nuclear atom in an unassailable position, one more step had yet to be taken to complete the picture and to give the nuclear atom a logically satisfying structure. This was to show that the Planck radiation formula can be derived from the Bohr theory and its stationary states. Einstein achieved this result in the year 1917, when he wrote the last in his series of monumental papers on the quantum nature of radiation. In some respects this is the most penetrating of this group of papers, for in it he not only clearly establishes that the interaction between a radiation field and atoms (or resonators, as he calls them) occurs via the emission and absorption of quanta or photons, but he also derives the Planck radiation formula from the most general principles, without making any assumptions about the nature of the resonators. At the same time, Einstein clarifies the phenomena of emission and absorption of radiation by atoms and shows that these processes are intimately related to the probabilities of an atom's passing from one state to another. Finally, in this paper he emphasizes the importance of taking into account the momentum of a quantum and in a sense thus foresees the Compton effect. This is indicated in Einstein's

Note: The reader's attention is drawn to the similar appearance of the symbol ν for the frequency and the italic *vee*, v , used to denote velocity.

efficient for that process and the density of the radiation of frequency corresponding to the energy difference between the two quantum states.

Since statistical equilibrium requires that the number of processes per unit time involving transitions of atoms from the higher to the lower state (emission of photons) equal the number of processes per unit time involving transitions of atoms from the lower to the higher state (absorption), Einstein sets up an equation expressing this condition. This equation involves the three Einstein coefficients, the energy density of the radiation, and the numbers of atoms in the two quantum states at any moment.

To derive the Planck formula Einstein now sets up two relationships among his three probability coefficients and uses the general statistical law (the famous Boltzmann law) for the distribution of atoms among possible atomic states to eliminate from his equation the number of atoms in each state. This last relationship introduces the temperature of the equilibrium ensemble of atoms and radiation as well as the energy difference between the two states. To obtain the two relations among his three probability coefficients Einstein considers, first, the limiting case of the temperature going to infinity, and second, the limiting case for which the Wien law is valid. In this way he eliminates the probability coefficients from his equilibrium equation and obtains the Planck formula for the energy density of black-body radiation. At the same time he derives, as a necessary condition, Bohr's hypothesis that in going from one state to another an atom always emits one photon whose frequency is given by the energy difference between the two states divided by Planck's constant.

One of the remarkable things in Einstein's derivation of Planck's formula is the appearance of the stimulated emission process, which seems to play a rather mysterious role and which was considered until recently as a rather curious theoretical feature of the problem without any apparent practical application. But during the last two decades Einstein's hypothesis of stimulated emission of radiation has received its most dramatic experimental verification in the development of the Maser and the Laser by Charles Townes and his collaborators. The word maser is derived from the first letters of the phrase "microwave amplification by the stimulated emission of radiation" and the word laser is obtained from the phrase "light amplification by the stimulated emission of radiation."

In both of these devices radiation of a given frequency is greatly amplified by allowing the photons of the radiation to stimulate excited atoms to emit additional photons of the same kind. The remarkable property of the amplified beam thus obtained is its very high coherence: The amplified beam consists of photons that are all of very nearly the same frequency and there is hardly any spreading of the beam at all. This means that very energetic, monochromatic beams of radiation can be obtained and sent over great distances without attenuation. The basis for this is given very

early in Einstein's paper when he points out that the emission and absorption of radiation is accompanied by a change in the momentum of the atom. Thus, when an atom is stimulated to emit a photon by a passing photon, the atom has momentum transferred to it whose direction is opposite to that of the passing photon. This means that the atom must emit another photon in the same direction as that of the passing photon. This is stated by Einstein as follows.

If as a result of incident radiation the process $Z_n \rightarrow Z_m$ (absorption) occurs, then an amount of momentum $(E_n - E_m)/c$ is transferred to the molecule in the direction of propagation of the radiation. If we have the process $Z_m \rightarrow Z_n$ for the case of incident radiation (stimulated emission), the magnitude of the transferred momentum is the same, but it is in the opposite direction.

