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A QUANTUM THEORY OF OPTICAL PHENOMENA

By J. C. Slater

Abstract

An attempt is made to present a consistent detailed theory of optical phenomena, based on the suggestion recently made by the author in collaboration with Bohr and Kramers. This suggestion is that atoms are radiating or absorbing continuously, during their stationary states, and that transitions influence radiation only in terminating the radiation characteristic of the old state, and substituting that of the new. The atoms, on the other hand, are supposed not to change their energy while radiating, but to change it discontinuously on transition. This necessitates giving up the detailed application of the conservation of energy in interaction between atoms and radiation. In the present paper, an additional suggestion is made, namely that resonance radiation is to be identified with the radiation carried out by the spherical wavelets which, by their interference with the external field, also produce absorption. This is practically a return to the classical picture of resonance radiation. *Statement of the theory* consists formally of two parts: the description of the behavior of atoms, and of radiation, when the two interact. The first involves the statement of the probabilities of transition of atoms, and is taken without change from Einstein. The probability of interruption of coherent vibrations is also discussed. The second requires the specification of the fields emitted by atoms in any steady state under the influence of any external field. These consist of spherical wavelets of the frequencies of the various quantum lines which the atom can emit or absorb in the stationary state in which it is. For emission frequencies, wavelets are emitted even in the absence of an external field; for absorption frequencies, external fields induce wavelets, similar to the wavelets of linearly bound electrons in electron theory, which on the one hand interfere with the external field to produce the phenomena of dispersion, etc., and on the other carry out the resonance radiation in all directions. Detailed descriptions of these fields are given. In a *discussion of the theory*, it is first shown that the assumptions which have been made about the field satisfy the correspondence principle, in that for large quantum numbers the field aproaches that which would be emitted classically on account of the interaction of an external field and a multiply periodic atom. On the other hand, it is shown that the field has a character essentially like that of classical electron theory, which is known to be in general agreement with experiments. Next, the energy and momentum relations at interaction of atoms and light are investigated, and it is shown that, although these quantities are not precisely conserved, still the assumptions as to atomic and radiation processes have been so made that they are conserved on an average over a great number of atomic processes. Finally the spectral resolution of emitted and absorbed radiation is considered; the theory gives a minimum breadth for the lines, depending on the finite length of wave trains resulting from the finite life in stationary states, and it is shown that Kirchhoff's law is obeyed, the emission and absorption lines being of the same breadth. By way of illustration, specific *application of the theory* is made to the simple examples of emission of light by bombardment of electrons at the resonance potential, resonance radiation, its quenching by presence of foreign gases, absorption, scattering, and dispersion.

I. Introduction

THE widespread feeling that the quantum theory of atomic structure and the electromagnetic theory of light are inconsistent with each other has tended to divide physicists into two opposing sections. Some, in their enthusiasm for the quantum theory, are willing to overlook the phenomena of optics; while others consider that the quantum theory is discredited by its failure to deal with optical problems. Such an unfortunate condition has naturally inspired many attempts to harmonize the two branches of theory. It has appeared from those attempts that the supposition of exact conservation of energy and momentum in atomic processes has been at the root of the difficulties. For in the quantum theory the energy of atoms must change by jumps; and in the electromagnetic theory the energy of a radiation field must change continuously. Once it is supposed that the total energy is the sum of the atomic energy and of the energy in some sort of radiation field, and that this total energy is conserved, there results the impossible situation that the sum of two quantities, one changing discontinuously and the other continuously, must be constant.

Two paths of escape from this difficulty have been followed with more or less success. The first is to redefine energy; the second to discard conservation. If atomic energy is to change discontinuously, then for conservation the energy of the field must change discontinuously also, and the idea that the energy of the field exists in discrete particles immediately presents itself. Einstein by his introduction of quanta of energy traveling through space has been the principal exponent of this first method. Optical theory on such an interpretation would be a set of laws telling in what paths the quanta travel; for these laws would determine how often an atom in any point of space would be struck by a quantum, and this is immediately connected with the strength of illumination at that point. A beginning of such a theory has been made by Duane,[1] who has suggested relations determining the deflection of quanta passing through

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[1] W. Duane, Proc. Nat. Acad. Sci. **9**, 158 (1923). See also G. Breit, Proc. Nat. Acad. Sci. **9**, 238 (1923).

diffraction gratings or crystals. A method of procedure somewhat more natural than Duane's would be to take advantage of the fact that the electromagnetic theory gives reasonable results, and to set up a sort of ghost field, similar to a classical field, whose function was in some way to guide the quanta. For example, the quanta might travel in the direction of Poynting's vector in such a field. The author was at one time of the opinion that this method was the most hopeful one for solving the problem. But any theory based on discrete quanta has the one fundamental disadvantage that it must find a substitute for wave theory even in explaining the nature of light itself, which the wave theory is perfectly competent to deal with. Such a theory must inevitably face the charge of lack of economy, since it introduces superfluous mechanism.

The other direction of escape from the conflict between quantum theory and wave theory has been to retain intact the quantum theory and as much of the wave theory as relates to the field, but to discard conservation of energy in the interaction between them. This is the point of view of Darwin[2] in a theory of dispersion which he put forward, but which, it is understood, he no longer defends. Darwin assumed that by the passage of light over an atom, the atom acquired a probability of sending out a spherical wave train to interfere with the external light, the probability depending on the strength of the incident light. By the cooperation of many of these interfering trains, the familiar phenomena of dispersion could be explained. The reason why such a theory cannot be right is that, in very weak light, only a very few atoms would be induced to send out wave trains, and these would not be enough to interfere properly; whereas it is known experimentally[3] that interference patterns can be obtained with weak light as well as with strong. In addition to Darwin's theory, there have been other attempts to treat the radiation field of quantum atoms by classical methods. Bohr[4] has suggested that atoms must become sources of spherical wavelets when external radiation strikes them. Ladenburg and Reiche[5] have given formulas for dispersion based essentially on the idea of such spherical wavelets. Neither of these suggestions has, however, gone as far as Darwin's theory in setting up a mechanism for the interaction between waves and atoms.

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[2] C. G. Darwin, Nature **110,** 841 (1922); Proc. Nat. Acad. Sci. **9,** 25 (1923).

[3] G. I. Taylor, Proc. Camb. Phil. Soc., **15,** 114 (1909).

[4] N. Bohr, Zeits. f. Phys., **13,** 117 (1923)

[5] Ladenburg, Zeits. f. Phys. **4,** 451 (1921); Ladenburg and Reiche, Naturwissenschaften, **11,** 584 (1923)

An attempt was made by the writer, in a note to Nature, enlarged upon in collaboration with Bohr and Kramers,[6] to contribute slightly to the solution of these difficulties. In the present paper, the suggestions made in those papers are developed into a more specific theory. The views suggested there had foundations similar to those of Darwin, and of Ladenburg and Reiche. It was supposed that energy was of two kinds, the continuously changing energy of the field and the discontinuously changing atomic energy, and that there was no exact conservation, but only a statistical conservation, so that the average rate of decrease of radiation energy would equal the average rate of increase of atomic energy, or vice versa. It was assumed that atoms under the influence of external light were induced to send out spherical wavelets of light, much like those sent out by the oscillators of Ladenburg and Reiche and not entirely dissimilar to Darwin's, and that those spherical wavelets interfered, giving the phenomena of dispersion, interference, etc. In addition, it was supposed that excited atoms emitted wavelets even in the absence of a field, to account for luminous radiation.

None of these points, as we have seen, was particularly original. But there was one suggestion in the paper, essentially new, which appeared to afford a more reasonable picture of optical phenomena than we had previously had. That was the suggestion that the wavelets sent out by an atom in connection with a given transition were sent out, not as a consequence of the occurrence of the transition, but as a consequence of the existence of the atom in the stationary state from which it could make that transition. On this assumption, the stationary state is the time during which the atom is radiating or absorbing; the transition from one state to another is not accompanied by radiation, but so far as the field is concerned, merely marks the end of the radiation or absorption characteristic of one state, and the beginning of that characteristic of another. The radiation emitted or absorbed during the stationary state is further not merely of the particular frequency connected with the transition which the atom is going to make; it includes all the frequencies connected with all the transitions which the atom could make. Then the atom is under no necessity of knowing what transition it is going to make ahead of time. In particular, the atom during a stationary state is supposed to be spontaneously emitting radiation of the various frequencies connected with transitions to states of lower energy, and to be capable of absorbing radiation connected with transitions to states of

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[6] J. C. Slater, Nature, p. 397, 1924; Bohr, Kramers, and Slater, Phil. Mag. **47,** 785 (1924); also Zeits. f. Phys. **34,** 69 (1924)

higher energy. Further, a "negative" absorption is assumed, similar to the ordinary absorption, but resulting in increase rather than decrease of the energy in the external field, and with frequencies corresponding to transitions to states of lower energy. Although the atom is radiating or absorbing during the stationary states, its own energy does not vary, but changes only discontinuously at transitions, as has always been supposed. It is quite obvious that the mechanism becomes possible only by discarding conservation.

The suggestion just described was of value in two different ways. In the first place, it furnished an immediate solution of the difficulties concerning dispersion and absorption by weak light. For all the atoms, in an ordinary substance, are in the normal state, and hence take part in absorption of radiation. Then the number of wavelets cooperating to produce the effect would be as great for weak light as for strong. In the second place, the suggestion makes possible a much more definite picture of the process of interaction of light and atoms, in time and space, than had been possible before. Light is emitted or absorbed in a perfectly definite time—the stationary state. In particular, this provides for a theory of the breadth of spectral lines, since that depends on the length of coherent wave trains, or the length of time during which the atom emits a train. It must be admitted that a theory of the kind suggested has unattractive features; there is an apparent duplication between the atoms on the one hand, and the mechanism of oscillators producing the field on the other. But this duplication seems to be indicated by the experimental facts, and it is difficult at the present stage to see how it is to be avoided.

