Absorption, emission, and linebreadths:A semihistorical perspective

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The development of the theory of the interaction of electromagnetic radiation with atoms and molecules is outlined. A fully classical analysis of absorption and emission is formulated in which particlular attention is paid to questions of detailed balance and to the sum rules obeyed by the susceptibility. Collision broadening is introduced through time-dependent dipole moment correlation functions, and brief discussions of interruption broadening and various frequency modulation models are given. The corresponding quantum mechanical analysis is presented with emphasis on the points in common with the classical approach. The importance of correspondence principles in bridging the gap between classical and quantum mechanical theories is stressed.

CONTENTS

INTRODUCTION AND MOTIVATION

A little over a year before the advent of the true quantum mechanics one of us (Van Vleck, 1924) published Parts I and II of a series of articles entitled "The Absorption of Radiation by Multiply Periodic Orbits and Its Relation to the Correspondence Principle and the Rayleigh-Jeans Law," henceforth referred to as *l.c.*[1] Part I was entitled "Some Extensions of the Correspondence Principle," and Part II gave the details of the "Calculation of Absorption by Multiply Periodic Orbits." Part III was to be concerned with the equilibrium beween absorption and emission under the Rayleigh-Jeans law. It was never written up for publication because in 1925 the author was busy writing his book *Quantum Principles and Line Spectra* (Van Vleck, 1926) and of course the advent of quantum mechanics presented innumerable research problems more timely than a purely classical investigation. The idea occurred to him to use the 50th anniversary of Parts I and II as the date for publishing a paper which would start with Part III and might even bear its title. Although he did not succeed in meeting the deadline, it still provided a partial motivation for collaborating on the present article. We use the term "partial" because even the classical portion (Part I) of the present paper goes considerably beyond what the senior author had in mind in 1924, as he was then thinking only in terms of absorption with infinitely sharp lines—no collision broadening or damping.

The presentation and calculations of Part I, which now follows, are entirely in terms of classical mechanics, and to some extent "old quantum theory." To some readers this may seem like a purely archival project, in which skeletons are taken from the family closet that are the victims of quantum mechanics. However, this is not really the case, although there are some reminiscences that may interest historians of science. In our opinion one has a better understanding of quantum mechanics, and an appreciation of its elegance, if one examines analogs in the earlier world of Fourier series and orbits. We are pleased to see this view taken by Rüdinger (1976) in an article commending Tomonaga's book on quantum mechanics (1962) because it starts, unlike most modern texts, by first developing a background in the old quantum theory. Many of the problems relating to linebreadth become clearer and simpler if first examined in the framework of classical mechanics. We might mention in particular, that in the appendix of the Born and Jordan (1930) book on the matrix form of quantum mechanics, a purely classical calculation is still given of the absorption.[2]

In concluding this introduction we should stress that

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*Work supported in part by the National Science Foundation.

[1] Part I of *l.c.* is reprinted in the van der Waerden (1967) historical compendium on the *Sources of Quantum Mechanics*.

[2] The calculation by Born and Jordan had been published earlier in a journal article (1925). Using a method only slightly different from that in *l.c.* they obtained a similar formula for the absorption.

the present paper does not pretend to be a comprehensive review of the subject of absorption, emission, and linebreadths, with references to hundreds of articles. A review of this type with emphasis on the effects of collisions on optical spectra in gases has been published by Breene (1951), while Poole and Farach (1971) have reviewed line broadening and relaxation in the context of magnetic resonance and Mössbauer work.

I. CLASSICAL THEORY

A. The absorption of radiation by (undisturbed) multiply periodic orbits

The title of this present section is the same as that of Part II of *l.c.* except for the insertion in parentheses of the word "undisturbed." This addition is to make it clear that the discussion and calculations of the present section, like all of *l.c.*, is for motions not interrupted by collisions or impacts, whereas this restriction does not apply after Sec. D.

In the dozen or so years between the advent of the Bohr atom and of quantum mechanics, in other words, the era of the old quantum theory, theoretical atomic calculations centered on multiply periodic motions. One doesn't encounter them often in the recent literature, but they are the classical analog of the Heisenberg system of representation, and involve the same kinds of series as often used by astronomers in celestial mechanics. For a detailed exposition thereof see, for instance, books by Born (1925) and Van Vleck (1926). Multiply periodic motions are characterized by a set of angle and action variables, and the multiple Fourier expansions related thereto, which have the form

$$x=\sum_{\tau_1=-\infty}^{\infty}\sum_{\tau_2=-\infty}^{\infty}\sum_{\tau_3=-\infty}^{\infty} x_{\tau_1\tau_2\tau_3}\exp[i(\tau_1 w_1+\tau_2 w_2+\tau_3 w_3)]\,, \tag{1}$$

for, say, the x coordinate.[3] As in *l.c.*, we assume that the system is one with three degrees of freedom associated with the motion of a particle of mass m and charge e, but the extension to more general systems with different degrees of freedom is an obvious procedure not involving any particular difficulties. The w's entering in (1) are called angle variables, and are three of the six canonical variables; the others are the conjugate action variables J_1, J_2, and J_3. The unperturbed Hamiltonian function, $\mathcal{H}$, is a function only of the J's so that we can write

$$\mathcal{H}=W_J(J_1,J_2,J_3)\,. \tag{2}$$

We use the notation W_J rather than E for the energy constant, both to avoid confusion with the electric field E, and because this was the nomenclature generally used in the 1920's. In the absence of such a field, Hamilton's equations are simply

$$\frac{dJ_k}{dt}=0\,, \tag{3a}$$

$$\frac{dw_k}{dt}=\omega_k\,, \tag{3b}$$

where

$$\omega_k=\frac{\partial W_J}{\partial J_k}\,,\quad (k=1,2,3)\,, \tag{3c}$$

so that the w_k's are linear functions, $w_k=\omega_k t+\epsilon_k$, of the time. It is convenient to use in place of (1) the abbreviated notation

$$x=\sum_{\tau} x_\tau \exp(i\omega_\tau t+i\epsilon_\tau)\,, \tag{4}$$

where τ represents the set of three integers τ_1, τ_2, τ_3 and

$$\omega_\tau=\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3\,, \tag{5a}$$

along with

$$\epsilon_\tau=\tau_1\epsilon_1+\tau_2\epsilon_2+\tau_3\epsilon_3\,. \tag{5b}$$

The reader should be careful not to confuse the ω_τ with the (angular) frequency ω of the applied field. In the old quantum theory the J's were the quantities which were equated to integral multiples of $\hbar$, so that

$$J_k=n_k\hbar\,. \tag{6}$$

Equation (4), as it stands, is valid only if there is no applied field. Perturbations by the latter make the w's cease to be linear functions of time, and the argument of the exponent in (4) must be replaced by $(\tau_1 w_1+\tau_2 w_2+\tau_3 w_3)$. Also, the coefficients x_τ of the exponents are in (4) no longer constant in time, but are still the same functions of the J's as in the absence of the field. How the perturbations of the J's and w's are calculated by adding to the Hamiltonian a term caused by the applied field is explained in *l.c.* and will not be repeated here. By employing the results of *l.c.* [combining Eqs. (32), (35), and (37) of *l.c.* and differentiating with respect to time], one finds that the rate at which a state having given initial values of J_1, J_2, and J_3 absorbs energy in a radiation field of density $u(\omega)$ is given by the expression

$$\frac{dW_J}{dt}=\frac{4\pi^2e^2}{3}\sum_{k=1}^{3}\sum_{\tau\geq 0}\tau_k\frac{\partial}{\partial J_k}\{\omega_\tau|d_\tau|^2[f(\omega_\tau,\omega)+f(\omega_\tau,-\omega)]u(\omega)\}\,, \tag{7}$$

where $\tau \geq 0$ means the summation is over only non-negative values of the combination overtone (5), and

$$|d_\tau|^2=|x_\tau|^2+|y_\tau|^2+|z_\tau|^2\,. \tag{8}$$

The functions $f(\omega_\tau, \pm\omega)$ are defined by

$$f(x,x_0)=\lim_{t\to\infty}\frac{\sin[(x-x_0)t]}{\pi(x-x_0)}\,, \\ =\delta(x-x_0)\,. \tag{9}$$

Here $\delta(x-x_0)$ denotes the Dirac δ function with the property $\int_{-\infty}^{\infty}f(x)\delta(x-x_0)dx=f(x_0)$. Equation (7) is also essentially the same (except for notational differences) as Eq. (38) of *l.c.* or as Eq. (24) on p. 419 of Born and Jordan's *Elementare Quantenmechanik* (1930) except that in both these cases the integration over ω has been carried out.

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[3] A discussion of action-angle variables can be found in the books by Born (1925), Van Vleck (1926), and Goldstein (1950).