Einstein points out two other important consequences of his derivation of the Planck formula. The first concerns the direction of photons emitted. Whereas, according to the classical wave theory of radiation, the radiation leaves the atom in the form of a spherical wave (that is, the emission occurs symmetrically in all directions), Planck's formula can be derived only if one assumes that the emission process is a directed one. This, as Einstein points out, must be true whether the emission is due to stimulation by a beam of incident radiation or whether it is spontaneous.

The second consequence concerns the momentum of radiation. As Einstein states in the last paragraph of his paper, almost all of the previous work on the interaction of atoms and radiation dealt with the energy exchange between the atom and the radiation field but neglected the momentum exchange because the momentum of the radiation is very small, so that the momentum transferred to the atom is negligible as compared to the energy. Einstein correctly concludes, however, that for theoretical considerations this momentum transfer is of extreme importance and must be taken into account just as energy interchange is. He states:

... But for theoretical considerations this small effect [momentum transfer] is on an equal footing with the energy transferred because momentum and energy are very intimately related to each other; a theory may therefore be considered correct only if it can be shown that the momentum transferred according to it from the radiation to the matter leads to the kind of motion that is demanded by thermodynamics.

This insight into the importance of the momentum of radiation was extremely prophetic for it contains in it the germ of the Compton effect. When Compton analyzed his experiments on the scattering of X-rays by electrons in 1923, he found that he could understand the results only if he

took into account the conservation of both energy and momentum in the interaction between the electron and the X-ray photon.

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EINSTEIN

The Quantum Theory of Radiation¹

THE FORMAL SIMILARITY OF THE spectral distribution curve of temperature radiation to Maxwell's velocity distribution curve is too striking to have remained hidden very long. Indeed, in the important theoretical paper in which Wien derived his displacement law

$$\rho = \nu^3 f\left(\frac{\nu}{T}\right) \quad (1)$$

he was led by this similarity to a farther correspondence with the radiation formula. He discovered, as is known, the formula [Wien's radiation formula]

$$\rho = \alpha \nu^3 e^{-\frac{h\nu}{kT}} \quad (2)$$

which is recognized today as the correct limiting formula for large values of $\frac{\nu}{T}$. Today we know that no consideration which is based on classical mechanics and electrodynamics can lead to a useful radiation formula; rather that the classical theory leads to the Rayleigh formula.

$$\rho = \frac{k\alpha}{h} \nu^2 T \quad (3)$$

After Planck, in his ground-breaking investigation, established his radiation formula

$$\rho = \alpha \nu^3 \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad (4)$$

on the assumption that there are discrete elements of energy, from which quantum theory developed very rapidly, Wien's considerations, from which formula (2) evolved, quite naturally were forgotten.

A little while ago I obtained a derivation, related to Wien's original idea, of the Planck radiation formula which is based on the fundamental assumption of quantum theory and which makes use of the relationship of Maxwell's curve to the spectral distribution curve. This derivation deserves consideration not only because of its simplicity, but especially because it appears to clarify the processes of emission and absorption of radiation in matter, which is still in such darkness for us. In setting down certain fundamental hypotheses concerning the absorption and emission of radiation by molecules that are closely related to quantum theory, I showed that molecules with a distribution of states in the quantum theoretical sense for temperature equilibrium are in dynamical equilibrium with the Planck radiation; in this way, the Planck formula (4) was obtained in a surprisingly simple and general way. It was obtained from the condition that the quantum theoretic partition of states of the internal energy of the molecules is established only by the emission and absorption of radiation.

If the assumed hypotheses about the interaction of matter and radiation are correct, they will give us more than just the correct statistical partition or distribution of the internal energy of the molecules. During absorption and emission of radiation there is also present a transfer of momentum to the molecules; this means that just the interaction of radiation and molecules leads to a velocity distribution of the latter. This must clearly be the same as the velocity distribution which molecules acquire as the result of their mutual interaction by collisions, that is, it must coincide with the Maxwell distribution. We must require that the mean kinetic energy which a molecule (per degree of freedom) acquires in a Planck radiation field of temperature T be

$$\frac{kT}{2};$$

this must be valid regardless of the nature of the molecules and independent of frequencies which the molecules absorb and emit. In this paper we wish to verify that this far-reaching requirement is, indeed, satisfied quite generally; as a result of this our simple hypotheses about the emission and absorption of radiation acquire new supports.