Although the suggestions of the previous paper appeared to help considerably in the task of making a consistent radiation theory, there was one point in which the problem remained in a rather unsatisfactory state. In the quantum theory, the emission and absorption of radiation have been considered as completely separated acts, while in classical theory they are combined into essentially a single process. It did not appear in the previous paper how these two quite different points of view could be combined. The difficulty appears only when light of a particular frequency is being simultaneously absorbed and emitted by a group of atoms. This includes the problems of scattering and of resonance radiation. In the quantum theory of resonance radiation, it has been supposed that atoms in their normal state could absorb energy, and pass to the excited state; then after a certain time in the excited state they re-emit the energy, just as they would emit it if they had been excited, say, by electron impact, and thus return to their normal state. Translated into the language of the present theory, this assumption would be that the atoms in the normal state emit wavelets which weaken the external field, while those in the excited state spontaneously emit wavelets of large intensity, just as if they were excited by impact, these wavelets forming the resonance radiation. In the classical theory, on the other hand, bound electrons are set into oscillation by the radiation field and emit wavelets which on the one hand interfere with the field and weaken it, producing the phenomena of absorption, while on the other hand, simply by virtue of being wavelets, they carry out radiation which is the scattered or resonance radiation. The connection of the two phenomena is inherent in the field equations, not merely in the assumptions of the classical theory as to the interaction of atoms and light. This connection must then be assumed if we are to retain the present theory, which is based on the field equations; and yet this is contrary to the quantum assumptions.

When we examine the difficulty presented here, we see that the assumed conservation of energy is again the cause of the trouble. The reason why we wish the emission to take place during the excited state and the absorption during the normal state, is simply a survival of the more restricted desire to have the emission take place at the transition from the excited to the normal state, the absorption at the transition from the normal to the excited state. But we are giving up exact conservation, and no reason remains why we should not assume that resonance radiation is emitted, not in the excited stationary state before the atom has its transition back to the normal state, but in the normal state just preceding that, before the atom is raised by resonance to the excited state. We shall now make this assumption, removing the necessity of separating the acts of emission and absorption, and returning essentially to the classical picture of resonance radiation.

If resonance radiation is emitted by atoms in the normal state, it follows that the atoms which are raised to the excited state by resonance do not radiate spontaneously any light of the resonance frequency, as they would if they were brought to that state by some other agency. We are then under the necessity of distinguishing those atoms that are brought to an excited state by resonance from those that are brought there by some other agency, and endowing the latter with a spontaneous radiation which the former do not possess. It should be clearly understood, however, that it is only spontaneous radiation of the resonance frequency which atoms brought to the excited state by resonance must be supposed not to possess; they have spontaneous radiation of all the other frequencies which an atom brought to the excited state by impact would have. And also they are supposed to be capable of "negative" absorption at the resonance frequency, as well as at other emission frequencies, so that they radiate some small amount of energy of the resonance frequency in this way; but we shall see that this is no greater than the energy radiated by each atom in the normal state.

One advantage of this picture of resonance radiation over the usual one is that it furnishes an explanation of the possibility of strong polarization of resonance radiation. This explanation is precisely that of the classical theory; the dipoles which produce the radiation are all called into play by the field, and vibrate in the direction of the electric vector of the field. This phenomenon, on the other hand, is extremely difficult to understand on the more usual interpretation.

On the basis of the assumption made in the previous paper concerning the emission of radiation during stationary states, and the present further assumption about the emission of resonance radiation during the normal state, it is possible to arrive at a complete and detailed picture of the interaction of radiation and atoms. Such a picture will be presented in this paper, in numerical detail. Although of course there may be many things about such a detailed theory which will turn out to be wrong, still it seems of considerable interest to know that the ideas presented here can be carried through consistently. The picture in the first place satisfies the primary requirements that all actions take place in time and space as we ordinarily think about them, and that the behavior outside the atom is described by Maxwell's equations, while the atom is described according to the theory of energy levels. But there are further conditions which the theory must meet. It must lead to optical results similar to the classical theory, for this is known to be empirically true. On the other hand, it must lead to formulas which satisfy the correspondence principle; the recent papers of Kramers[7] and of Van Vleck[8] show how this is to be done.

Finally, and most important, the probabilities of transition, and the behavior of the field, must be so related that energy and momentum are conserved on the average, in spite of the lack of exact conservation. And they must be so related that, in thermal equilibrium, the atomic energy distribution will be Boltzmann's, and the radiation energy distribution will be Planck's. In the next section we shall state the theory which is being suggested. Then there will be a section in which it will

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[7] H. A. Kramers, Nature, May 10 1924, p. 273; Aug. 30 1924, p. 310.

[8] J. H. Van Vleck, Phys. Rev. **24**, 330 (1924)

be shown that this theory satisfies all the various requirements enumerated above. Finally, we shall give a section with a number of examples of the application of the theory in important particular cases.[9]

II. Statement of Theory

Probabilities of transition of atoms. Consider the energy levels and transitions of an atom. By Bohr's frequency condition, we associate with every transition between two energy levels i and j a frequency $\nu_{ij}=\nu_{ji}$, given by the equation $h\nu_{ij}=|E_i-E_j|$, where E_i and E_j are the energies in the two states. By Bohr's correspondence principle, we associate also with each transition a certain amplitude $D_{ij}=D_{ji}$, which is some sort of mean of the amplitude of a certain harmonic in the actual motion of the atom, taken by a method not yet known for motions intermediate between the initial and final states of the atom. This amplitude is supposed to be connected with the probability of transition, or with the intensity of emitted or absorbed light. In particular, if D_{ij} is zero, the transition does not take place. These two constants, ν_{ij} and D_{ij}, for each transition, are the only atomic constants which enter into the theory of the interaction of the atom with light.

Let us now fix our attention on an atom which enters a particular stationary state i, at a particular instant. We assume, following Einstein,[10] that as soon as it enters the state, it acquires separate probabilities

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[9] Since this paper was written, my attention has been called to a recent paper by R. Becker (Zeits. f. Phys. **27**, 173, 1924), treating similar problems by somewhat similar methods, and based also on the assumptions of the paper by Bohr, Kramers, and the author. In several important points, Becker's treatment differs fundamentally from that of the present paper. The most important of these is the matter of resonance radiation, on which a new assumption is made in the present work. Becker supposes that the probability of forced transition is compensated, not by the term $(E\cdot\dot{p})$ alone in the interaction of external radiation and the forced oscillators, but by the whole quantity $2(\ddot{p})^2/3c^3\pm(E\cdot\dot{p})$ for these oscillators, the first part of which we identify with resonance radiation. On account of the two signs in the second term, one for the positive and one for the negative oscillator, these quantities have different magnitudes for the two oscillators; and Becker is under the necessity of choosing different p's for them, in order to secure conservation of energy, thereby losing his connection with the correspondence principle except in the limiting case where the resonance radiation can be neglected. Further, although he does not calculate it, his assumptions do not appear to satisfy the conservation of momentum, except again in the limiting case where resonance radiation is negligible. In the question of broadening of spectral lines, Becker agrees with the present work in making the broadening depend symmetrically on the properties of the two states; but his methods do not lead to such a definite theory of broadening as is given here, and he does not make the connection with probabilities of interruption which is at the basis of the present work.

[10] A. Einstein, Phys. Zeits. **18**, 121, 1917.

for having transitions to each of the other stationary states of which the atom is capable. In particular, it acquires a probability $A_{i\rightarrow j}dt$ of having a transition in time dt to each state j of lower energy, where[11]

$$A_{i\rightarrow j}=16\pi^4\nu_{ij}^3e^2D_{ij}^2/3c^3h\ . \tag{1}$$

We shall call this the probability of a spontaneous transition, or of spontaneous emission. Next, it acquires an additional probability of transition to any state j of either higher or lower energy, if there is an external radiation field present whose spectrum includes energy in the neighborhood of the frequency ν_{ij}. In particular, if the specific energy density is independent of frequency through a small region of frequencies about ν_{ij} (that is, as we shall later see, if it is constant over the absorption line) and equals $\rho(\nu_{ij})$, the probability of transition to state j in time dt will be assumed to be $B_{i\rightarrow j}\rho(\nu_{ij})dt$, where

$$B_{i\rightarrow j}=2\pi^3e^2D_{ij}^2/3h^2\ . \tag{2}$$

If $\rho(\nu)$ is not independent of ν, the expression for this part of the probability will be assumed to be of the form

$$\int B_{i\rightarrow j}(\nu)\ \rho(\nu)d\nu dt\ , \tag{3}$$

where $B_{i\rightarrow j}(\nu)$ is a function of ν of the nature of an absorption curve, with a sharp maximum at $\nu=\nu_{ij}$, and such that $\int B_{i\rightarrow j}(\nu)d\nu=B_{i\rightarrow j}$. The precise formula for $B_{i\rightarrow j}(\nu)$ will be given later, in (12). Then in the particular case where $\rho(\nu)=$ a constant $=\rho(\nu_{ij})$, we can take it out of the integral in (3), and arrive at the formulation first given. The kind of transition contemplated in (3) will be called a forced transition. If it is a transition to a state of higher energy, it will be called forced absorption, or merely absorption; if it is to a state of lower energy, it will be called forced emission. In addition to these probabilities of transition, the atom in the ith state may be subject to collisions which can result in a change of stationary state, We may write the probability of such successful collision in time dt, resulting in a transition to state j, as $K_{i\rightarrow j}dt$. If j is a state of higher energy than i, the collision will be one of the first kind; if j is of lower energy, it will be of the second kind. The quantity $K_{i\rightarrow j}$ must be supposed to depend both on the number of particles per unit volume which are capable of colliding successfully with the atom in question, and which consequently possess the proper energy; and on the specific properties of the atom. No attempt will be made at present to evaluate this quantity.

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[11] The formulas given for $A_{i\rightarrow j}$ and $B_{i\rightarrow j}$ in terms of D_{ij} and ν_{ij} come directly from the correspondence principle, and have often been derived.

All of the probabilities enumerated above are supposed to operate simultaneously and independently. We shall denote by $P_{i\to j}$ the total probability for a transition from state i to state j in unit time. Then we have

$$P_{i\to j}=(A_{i\to j}\text{ or }0)+\int B_{i\to j}(\nu)\rho(\nu)d\nu+K_{i\to j}\ , \tag{4}$$

where the notation ($A_{i\to j}$ or 0) means that the term $A_{i\to j}$ is present if the state j is of lower energy than the state i, but not in the opposite case. We shall further denote by P_i the total probability of a transition from state i to any other state in unit time. Then

$$P_i=\Sigma\ (j)P_{i\to j}\ , \tag{5}$$

the summation being over all j's.