It should be stressed in making comparison with *l.c.* that we have used somewhat different notation to conform to modern usage. In 1924 there was no Dirac $\hbar$ to reduce the number of factors of 2π. We now use angular rather than true frequencies, and J_k, w_k, ω_τ, ω are, respectively, the same as $J_k/2\pi$, $2\pi w_k$, $2\pi\omega_\tau$, and $2\pi\omega$ of *l.c.* Also, both for convenience and in conformity with present practice, we use exponential rather than cosine series, so that a typical pair of terms in the multiple Fourier expansion is $x_\tau \exp(i\omega_\tau t + i\epsilon_\tau) + x_\tau^* \exp(-i\omega_\tau t - i\epsilon_\tau)$ compared with $x_\tau \cos(2\pi\omega_\tau t + \epsilon_\tau)$ of *l.c.* The condition that x be real requires that $x_\tau = x_{-\tau}^*$, and the time average of x^2 for a given state J_1, J_2, J_3 is

$$\overline{x^2} = 2\sum_{\tau\geq 0} |x_\tau|^2, \tag{10}$$

since the only terms which do not vanish on averaging the square of (4) over all phases (epoch angles) ϵ_τ are the cross terms connecting τ and $-\tau$. In the presence of the field, Eq. (7) is no longer exact, but is adequate for our purposes as it is to be understood that all the quantities appearing in (7) are to be computed in the absence of the field; in other words, Eq. (7) already involves a factor of $u \propto E^2$, and any higher orders of E can be disregarded. In *l.c.* we used ρ to denote the density of radiant energy, but in the present paper we will use u for this density, as we wish to use ρ to denote the density of atoms in J space, or more generally in phase space.

We now assume that the distribution in J space conforms to classical statistical mechanics, so that the number of atoms or molecules in an element $dJ_1 dJ_2 dJ_3$ is $\rho_J dJ_1 dJ_2 dJ_3$, with

$$\rho_J = NCe^{-W_J/kT}, \tag{11}$$

where N is the number of atoms or molecules per unit volume, and

$$1/C = \int\int\int e^{-W_J/kT} dJ_1 dJ_2 dJ_3 .$$

In general the Boltzmann distribution relates to density in phase space whose dimensionality is twice the number of degrees of freedom, so that basically we ought to consider the volume element $dJ_1 dJ_2 dJ_3 dw_1 dw_2 dw_3$. However, the w coordinates have already been averaged over in obtaining Eq. (7), and they are not involved in the Boltzmann exponent. We can therefore take the rate of absorption by the ensemble to be

$$N\left\langle \frac{dW_J}{dt} \right\rangle_{\text{abs}} = \int\int\int \rho_J \frac{dW_J}{dt} dJ_1 dJ_2 dJ_3 , \tag{12}$$

where dW_J/dt is given by (7). The ensemble average, which we denote by $\langle \ldots . \rangle$, is not to be confused with the time average for a single state, which we denote by a bar as in Eq. (10). When (7) is substituted in (12) a partial integration with respect to the J's suggests itself, as it gets rid of having to take the derivative of the δ function. This procedure works rather neatly, as thanks to the relation

$$\omega_\tau = \tau_1 \frac{\partial W_J}{\partial J_1} + \tau_2 \frac{\partial W_J}{\partial J_2} + \tau_3 \frac{\partial W_J}{\partial J_3}$$

[cf. Eqs. (3) and (5)] the expression (12) is transformed into

$$N\left\langle \frac{dW_J}{dt} \right\rangle_{\text{abs}} = \frac{4\pi^2 e^2}{3kT} \int\int\int \sum_{\tau\geq 0} \rho_J \omega_\tau^2 |d_\tau|^2 \times [f(\omega_\tau, \omega) + f(\omega_\tau, -\omega)] \times u(\omega) dJ_1 dJ_2 dJ_3 , \tag{13}$$

provided we can neglect the terms at the limits in the partial integration. This is allowable for all systems for which classical Boltzmann statistics have a meaning. One limit usually corresponds to an infinitely high energy and vanishing Boltzmann factor, and the other to the vanishing of other factors (i.e., the amplitude for an oscillator or the frequency for a rotator). Of course Boltzmann statistics cannot be applied to a real Rutherford atom, as it would make electrons condense infinitely near to the nucleus. Also, we make our calculation for the electric rather than the magnetic moment, since consistent Boltzmann statistics gives zero magnetic moment because of the Bohr-van Leeuwen theorem [for details and references see p. 94 ff of Van Vleck (1932)]. One could, however, use classical *ad hoc* models like that of Langevin in connection with the present formalism.

B. Equilibrium of multiply periodic orbits under the Rayleigh-Jeans law

One must now integrate expression (13) over the frequency distribution of the impressed electric field. Because of the δ-function property of the factor $f(\omega_\tau, \omega)$, we find that the rate of absorption is

$$N\left\langle \frac{dW_J}{dt} \right\rangle_{\text{abs}} = \frac{4\pi^2 e^2}{3kT} \int\int\int \sum_{\tau\geq 0} \omega_\tau^2 |d_\tau|^2 u(\omega_\tau) \rho_J dJ_1 dJ_2 dJ_3 . \tag{14}$$

[The term $f(\omega_\tau, -\omega)$ makes no contribution as ω_τ and ω are both positive.]

According to electromagnetic theory, an electron radiates energy at a rate $(2/3c^3)e^2\dot{v}^2$ and so the rate of spontaneous radiation is

$$N\left\langle -\frac{dW_J}{dt} \right\rangle_{\text{emis}} = \frac{4e^2}{3c^3} \int\int\int \sum_{\tau\geq 0} \omega_\tau^4 |d_\tau|^2 \rho_J dJ_1 dJ_2 dJ_3 . \tag{15}$$

Comparing (14) and (15) we see that there is perfect balance between absorption and emission, provided the radiation energy density is given by the Rayleigh-Jeans law

$$u(\omega) = \frac{kT}{\pi^2 c^3} \omega^2. \tag{16}$$

This result is valid for any multiply periodic system, and furthermore it applies term by term, i.e., to each combination overtone separately. Furthermore by going back to the calculations of *l.c.* [cf. Eqs. (11), (44), and (45) and remarks on pp. 336, 363] one finds that for the absorption and emission associated with a given combination overtone the changes in J_1, J_2, J_3 are in the ratio $\tau_1 : \tau_2 : \tau_3$, so that not only do the books balance energetically, but also there is no orbital distortion, i.e., absorption and emission change the shape in the same way.

The results presented in the preceding paragraph are essentially what the senior author had in mind for Part III of *l.c.* At this juncture we should mention that calculations of a nature closely related thereto were published by Niessen (1924), and by Born and Jordan (1924). Instead of integrating over phase space and making a partial integration as we do in going from (12) to (13), these authors both used basically Fokker–Planck fluctuation theory, but the essential points are that they still had to make, as they did, the calculation of absorption by a multiply periodic orbit and use statistical distributions in extrapolating to quantum theory. The classical balance between absorption and emission under the Rayleigh–Jeans law is implicit in their work, but not explicitly noted. Instead, in the twilight days of the old quantum theory before quantum mechanics, they were anxious to obtain equilibrium under the Planck radiation formula. This can be achieved if $-\rho/kT$ is replaced by $(\rho_r - \rho_s)/\hbar\omega_{rs}$ as these authors did on the grounds that in quantum theory difference quotients replace differences. On the other hand they assumed that the amplitude factors entered in the same way as classically, or, more precisely cancelled out in comparing absorption and emission in the same way as in classical theory. Fifty years later, a hybrid calculation is less appealing than one which is purely classical. Granted that the Rayleigh–Jeans law has its ultraviolet catastrophe (infinite radiation energy density), still there is a certain elegance to the balance between absorption and emission in a consistently classical framework.