In order to obtain this result, however, we must enlarge, in a definite way, the previous fundamental hypotheses which were related entirely to the exchange of energy. We are faced with this question: Does the molecule suffer a push, when it absorbs or emits the energy ϵ ? As an example we consider, from the classical point of view, the emission of radiation. If a

¹ Albert Einstein, *Physikalische Zeitschrift*, 18 (1917), 121-128—trans. Editors.

body emits the energy ϵ , it acquires a backward thrust [impulse] $\frac{\epsilon}{c}$ if all the radiation ϵ is radiated in the same direction. If, however, the radiation occurs through a spatially symmetric process, for example, spherical waves, there is then no recoil at all. This alternative also plays a role in the quantum theory of radiation. If a molecule, in going from one possible quantum theoretic state to another, absorbs or emits the energy ϵ in the form of radiation, such an elementary process can be looked upon as partly or fully directed in space, or also as a symmetric (non-directed) one. It turns out that we obtain a theory that is free of contradictions only if we consider the above elementary processes as being fully directed events; herein lies the principal result of the considerations that follow.

FUNDAMENTAL HYPOTHESES OF THE QUANTUM THEORY—CANONICAL DISTRIBUTION OF STATES

According to the quantum theory, a molecule of a definite kind may, aside from its orientation and its translational motion, be in one of only a discrete set of states $Z_1, Z_2, \dots, Z_n, \dots$ whose (internal) energies are $\epsilon_1, \epsilon_2, \dots, \epsilon_n, \dots$. If the molecules of this kind belong to a gas of temperature T , then the relative abundance W_n of the state Z_n is given by the statistical mechanical canonical partition function for states

$$W_n = p_n e^{-\frac{\epsilon_n}{kT}} \quad (5)$$

In this formula $k = \frac{R}{N}$ is the well-known Boltzmann constant, p_n a number that is independent of T and characteristic of the molecule and the state, which we may call the statistical "weight" of the state. Formula (5) can be derived from the Boltzmann principle or purely from thermodynamics. Equation (5) is the expression of the most far-reaching generalization of the Maxwellian distribution of velocities.

The latest important advances in quantum theory deal with the theoretical determination of the quantum theoretical possible states Z_n and their weights p_n . For the principal part of the present investigation, it is not necessary to have a more detailed determination of the quantum states.

HYPOTHESES ABOUT THE ENERGY EXCHANGE THROUGH RADIATION

Let Z_n and Z_m be two possible quantum theoretical states of a gas molecule whose energies ϵ_n and ϵ_m respectively, satisfy the inequality

$$\epsilon_m > \epsilon_n$$

Let the molecule be able to pass from the state Z_n to the state Z_m by absorbing the radiation energy $\epsilon_m - \epsilon_n$; similarly let the transition from state Z_n to the state Z_m be possible through the emission of this amount of energy. Let the radiation emitted or absorbed by the molecule for the given index and combination (m, n) have the characteristic frequency ν .

We now introduce certain hypotheses about the laws which are decisive for these transitions. These hypotheses are obtained by carrying over the known classical relations for a Planck resonator to the unknown quantum theoretical relations.

Emission

A Planck resonator that is vibrating radiates energy, according to Hertz, in a known way independently of whether it is stimulated by an external field or not. In accordance with this, let a molecule be able to pass from the state Z_m to the state Z_n with the emission of radiant energy $\epsilon_m - \epsilon_n$ of frequency ν without being excited by any external cause. Let the probability dW for this to happen in the time dt be

$$dW = A_m^n dt \quad (A)$$

where A_m^n is a characteristic constant for the given index combination.

The assumed statistical law corresponds to that of a radioactive reaction: that elementary process of such a reaction in which only γ -rays are emitted. We need not assume that this process requires no time; this time need only be negligible compared to the times which the molecule spends in the states Z_1 , and so on.