Probability of interruption of coherent vibrations. The radiation field emitted by an atom will be described by giving the electrical moment or polarization of an oscillating dipole, from which the field of the atom can be computed by the Hertz solutions of the field equations. It will be assumed that this polarization, which we shall denote by p_i, is the sum of a number of partial polarizations, $p_{i\to j}$, each connected with a separate transition to another state j, the natural frequency of the partial polarization $p_{i\to j}$ being ν_{ij}. This analysis of the total polarization into a number of partial polarizations is analogous to the analysis of the actual multiply periodic polarization of the atom into a number of terms, one for each harmonic present in the motion. We shall speak of a term $p_{i\to j}$ as an oscillator. An oscillator can consist of two parts, (1) a spontaneous part, independent of the external field, present only when the energy of state j is less than that of state i, and when the atom was not raised to its state i by resonance radiation of frequency ν_{ij}, and (2) a forced part, similar to the oscillation of a bound electron under the action of an external field on classical theory, and with the same sign as in classical theory if the state j has greater energy than i, but with the opposite sign if state j has less energy. These parts of the oscillator will be referred to as the spontaneous oscillator, and the positive and negative forced oscillators. We now wish to consider the length of time during which the vibrations of the oscillator $p_{i\to j}$ remain coherent. This determines the inherent breadth of spectral lines; and, taken in connection with Doppler effect, etc., it determines the observed breadth.

An atom in the ith state has a probability P_i of suffering in unit time a transition, after which of course it will no longer be in the ith state. Thus there is a probability P_i that the vibrations of each of the oscillators $p_{i\to j}$ will simultaneously cease. But we shall assume that, in addition to this probability P_i of ceasing its oscillation altogether, each oscillator $p_{i\to j}$ has also an independent probability P_j of suffering an interruption, in which it ceases its oscillation as if it were leaving the state, but immediately begins again as if it were entering the same state. This term P_j is the same as the probability that an atom in the jth state will leave that state. It is thus different for the various oscillators $p_{i\rightarrow j}$ of the state i connected with different j's, so that the interruptions of this kind come at different times for different oscillators. Each oscillator may be interrupted a number of times in the course of a stationary state. The combined probability that an oscillator $p_{i\rightarrow j}$ will suffer either an interruption or a complete cessation is the sum, P_i+P_j. Either an interruption or a cessation is supposed to result in a complete breaking off of coherence in the emitted radiation. On the other hand, the coherence is supposed to be perfect in the time between these interruptions; spontaneous oscillators vibrate exactly sinusoidally, and forced oscillators act like bound electrons with no damping, so that the whole lack of coherence in the radiation arises from the interruptions, and the finite length of wave trains. The reason for the introduction of the interruptions of oscillators without transitions of the atom is to preserve Kirchhoff's law in cases where oscillators of atoms both in the state i and in the state j take part in emission and absorption of radiation of frequency ν_{ij}. In order that the emission and absorption lines may be of the same breadth, which Kirchhoff's law demands, the time of coherent vibration must be the same for oscillators $p_{i\rightarrow j}$ and $p_{j\rightarrow i}$. This we have secured by making the probability of interruption for each equal to P_i+P_j, which is symmetrical in i and j. It remains, of course, to be shown later that the equality of time during which coherent vibration is emitted or absorbed is a sufficient reason for actual equality of breadth in the spectral lines of absorption and emission.

The radiation field of an atom: *Spontaneous oscillators*. We assume that the spontaneous part of the oscillator $p_{i\rightarrow j}$, which we shall denote by $p^s_{i\rightarrow j}$, has when it occurs an amplitude eD_{ij}, where e is the electronic charge, a frequency ν_{ij}, and a phase determined by chance. This completes the formulation, except for stating when a spontaneous oscillation occurs. We have already stated that such an oscillator is present when the following two conditions are satisfied: (a) The energy of state j is less than that of state i; (b) the atom was not brought to the state i by resonance radiation of frequency ν_{ij}. We shall now slightly amend the condition (b), and make it more precise, bringing in the idea of interruptions as outlined in the preceding paragraph. The restatement of (b) will be: The interruption of the oscillator $p_{i\rightarrow j}$ just preceding the time of continuous vibration which we are considering was not a result of the probability term (3). There are then two cases in which, according to (b), spontaneous polarization $p_{i\to j}$ is absent: First, when the atom has just entered the state i from the state j, on account of the term (3) in the probability of transition from state j to state i, but when the oscillator $p_{i\to j}$ has not yet had an interruption while the atom has been in the state i; second, when the atom has been in the state i long enough so that the oscillator $p_{i\to j}$ has had interruptions, and when the last previous interruption was on account of the term (3) in the probability P_j of interruption which this oscillator possesses. In justification of this precise assumption we see that a consequence of it is that when there is no resonance, so that $\int B_{j\to i}(\nu)\rho(\nu)d\nu=0$, all the atoms in the state i have spontaneous oscillators $p^s{}_{i\to j}$. Further, when no atoms reach state i except on account of this term, none possess spontaneous oscillators; for P_j can contain no terms except (3), and hence no oscillators $p_{i\to j}$, either after a transition or an interruption, satisfy the condition (b). Thus in the two limiting cases, of complete resonance or complete lack of resonance, the assumption is what we should desire. In intermediate cases, the justification of the assumption will come by showing that conservation of energy results from it.

The radiation field of an atom: *Forced oscillators.* Before stating in detail our assumptions about the forced oscillators, there are several approximations and simplifications which are to be made in the present paper, and which will be described. First, in absorption formulas and similar places, we shall work only to the first order in $1/(\nu_{ij}-\nu)$. Then we shall replace $1/(\nu_{ij}^2-\nu^2)$ by $1/[2\nu_{ij}(\nu_{ij}-\nu)]$, etc. This will in future be done without comment. Second, we shall assume that the atoms have equal probability of orientation in any direction, and shall work throughout with average values over all orientations; or, what amounts to the same thing, we shall assume that the atoms are isotropic.[12] We shall further assume all states to have the same a priori probability. It is probable that a more complete theory, in which these simplifications were not made, would encounter only additional complications, without additional difficulties of an essential kind.

It will be assumed that the spectral resolution for the external electric field is

$$E_x=\Sigma\,(n)\,A_{nx}\cos 2\pi\nu_n t+B_{nx}\sin 2\pi\nu_n t\,, \qquad \nu_n=n/T \tag{6}$$

where T is a very long time. There are to be similar resolutions for E_y and E_z. The coefficients A_{nx} of the field should not be confused with the terms $A_{i\to j}$ in the probability of transition.

[12] See Van Vleck, l.c.,[8] note 25, p. 344.

We are now ready to write our detailed assumption about the forced part of the oscillator $p_{i\to j}$, which we shall call $p^f{}_{i\to j}$. We assume that the last interruption of the oscillator came at time t_o. Then for times after t_o, and until the next interruption, we assume that its value, averaged as stated over all orientations of the atom, is[13]

$$(p^f{}_{i\to j})_x = \pm\frac{e^2D_{ij}{}^2}{12h}\sum(n)\ \frac{A_{nx}}{\nu_{ij}-\nu_n}\{\cos 2\pi\nu_n t-\cos 2\pi[\nu_{ij}t-(\nu_{ij}-\nu_n)t_0]\}$$
$$+\frac{B_{nx}}{\nu_{ij}-\nu_n}\{\sin 2\pi\nu_n t-\sin 2\pi[\nu_{ij}t-(\nu_{ij}-\nu_n)t_0]\} \qquad (7)$$

with similar values for the y and z components. The positive sign is to be taken for positive oscillators, where the energy in the jth state is greater than in the ith, the negative sign in the opposite case of negative oscillators. Eq. (7) can also be written

$$(p^f{}_{i\to j})_x = \pm\frac{e^2D_{ij}{}^2}{12h}\sum(n)\ \frac{A_{nx}}{\nu_{ij}-\nu_n}\{[1-\cos 2\pi(\nu_{ij}-\nu_n)\ (t-t_0)]\cos 2\pi\nu_n t$$
$$+[\sin 2\pi(\nu_{ij}-\nu_n)\ (t-t_0)]\sin 2\pi\nu_n t\}$$
$$+\frac{B_{nx}}{\nu_{ij}-\nu_n}\{[1-\cos 2\pi(\nu_{ij}-\nu_n)(t-t_0)]\sin 2\pi\nu_n t \qquad (8)$$
$$-[\sin 2\pi(\nu_{ij}-\nu_n)(t-t_0)]\cos 2\pi\nu_n t\}$$

The polarization is seen to depend on the time $(t-t_o)$ which has elapsed since the last interruption. In most applications, we are interested only in .the average of $(p^f{}_{i\to j})$ taken over all values of $(t-t_o)$. This is found in Note 1, and is

$$\overline{(p^f{}_{i\to j})_x} = \pm\frac{e^2D_{ij}{}^2}{12h}\sum(n)\frac{\nu_{ij}-\nu_n}{[\nu_{ij}-\nu_n]^2+[(P_i+P_j)/2\pi]^2}(A_{nx}\cos 2\pi\nu_n t+B_{nx}\sin 2\pi\nu_n t)$$
$$+\frac{(P_i+P_j)/2\pi}{[\nu_{ij}-\nu_n]^2+[(P_i+P_j)/2\pi]^2}(A_{nx}\sin 2\pi\nu_n t-B_{nx}\cos 2\pi\nu_n t)\ . \qquad (9)$$

A variation of this equation is obtained by substituting for D_{ij} from (1); this gives simply a different form for the constant. In terms of this value we can write the whole average moment for all the oscillators $p_{i\to j}$ combined. We shall be interested in the particular form which this equation

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[13] The polarization (7) can be considered as being derived in either of two ways. In the first place, it follows directly from the correspondence principle. In the second place, it results if we apply the conditions of conservation of energy and momentum on the average. Both these conditions will be discussed in the next section. It is noteworthy that the two independent requirements lead to the same result; or, expressing it differently, that the same assumption can satisfy both conditions.

takes at frequences ν_n which are outside any of the absorption lines, so that $(\nu_{ij}-\nu_n) > > (P_i+P_j)/\pi$ for all j's. Then the formula is

$$\Sigma(j)\overline{(p^f{}_{i\to j})_x} = \frac{c^3}{64\pi^4}\sum(n)\left[\sum(r)\frac{A_{r\to i}}{\nu_{ir}{}^3(\nu_{ir}-\nu_n)} - \sum(s)\frac{A_{i\to s}}{\nu_{is}{}^3(\nu_{is}-\nu_n)}\right] \times\left[A_{nx}\cos 2\pi\nu_n t + B_{nx}\sin 2\pi\nu_n t\right], \qquad (10)$$

where r is to be summed over all states for which the energy is greater than for the state i, and s over all states for which the energy is less. This concludes the formulation of the polarization of the dipole connected with an atom in the ith state, and consequently of the radiation field emitted by such an atom during its stationary state.