C. The statistical and nonstatistical formulations of the correspondence principle for absorption

In working on the present article the following alternative formulation of the correspondence principle for absorption was revealed which is somewhat different from the form presented in *l.c.* The Einstein (1917) A and B coefficients connecting two states r and s satisfy the relation

$$B_{rs} = B_{sr} = \frac{\pi^2 c^3}{\hbar\,\omega_{rs}^3}\,A_{rs}\,, \tag{17a}$$

where

$$\hbar\,\omega_{rs} = W_r - W_s > 0\,. \tag{17b}$$

Likewise the Planck radiation formula is

$$u(\omega) = \frac{\hbar\,\omega^3}{\pi^2 c^3}\left[\exp\frac{\hbar\,\omega}{kT} - 1\right]^{-1}. \tag{18}$$

Let us suppose that the upper state r differs from s by τ_1, τ_2, τ_3, respectively in the values of the quantum numbers associated with J_1, J_2, J_3. In the early days, before 1924, the correspondence principle was applied only to spontaneous emission, and as a result it was required that asymptotically for large quantum numbers

$$\omega_{rs} \to \omega_\tau\,, \tag{19a}$$

$$A_{rs} \to \frac{4e^2}{3c^3}\,|d_\tau|^2\,\frac{\omega_\tau^4}{\hbar\,\omega_\tau}\,, \tag{19b}$$

by analogy with Eq. (15). The excess of ordinary, i.e., positive absorption over induced emission (also called negative absorption) for a given transition is

$$\hbar\omega_{rs} B_{sr}[\rho_s - \rho_r]u(\omega_{rs}) \to \frac{4\pi^2 e^2}{3kT}\,\omega_\tau^2\,|d_\tau|^2 \rho_J u(\omega_\tau)\,. \tag{20}$$

The asymptotic value indicated by the arrow is a consequence of (11), (17), (19), and the fact that

$$\begin{aligned}\rho_r - \rho_s &\to (d\rho_J/dW_J)\hbar\omega_\tau\,,\\ &= -(\rho_J/kT)\hbar\omega_\tau\,.\end{aligned} \tag{21}$$

The right side of (20) agrees exactly with the corresponding factor in (13), and this fact shows that correspondence principle considerations apply just as well to absorption as to emission and are mutually consistent. One could equally well start with absorption as with emission. This result seems almost trivial nowadays, inasmuch as classical is generally a limiting case of quantum mechanics. Still it is interesting that in the partial integration that took (12) into (13), and also in (20), one has $d\rho/dW$ in place of $-\rho/kT$ if one assumes a nonequilibrium distribution in which the density of states is an arbitrary function of the energy W. If $d\rho/dW > 0$ one would have a classical net negative absorption. Usually one associates laser action entirely with quantum mechanics, and inverted populations. However, even in classical theory one can have similar behavior if the derivative $d\rho/dW$ is positive.

The form of the correspondence principle which we have presented is to be contrasted with the original version in *l.c.* which, because of (17) and (19), took the form

$$\hbar\omega_{rs}B_{sr}\,u(\omega_{rs}) - \hbar\omega_{st}B_{st}u(\omega_{st}) \to \frac{4\pi^2 e^2}{3}\sum_{k=1}^{3}\tau_k\,\frac{\partial}{\partial J_k}\left[\omega_\tau|d_\tau|^2 u(\omega_\tau)\right], \tag{22}$$

where the states r, s, t are identified with $J_1 + \tau_1\hbar$, $J_2 + \tau_2\hbar$, $J_3 + \tau_3\hbar$, with J_1, J_2, J_3, and with $J_1 - \tau_1\hbar$, $J_2 - \tau_2\hbar, J_3 - \tau_3\hbar$, respectively. The right-hand side of (22) does indeed agree with the corresponding part of (7) when we use the δ-function property of f [Eq. (9)]. It should be remarked that (7) and also the right-hand side of (22) contain terms in $du/d\omega$ inasmuch as $\partial u(\omega_\tau)/\partial J_k = (du/d\omega_\tau)\partial\omega_\tau/\partial J_k$. On the other hand the absorption involved in (13) or the right-hand side of (20) is directly proportional to the radiation energy density u. In (22) one compares the classical absorption with the excess of the positive absorption from a given state over the negative absorption going down from it, whereas (20) is concerned with the excess of the positive over negative absorption for one given transition. The form (20) of the correspondence principle for absorption involves statistical considerations, and the density of states, as evidenced by a factor involving the temperature, whereas this is not true of the form (22), which is consequently nonstatistical.

In concluding the present section it is rather amusing for one of us to recall the circumstances which led him to discover the correspondence principle for absorption. In 1924 he mentioned to Gregory Breit, then at the University of Minnesota, that he could not understand how there could be any classical analog of negative absorption. Breit replied that classically there could be fluctuations up and fluctuations down. This Van Vleck took to mean that there could be classical analogs of the transitions $s \to t$ and $s \to r$ on the right side of (22), so he made the classical calculations with multiply periodic orbits that led to (7) and (22). However, Breit had in mind only the fact that depending on the phase relations, a light wave can receive work from a system, rather than doing work thereon. There was no acknowledgment to Breit in *l.c.*, although there is in the preliminary note in J. Opt. Soc. America (Vol. 9, p. 27, 1924) because, as Van Vleck remembers it, Breit overmodestly objected that the phase considerations were nothing as explicit as what Van Vleck construed Breit's remark to mean. It is interesting in this connection to quote from a paper recently published (1975) by R. H. Stuewer, a historian of science, on the theoretical ideas of G. N. Lewis, the physical chemist. Lewis was very skeptical about stimulated emission. In an effort to dispel this skepticism Einstein wrote to Lewis "The sign in front of the absorbed radiation depends on the phase of the oscillator, and is therefore just as probably positive as negative." This is precisely the gist of Breit's remarks that led Van Vleck to produce *l.c.*

D. The Kramers–Kronig relation and the f-sum rule

There are two important relations which must be satisfied by an expression for the absorption coefficient if it is correct. These relations are usually expressed as integrals involving the imaginary part of the complex susceptibility which connects the polarization $P(\omega)$ and the field $E(\omega) = E_0 \exp(i\omega t)$ according to the formula $P(\omega)/E(\omega) = \chi(\omega) = \chi'(\omega) + i\chi''(\omega)$. The rate of absorption of energy, the absorption coefficient $B(\omega)$, and $\chi''(\omega)$ are connected by the relations

$$N\left\langle\frac{dW_J}{dt}\right\rangle_{\rm abs} = B(\omega)u(\omega)\,, \tag{23a}$$

$$B(\omega) = 4\pi\omega\chi''(\omega)\,. \tag{23b}$$

The so-called Kramers–Kronig relation relevant for our purposes is

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)}{\omega}\,d\omega = \chi'(0)\,, \tag{24}$$

where $\chi'(0)$ is the static susceptibility. We follow the customary modern usage in taking the limits of integration in (24) and later equations to be from $-\infty$ to $+\infty$. This is a purely formal procedure. One usually computes the absorption only for positive values of ω, as we did in obtaining Eq. (14). We could instead integrate from 0 to ∞ and insert an extra factor 2 on the left side of (24), inasmuch as χ'' is an odd function of ω. It should be noted that when the integral extends from $-\infty$ to ∞, both the f terms in (13) make equal contributions.

There are also Kramers–Kronig relations which are more general than (24) and which express $\chi'(\omega)$ $(\omega \neq 0)$ as an integral involving $\chi''(\omega)$ and also $\chi''(\omega)$ in terms of $\chi'(\omega)$, but we will not make use of these other formulas. The Kramers–Kronig relations can be derived (Kramers, 1927) on the basis of very general function theory arguments, involving the absence of singularities in the complex plane, which would make the effects of a disturbance felt before it exists. However, we will not give the general proof, and instead proceed to show that (24) is satisfied for an undisturbed multiply periodic orbit.

On expressing χ'' in terms of $\langle dW_J/dt\rangle_{\rm abs}$ by means of (23) and then utilizing (13) along with the δ function property of the f factors [Eq. (9)] one finds that

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)}{\omega}\,d\omega = \frac{e^2}{3kT}\int\!\!\int\!\!\int 2\sum_{\tau\geq 0}|d_\tau|^2\rho_J\,dJ_1dJ_2dJ_3\,. \tag{25}$$

We must now compute the static susceptibility, $\chi'(0)$, which is given by

$$\chi'(0) = \frac{P}{E} = \left(\frac{e}{E}\right)\int\!\!\int\!\!\int x\rho_J^E\,dJ_1dJ_2dJ_3dw_1dw_2dw_3\,, \tag{26}$$

where ρ_J^E is the density in the presence of the static field E, which is different from ρ_J, which denotes the density when $E = 0$. As we are throughout interested only in linear response, we can take

$$\begin{aligned}\rho_J^E &= \rho_J \exp\left(\frac{exE}{kT}\right),\\ &\simeq \rho_J\left(1 + \frac{exE}{kT}\right).\end{aligned} \tag{27}$$

We assume that the polarization vanishes in the absence of a field (no ferroelectric effects) and so the integral in (26) vanishes when $E = 0$.[4] Thus Eq. (26) becomes

$$\chi'(0) = \frac{e^2}{kT}\int\!\!\int\!\!\int \overline{x^2}\,\rho_J\,dJ_1dJ_2dJ_3\,, \tag{28}$$

where $\overline{x^2}$ means the average over the w's (equivalent to a time average) for a state of given J_1, J_2, J_3. When we use (8), (10) and the fact the system is isotropic, we see that (28) is equivalent to (25), and so the Kramers–Kronig relation (24) is satisfied.[5]

The reader should not form the impression from (28) that $\chi'(0)$ is necessarily inversely proportional to T, as in Curie's law. For example, in the case of the harmonic oscillator the integral in (28) is, except for a constant factor, the same as the mean potential energy $\frac{1}{2}kT$, and then $\chi'(0)$ is independent of T. The general validity of expression (28) in classical mechanics is discussed in greater detail on p. 37 of Van Vleck's *Electric and Magnetic Susceptibilities* (1932), where the equivalent of (28) is called a "generalized Langevin–Debye formula."