Incident Radiation

If a Planck resonator is in a radiation field, the energy of the resonator changes because the electromagnetic field of the radiation does work on the resonator; this work can be positive or negative depending on the phases of the resonator and the oscillating field. In accordance with this, we introduce the following quantum theoretical hypothesis. Under the action of the radiation density ρ of the frequency ν a molecule in state Z_n can go over to state Z_m by absorbing the radiation energy $\epsilon_m - \epsilon_n$ in accordance with the probability law

$$dW = B_m^n \rho dt \quad (B)$$

In the same way, let the transition $Z_m \rightarrow Z_n$ under the action of the radiation also be possible, whereby the radiation energy $\epsilon_m - \epsilon_n$ is emitted according to the probability law

$$dW = B_m^n \rho dt \quad (B')$$

B_m^n and B_n^m are constants. We call both processes "changes of states through incident radiation."

The question presents itself now as to the momentum that is transferred to the molecule in these changes of state. We begin with the events associated with incident radiation. If a directed bundle of rays does work on a Planck resonator, then an equivalent amount of energy is removed from the bundle. This transfer of energy results, according to the law of momentum, to a momentum transfer from the beam to the resonator. The latter therefore experiences a force in the direction of the ray of the radiation beam. If the energy transferred is negative, the force acting on the resonator is opposite in direction. In the case of the quantum hypothesis, this clearly means the following. If, as the result of incident radiation, the process $Z_n \rightarrow Z_m$ occurs, then an amount of momentum

$$\frac{\epsilon_m - \epsilon_n}{c}$$

is transferred to the molecule in the direction of propagation of the bundle of radiation. If we have the process $Z_m \rightarrow Z_n$ for the case of incident radiation, the magnitude of the transferred momentum is the same, but it is in the opposite direction. If a molecule is simultaneously exposed to many bundles of radiation, we assume that the total energy $\epsilon_m - \epsilon_n$ is taken from or added to just one of these bundles, so that even in this case the momentum

$$\frac{\epsilon_m - \epsilon_n}{c}$$

is transferred to the molecule.

In the case of emission of energy by radiation by a Planck resonator, there is no net transfer of momentum to the resonator because, according to classical theory, the emission occurs as a spherical wave. However, we have already noted that we can arrive at a contradiction-free quantum theory only if we assume that the process of emission is a directed one. Every elementary process of emission ($Z_m \rightarrow Z_n$) will then result in a transfer to the molecule of an amount of momentum

$$\frac{\epsilon_m - \epsilon_n}{c}$$

If the molecule is isotropic, we must take every direction of emission as equally probable. If the molecule is not isotropic, we arrive at the same result if the orientation changes in a random way in the course of time. We must, in any case, make such an assumption also for the statistical laws

(B) and (B') for incident radiation since otherwise the constants B_m^n and B_n^m would have to depend on direction, which we can avoid by assuming isotropy or pseudo-isotropy (through setting up temporal mean values).

DERIVATION OF THE PLANCK RADIATION LAW

We now enquire about those effective radiation densities ρ which must prevail in order that the energy exchange between molecules and radiation as a result of the statistical laws (A), (B) and (B') shall not disturb the distribution of molecular states present as a consequence of equation (5). For this, it is necessary and sufficient that on the average, per unit time, as many elementary processes of type (B) take place as processes (A) and (B') together. This condition gives as a result of (5), (A), (B), (B'), for the elementary processes corresponding to the index combination (m, n) the equation

$$p_n e^{-\frac{\epsilon_n}{kT}} B_n^m \rho = p_m e^{-\frac{\epsilon_m}{kT}} (B_m^n \rho + A_m^n)$$

If, further, ρ is to become infinite as T does, the constants B_m^n and B_n^m must satisfy the relation

$$p_n B_n^m = p_m B_m^n \quad (6)$$

We then obtain as the condition for dynamical equilibrium the equation

$$\rho = \frac{A_m^n / B_m^n}{e^{\frac{\epsilon_m - \epsilon_n}{kT}} - 1} \quad (7)$$

This is the dependence of the radiation density on the temperature that is given by the Planck law. From the Wien displacement law (1) it then follows immediately that

$$\frac{A_m^n}{B_m^n} = \alpha \nu^3 \quad (8)$$

and

$$\epsilon_m - \epsilon_n = h\nu \quad (9)$$

where α and h are universal constants. To obtain the numerical values of α and h we must have an exact theory of electrodynamic and mechanical

processes; we content ourselves for the moment with the Rayleigh law in the limit of high temperatures, where the classical theory is valid in the limit.