III. DISCUSSION OF THEORY

The correspondence principle. The polarization assumed in the preceding section satisfies the condition of the correspondence principle, that it should degenerate for high quantum numbers to the polarization which would be produced in the actual orbital motions of the electrons in the atom under the same external field. This has been shown both by Kramers and by Van Vleck, in the papers quoted above. We begin with formula (10). We suppose any particular stationary state to be described by a set of quantum numbers $n_1 \ldots n_p$. Let the state i be described by a particular set $n_1' \ldots n_p'$, and let the state r be described by $n_1'+\tau_1, \ldots n_p'+\tau_p$, where some of the τ's may be positive, some negative. Now let us pair off with this state r a particular state s whose quantum numbers are $n_1'-\tau_1, \ldots n_p'-\tau_p$. Then the transitions from state i to r, and from i to s, are connected by the correspondence principle with the same harmonic in the actual motion. As we approach high quantum numbers, the constants D_{ir} and D_{is}, ν_{ir} and ν_{is}, for these two transitions, will approach each other. Then the difference between the two terms, one positive and the other negative, in (10), corresponding to those particular transitions, will become relatively small as the quantum numbers become large. We note that $A_{r\to i}$ contains a factor h in the denominator. Then a set of two terms, paired as described, will be the difference of two quantities which, in the limit of high quantum numbers, approach each other, divided by h. Now if we replace this difference divided by h, by a derivative with respect to a phase integral J, as is usual in correspondence principle, the resulting formula is, to the approximation with which we are working, precisely the formula found for the polarization produced classically in the multiply periodic atom by the external field. It is noted that we used the formula (10), which holds only at a distance from absorption lines, in this deduction. This is simply because the breadth of spectral lines is a characteristic quantum theory phenomenon, for which we can expect no classical analogy. The classical multiply periodic system would give no sharp lines at all, for its energy and frequency would change with the time.

Optical phenomena and classical bound electrons. It is a very remarkable fact, pointed out by Van Vleck,[14] that although the classical dispersion by a multiply periodic system involves complicated terms, still the quantum dispersion formula (10), where differences are substituted for derivatives, consists of a series of terms each of which behaves formally like the contribution of a bound electron on the classical theory. It appears that this is the real explanation of the fact that it has been possible to obtain a dispersion theory capable of representing the truth so well by means of the classical theory of elastically bound electrons. Even within the absorption lines there is a similar situation, in which our assumptions, derived with the multiply periodic system in mind, still give results suggesting linear oscillators. On examination, it will be seen that the complete forced polarization, on the present theory, is the sum of two parts, that given by (10), and terms in the natural frequences ν_{ij}, which reduce the amplitude of a forced oscillator to zero at the beginning of its vibration. Formula (7) consists precisely of these two terms, one having a frequency ν_n, the other ν_{ij}, and the second having such a phase that the two cancel each other at $t=t_0$. But the use of the two kinds of terms amounts to setting up our polarization by analogy, not with the steady forced perturbation of a classical multiply periodic system, but with the perturbations as they build up from zero.[15] This is necessary in order that we may explain the broadening of lines by a mechanism of interruptions such as we have used. But the result of it is that (7) is precisely the kind of forced motion which a classically bound electron would have while its amplitude was building up from zero, and the formulas which result from it are just the ones to which we are led by Lorentz's theory of broadening of lines by collisions.

The present theory, then, arrives at qualitatively the same kind of forced polarization as the classical theory, although no suggestion of linear restoring forces lies at the bottom of it. But it is known that for

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[14] Van Vleck, l.c.,[8] p. 346.

[15] Kramers and Van Vleck retain merely the terms in their results which vibrate with the impressed frequency. But if also the terms representing the building up of the perturbations from zero are retained in the classical derivation, it is found that the whole forced polarization can be written as a derivative with respect to a phase integral. When this is replaced by a difference, the terms are exactly the terms of the formula (7).

the explanation of optical phenomena, the classical theory is qualitatively satisfactory. We may then expect that the present theory will have the same success. Quantitatively, the classical theory was not so fortunate. The present work suggests why that may have been true. The constant of the polarization of a classically bound electron depends on e/m, and this is the same for all electrons. But experimental values were found which almost invariably differed from the true value of e/m. On the present theory, the constant is different, involving the amplitude D_{ij}, which can have almost any value. Whether the polarization predicted by the present formulas is in accord with experiment is largely a question for the future. In the matter of broadening of lines, too, the classical theory found itself rather unable to deal with the situation. The present theory, with its result that the broadening depends on P_i+P_j, leads to definite results which, it seems, may be useful in explaining the observations. Of course, we must always remember that there are other causes of broadening in addition to the intrinsic broadening connected with the probability P_i+P_j, Doppler effect, Stark effect from neighboring atoms, etc.

Conservation of energy. The present theory has just been shown to be in accordance with the correspondence principle, and to be qualitatively similar to classical dispersion theory. Now we shall approach the more difficult tasks of showing that the conservation of energy and momentum are satisfied in general in the interaction of radiation and atoms, on the average, and that the theory leads to the proper relations in thermal equilibrium. Energy and momentum we are assuming to be of two kinds, the atomic energy and momentum of the atoms in their stationary states, and the radiation energy and momentum located in the field of the oscillators. The energy and momentum arising from the electrostatic part of the field of the oscillators, their so-called constitutive energy, is not included; its place is taken in the general scheme by the atomic energy. Now if energy and momentum are on the average conserved, it must be because the average rate of decrease of the discontinuously changing atomic quantity equals the average rate of increase of the quantity in the field, or vice versa. We shall find, in fact, that not only is there conservation in general, but that there is also conservation among the particular frequencies. That is, the rate of decrease of atomic energy and momentum in consequence of a particular transition $i\rightarrow j$ or $j\rightarrow i$, is just compensated by the rate of increase of the corresponding quantities in the field on account of the oscillators $p_{i\rightarrow j}$ or $p_{j\rightarrow i}$ of the atoms in the two states. We must then compute the quantities involved in these statements, and verify their correctness.

Let us consider a situation in which the number of atoms in each stationary state is independent of time. This includes almost all the problems we are interested in. Let the number of atoms in the ith state be N_i and in the jth N_j. Then $N_iP_{i\to j}$ atoms make the transition $i\to j$ per second, and $N_jP_{j\to i}$ make the transition $j\to i$. Let us suppose for convenience that the ith state has larger energy. Then in each of the transitions $i\to j$, atomic energy decreases by $h\nu_{ij}$, and in each transition $j\to i$ it increases by the same amount. The rate of decrease of atomic energy on account of these transitions is then $(N_iP_{i\to j}-N_jP_{j\to i})h\nu_{ij}$. Now we can substitute the expression given in Eq. (4) for the P's. The terms in $K_{i\to j}$ and $K_{j\to i}$ in the resulting expression are supposed to be compensated directly by increase of energy of colliding bodies at collisions. Then the part of the rate of decrease of atomic energy connected with emission or absorption of radiation of frequency ν_{ij} is

$$N_iA_{i\to j}h\nu_{ij}+(N_i-N_j)\int B_{i\to j}(\nu)\rho(\nu)d\nu h\nu_{ij}\ . \tag{11}$$

Next we must find the rate of increase of energy in the field on account of the oscillators $p_{i\to j}$ and $p_{j\to i}$. This is a simple problem in electromagnetic theory. We have an oscillating dipole exposed to an external field and wish to know the rate at which the energy of the field increases on account of the presence of the dipole. This is known to be the sum of two parts: the rate at which the dipole would radiate if the external field were absent, but if the dipole still had its same amplitude, which is $2(\ddot{p})^2/3c^3$, if p is the moment; and the additional rate of radiation on account of interference with the external field, which is $-(E\cdot\dot{p})$. A term of the first kind arises from both the spontaneous and forced parts of the polarization, that from the spontaneous oscillators representing ordinary emission of light, and that from the forced oscillators being resonance radiation. A term of the second kind arises only from the forced oscillators, for the spontaneous oscillators are not in any phase relation with the field E, and the average of $(E\cdot\dot{p})$ for them is zero. We shall as a matter of fact find that the term $N_iA_{i\to j}h\nu_{ij}$ in (11) is compensated by the term $2(\ddot{p})^2/3c^3$ for the whole polarization, spontaneous and forced; while the remaining term is compensated by the quantity $-(E\cdot\dot{p})$ for the forced oscillators. In Note 2 the necessary computations are made. It is there found that the rate of radiation from a spontaneous oscillator of amplitude D_{ij} and frequency ν_{ij} is $A_{i\to j}h\nu_{ij}$. In order to state the results for the forced oscillators, it is most convenient first to give our definition of $B_{i\to j}(\nu)$. We assume that it is given by

$$B_{i\to j}(\nu)=B_{i\to j}\frac{(1/\pi)[(P_i+P_j)/2\pi]}{[\nu_{ij}-\nu]^2+[(P_i+P_j)/2\pi]^2}\ . \tag{12}$$

This satisfies the condition that $\int B_{i\rightarrow j}(\nu)d\nu = B_{i\rightarrow j}$, and gives a dependence on ν which has precisely the form of the absorption curve. Then we find, in terms of this function, that the average rate of radiation by a forced oscillator as described in (8), on account of the term $2(\ddot{p})^2/3c^3$, is

$$\frac{A_{i\rightarrow j}h\nu_{ij}}{P_i+P_j}\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu\ . \tag{13}$$

Further, the rate of radiation by a forced oscillator on account of the term $-(E\cdot\dot{p})$ is

$$\pm h\nu_{ij}\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu\ , \tag{14}$$

the positive sign referring to the forced polarization $p^f{}_{i\rightarrow j}$, the negative to $p^f{}_{j\rightarrow i}$.