The other important general relation besides the Kramers–Kronig one is the so-called f-sum rule, which states that

$$\int_{-\infty}^{\infty}\omega\chi''(\omega)\,d\omega = \frac{N\pi e^2}{m}\,, \tag{29}$$

for a particle of change e and mass m. To prove that this formula is valid we first express $\omega\chi''$ in terms of $\langle dW_J/dt\rangle_{\rm abs}$ by means of (23) and obtain an explicit formula for $\langle dW_J/dt\rangle_{\rm abs}$ by substituting (7) and (12). The integrations over ω can immediately be performed because

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[4] From this assumption it also follows that the normalization of the density is unaffected by the field to first order in E.

[5] In this analysis we have identified $\chi'(0)$ with the isothermal susceptibility. The validity of this procedure, ordinarily well warranted, is discussed in Sec. II.C.

of the δ-function property of the f factors [Eq. (9)]. One thus obtains

$$\int_{-\infty}^{\infty} \omega\chi''(\omega)d\omega = \frac{\pi e^2}{3}\int\int\int \sum_{k=1}^{3}\sum_{\tau\geq 0} 2\tau_k \frac{\partial}{\partial J_k}\{\omega_\tau|d_\tau|^2\}\rho_J dJ_1dJ_2dJ_3 . \tag{30}$$

At this stage it is appropriate to say something about Poisson brackets. The Poisson bracket of any two functions a, b, of a set of canonical variables satisfying Hamilton's equations is commonly written as $\{a, b\}$ and is defined classically as

$$\{a, b\} = \sum_{k=1}^{3}\left(\frac{\partial a}{\partial q_k}\frac{\partial b}{\partial p_k} - \frac{\partial a}{\partial p_k}\frac{\partial b}{\partial q_k}\right) . \tag{31}$$

The corresponding definition in quantum mechanics, as most readers know, is $(ab - ba)/i\hbar$; that the quantum-mechanical definition goes asymptotically into the classical one was first demonstrated by Dirac (1926) as well as having been discovered independently by Slater, who withheld publication because of the appearance of Dirac's paper. The beautiful property of the Poisson brackets is that their values are independent of which set of canonical variables one chooses to use in the denominators of (31) provided only that they relate to the same dynamical system at the same instant of time. The proof of the invariance of the choice of variables is not given in textbooks as often as it should be. For a good reference see Goldstein's *Classical Mechanics* (1950), p. 250.

Because of the invariance property derived in the preceding paragraph it follows immediately that if $q_1, \ldots, p_3$ and $Q_1, \ldots, P_3$ are two sets of canonical variables evaluated at the same value of the time, one has

$$\{Q_k, P_l\} = \delta_{kl} , \tag{32a}$$

$$\{Q_k, Q_l\} = \{P_k, P_l\} = 0 , \tag{32b}$$

inasmuch as (31) is obviously satisfied for the choice $q_1 = Q_1, \ldots, p_3 = P_3$. [One should be cautioned that (32) is not valid if the numerator and denominator in (31) are evaluated at different values of the time.]

The ordinary Cartesian coordinates x, y, z, p_x, p_y, p_z, as well as the angle and action variables, are canonical sets. Consequently the relations (32) are fulfilled if we take $Q_i = w_i$ and $P_i = J_i$. The multiple Fourier expansion of x is given by (1) and the corresponding expression for p_x is

$$p_x = m\sum_{\tau} i\omega_\tau x_\tau \exp[i(\tau_1 w_1 + \tau_2 w_2 + \tau_3 w_3)] , \tag{33}$$

where ω_τ is a function of J_1, J_2, J_3 [Eq. (3)]. To satisfy (32) it is required that all terms in the multiple Fourier expansion of the Poisson bracket vanish except for the constant term $\{Q_k, P_k\}$ which results from the multiplication of x_τ into $p_{x(-\tau)}$ etc., and it is only this term in which we are interested for present purposes. So by use of (1) and (33) in (32) one has

$$\begin{aligned}\{x, p_x\} &= \sum_{k=1}^{3}\left(\frac{\partial x}{\partial w_k}\frac{\partial p_x}{\partial J_k} - \frac{\partial x}{\partial J_k}\frac{\partial p_x}{\partial w_k}\right) ,\\ &= \sum_{k=1}^{3}\sum_{\tau\geq 0} 2m\tau_k\frac{\partial}{\partial J_k}\{\omega_\tau|x_\tau|^2\} = 1 .\end{aligned} \tag{34}$$

There are also similar expressions for $\{y, p_y\}$ and $\{z, p_z\}$. So, using (34) and the definition (8) of $|d_\tau|^2$ we see that the right-hand side of (30) is merely $(\pi e^2/m)\int\int\int\rho_J \times dJ_1dJ_2dJ_3 = N\pi e^2/m$. Consequently (29) is proved. It is not necessary that there be a Boltzmann distribution such as in (11). Instead all the atoms could be in the same state J_1, J_2, J_3. In other words the f-sum rule is nonstatistical in nature (except for averaging over the phases involved in the w's).

A few remarks, mainly of a historical nature, may now be made about the f-sum rule. Since the asymptotic relation (22) is valid for arbitrary $u(\omega)$, we can take $u(\omega) = 1$, and if we then sum over all states r, t connected by dipole transitions to the given state s, then (22) becomes

$$\begin{aligned}\sum_{r}\hbar\omega_{rs}B_{sr} - \sum_{t}\hbar\omega_{st}B_{st} &\rightarrow \frac{4\pi^2e^2}{3}\sum_{k=1}^{3}\tau_k\frac{\partial}{\partial J_k}\{\omega_\tau|d_\tau|^2\}\\ &= \frac{2\pi^2e^2}{m} .\end{aligned} \tag{35}$$

Here we have inserted on the right side the value which it acquires because of (8) and the Poisson bracket relation (34). It is natural to propose that this value also applies in quantum theory, so that the asymptotic arrow in (35) is replaced by an equality sign. Then both in classical and in quantum theory, the absorption in a radiation field of uniform unit spectral density (a purely formal concept) is $2\pi^2e^2/m$, quite irrespective of the state the atom is in, or the nature of its dynamics, provided only that they are Hamiltonian and there are three degrees of freedom (as in *l.c.*).[6]

The proposal that the left side of (35) have the value $2\pi^2e^2/m$ was made independently by Kuhn and by Thomas in 1925. In their paper on dispersion, written slightly earlier, Kramers and Heisenberg (1925) used a notation equivalent to writing the left-hand side of (35) as $2\pi^2e^2m^{-1}\sum_i f_i$, where the summation over i includes both r and t. The letter f was used in the same fashion by Reiche and Thomas (1925), and the Kuhn–Thomas proposal was that $\sum_i f_i = 1$. This relation is the equivalent of the diagonal part of the familiar formula $(qp - pq)/i\hbar = 1$ of matrix quantum algebra, but of course the language was unknown in 1925. The Kuhn paper is appropriately printed as the last article in the first half, "Towards Quantum Mechanics," of the van der Waerden (1967) quantum-historical compendium, while Part II, "Matrix Mechanics," appropriately opens with the Heisenberg (1925) paper which Kronig calls "the turning point" and which van der Waerden (1967) characterizes as the discovery of a "small path that led from the darkness towards the light of a new physics." The reason for the term "f-sum rule" is a purely historical one, arising from the use of the letter f in the early papers, as we have mentioned, and is not a happy or informative choice of terminology. It should be mentioned in this connection that Kuhn suggested that the expression given on the left-hand side of (35) has the value $2\pi^2e^2/m$, not because of the correspondence principle argument indicated schematically in Eq. (35), but instead because this particular value made the Kramers dispersion formula reduce to the

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[6] If unit energy density is relative to the true rather than the angular frequency distribution $\pi e^2/m$ occurs in place of $2\pi^2e^2/m$.

classical Thomson formula if the frequency of the impressed light is high compared to the frequencies associated with atomic binding. This is a more physical argument based on the idea that with high frequencies quantum discreteness is unimportant. It is sometimes stated in the literature (e.g., Heisenberg, 1925) that Thomas also was led to the f-sum rule by the same dispersion argument as Kuhn's, but instead Thomas used the more immediate type of correspondence principle analysis schematized in Eq. (35). A year before the papers of Thomas and Kuhn, one of us showed (p. 359 of *l.c.*) that the right side of (35) had the value $2\pi^2e^2/m$,[7] something not previously noted, and in a footnote suggested that the left or quantum side might also have this value, but dismissed the suggestion as "tempting but probably futile." The grounds for this dismissal sound today rather naive, viz. disagreement with some questionable x-ray data and especially the surmisal that there would then result a nonzero probability of transition to nonexistent states. Actually there is an additive constant in all the B's which cancels out of the difference on the left side of (35) and which is determined by the boundary condition that there be vanishing of the transition probability to nonexistent states. This type of boundary condition was used in the pre-quantum mechanical papers of Goudsmit and Kronig, Russell, and Sommerfeld and Hönl, who developed sum rules for calculating relative intensities in Zeeman and multiplet components, but for the most part their papers had not appeared when *l.c.* was written. Van Vleck was led to an incorrect value of this constant by employing even for small quantum numbers a relation between classical and quantum amplitudes only warranted asymptotically [Eq. (10) of *l.c.*].