Equation (9) is, as we know, the second principal rule in Bohr's theory of spectra, about which we may assert, following upon Sommerfeld's and Epstein's completion of the theory, that it belongs to the most fully verified domain of our science. It also contains implicitly the photochemical equivalent law, as I have already shown.

METHOD FOR CALCULATING THE MOTION OF MOLECULES IN RADIATION FIELDS

We now turn our attention to the investigation of the motion imparted to our molecules by the radiation field. We make use in this of a method that is known to us from the theory of Brownian motion and which I have often used in investigating motions in a region containing radiation. To simplify the calculation, we shall carry it through for the case in which the motion occurs only along the X-direction of the coordinate system. We further content ourselves with calculating the mean value of the kinetic energy of the translational motion, and thus dispense with proof that these velocities v are distributed according to the Maxwell law. Let the mass M of the molecule be large enough so that higher powers of $\frac{v}{c}$ can be neglected relative to lower ones; we can then apply the usual mechanics to the molecule. Moreover, without any loss in generality, we may carry out the calculation as though the states with indices m and n were the only ones the molecule can be in.

The momentum Mv of a molecule undergoes two kinds of changes in the short time τ . Even though the radiation is the same in all directions, the molecule, because of its motion, will experience a resistance to its motion that stems from the radiation. Let this opposing force be Rv , where R is a constant to be determined later. This force would ultimately bring the molecule to rest if the randomness of the action of the radiation field were not such as to transfer to the molecule a momentum Δ of alternating sign and varying magnitude; this random effect will, in opposition to the previous one, sustain a certain amount of motion of the molecule. At the end of the given short time τ the momentum of the molecule will equal

$$Mv - Rv\tau + \Delta$$

Since the velocity distribution is to remain constant in time, the mean of the absolute value of the above quantity must equal that of the quantity

Mv ; thus, the mean values of the squares of both quantities averaged over a long time or over a large number of molecules must be equal:

$$(\overline{Mv - Rv\tau + \Delta})^2 = (\overline{Mv})^2$$

Since we have taken into account the influence of v on the momentum of the molecule separately, we must discard the mean value $v\Delta$. On developing the left-hand side of the equation we thus obtain

$$\overline{\Delta^2} = 2\overline{RMv^2}\tau \quad (10)$$

The mean value $\overline{v^2}$ which the radiation of temperature T by its interaction imparts to the molecule must just equal the mean value $\overline{v^2}$ which the gas molecule acquires at temperature T according to the gas law and the kinetic theory of gases. For otherwise the presence of our molecules would disturb the thermal equilibrium between thermal radiation and an arbitrary gas of the same temperature. We must therefore have

$$\frac{\overline{Mv^2}}{2} = \frac{kT}{2} \quad (11)$$

Equation (10) thus goes over into

$$\frac{\overline{\Delta^2}}{\tau} = 2RkT \quad (12)$$

The investigation is now to be carried through as follows. For a given radiation density ($\rho(v)$) we shall be able to compute $\overline{\Delta^2}$ and R by means of our hypotheses about the interaction between radiation and molecules. If we put this result into (12), this equation will have to be identically satisfied when ρ is expressed as a function of v and T by means of Planck's equation (4).

COMPUTING R

Let a molecule of the given kind be in uniform motion with speed v along the X-axis of the coordinate system K . We inquire about the momentum transferred on the average from the radiation to the molecule per unit time. To calculate this we must consider the radiation from a coordinate system K' that is at rest with respect to the given molecule. For we have formulated our hypotheses about emission and absorption only for molecules at rest. The transformation to the system K' has often been performed in the literature. Nevertheless, I shall repeat the simple considerations here for the sake of clarity.