The total increase of field energy on account of the term $-(E\cdot\dot{p})$ arises from N_i dipoles with the polarization (14) taken with the positive sign and N_j with the same polarization but the negative sign. It is thus exactly the second term of (11) (where now we are to understand that the function (12) is substituted in (11)) so that the rate of decrease of atomic energy on account of forced transitions is just equal to the rate of increase of energy of the field on account of the interaction between the forced oscillators and the field, connected with the term $-(E\cdot\dot{p})$. It remains to show that the first term in (11), the rate of decrease of atomic energy on account of spontaneous transitions, is equal to the rate of increase of radiation energy on account of the term $2(\ddot{p})^2/3c^3$ for all the oscillators, spontaneous and forced together. To do this, we must find the number of atoms in the state i which have spontaneous oscillators. This is N_i, multiplied by the fraction of N_i whose last previous interruption was neither an interruption of an oscillator in the ith state on account of the term (3) in its probability of interruption P_i, nor a transition from state j to state i on account of the same term in its probability of transition. In Note 3, it is shown that this fraction is

$$1-\frac{N_i+N_j}{N_i}\ \frac{\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu}{P_i+P_j}\cdot \tag{15}$$

Then the total rate of increase in energy of the field on account of the term $2(\ddot{p})^2/3c^3$ is the sum of $N_iA_{i\rightarrow j}h\nu_{ij}$ multiplied by the fraction (15), increased by (N_i+N_j) times the quantity (13). That is, it is

$$N_iA_{i\rightarrow j}h\nu_{ij}\left(1-\frac{N_i+N_j}{N_i}\ \frac{\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu}{P_i+P_j}\right) +\frac{(N_i+N_j)A_{i\rightarrow j}h\nu_{ij}}{P_i+P_j}\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu = N_iA_{i\rightarrow j}h\nu_{ij}\ . \tag{16}$$

This is equal to the first term in (11), so that the conservation of energy is secured.

Conservation of momentum. In stating the laws of probability for transitions, no mention was made of the momentum gained or lost by an atom in its transition. We shall make the same assumptions as Einstein.[10] In the first place, in every transition from state i to j, in which the atom either gains or loses energy $h\nu_{ij}$, it is assumed that the momentum of the atom in some direction changes by $h\nu_{ij}/c$. The direction is determined as follows: (a) If the transition is a spontaneous one, on account of the probability $A_{i\rightarrow j}$, the direction is random. (b) If the transition is a forced one, we can state the condition most simply if the external field happens to be a plane wave. Then the momentum is in the same direction that the wave is travelling, or the opposite direction, depending on whether the induced transition is an absorption, with increase of atomic energy, or an emission, respectively. When the external field has not this simple character, we must analyze it into many plane waves travelling in all directions. We can write the probability of an induced transition as a sum of terms, one arising from each plane wave. We can then say that the chance that the direction of the momentum lies in any solid angle is equal to the fractional contribution to the total probability of transition made by waves whose wave normals lie in this solid angle (or, for induced emission, whose directions lie in the opposite solid angle). That is, we regard each plane wave as contributing an independent probability of directed momentum interchange in its own direction.

From these assumptions, we can find the average rate of increase of atomic momentum in any direction. The spontaneous transitions contribute nothing, for the direction of impulse in such transitions is random, and the average in any direction is zero. In treating the induced transitions, we can consider separately the effect of plane waves in different directions. Let us fix our attention on a solid angle of directions, say $d\omega$, about a particular direction n, and let us denote by $\rho_n(\nu)d\omega$ the energy density in the particular plane waves whose wave normals are included in this solid angle. Then the contribution of these waves to the probability of induced transitions is $\int B_{i\rightarrow j}(\nu)\rho_n(\nu)d\nu d\omega$. The number of transitions per second from the ith to the jth state induced by this part of the field is N_i times this probability, and from the jth to the ith state N_j times it. We may say that in each of the transitions of the first variety, atomic momentum in the direction of n decreases by $h\nu_{ij}/c$, while in each transition of the second variety atomic momentum in the same direction increases by the same amount. Thus the net rate of increase of atomic momentum in the direction n, in consequence of these transitions, is

$$(N_j - N_i)h\nu_{ij}/c \int B_{i\to j}(\nu)\rho_n(\nu)d\nu d\omega \tag{17}$$

It is next necessary to compute the change in momentum of the field in any direction. In the first place, there is no momentum change on account of spontaneous radiation or resonance radiation, for in each of these cases the energy is carried out in spherical waves, which on the average carry no momentum. The only momentum change results from the interaction of the external field with the wavelets emitted by the forced oscillators. Here again we can separate the external field into a collection of plane waves, and consider only those whose directions lie in the same solid angle as before. In treating the interaction of such a plane wave with the wavelet of a forced oscillator, we need take account only of that part of the polarization of the oscillator produced by the electric field of the particular plane wave in question; for any other term in the polarization will have a phase which is statistically independent of the phase of our plane wave, and the effect will cancel on the average. Then we must find the rate of change of momentum in the field on account of interaction of a plane wave, and a spherical wave in a phase relation to it. It can be shown generally that in such a case the momentum of the field in the direction in which the plane wave is travelling decreases at a rate equal to the rate of decrease of energy in the field, divided by c. For the rate at which the energy of the field decreases, in consequence of the interaction of an external field and the field emitted by an oscillator of moment p, is $(E\cdot\dot{p})$, and the rate at which the momentum of the field decreases is the vector $[\dot{p}\times H]/c$. Now let us analyze the plane wave into components polarized at right angles to each other, and consider one of the components. In general, these components will be independent of each other, so that we need consider only the interaction of each with the part of the polarization which it produces. Choose the x axis as the direction of E, the y axis as the direction of H. Then $E_x = H_y$. Further, for the part of the polarization we are interested in, p is in the x direction. Then $(E\cdot\dot{p}) = E_x\dot{p}_x$, and $[\dot{p}\times H]/c$ is a vector at right angles to both x and y—that is, in the direction z, or the direction of the wave normal—with an amplitude $(\dot{p}_x H_y)/c = (E_x\dot{p}_x)/c$. Thus the result is proved.

The rate of increase in energy of the field on account of the term $(E\cdot\dot{p})$ has already been found, in (14). Then we see, by the result above, that the rate of decrease in momentum of the field in the direction n of the wave normal of our plane waves, on account of a positive forced oscillator

$p^{f}{}_{j\to i}$ is $h\nu_{ij}/c \int B_{i\to j}(\nu)\rho_n(\nu)d\nu d\omega$, and by a negative forced oscillator the negative of this. The total rate of decrease of momentum of the field in this direction, on account of the interaction between the plane waves whose normals are included in $d\omega$, and all the atoms, is just equal to (17), the rate of increase of atomic momentum on account of the same part of the external field. Thus the conservation of momentum is satisfied.

Spectral distribution and thermal equilibrium. It is assumed that in thermal equilibrium the atomic energy is distributed according to Boltzmann's distribution, and the radiation energy is distributed among the various frequencies according to Planck's law. Then the mechanism of interaction between atomic energy and radiation energy must satisfy the condition that it disturbs neither of these distributions. This involves two distinct conditions. First, the laws of probability of transition must be such that the atomic distribution is not affected by interaction with black radiation; second, the radiation emitted and absorbed by atoms must be such that the energy density of Planck's law is not affected by the interaction. The first of these conditions is automatically satisfied by the assumptions of probability that we have made; for these assumptions were taken directly from Einstein, and were made by him simply to secure the result we desire. As a result of the assumption regarding the probability of transition, together with the value $h\nu_{ij}$ of the energy change connected with a transition, the distribution of energy between stationary states is not affected by the presence of black radiation of the temperature of the atoms. The additional assumptions about momentum, in a similar way, bring it about that Maxwell's distribution of velocity among the translational coordinates of the molecules is not affected by radiation. On the other hand, the condition that the energy distribution in the field is not to be affected by the interaction is a new condition, which must be proved. In the first place, the conservation of energy, which we have already verified, shows us that there can be no net increase or decrease in the energy of the field on account of the oscillators connected with the two transitions $i\to j$ and $j\to i$; for in thermal equilibrium as many atoms make this transition in one direction as in the other, so that the atomic energy does not change in consequence of the transition, and hence the energy of the field cannot change either. But it must be shown that this transition not only does not change the total energy of the field, but also does not alter the spectral distribution. To do this, it is necessary to show that emission and absorption lines have the same spectral distribution; that is, that Kirchhoff's law is obeyed. We must therefore investigate the spectral distributions. For generality, we shall not limit ourselves to thermal equilibrium for the moment.

The spectral distribution of the absorption curve is given directly from the absorption probability coefficient $B_{i\rightarrow j}(\nu)$, or from the term in the forced polarization (9) out of phase with the external field; we can best specify the distribution from the ratio $B_{i\rightarrow j}(\nu)/B_{i\rightarrow j}$, given in (12), for this is a quantity which integrates to unity. It is easily shown that this function represents a narrow line whose width in frequency measure, between the points where the curve has half value, is $(P_i+P_j)/\pi$. Now we must compute the spectral distribution of the radiation emitted by the forced oscillators, and see if they have the same distribution. This is a task in Fourier analysis, and is carried out in Note 4. There it is shown that the relative distribution of intensity in the radiation of the spontaneous oscillators is in fact $B_{i\rightarrow j}(\nu)/B_{i\rightarrow j}$. The distribution for the resonance radiation is naturally dependent on the spectral distribution of the incident light which induces the polarization, and is a rather complicated function. But in the case of thermal equilibrium, the external field is a field of continuous radiation, and the energy density can be considered constant over the absorption line. In this special case, the spectral resolution of the resonance radiation also reduces to $B_{i\rightarrow j}(\nu)/B_{i\rightarrow j}$. Thus Kirchhoff's law is verified, and the conditions for thermal equilibrium satisfied. In the more general case where the inducing light is not of uniform energy density, there seem to be no experiments to test the results of Note 4 as to the spectral resolution of the resonance radiation; but it seems likely that such experiments could be devised, and it would be of considerable interest to try them.