E. The method of correlation functions and the Wiener–Khintchine formula

We now turn from the study of multiply periodic orbits described by angle and action variables to a modern method of attack, based on correlation functions and the Wiener–Khintchine formula.

By the correlation function associated with a time-dependent quantity we mean the average $\langle f(t)f(t')\rangle$ taken over an ensemble of atoms so that all differences in phase and state are ironed out. (Alternatively we could average over t with fixed $t'-t$, if all atoms over a very long time interval have the same average history—essentially the ergodic hypothesis.) The Wiener–Khintchine formula states that the "power spectral density" $\mathcal{P}(\omega,f)$ of $f(t)$ associated with a frequency ω is $1/\pi$ times the Fourier transform of the correlation function, i.e.,

$$\mathcal{P}(\omega,f)=\frac{1}{\pi}\int_{-\infty}^{\infty}\langle f(t)f(t')\rangle e^{i\omega(t'-t)}d(t'-t)\,. \tag{36}$$

What is meant by "power spectral density" is clear if we write down the further relation

$$\int_0^{\infty}\mathcal{P}(\omega,f)d\omega=\langle f(t)^2\rangle\,. \tag{37}$$

Thus $\mathcal{P}(\omega,f)$ tells us what the power spectrum of $f(t)$ is like on the average. We use the term power because it refers to expenditure of energy per unit time if we regard $\int f(t)^2dt$ as energy, but in this connection it is to be understood that we use "power" and "energy" in a purely heuristic sense, so that we can visualize the results in terms of, say, ac currents, but the dimensions of $f(t)^2$ and $f(t)^2t$ need not be those of power and energy in the literal sense. A word should be said about the meaning of the notation $\langle\cdots\rangle$ in (36). As in Sec. I.A it denotes an average over an ensemble, so that

$$\langle\cdots\rangle=C\int\cdots\int(\cdots)e^{-W/kT}dx\ldots dp_z\,,$$

if one is calculating in phase space or

$$\langle\cdots\rangle=C\int\cdots\int(\cdots)e^{-W_J/kT}dJ_1dJ_2dJ_3\,,$$

if one is using angle and action variables and has already averaged over the arbitrary epoch or phase angles associated with the angle variables w_1, w_2, w_3. With either procedure the constant *of proportionality* C is, of course, determined by the requirement that the number of molecules per unit volume is N.

The Wiener–Khintchine theorem is remarkable in two respects. In the first place, it has a simplicity ideally adapted to statistical systems. Unless otherwise stated it will be assumed that $\langle f(t)f(t')\rangle$ is a real function of only the argument $t'-t$. It is furthermore (until one passes to quantum mechanics) an even function of $t'-t$, as there is nothing to distinguish between $\langle f(t)f(t')\rangle$ and $\langle f(t')f(t)\rangle$. It is the richness of the physical content of the assumption that $\langle f(t)f(t')\rangle$ depends only on $t'-t$ that gives the Wiener–Khintchine theorem its usefulness and vitality.

The other reason the theorem is remarkable is that it was not derived until 1930, when it appeared in a rather abstract mathematical paper of Wiener's not particularly concerned with physics. Subsequently, it was discovered independently by Khintchine in 1934. When one thinks of all the complicated abstract mathematics and physics that was developed by 1930 it is hard to believe that this beautifully simple theorem had not been discovered earlier (just as the so called Plancherel theorem we mention later was used by the elder Lord Rayleigh, without the niceties of rigor, in 1889, some twenty years before Placherel's 1910 paper (see Kemble, 1937).

The proof of the Wiener–Khintchine theorem is exceedingly simple, and at the same time sheds light on its meaning. The Fourier integral description of $f(t)$

$$f(t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}g(\omega)e^{i\omega t}d\omega\,, \tag{38}$$

where

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[7] Van Vleck did not use Poisson brackets to establish the relation (34) basic to the proof, but instead used a rather cumbersome variational method given in Appendix I of his 1926 book, but quoted in advance in *l.c.* He derived the Lagrange bracket relation $\sum_{\tau\geq 0}\partial/\partial J_k\,(2m\omega_\tau|d_\tau|^2)=1$ rather than the Poisson one (34), but either approach works equally well. With the Poisson approach the factor 3 in the denominator of (7) is canceled out by summing over k. The Lagrange brackets differ from the Poisson ones in that the summation over the canonical variables is in the numerator rather than in the denominator. For a description of the relation between Lagrange and Poisson brackets see Goldstein (1950). Van Vleck in his *Quantum Principles and Line Spectra*, written in 1925, treated canonical transformations by means of Lagrange rather than Poisson brackets, as at the time it was not realized that, in quantum mechanics, Poisson brackets would be the more useful of the two alternatives.

$$g(\omega)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt\,. \tag{39}$$

An immediate consequence of (38) and (39) is the well known Plancherel relation

$$\int_{-\infty}^{\infty} f(t)^2dt=\int_{-\infty}^{\infty}|g(\omega)|^2d\omega=2\int_0^{\infty}|g(\omega)|^2d\omega\,. \tag{40}$$

The proof of (40) except perhaps for questions of rigor consists in writing down $f(t)^2$ as a product of two integrals of the type (38), and integrating over a long period of time. This has the effect of introducing a δ function, $\delta(\omega'-\omega'')$, in the double integral, which thus becomes a single integral given by the right side of (40). Evidently $2|g(\omega)|^2d\omega$ is the "energy" associated with $f(t)$ in the frequency interval ω, $\omega+d\omega$, since we must consider both $+\omega$ and $-\omega$ (or alternatively the factor 2 associated with the cross product of terms in $+\omega$ and $-\omega$ [cf. Eq. (10)]). To establish the Wiener-Khintchine relation (36) we must show that

$$2|g(\omega)|^2=2T\mathcal{P}(\omega,f) \tag{41}$$

assuming $f(t)$ vanishes for $|t|>T$. Now from (39) we have

$$\langle g(\omega)g(\omega)^*\rangle=\frac{1}{2\pi}\int_{-T}^{T}\int_{-T}^{T}\langle f(t)e^{i\omega t}f(t')\,e^{-i\omega t'}\rangle\,dtdt'\,,$$
$$=\frac{1}{2\pi}\int_0^{2T}dt_2\int_{-(2T-t_2)}^{2T-t_2}\langle f(0)f(t_1)\rangle e^{i\omega t_1}dt_1\,.$$

Here we have changed variables from t,t' to $t_1=t-t'$ and $t_2=t+t'$ and utilized the fact that $\langle f(t)f(t')\rangle$ is an even function only of $t-t'$, which is the crux of any argument based on the Wiener–Khintchine relation. We now assume the $\langle f(0)f(t_1)\rangle$ converges to zero as $t_1\rightarrow\pm\infty$. [If $f(t)$ has a "dc" component so that $\int_{-\infty}^{\infty}f(t)dt\neq 0$ this component can be subtracted out and $f(t)$ redefined. The dc component would correspond to a "delta" function at $\omega=0$ in the integral (36).] Because of the convergence of $\langle f(0)f(t_1)\rangle$ to zero, the limits of integration on t_1 can be treated as $\pm\infty$, since T can be made arbitrarily large. When the limits in the integration over t_1 are changed to $\pm\infty$ we have exactly the desired relation:

$$2\langle|g(\omega)|^2\rangle=\frac{2T}{\pi}\int_{-\infty}^{\infty}\langle f(0)f(t_1)\rangle e^{i\omega t_1}dt_1\,,$$
$$=2T\mathcal{P}(\omega,f)\,.$$

With the Wiener-Khintchine theorem all our relations regarding emission and absorption can be derived very simply, provided we utilize the fact that for a well behaved function the Fourier integral expansion of df/dt is the same as that of f except for a factor $i\omega$, or in other words

$$\mathcal{P}(\omega,df/dt)=\omega^2\mathcal{P}(\omega,f)\,. \tag{42}$$

Thus since an electron radiates energy at the rate $(2/3c^3)e^2\dot{v}^2$, its radiated power spectrum can be expressed equally well as

$$N\left\langle-\frac{dW}{dt}\right\rangle_{\text{emis}}=\frac{2e^2N\mathcal{P}(\omega,p_x)\omega^2}{c^3m^2}\,, \tag{43}$$

or as

$$N\left\langle-\frac{dW}{dt}\right\rangle_{\text{emis}}=\frac{2e^2N\mathcal{P}(\omega,x)\omega^4}{c^3}\,. \tag{44}$$

(The factor 3 in the denominator has disappeared because there are x,y,z components.)