Relative to K the radiation is isotropic, that is, the quantity of radiation in a solid angle $d\kappa$ in the direction of the radiation in a frequency range $d\nu$ is

$$\rho d\nu \frac{d\kappa}{4\pi} \quad (13)$$

where ρ depends only on the frequency ν but not on the direction of the radiation. This special beam corresponds to a special beam in the system K' which is also characterized by a frequency range $d\nu'$ and a solid angle $d\kappa'$. The volume density of this special beam is

$$\rho'(v', \phi') d\nu' \frac{d\kappa'}{4\pi} \quad (13')$$

This defines ρ' . It depends on the direction of the radiation which, in the familiar manner, is defined by the angle ϕ' it makes with the X' axis and which its projection on the Y', Z' plane makes with the Y' axis. These angles correspond to the angles ϕ and ψ which in an analogous manner determine the direction of $d\kappa$ in K .

To begin with, it is clear that the same transformation law between (13) and (13') must hold as between the amplitudes A^2 and A'^2 of a plane wave moving in the corresponding direction. Hence, to our desired approximation we have

$$\frac{\rho'(v', \phi') d\nu' d\kappa'}{\rho(v) d\nu d\kappa} = 1 - 2 \frac{\nu}{c} \cos \phi \quad (14)$$

or

$$\rho'(v', \phi') = \rho(v) \frac{d\nu}{d\nu'} \frac{d\kappa}{d\kappa'} \left(1 - 2 \frac{\nu}{c} \cos \phi \right) \quad (14')$$

The relativity theory further gives the formulae, valid to the desired approximation,

$$\nu' = \nu \left(1 - \frac{\nu}{c} \cos \phi \right) \quad (15)$$

$$\cos \phi' = \cos \phi - \frac{\nu}{c} + \frac{\nu}{c} \cos^2 \phi \quad (16)$$

$$\psi' = \psi \quad (17)$$

From (15) it follows, to the same approximation, that

$$\nu = \nu' \left(1 + \frac{\nu}{c} \cos \phi' \right).$$

Hence, again to the desired approximation

$$\rho(v) = \rho \left(\nu' + \frac{\nu}{c} \nu' \cos \phi' \right)$$

or

$$\rho(v) = \rho(\nu') + \frac{\partial \rho(\nu')}{\partial \nu'} \left(\frac{\nu}{c} \nu' \cos \phi' \right) \quad (18)$$

Further, according to (15), (16), and (17)

$$\begin{aligned} \frac{d\nu}{d\nu'} &= \left(1 + \frac{\nu}{c} \cos \phi' \right) \\ \frac{d\kappa}{d\kappa'} &= \frac{\sin \phi' d\phi' d\psi'}{\sin \phi d\phi d\psi} = \frac{d(\cos \phi)}{d(\cos \phi')} = 1 - 2 \frac{\nu}{c} \cos \phi' \end{aligned}$$

As a result of these two equations and equation (18), equation (14') goes over into

$$\rho'(v', \phi') = \left[(\rho)_{\nu'} + \frac{\nu}{c} \nu' \cos \phi' \left(\frac{\partial \rho}{\partial \nu'} \right)_{\nu'} \right] \left(1 - 2 \frac{\nu}{c} \cos \phi' \right) \quad (19)$$

With the aid of (19) and our hypotheses about the radiation from and radiation onto molecules, we can easily calculate the average momentum transferred to the molecule per unit time. Before we can do this, however, we must say something to justify our procedure. It may be objected that equations (14), (15), (16) are based on Maxwell's theory of the electromagnetic field that is not consistent with the quantum theory. This objection deals, however, more with the form than with the substance of the problem. For, no matter how the theory of electromagnetic processes may be formulated, in any case the Doppler principle and the law of aberration still remain, and hence also the equations (15) and (16). Moreover, the validity of the energy relationship (14) certainly extends beyond that of the wave theory; this transformation law is also valid, for example, according to relativity theory, for the energy density of a mass of infinitesimally small rest density that is moving with the [quasi-] speed of light. We may therefore assert the validity of equation (19) for any theory of radiation.