IV. Examples of Application of the Theory

In treating a specific problem by the methods outlined here, the first step is to find, either from atomic models or in some other way, the values of the constants D_{ij} and ν_{ij} associated with the various transitions with which the problem deals. Next, the probabilities of transition must be ascertained. The term $A_{i\rightarrow j}$ can be at once computed. If the value of the external radiation field is given, we can find $\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu$. In case $\rho(\nu)$ is constant over the absorption line, this is simply $B_{i\rightarrow j}\rho(\nu_{ij})$, where $B_{i\rightarrow j}$ is directly computed. If on the other hand $\rho(\nu)$ is not constant, we must perform the integration, using (12) for $B_{i\rightarrow j}(\nu)$. The formula involves the probabilities P_i+P_j, and hence implicitly $B_{i\rightarrow j}(\nu)$ itself; but in practical cases this term is negligible, for $\rho(\nu)$ is almost always so small that $B_{i\rightarrow j}\rho(\nu_{ij})$ can be neglected in comparison with $A_{i\rightarrow j}$. We must, however, evaluate the rest of the probability before such an integration can be performed. The remaining terms in the probability arise from collisions. We do not at present know the exact formulas for these probabilities, but approximate formulas can be easily set up.

Having determined the probabilities of transition, the next task is to find the number of atoms in each stationary state. To do this, we first set up a set of equilibrium equations, stating that the number of atoms in each stationary state is to be independent of time. For the *i*th state, for example, we find as the number of atoms entering the state per unit time from all other states, $N_aP_{a\to i}+N_bP_{b\to i}+\ldots$, and as the number leaving per unit time $N_i(P_{i\to a}+P_{i\to b}+\ldots)=N_iP_i$. Then the condition that N_i be independent of time is

$$N_aP_{a\to i}+N_bP_{b\to i}+\cdots\cdots-N_iP_i=0\ . \tag{18}$$

There will be one of these equations for each of the stationary states. Thus there is a set of homogeneous linear equations, one equation for each variable. The solution of these equations presents interesting results, which however need not concern us here. So far as I know, the general equations were first set up and solved by Mr. S. Rosseland, although he has not published them. It can be easily shown that the determinant of coefficients always vanishes, so that the equations always have an infinite number of solutions, and determine the ratios of the N's. When an additional condition specifies the total number of atoms, the N's are determined.

When we have found the number of atoms in the various stationary states, we can investigate the energy interchanges involved in the radiation processes directly from the principle of conservation. Thus we can compute the amount of energy absorbed on account of the term $B_{i\to j}\rho(\nu_{ij})$, and the amount radiated either spontaneously or as resonance radiation. We can further find the amount of kinetic energy brought to or from the system by collisions. In the steady state, such as we are assuming, there will be energy equilibrium; that is, the energy brought into the system, by radiation and collisions, will equal the energy taken out, by other types of radiation and collisions. In general, there is no equilibrium in each mechanism separately, however; radiation will be flowing in, in some frequencies, in which there is absorption, and out in others, where there is fluorescence, resonance, or emission of other types; and kinetic energy will be flowing in, in collisions of the first kind, out in collisions of the second kind. The atoms in general travel from one state to another in cycles, being excited by one agency, returning to the normal state by another, so that the number making a particular transition in one direction is in general different from the number making it in the other. Only in the special case of thermal equilibrium is there equilibrium in each separate agency, and an equal number of atoms making each transition in each direction.

We can now go on to discuss in detail the radiation emitted and absorbed. We consider each natural frequency ν_{ij} separately. Then in the first place we may find the reaction of the atoms on the external field. To do this, we separate the field into polarized monochromatic plane waves, such as are used in optical theory, and on account of the independence of phase between such waves we can treat them separately. Then we can compute the dispersion, refractive index, etc., exactly as in the ordinary treatments of classical theory, only substituting for the polarization of an electron used in classical theory the average values for polarization of forced oscillators given in (9). Having found the reaction of the atom on the field, we next find the nature of the emitted light. We compute the number of excited atoms which have spontaneous oscillators, and find the radiation emitted by them. Also we investigate the scattered or resonance radiation.

In an actual problem, there are of course many other complications which enter. The greatest of these is generally the change in character of the radiation as it passes through the body. If the substance is strongly absorbing, the spectral distribution of the external field in the region in which we are interested may change entirely in passing through the body. Further, the rescattering or reresonating of radiation generally adds to the complication. In the simple problems which we treat here, however, these difficulties will be left out of consideration; they would naturally be treated in making definite applications of the theory to special problems. We shall now pass to several simple examples.

Emission by bombardment at the resonance potential. It is assumed that atoms in the normal state (which we shall call j) are subject to bombardment by electrons, which possess the energy necessary to raise them to the first excited state i. There is supposed to be no external radiation of the resonance frequency. Then, if $K_{j\to i}$ is the probability of collision, we have $P_{j\to i}=K_{j\to i}$, $P_{i\to j}=A_{i\to j}$, and all the other P's are zero. Then there is only one equation for the N's, $N_jP_{j\to i}=N_iP_{i\to j}$, or, if $N=N_i+N_j$,

$$N_i=N\frac{P_{j\to i}}{P_{i\to j}+P_{j\to i}}=N\frac{K_{j\to i}}{A_{i\to j}+K_{j\to i}}\,;\; N_j=N\frac{P_{i\to j}}{P_{i\to j}+P_{j\to i}}=N\frac{A_{i\to j}}{A_{i\to j}+K_{j\to i}}\,.$$

The number in the excited state i depends directly on $K_{j\to i}$, vanishing if there are no electron impacts. There is radiation of energy $N_iA_{i\to j}h\nu_{ij}$ per second. On the other hand, kinetic energy of the equal amount $N_jK_{j\to i}h\nu_{ij}$ per second is brought into the system by the electrons. The radiation is in a line of frequency breadth $(A_{i\to j}+K_{j\to i})/\pi$. It is entirely spontaneous radiation.

Resonance radiation, its quenching by collisions of the second kind, and absorption. Again we have two stationary states j and i. Now, however, there is an external energy density $\rho(\nu_{ij})$, constant over the absorption line. Further, excited atoms have a probability $K_{i\to j}$ of collision of the second kind, either with slow moving electrons or with gas molecules, but there are no collisions of the first kind. Then $P_{j\to i}=B_{j\to i}\rho(\nu_{ij})=B_{i\to j}\rho(\nu_{ij})$, $P_{i\to j}=A_{i\to j}+B_{i\to j}\rho(\nu_{ij})+K_{i\to j}$, $P_i+P_j=A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}$. The numbers of atoms in the two states are then

$$N_i=N\frac{B_{i\to j}\rho(\nu_{ij})}{A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}}\,,\quad N_j=N\frac{A_{i\to j}+B_{i\to j}\rho(\nu_{ij})+K_{i\to j}}{A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}}\,. \tag{19}$$

For all ordinary cases, $B_{i\to j}\rho(\nu_{ij})$ is negligible in comparison with $A_{i\to j}$, so that only a negligible number of atoms are in the excited state. Since all the atoms are brought to the excited state by resonance, none of them have spontaneous oscillators. Then, since the forced oscillators of an atom in the excited state are no larger than those of an atom in the normal state, the excited atoms make an entirely negligible contribution to the resonance radiation. On the other hand, we know by conservation that the rate of radiation of resonance radiation by the normal atoms is directly connected with the number of excited atoms, and is

$$N_iA_{i\to j}h\nu_{ij}=N\frac{A_{i\to j}B_{i\to j}\rho(\nu_{ij})h\nu_{ij}}{A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}}\,. \tag{20}$$

It is observed that, as $K_{i\to j}$ is made large, this decreases, and can be made as small as we please. This is the phenomenon of quenching of resonance radiation by collisions of the second kind. The rate of absorption of radiation from the external field is

$$(N_j-N_i)B_{i\to j}\rho(\nu_{ij})h\nu_{ij}=N\frac{(A_{i\to j}+K_{i\to j})B_{i\to j}\rho(\nu_{ij})h\nu_{ij}}{A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}} \tag{21}$$

or approximately $NB_{i\to j}\rho(\nu_{ij})h\nu_{ij}$. The excess of radiation absorbed over radiation emitted is

$$N\frac{K_{i\to j}B_{i\to j}\rho(\nu_{ij})h\nu_{ij}}{A_{i\to j}+2B_{i\to j}\rho(\nu_{ij})+K_{i\to j}} \tag{22}$$

which is also equal to $N_iK_{i\to j}$, the rate at which kinetic energy is being taken from atoms by collisions of the second kind. If $K_{i\to j}$ is zero, so that there are no collisions, all the energy which is removed from the initial beam is sent out again as resonance radiation. As $K_{i\to j}$ becomes large, however, more and more of the energy absorbed is converted into kinetic energy, and thus is lost as light energy. The amount absorbed from the external beam is very nearly independent of the presence or absence of collisions of the second kind, however. When $K_{i\rightarrow j}$ is small, the phenomenon described here is that of resonance radiation; when it is large, it is essentially the familiar optical process of "true" absorption, in which the energy removed from the beam is not reradiated, but is converted into kinetic energy. The momentum interchange is also of interest in this problem. Suppose the external field is a plane wave. Then the atoms receive momentum of the quantity (21) divided by c, in the direction of the beam. There is then a force of this amount exerted on the atoms by the light; this is simply the radiation pressure. Like the absorption, its amount is very nearly independent of whether the energy abstracted from the incident beam is reradiated or is converted into kinetic energy.

The resonance radiation emitted in these processes is emitted by the vibration of the forced oscillators, and thus shows polarization characteristic of the incident light. The destruction of this polarization by a magnetic field is, of course, outside the province of the present paper, which is not considering magnetic effects explicitly. The radiation is emitted in the form of a line of breadth $(A_{i\rightarrow j}+2B_{i\rightarrow j}\rho(\nu_{ij})+K_{i\rightarrow j})/\pi$. As $K_{i\rightarrow j}$ increases, and the resonance radiation decreases in amount, it is seen that the line is broadened. As far as the influence of the atoms on the incident light is concerned, this problem is that of anomalous dispersion. There is an absorption line, of the breadth just given, inside which the index of refraction goes through changes of the characteristic nature. The total strength of this line is nearly independent of the collisions. On the other hand, the breadth of the line increases with $K_{i\rightarrow j}$ with corresponding decrease of the intensity corresponding to any frequency, and the breadth may become very considerable for large pressures of gas capable of colliding with the atoms. Of course, it must not be forgotten that there may be other factors influencing the broadening in addition to the lack of coherence in the wave trains, so that the figure given refers to a minimum breadth for the line. The principal effect of this kind when the line is narrow is Doppler effect; when the line is broad, there is probably also broadening on account of Stark effect from neighboring atoms.

It is well to call attention to the various interpretations of the term absorption which have been made by various authors. By some, the term is used, as we have used it, to refer to the weakening of the incident beam. By others, however, it is used to indicate the net amount of light disappearing on account of the process, or the difference between the amount removed from the incident light and the amount re-emitted. The present theory gives a perfectly definite picture of the phenomena concerned, so that if it is adopted there need be at least no confusion as to the physical processes, whichever definition of the words may be preferred.