We must now calculate the rate of absorption of radiation. To do this we rely heavily on Liouville's theorem. The rate of absorption in a field $E_0\cos(\omega t-\epsilon)$ at a given time t is

$$N\langle dW/dt\rangle_{\text{abs}}=\frac{e}{m}\int\cdots\int p_x(t)(\rho^E-\rho)dx\ldots dp_z$$
$$\times E_0\cos(\omega t-\epsilon)\,, \tag{45}$$

where ρ^E is the instantaneous density in phase space $dx\ldots dp_z$, and ϵ is some phase angle. The value of ρ^E is not the same as the value ρ for $E=0$, because the medium is unpolarized, i.e., $\langle p_x\rangle=0$ unless there is a field E. This fact permits us to write $\rho^E-\rho$ in place of ρ^E in (45). What we can do is to trace the field back to a much earlier time $t-\theta$ before the field is applied, at which point ρ^E had the value $\rho^E=\rho=NC\exp(-W/kT)$, where $W(x_0,\ldots,p_{z0})$ is the "inner energy" exclusive of the applied field.

The systems occupying an element of volume $d\Gamma=dx_0\ldots dp_{z0}$ at time $t-\theta$ are carried over into an element $d\Gamma'=dx\ldots dp_z$ at time t, and because of Liouville's theorem $d\Gamma=d\Gamma'$. Hence the proper value of $\rho^E-\rho$ to use in (45) is

$$\rho^E-\rho=NC\{\exp[-W(x_0,\ldots,p_{z0})/kT$$
$$-\exp[-W(x,\ldots,p_z)/kT]\}\,.$$

Now the rate at which the applied field changes W is $(e/m)p_x(t)E_0\cos(\omega t-\epsilon)$ and so to first order in E

$$\rho^E-\rho\equiv\Delta\rho(t,\theta)=\frac{eE_0\rho}{mkT}\int_{t-\theta}^{t}p_x(t')\cos(\omega t'-\epsilon)dt'\,. \tag{46}$$

In virtue of (46), expression (45) becomes

$$N\langle dW/dt\rangle_{\text{abs}}=\frac{e^2E_0^2}{m^2kT}\int\cdots\int\left[\int_{t-\theta}^{t}p_x(t)p_x(t')\cos(\omega t-\epsilon)\cos(\omega t'-\epsilon)dt'\right]\rho dx\ldots dp_z\,,$$
$$=\frac{e^2E_0^2N}{m^2kT}\int_{t-\theta}^{t}\langle p_x(t)p_x(t')\rangle\cos(\omega t-\epsilon)\cos(\omega t'-\epsilon)dt'\,. \tag{47}$$

Now, as already noted $\langle p_x(t)p_x(t')\rangle$ is on the average an even, real function of only the argument $t'-t$. Any term involving $\exp[i\omega(t'+t)]$ rather than $\exp[i\omega(t'-t)]$ will average to zero if the ensemble has a random distribution of phases. The limit of integration, $t-\theta$, can be replaced by $-\infty$ since all correlation is lost after a sufficiently long time interval according to the assumptions underlying the Wiener–Khintchine formula. Furthermore $E_0\cos(\omega t-\epsilon)$ is connected with the radiant energy density $u(\omega)$ by the relation $E_0^2/8\pi=\frac{1}{3}u(\omega)$, but the factor $\frac{1}{3}$ goes out when we allow for the fact that there is also work done by the y and z components of the radiation field, and so, using (36), we have

$$N\langle dW/dt\rangle_{\rm abs} = \frac{2\pi^2 e^2}{kTm^2}\, Nu(\omega)\mathcal{P}(\omega, p_x)\,, \tag{48}$$

or equivalently, because of (42) and the fact that $p_x = m dx/dt$,

$$N\langle dW/dt\rangle_{\rm abs} = \frac{2\pi^2 e^2 N u(\omega)\mathcal{P}(\omega, x)\omega^2}{kT}\,. \tag{49}$$

From comparison of (48) with (43), or equally well, of (49) with (44) it follows immediately that there is equilibrium between absorption and emission if the energy density has the Rayleigh–Jeans value (16).

The Kramer–Kronig relation and the f-sum rule also follow immediately. To prove the Kramers–Kronig relation (24) we simply take $f = x$ in (36) and express the integrand in (37) in terms of χ''/ω by combining (23) and (49), noting that a factor of 2 arises because the region of integration is half as big in (37) as in (24). To prove the f-sum rule we take $f = p_x$ and express the integrand in (37) in terms of $\chi''\omega$ by means of (23) and (48). One thus finds that the integral on the left side of (29) is $Ne^2\pi[\langle p_x^2\rangle/kT]$; the bracketed factor is simply $1/m$ by equipartition and so (29) is established.

The simplicity and power of the correlation function method cannot be overestimated, especially in the historical context. Planck thought the proof of the balance between absorption and emission under the Rayleigh–Jeans law just for a harmonic oscillator or two-dimensional rotator of sufficient importance to warrant inclusion in the editions of his *Wärmestrahlung* published in the 1920's even though these dynamical systems were highly simplified and idealized ones. When in 1924 one of us found that the balance held generally in multiply periodic systems, we hoped that it might be referred to in future editions of Planck's book, which never appeared for a variety of reasons, perhaps most notably the quantum mechanical revolution. The calculation of absorption by multiply periodic orbits (the most general undisturbed relevant classical dynamical system) was a somewhat laborious one as made by applying perturbation theory with angle and action variables as in *l.c.* One can, however, also obtain our final formula (13) simply by using (49) and assuming x to be described by a multiple Fourier series of the type given in Eq. (1). To see this we note that in $\langle x(t)x(t')\rangle$ the only terms that don't drop out in averaging over all phases are the cross terms between a given τ and $-\tau$ [cf. Eq. (10)]. Thus (36) becomes

$$\mathcal{P}(\omega, x) = 2\sum_{\tau\geq 0} |x_\tau|^2[f(\omega_\tau, \omega) + f(\omega_\tau, -\omega)]\,, \tag{50}$$

where $f(\omega_\tau, \omega)$ is a δ function as in Eq. (9). The extra factor $\frac{1}{3}$ found in (13) but not in (49) is because of the definition (8).

However the greatest service of all provided by the correlation function approach is that it frees us from the assumption that the system be undisturbed. All the analysis in Sec. I.A–I.D applied only to undamped systems with infinitely sharp lines. The proofs in the present section of the equilibrium under the Rayleigh–Jeans law, the Kramers–Kronig relation, and the f-sum rule apply even when the system is disturbed by collisions, provided there are no sudden discontinuities. However, the traditional models in which velocities and positions are discontinuous at collisions can cause trouble, as we shall see in the next section, though even the troubles can be enlightening.

F. Line shape with traditional collision-interrupted models

The method of correlation functions which we have presented is so general that it does not tell us specifically what is going on unless we adopt some sort of a definite model. In this respect it is a little reminiscent of thermodynamics. We therefore examine the situation when the atoms or molecules are interrupted by collisions so that the lines are not infinitely sharp. We will assume that at a collision there is no correlation ("hangover") with what has been going on before. We use the term traditional to indicate we are not at present talking about an "*FM*" type of collision theory in which the frequency is changed at collision but not the phase. Instead we assume, as in the traditional impact theories, that there is no persistence in phase. Consequently, instead of $t-\theta$ being an arbitrarily large negative time, as in the uninterrupted model, we need run the time back to values of θ distributed according to the usual random law that the probability that a collision last occured at a time in the interval $-\theta$, $-\theta+d\theta$ is given by $\gamma e^{-\gamma\theta}d\theta$, where $1/\gamma$ is the mean duration of the interval between collisions. Consequently, since all correlation is destroyed by the collision, and since $\langle f(t)f(t')\rangle$ is still an even function of $t'-t$, we must use in place of (36)

$$\mathcal{P}(\omega, f) = \frac{2}{\pi}\int_0^\infty \gamma e^{-\gamma\theta}d\theta \int_{-\theta}^{0} \langle f(t)f(t')\rangle \cos[\omega(t'-t)]\,d(t'-t)\,. \tag{51}$$