The radiation belonging to the solid angle $d\kappa'$ would, according to (B), give rise to

$$B_n^m \rho'(v', \phi') \frac{d\kappa'}{4\pi}$$

elementary processes per second of radiation events of the type $Z_n \rightarrow Z_m$ if the molecule after each such process immediately returned to state

Z_n . Actually, however, the time of lingering in state Z_n , according to (5), is

$$\frac{1}{S} p_n e^{-\frac{\epsilon_n}{kT}}$$

where we have used the abbreviation

$$S = p_n e^{-\frac{\epsilon_n}{kT}} + p_m e^{-\frac{\epsilon_m}{kT}} \tag{20}$$

The number of these processes per second is therefore actually

$$\frac{1}{S} p_n e^{-\frac{\epsilon_n}{kT}} B_n^m \rho'(v', \phi') \frac{d\kappa'}{4\pi}$$

In each of these elementary processes the momentum

$$\frac{\epsilon_m - \epsilon_n}{c} \cos \phi'$$

is transferred to the molecule in the direction of the X' -axis. In an analogous manner we find, based on (B') that the corresponding number of elementary processes of radiation events of type $Z_m \rightarrow Z_n$ per second is

$$\frac{1}{S} p_m e^{-\frac{\epsilon_m}{kT}} B_m^n \rho'(v', \phi') \frac{d\kappa'}{4\pi}$$

and in each such elementary process the momentum

$$-\frac{\epsilon_m - \epsilon_n}{c} \cos \phi'$$

is transferred to the molecule. The total momentum transferred to the molecule per unit time by incident radiation is, keeping in mind (6) and (9),

$$\frac{h\nu'}{cS} p_n B_n^m \left(e^{-\frac{\epsilon_n}{kT}} - e^{-\frac{\epsilon_m}{kT}} \right) \int \rho'(v', \phi') \cos \phi' \frac{d\kappa'}{4\pi}$$

where the integration is to be taken over all solid angles. Carry this out, and we obtain with the aid of (19) the value

$$-\frac{h\nu}{c^2 S} \left(\rho - \left(\frac{1}{3} \right) v \frac{\partial \rho}{\partial v} \right) p_n B_n^m \left(e^{-\frac{\epsilon_n}{kT}} - e^{-\frac{\epsilon_m}{kT}} \right) v.$$

Here we have represented the effective frequency again with ν and not with ν' . This expression gives, however, the total momentum transferred on the average to a molecule moving with speed v . For it is clear that those elementary processes of emission of radiation not induced by the action of the radiation field have no preferred direction as seen from system K' and hence, on the average, cannot transfer any momentum to the molecule. We thus obtain as the final result of our considerations

$$R = \frac{h\nu}{c^2 S} \left(\rho - \frac{1}{3} v \frac{\partial \rho}{\partial v} \right) p_n B_n^m e^{-\frac{\epsilon_n}{kT}} \left(1 - e^{-\frac{h\nu}{kT}} \right) \tag{21}$$

CALCULATING $\bar{\Delta}^2$

It is much easier to calculate the random effect of the elementary processes on the mechanical behavior of the molecule. For we can calculate this for a molecule at rest for which the approximation which we have been using applies.

Let some event cause the momentum λ to be transferred to a molecule in the X direction. This momentum is to be of varying magnitude and direction from moment to moment. However, let λ obey a statistical law such that its average value vanishes. Then let $\lambda_1, \lambda_2, \dots$ be the momenta which are transferred to the molecule in the X -direction by various operating causes that are independent of each other so that the total momentum that is transferred is

$$\Delta = \sum \lambda_{\nu}$$

We then have (if for the individual λ_{ν} their mean values $\bar{\lambda}_{\nu}$ vanish)

$$\bar{\Delta}^2 = \sum \lambda_{\nu}^2 \tag{22}$$

If the mean values $\bar{\lambda}_{\nu}^2$ of the individual momenta are all equal to each other ($= \bar{\lambda}^2$) and if l is the total number of processes giving rise to momenta, we have the relation

$$\bar{\Delta}^2 = l \bar{\lambda}^2 \tag{22a}$$

According to our hypothesis, in each process of incident radiation and outflowing radiation, the momentum