Scattering and normal dispersion. The problem of scattering is supposed to be essentially the same as resonance radiation, except that the frequency of the incident light lies far from the frequency of the absorption line. The formulas are the same as in the previous example, except that $B_{i\rightarrow j}\rho(\nu_{ij})$ is to be replaced by $\int B_{i\rightarrow j}(\nu)\rho(\nu)d\nu$. On account of the very small value of $B_{i\rightarrow j}(\nu)$ for a ν far from the natural frequency, this will be an extremely small quantity. The number of atoms brought to the upper state is thus very minute. Still, it is not zero; just as in the case of ordinary resonance, the amount of energy scattered is compensated by the spontaneous transitions of atoms from the higher to the lower state. All the atoms brought to the upper state are brought on account of resonance, so that they do not have spontaneous oscillators; the scattered radiation comes from the forced vibrations of the oscillators of the atoms, which are practically all in the lower state. We see that it is possible, in this case, to have the probability $A_{i\rightarrow j}$ connected with radiation, not of the natural frequency, but of the entirely different frequency of the scattered light. The effect of the process on the incident light is the ordinary dispersion. The vibrations of the forced oscillators are almost precisely in phase with the field, so that there is only very slight absorption—just enough, if there is no conversion of the absorbed energy into kinetic energy, to compensate for the scattered energy. The radiation pressure is found directly from the absorption.

When we inquire as to the exact amount of scattering, or the exact spectral constitution of the scattered light, we see at once that the present theory is not complete enough to answer our question. It will be recalled that we are deliberately working only to the first power of $1/(\nu_{ij}-\nu)$. Thus as the frequency of the light gets further and further from ν_{ij}, our formulas become more and more inaccurate. They cannot give the variation of scattering with frequency found either in Rayleigh's scattering formula, or Thomson's formula; for on examination it is seen that both of these results depend on higher powers of $1/(\nu_{ij}-\nu)$. The reason why the present theory was not carried to a higher degree of approximation was because it was believed that the phenomena at a distance from the absorption line demanded consideration by themselves, and it was thought better to give formulas which made no pretense of treating them exactly, rather than to include terms which appeared to apply to them, but which were of doubtful validity. It should be understood that we can change the assumptions of the present paper about as much as we please, outside the absorption line, without changing in an essential way the results we have described. The reason is that in the phenomena we have been principally discussing, the absorption line is of such great importance as to outweigh entirely the other regions of the spectrum. It is very probable, then, that satisfactory numerical assumptions about scattering can be made; and there seems at any rate no reason to think the qualitative explanation given here is not satisfactory.

Problems with more than two stationary states. In the problems which we have so far discussed, much simplification has resulted from the fact that atoms occurred in only two stationary states. In most problems, it is not so simple as this. No problems of great complication will be treated in detail here; they involve no new principles. But it may be useful to describe a few, to indicate what a variety of problems the theory is capable of dealing with. The general problem of emission of spectra after ionization by bombardment could be treated, except for the initial stages, where the electron and ion are just recombining; this process could not be included, for we are dealing here only with periodic systems, which give oscillations of sharply defined natural frequencies; while a free electron is not such a system. The problem of fluorescence could also be treated, in a general way. There are not many problems in which absorption by excited atoms is of importance; but absorption by band spectra, where the absorbing molecules are distributed among stationary states of a number of rotational quantum numbers, would be a good example of such a problem which could be attacked. In addition, of course all problems of dispersion by gases in their normal state could be brought under the theory.

All the problems which have been discussed are problems of kinetic equilibrium, in which the number of atoms in each state remains constant. But in all of them, the system has been receiving energy, and converting it irreversibly into some other form of energy. There is the special case of thermal equilibrium, in which there is no such irreversible conversion; and this problem, as indicated at the end of the last section, can also be treated by the present methods. As a matter of fact, however, the problems in which we are practically interested are generally problems where thermal equilibrium does not occur, but where somewhere in the system there are parts with energy far greater than the energy corresponding to thermal equilibrium at the temperatures we are accustomed to—swift electrons, or radiation of large intensity in the visible or ultraviolet region. And we are generally concerned with the processes which occur in the course of the degradation of this energy to more ordinary form.

NOTE I

We wish to find the average of the forced polarization (8) over atoms with all possible values of $(t-t_0)$, the length of time which has elapsed since the last interruption. Let us for brevity denote $(t-t_0)$ by θ. Then we must find the fraction of all atoms for which θ is between a certain value θ and $\theta+d\theta$, multiply (8) by this fraction, and integrate over all values of θ.

Consider a certain number N_0 of atoms whose oscillators $p_{i\rightarrow j}$ entered continuous motions approximately simultaneously. Let N be the number of these oscillators which have not yet had an interruption at time t, after this. The probability that any oscillator will be interrupted is P_i+P_j; so that a number $N(P_i+P_j)dt$ have interruptions in dt. Then $dN/dt=-N(P_i+P_j)$, $N=N_0e^{-(P_i+P_j)t}$. Now the number of oscillators $p_{i\rightarrow j}$ entering continuous motions in unit time equals the number leaving such motions, or the number $N_i(P_i+P_j)$ having interruptions. Then $N_i(P_i+P_j)d\theta$ entered continuous motions between times $t-\theta$ and $t-(\theta+d\theta)$. Of these, $N_i(P_i+P_j)e^{-P_i(+P_j)\theta}d\theta$ survive in their continuous motions at time t, when we are performing our integration. Thus the fraction of oscillators for which θ is between θ and $\theta+d\theta$ is $(P_i+P_j)e^{-(P_i+P_j)\theta}d\theta$.

Having found this fraction, we must substitute θ for $(t-t_0)$ as it appears in (8), multiply (8) by the fraction, and integrate from $\theta=0$ to $\theta=\infty$. The integration is simply performed, and results after slight reduction in (9).

NOTE 2

Rate of radiation from a spontaneous oscillator. For this oscillator we have $p=eD_{ij}\cos 2\pi(\nu_{ij}t-\alpha)$, where α is a phase angle. The average rate of radiation is the time average of $2(\ddot{p})^2/3c^3$. We find immediately that $2(\ddot{p})^2/3c^3=(32\pi^4\nu_{ij}{}^4e^2D_{ij}{}^2/3c^3)\cos^2 2\pi(\nu_{ij}t-\alpha)$, of which the time average is $(16\pi^4\nu_{ij}{}^4e^2D_{ij}{}^2)/3c^3$, which by (1) equals $A_{i\rightarrow j}h\nu_{ij}$.

Rate of resonance radiation from a forced oscillator. The radiation from the forced oscillators cannot be found directly from the average amplitude given in (8); for the radiation depends on the mean square amplitude, and this is in general different from the square of the mean amplitude. We must make some assumption about the behavior of an individual oscillator, in order to obtain a relation between the mean square and the square of the mean. Consider the term in the external field of frequency

ν_n, and let us schematically represent this part of the field by E_x, E_y, E_z. Then we assume that a particular oscillator has its moment in a definite direction, and that the magnitude of the part of the oscillator's moment arising from the term ν_n in the field is proportional to the component of E_x, E_y, E_z in this direction. That is, if we schematically represent the particular part of the moment we are interested in by p, its magnitude by $|p|$, and its direction by n, then $|p| = k[E_x\cos(nx)+E_y\cos(ny)+E_z\cos(nz)]$. We have then $p_x = k[E_x\cos^2(nx)+E_y\cos(nx)\cos(ny)+E_z\cos(nx)\cos(nz)]$. Next we assume that the directions n of oscillators are all equally probable, so that we get $\overline{p_x}$ by averaging over n. Using the fact that the average of $\cos^2(nx)$ is 1/3, and of $\cos(nx)$ zero, we have $\overline{p_x} = \frac{1}{3}kE_x$. Further, we have $p^2 = k^2[E_x^2\cos^2(nx)+E_y^2\cos^2(ny)+E_z^2\cos^2(nz)+2E_xE_y\cos(nx)\cos(ny)+\text{etc.}]$ The average of this is similarly $\frac{1}{3}k^2[E_x^2+E_y^2+E_z^2] = 3[(\overline{p_x})^2+(\overline{p_y})^2+(\overline{p_z})^2]$. Thus the mean square amplitude is three times the square of the mean amplitude. In a more complete discussion than this, it would be necessary to consider the case where the polarization of an oscillator was determined in a more complicated way from the external field than what we have assumed; for the present assumption would presumably apply only in the simplest cases. It is to be expected, however, that the final results would be the same in more complicated cases.

To compute the radiation, we take (8) for the moment, find its second derivative, and square it. Next we multiply by 3, to convert from square of the mean to mean square, as shown above. The second derivative is, to the accuracy with which we are working, $-4\pi^2\nu_{ij}^2$ times the polarization itself. The square involves terms in the squares and products of the A's and B's. We must now average over an ensemble of external fields, having a great variety of values of the A's and B's, but all consistent with the same macroscopic spectral distribution. In this averaging, the products of A's and B's all vanish, on account of random phases in different systems of the ensemble, while the squares A_{nx}^2 and B_{nx}^2 are replaced by average values $\overline{A_{nx}^2}$ and $\overline{B_{nx}^2}$. We must next average over time as it appears explicitly in $\cos 2\pi\nu_n t$ and $\sin 2\pi\nu_n t$. The result of these processes, after multiplying by $2/3c^3$ is

$$\frac{2(\ddot{p}'_{i\to j})_x^2}{3c^2 3c^3} = \frac{\pi^4\nu_{ij}^4 e^4 D_{ij}^4}{9c^3h^2}\sum(n)\frac{(\overline{A_{nx}^2}+\overline{B_{nx}^2})}{(\nu_{ij}-\nu_n)^2}\{[1-\cos 2\pi(\nu_{ij}-\nu_n)\ (t-t_0)]^2 + [\sin 2\pi(\nu_{ij}-\nu_n)\ (t-t_0)]^2\}\ .$$

Next we average over oscillators with different values of $(t-t_0)$, substituting θ for $(t-t_0)$, multiplying the quantity above by