If we now assume that $f = x$ and that x is given by a multiple Fourier series $x = \sum_\tau x_\tau \exp(i\omega_\tau t + i\epsilon_\tau)$ then, as usual the only terms that persist on averaging over all phases are those resulting from multiplication of x_τ into $x_{-\tau}$. Since

$$\cos a \cos b = \tfrac{1}{2}[\cos(a-b) + \cos(a+b)]\,, \tag{52a}$$

$$\int_0^\infty e^{a\theta}\cos b\theta\, d\theta = \frac{a}{a^2+b^2}\,, \tag{52b}$$

we find that $\mathcal{P}(\omega, x)$ is still given by expression (50) provided we define $f(\omega_\tau, \omega)$ not as a delta function, as previously, but instead as

$$f(\omega_\tau, \omega) = \frac{\Delta\omega}{\pi[(\omega_\tau - \omega)^2 + \Delta\omega^2]}\,, \quad (\Delta\omega = \gamma)\,. \tag{53}$$

If we assume the Fourier coefficients of p_x differ from those of x by a factor of $im\omega_\tau$ as in Eq. (33), then $\mathcal{P}(\omega, p_x)$ differs from $\mathcal{P}(\omega, x)$ only by the extra factor $m^2\omega_\tau^2$ inside the summation in (50). From (23) it follows that the expression for the absorptive part of the susceptibility is

$$\chi''(\omega) = \frac{\pi N e^2\omega}{kT}\sum_{\tau\geq 0} |x_\tau|^2[f(\omega_\tau, \omega) + f(\omega_\tau, -\omega)], \tag{54}$$

provided we use (49), i.e., work with the correlation in x. On the other hand if we employ (48), i.e., work with the correlations in the momentum p_x, we find

$$\chi''(\omega)=\frac{\pi N e^2}{\omega kT}\sum_{\tau\geq 0}\omega_\tau^2\,|x_\tau|^2[f(\omega_\tau,\omega)+f(\omega_\tau,-\omega)]\,, \qquad (55)$$

where both cases $f(\omega_\tau, \pm\omega)$ are given by (53). The two expressions (54) and (55) are not the same except in the resonance region$(\omega_\tau \pm \omega) \to 0$ or in the limit $\Delta\omega \to 0$, i.e., infinitely sharp lines. Then (54) and (55) are the same and in the narrow linewidth limit reduce to the expression previously derived for uninterrupted systems.

What is the cause for the discrepancy? It is that because of the assumption of infinitely sharp collisions, x is not a well behaved function. A valid multiple Fourier series for p_x cannot be obtained by term differentation of the series for x, as in (33). Instead at each collision the coordinate x changes abruptly and the momentum p_x is infinite.

Since

$$\int_{-\infty}^{\infty}\frac{\Delta\omega d\omega}{(\omega\pm\omega_\tau)^2+\Delta\omega^2}=\pi\,,$$

one finds that (54) satisfies the Kramers–Kronig relation (24), and that (55) satisfies the f-sum rule (29). But the reverse is not true (unless $\Delta\omega \to 0$). In fact it is clear from physical considerations that (55) cannot be correct at low frequencies since according to (55) the absorption approaches a constant value and the susceptibility has a singularity, whereas actually the absorption should be proportional to ω^2, and the susceptibility to ω. On the other hand (54) behaves improperly at high frequencies, as the resulting f-sum integral (29) diverges.

It is clear that one cannot obtain an expression for the line shape which is of Lorentzian form, and which is a good approximation for the whole frequency spectrum. To be sure there is balance between absorption and emission under the Rayleigh–Jeans law if one consistently uses the same kind of correlation function in both cases [i.e., mates (54) with (44) if one considers the correlation in x, and (55) with (43) if one considers that in p_x].

It is futile to inquire whether (54) or (55) is basically correct, since neither is completely. However, (54) is probably a good approximation from low frequencies up to the resonance region, and at high frequencies no formula of the Lorentzian (rather than, say, Gaussian) type can possibly be right, as $\int_0^\infty \chi''(\omega)\omega^n d\omega$ should be finite for any value of n (unless one uses a physically incorrect model in which the intermolecular approach has an infinitely sharp boundary). Van Vleck and Weisskopf (1947) (also Van Vleck and Margenau, 1949) appear to give the impression that (54) was the ultimate Lorentzian-type answer which was generally correct. Instead it is well known that in the high-frequency region one should use the so-called statistical theory of broadening, where the intermolecular fields are treated as static (see Sec. I.G).

There is a nice physical distinction between (54) and (55). The result (55) is what one obtains with the impact model, and assumes the frequency of radiation is so high that it does not affect the Boltzmann distribution, or do any substantial work at collisions because during a collision one averages over a large number of phases of the radiation. In this case, which we call (a), the Boltzmann equilibrium must be restored at collisions by forces other than the applied field. On the other hand, one obtains (54) in the case, which we call (b) when the variation of the field is sufficiently slow so that the Boltzmann factor includes the instantaneous value of the potential energy $-exE$ associated with the field, and is thus maintained because of this field.

To prove the validity of the statements made in the previous paragraph we go back to the basic formula (45) for the work being done by the applied field. Various atoms or molecules differ in the value of the time $t-\theta$ when the last collision occurred, so that we have in place of (45)

$$N\,\langle dW/dt\rangle_{\rm abs}=\frac{e\gamma}{m}\int\int\cdots\int_0^\infty E_0\cos(\omega t-\epsilon)F(t,\theta)e^{-\gamma\theta}d\theta\,dx\cdots dp_z. \qquad (56)$$

With situation (a) we take

$$F(t,\theta)=p_x(t)\Delta\rho(t,\theta)\,, \qquad (57)$$

where $\Delta\rho(t,\theta)$ is given by the right side of (46) and $t-\theta$ is the time when the last collision occurred. In case (b) there are two effects or corrections to (57) which must be considered. One is that right after the collision, the value of the density is $\rho^E = \rho\exp[eEx/kT]$, so that now, to first order in E

$$\rho^E(t,\theta)-\rho=\Delta\rho(t,\theta)+\rho eE(t-\theta)x(t-\theta)/kT\,.$$

The other correction is for the impulsive work at collision, which is equal to $eEx\delta\rho$, where $\delta\rho$ is the change in density corresponding to adjustment to the equilibrium value of the field, i.e.,

$$\delta\rho(t,\theta)=\rho eE(t)x(t)/kT-(\rho^E(t,\theta)-\rho)\,,$$

where $\rho^E(t,\theta)$ is evaluated just before the collision at time t. There are γ collisions per second, and so the effect of the two corrections is to make the proper value of $F(t,\theta)$ to be used in (56).

$$F(t,\theta)=(\rho^E(t,\theta)-\rho)p_x(t)+m\gamma\left(\rho\frac{eE(t)x(t)}{kT}-\rho^E(t,\theta)+\rho\right)x(t)\,. \qquad (58)$$

The evaluation of the integral in the bracketed factor of (56) is now an elementary, though slightly tedious process. Since expression (56) is already of order E we can use for x and p their unperturbed values, viz.

$$x=\sum_\tau x_\tau e^{i\omega_\tau t+i\epsilon_\tau}\,,$$

$$p_x=m\sum_\tau i\omega_\tau x_\tau e^{i\omega_\tau t+i\epsilon_\tau}\,.$$

The products of the trigonometric factors can be reduced out by relations similar to those given in (52a). Only the resulting Fourier terms, which are independent of t and which hence depend only on θ, need be retained when account is taken of the randomness of phases. [Viz. different atoms are exposed to random values of the phase ϵ of the electric field, and in the multiple Fourier series for x and p_x the phases ϵ_τ are given by $\epsilon_1\tau_1+\epsilon_2\tau_2+\epsilon_3\tau_3$, where the ϵ_i are random; cf. Eq. (5). It is also obvious from physical considerations that there can be no terms involving the absolute time in the final result.] The terms proportional to γ^2 in (56) when (58) is used can be converted into terms linear in γ by partial integration, and expression (56) is thus reduced to a sum of integrals of the form (52b). One thus finds that one does indeed obtain (54) or (55) depending on whether one employs (58) or (57).

We should also mention that (54) can be obtained by a method due to Karplus and Schwinger (1948). They make a quantum-mechanical density matrix calcultion, but the adaption to the classical case is immediate and so we will not reproduce it here. Their method has the advantage that it is not necessary to assume "hard" collisions which completely restore the density to its equilibrium value each time. It is only necessary that it tend toward this value. Their analysis is based on a consideration of the imaginary part of the polarization rather than the direct calculation of the absorption. It is simpler to use the correlation based on x rather than p_x, but it is physically rather informative to see how the impulsive work and adjustments at collision are involved; they do not show up explicitly when one works with x instead of p_x.