$$\lambda = \frac{h\nu}{c} \cos \phi$$

is transferred to the molecule. Here ϕ is the angle between the X-axis and some randomly chosen direction. Hence, we obtain

$$\bar{\lambda}^2 = \frac{1}{3} \left(\frac{h\nu}{c} \right)^2.$$

Since we assume that all the elementary processes that are present are to be considered as events that are independent of each other, we may apply (22a); l is then the number of all elementary processes that occur in the time τ . This is twice as large as the number of radiation-incident processes $Z_n \rightarrow Z_m$ in the time τ . We thus have

$$l = \frac{2}{3} P_n B_n e^{-\frac{e_n}{kT}} \rho \tau \quad (24)$$

From (23), (24) and (22) we thus obtain

$$\frac{\Delta^2}{\tau} = \frac{2}{3S} \left(\frac{h\nu}{c} \right)^2 P_n B_n e^{-\frac{e_n}{kT}} \rho \quad (25)$$

RESULTS

In order now to show that the momenta transferred from the radiation to the molecule according to our basic hypotheses never disturb the thermodynamic equilibrium, we need only introduce the values for $\frac{\Delta^2}{\tau}$ and R calculated in (25) and (21) respectively after the quantity

$$\left(\rho - \left(\frac{1}{2} \lambda \right) \nu \frac{\partial \rho}{\partial \nu} \right) \left(1 - e^{-\frac{h\nu}{kT}} \right)$$

in (21) is replaced by

$$\frac{\rho h\nu}{3RT}$$

from (4). We then see that our fundamental equation (12) is satisfied identically.

The above consideration lends very strong support to the hypotheses introduced earlier for the interaction between matter and radiation by means of absorption and emission, and through incident and outgoing radiation. I was led to these hypotheses in trying to postulate in the simplest possible way a quantum behavior of molecules that is analogous to

the Planck resonators of classical theory. We obtained, without effort, from the general quantum assumption for matter, the second Bohr rule (equation (9)) as well as Planck's radiation formula.

Most important, however, appears to me the result about the momentum transferred to the molecule by incoming and outgoing radiation. If one of our hypotheses were altered, the result would be a violation of equation (12); it appears hardly possible, except by way of our hypotheses, to be in agreement with this relationship which is demanded by thermodynamics. We may therefore consider the following as pretty well proven.

If a beam of radiation has the effect that a molecule on which it is incident absorbs or emits an amount of energy $h\nu$ in the form of radiation by means of an elementary process, then the momentum $h\nu/c$ is always transferred to the molecule, and, to be sure, in the case of absorption, in the direction of the moving beam and in the case of emission in the opposite direction. If the molecule is subject to the simultaneous action of beams moving in various directions, then only one of these takes part in any single elementary process of incident radiation; this beam alone then determines the direction of the momentum transferred to the molecule.

If, through an emission process, the molecule suffers a radiant loss of energy of magnitude $h\nu$ without the action of an outside agency, then this process, too, is a directed one. Emission in spherical waves does not occur. According to the present state of the theory, the molecule suffers a recoil of magnitude $h\nu/c$ in a particular direction only because of the chance emission in that direction.

This property of elementary processes as expressed by equation (12) makes a quantum theory of radiation almost unavoidable. The weakness of the theory lies, on the one hand, in its not bringing us closer to a union with the wave theory, and, on the other hand, that it leaves the time and direction of the elementary processes to chance; in spite of this, I have full confidence in the trustworthiness of this approach.

Only one more general remark. Almost all theories of thermal radiation rest on the considerations of the interaction between radiation and molecules. But, in general, one is satisfied with dealing only with the energy exchange, without taking into account the momentum exchange. One feels justified in this because the momentum transferred by radiation is so small that it always drops out as compared to that arising from other dynamical processes. But for the theoretical considerations, this small effect is on an equal footing with the energy transferred by radiation because energy and momentum are very intimately related to each other; a theory may therefore be considered correct only if it can be shown that the momentum transferred accordingly from the radiation to the matter leads to the kind of motion that is demanded by thermodynamics.