$(P_i+P_j)e^{-(P_i+P_j)\theta}d\theta$, and integrating from zero to infinity, just as in note (1). At the same time, we can also make the substitution

$$\pi^4\nu_{ij}{}^4e^4D_{ij}{}^4/(9c^3h^2)=A_{i\to j}B_{i\to j}h\nu_{ij}/(32\pi^3),$$

which results from equations (1) and (2). Then the result is

$$\frac{A_{i\to j}B_{i\to j}h\nu_{ij}}{16\pi^3}\sum(n)\frac{\overline{A_{nx}{}^2}+\overline{B_{nx}{}^2}}{[\nu_{ij}-\nu_n]^2+[(P_i+P_j)/2\pi]^2}.$$

To get the total radiation, we add together the contributions of the x, y, and z components of polarization, and thus obtain $\overline{A_{nx}{}^2}+\overline{A_{ny}{}^2}+\overline{A_{nz}{}^2}+\overline{B_{nx}{}^2}+\overline{B_{ny}{}^2}+\overline{B_{nz}{}^2}$ under the summation sign. But this is the square of the amplitude of the electric vector for the component of the external field of the frequency n/T, averaged, or twice the time average square of the vector. In a radiation field of the kind we are considering, the average square of the electric vector equals the average square of the magnetic vector, and each in turn equals 4π times the energy density. Then the sum of the squares of the amplitudes above can be replaced by 8π times the energy density of the components of frequency n/T. Next we replace the summation over the separate components of the Fourier series by an integration over the frequency ν. We regard the contribution of the term n as arising from a small frequency interval $d\nu=(n+1)/T-n/T=1/T$. We write the energy density in this small interval as $\rho(\nu)d\nu$. Thus we have the identification of the sum of squares of amplitudes with $8\pi\rho(\nu)d\nu$. Replacing the summation by an integration, our quantity now becomes

$$\frac{A_{i\to j}B_{i\to j}h\nu_{ij}}{2\pi^2}\int\frac{\rho(\nu)d\nu}{[\nu_{ij}-\nu_n]^2+[(P_i+P_j)]/2\pi]^2}=\frac{A_{i\to j}h\nu_{ij}}{P_i+P_j}\int B_{i\to j}(\nu)\rho(\nu)d\nu$$

Rate of absorption by forced oscillator. We take the x component of forced polarization (8), differentiate it once, and multiply it by E_x from (6). As in the last paragraph, we have terms in squares and products of A's and B's, and as before we average over an ensemble of external fields, so that products drop out, and squares are replaced by mean squares. Next we average over time, and finally over all values of $(t-t_0)$. Then we add the contributions of the x, y, and z components, and as before substitute $8\pi\rho(\nu)d\nu$ in place of the sum of squares of amplitudes, and integrate over $d\nu$ instead of summing. The process involves no difficulties, and the result is as given in (14). We could equally well take advantage of the average of the forced polarization over $(t-t_0)$, which we have already performed to derive (9). In that case, we should differentiate (9), multiply by (6), and proceed as before, except that we no longer have to average over $(t-t_0)$. Only the second term of (9), out of phase with the field, survives the averaging over time, and the result comes out immediately.

NOTE 3

We shall first find the fraction of oscillators $p_{i\to j}$ whose last interruption was an interruption of an oscillator in the ith state on account of the term (3). $N_i\int B_{i\to j}(\nu)\rho(\nu)d\nu$ such interruptions occur per second; whereas, as we saw in Note 1, the total number of interruptions per second resulting in oscillators entering the ith state is $N_i(P_i+P_j)$. Thus the fraction we desire is $[N_i/N_i(P_i+P_j)]\int B_{i\to j}(\nu)\rho(\nu)d\nu$. Next we shall find the fraction of oscillators $p_{i\to j}$ whose last interruption was a transition from state j on account of the term (3). $N_j\int B_{i\to j}(\nu)\rho(\nu)d\nu$ such transitions occur per second, so that this fraction is

$$[N_j/N_i(P_i+P_j)]\int B_{i\to j}(\nu)\rho(\nu)d\nu.$$

Then the total fraction of oscillators $p_{i\to j}$ which are brought to their continuous motion by resonance is

$$[(N_i+N_j)/N_i(P_i+P_j)]\int B_{i\to j}(\nu)\rho(\nu)d\nu;$$

and the fractions which are brought up by some other agency is unity minus this, or (15).

NOTE 4

Spectral resolution of radiation from spontaneous oscillators. To find a spectral resolution of emitted energy, we analyze the polarization in Fourier series: $p=\Sigma(n)\alpha_n\cos 2\pi\nu_n t+\beta_n\sin 2\pi\nu_n t$ where $\nu_n=n/T$, for times between zero and T. Then we may say that $\overline{\alpha_n{}^2+\beta_n{}^2}\,d\nu$ is proportional to the contribution to the energy emission of frequencies between ν and $\nu+d\nu$. The fractional contribution is the ratio of this quantity to its integral over all frequencies. By finding the fractional contribution in this way, we do not have to concern ourselves with constant multipliers. In the present case, the average sign indicates that we are to average over all lives of oscillators, θ.

For the spontaneous oscillator, the amplitude is proportional to $\cos 2\pi(\nu_{ij}t-\alpha)$ for all times from $t=t_0$ to $t=t$. The averaging removes the effect of the initial instant and of the initial phase, so that we can disregard them, and say that the amplitude is proportional to $\cos 2\pi\nu_{ij}t$ from $t=0$ to θ. Then we have as the coefficients of the Fourier series

$$\alpha_n=(2/T)\int_0^\theta \cos 2\pi\nu_{ij}t\cos 2\pi\nu_n t\,dt\ ,\ \beta_n=(2/T)\int_0^\theta \cos 2\pi\nu_{ij}t\sin 2\pi\nu_n t\,dt\ ,$$

where the integration is from zero to θ because the amplitude is zero outside those limits. These products of two cosines or a cosine and a sine can be transformed into

$$\tfrac{1}{2}(\cos 2\pi(\nu_{ij}+\nu_n)t+\cos 2\pi(\nu_{ij}-\nu_n)t)$$

and

$$\tfrac{1}{2}(\sin 2\pi(\nu_{ij}+\nu_n)t-\sin 2\pi(\nu_{ij}-\nu_n)t)$$

respectively. We next integrate. In the integration, the terms in functions of $(\nu_{ij}+\nu_n)$ will be divided by that quantity, while the other terms will be divided by the much smaller $(\nu_{ij}-\nu_n)$. To the approximation to which we are working, we need retain only the second kind of terms. We then have

$$\alpha_n=\frac{\sin 2\pi(\nu_{ij}-\nu_n)\theta}{T\cdot 2\pi(\nu_{ij}-\nu_n)}\,,\quad \beta_n=-\frac{1-\cos 2\pi(\nu_{ij}-\nu_n)\theta}{T\cdot 2\pi(\nu_{ij}-\nu_n)}\,.$$

We square these, add them, and average over lengths of life θ. By methods similar to those of Note 1, it is easily seen that the fraction of the total oscillators whose whole life is between θ and $\theta+d\theta$ is the same as the fraction which have existed in their uninterrupted state this length of time, so that the averaging process is exactly what we have used before. We then multiply by $d\nu$, and divide the result by the integral of the same quantity over all ν's, so as to convert it into a fraction. The result is easily found to be $B_{i\to j}(\nu)/B_{i\to j}$.

Radiation from forced oscillators. On account of the complication of the mathematics, the derivation will not be given here in detail. We must first find the coefficients of the Fourier series, as for the spontaneous oscillators. But the problem is more difficult, because the polarization is no longer a simple periodic term, but is itself a series (8). To avoid confusion with the index n of that series, we may denote the coefficients of our new series by α_m, β_m. Each of these is a series in n, linear in the A's and B's. Next we find $\alpha_m{}^2+\beta_m{}^2$, obtaining series in the squares and products of the A's and B's, and as usual we average over many fields, replacing the resulting sum of mean square amplitudes by the energy density, and the summation over n by an integration over ν. We then obtain $\alpha_m{}^2+\beta_m{}^2$ as an integral over ν; and this can be transformed into

$$\alpha_m{}^2+\beta_m{}^2=\text{constant}\times\int\rho(\nu)d\nu\Bigg[-\frac{\sin^2\pi(\nu-\nu_m)\theta}{(\nu-\nu_m)^2(\nu-\nu_{ij})\,(\nu_{ij}-\nu_m)}$$
$$+\frac{\sin^2\pi(\nu_{ij}-\nu_m)\theta}{(\nu_{ij}-\nu_m)^2(\nu-\nu_m)\,(\nu-\nu_{ij})}+\frac{\sin^2\pi(\nu-\nu_{ij})\theta}{(\nu-\nu_{ij})^2(\nu_{ij}-\nu_m)(\nu-\nu_m)}\Bigg]\,.$$

In general, this is too complicated to give information of interest. We shall consider it first in case $\rho(\nu)$ is constant, which is the case we meet in thermal equilibrium, and in most other problems. Then it can be taken outside the integral sign. The integrations can then be performed, the denominator being developed in partial fractions. The result, after averaging over θ, and converting to a fractional contribution, proves to be $B_{i\to j}(\nu_m)/B_{i\to j}$.

When the external field has a spectral distribution which is not constant within the line, there is no physical way of saying just what the character of the emitted light should be. If in particular the external field is monochromatic and its frequency is appreciably different from the natural frequency, it can be seen from the formula above that the emitted light consists of two lines of equal intensity, one with its center at the natural frequency, the other with its center at the impressed frequency, the intensity becoming rapidly less as the impressed frequency moves away from the natural frequency. If such monochromatic light were projected into a gas of atoms of this kind, the external effect would be quite different according as the gas showed "real" absorption or not—that is, according to whether there were other methods of going from the upper to the lower state than by the probabilities $A_{i\to j}+\int B_{i\to j}(\nu)\rho(\nu)d\nu$. If there were "real" absorption, this would be much greater for the light of the natural frequency than for that of the impressed frequency. The light of the natural frequency would be practically completely absorbed inside the gas, in a way somewhat similar to the situation in the familiar reversal of spectral lines; and the light of the impressed frequency would escape, and be interpreted as scattered light. If on the other hand there were no "real" absorption, and the gas were in the situation where it could emit resonance radiation, the light of the natural frequency could escape as well as that of the impressed frequency. In experiments at a great distance from the absorption line, as has been pointed out in the body of the paper, there is no reason to suppose that these results hold.

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HARVARD UNIVERSITY,
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