Another illustration of the limitations of the Lorentzian approximation is provided by our previous calculation (1966) of the absorption by an oscillator which is coupled to a continuum of oscillators through a bilinear interaction. The exact expression for the susceptibility was found to have the form

$$\chi''(\omega)=\frac{e^2}{m}\frac{\operatorname{Im}G(\omega)}{[\omega_0^2-\omega^2+\operatorname{Re}G(\omega)]^2+[\operatorname{Im}G(\omega)]^2}\ , \qquad (59)$$

where $\operatorname{Im}G(\omega)$ and $\operatorname{Re}G(\omega)$ are odd and even functions of the frequency, respectively. The "linewidth" $\operatorname{Im}G(\omega)$ had the property of vanishing when $|\omega|$ fell outside the bandwidth of modes coupling to the primary oscillator. Near resonance (56) reduces to the Lorentzian form

$$\chi''(\omega)=\frac{e^2}{2m\omega_0}\frac{\gamma}{(\overline{\omega}_0-\omega)^2+\gamma^2}$$

with $\overline{\omega}_0\approx\omega_0+\operatorname{Re}G(\omega_0)/2\omega_0$ and $\gamma\approx\operatorname{Im}G(\omega_0)/2\omega_0$. However, at low frequencies, $\omega\ll\omega_0$, we have

$$\chi''(\omega)=\frac{e^2}{m}\frac{\operatorname{Im}G(\omega)}{[\omega_0^2+\operatorname{Re}G(0)]^2}$$

so that the frequency dependence of $\chi''(\omega)$ as $\omega\to 0$ is determined by that of $\operatorname{Im}G(\omega)$, which in turn reflects the low-frequency limit of the density of states of the perturbing oscillators as well as any variation with frequency in the coupling constant. It is interesting to note that if we take $\operatorname{Re}G(\omega)=0$, $\operatorname{Im}G(\omega)\sim\omega$, Eq. (59) gives exactly the same dependence of the susceptibility on frequency as does the venerable damped harmonic oscillator $m\ddot{x}+b\dot{x}+ax=eE$. It then becomes identical with a formula derived by Gross (1955a) by a somewhat different method based on a Brownian motion analysis. His model assumes that collisions can change velocities but not positions, and so does not encounter the difficulties mentioned at the beginning of the present section.

G. Line broadening by frequency modulation

The interruption model of collision broadening discussed in the preceding section is appropriate for characterizing collisions which restore the system to thermal equilibrium. As such it is a model which is better suited to describing the relaxation of rotating dipoles than harmonic oscillators, since in the latter case it requires in general a complete change in position of a harmonically bound particle (like a pendulum suddenly being switched from one side to the other) whereas the reorientation of a dipole at collision is a much less drastic readjustment.[8] A class of models which are useful in simulating the effects of collisions on those systems where the harmonic oscillator is the appropriate classical analog employ a stochastic modulation of the oscillator frequency.

In discussing the frequency modulation (FM) models it is convenient to work with the function $\eta=p+im\omega_0x$ and its complex conjugate η^*. In the absence of perturbations η satisfies the equation.

$$\frac{d\eta}{dt}=i\omega_0\eta\,. \qquad (60)$$

The effect of collisions is simulated by adding to the right side of (60) a term $\delta\omega_0(t)\eta$, where $\delta\omega_0(t)$ is a random function. With $\delta\omega_0$ included the solution to the counterpart of (60) is given by

$$\eta(t)=\eta(0)\exp\Big[i\omega_0t+i\int_0^t\delta\omega_0(t')dt'\Big]\,. \qquad (61)$$

The calculation of the absorption line shape is carried out by relating $\mathcal{P}(\omega,x)$ to the Fourier transform of $\langle x(0)x(t)\rangle$ and then expressing $x(t)$ as a combination of $\eta(t)$ and $\eta(t)^*$. In such a procedure it is understood that the bracket $\langle\cdots\rangle$ refers to an average over the fluctuations in $\delta\omega_0$ as well as a thermal average. The resulting expression for the power spectrum has the form (50) with the function $f(\omega_0,\omega)$ given by

$$f(\omega_0,\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{i(\omega_0-\omega)t}\phi(t)\,, \qquad (62)$$

where

$$\phi(t)=\left\langle\exp\left[i\int_0^t\delta\omega_0(t')dt'\right]\right\rangle_\delta\ , \qquad (63)$$

in which the symbol $\langle\cdots\rangle_\delta$ refers explicitly to the average over the fluctuations in the frequency.

In all of the FM models, the line shape is related to the Fourier transform of the function $\phi(t)$. As discussed by Kubo (1961) the differences in the various models relate to assumptions about the time dependence of the fluctuations. We will develop in some detail models incorporating Gaussian and Poisson modulation, as these are the most useful in interpreting atomic spectra. The Gaussian model corresponds to keeping the first nonvanishing term in the expansion of $\ln\phi(t)$ in powers of $\delta\omega_0$. We have

$$\ln\phi(t)=-\frac{1}{2}\int_0^t dt'\int_0^t dt''\langle\delta\omega_0(t')\delta\omega_0(t'')\rangle_\delta+\cdots$$

with the assumption $\langle\delta\omega_0(t')\rangle_\delta=0$. The line shape is seen to depend on the correlation of the fluctuations in the frequency. With no preferred point in time $\langle\delta\omega_0(t')\delta\omega_0(t'')\rangle_\delta$ will be a function of $t''-t'$ so that we have

$$\phi(t)=\exp\left[-\int_0^t(t-t_1)R(t_1)dt_1\right]\,, \qquad (64)$$

where $R(t_1)=\langle\delta\omega_0(0)\delta\omega_0(t_1)\rangle_\delta$. The variation of $f(\omega_0,\omega)$ depends on the difference frequency $|\omega-\omega_0|$ relative to the decay rate of the fluctuations. A simple and useful approximation is to take $R(t)=\langle\delta\omega_0^2\rangle_\delta\exp[-\lambda t]$. As discussed in this journal by Anderson and Weiss (1953), the line shape assumes qualitatively different forms in the two limits $|\omega-\omega_0|\ll\lambda$ and $|\omega-\omega_0|\gg\lambda$. If $|\omega-\omega_0|\ll\lambda$ we have

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[8] This difficulty has been stressed by Gross (1955a).

$$\phi(t)=\exp[-\gamma|t|], \tag{65}$$

where $\gamma=\langle\delta\omega_0^2\rangle_\delta/\lambda$. Using (65), we obtain a Lorentzian form for $f(\omega_0,\omega)$ with the width equal to γ. With Gaussian modulation the Lorentzian form is seen to correspond to the rapid modulation limit (Bloembergen, Purcell, and Pound, 1946). On the other hand, if $|\omega-\omega_0|\gg\lambda$, we have the static limit where

$$\phi(t)=\exp[-\tfrac{1}{2}\langle\delta\omega_0^2\rangle_\delta t^2], \tag{66}$$

which leads to a Gaussian line shape with root mean square width $\langle\delta\omega_0^2\rangle_\delta^{1/2}$.

Equation (64) for $\phi(t)$ is an exact result if the fluctuations have a Gaussian distribution. It is frequently a good approximation in situations where the oscillator is continually under the influence of a large number of weak perturbers, as, for example, occurs in the case of sharp line optical transitions in solids where the fluctuations in the frequency are caused by the Raman scattering of phonons.

The model of Poisson modulation is appropriate to a situation where the modulation occurs as a sequence of irregular pulses of short duration. As such it is a suitable model for describing pressure broadening in gases, where the random collisions between atoms generate the fluctuations in the frequency. We assume there are N_ν independent perturbers in a box of volume V and that the kth perturber causes a frequency fluctuation $\delta\omega_k$ if it is within a distance a of the oscillator; otherwise it has no effect. The function $\phi(t)$ is then given by

$$\begin{aligned}\phi(t)&=\prod_{k=1}^{N_\nu}\left\langle\exp\left[i\int_0^t\delta\omega_k(t')dt'\right]\right\rangle_\delta\\&=\prod_{k=1}^{N_\nu}\left\{1\cdot+\left\langle\exp\left[i\int_0^t\delta\omega_k(t')dt'\right]-1\right\rangle_\delta\right\},\\&=\exp\left[\sum_{k=1}^{N_\nu}\left\langle\exp\left[i\int_0^t\delta\omega_k(t')dt'\right]-1\right\rangle_\delta+\mathcal{O}\left(\frac{N_\nu a^3}{V}\right)\right],\\&=\exp\left[N_\nu\left\langle\exp\left[i\int_0^t\delta\omega_k(t')dt'\right]-1\right\rangle_\delta\right],\end{aligned}\tag{67}$$

assuming all perturbers are identical. The connection between (67) and the Poisson distribution becomes apparent if we consider a related problem (Kubo, 1961). Let $\nu(\mathbf{r}_j)=1$ if the jth perturber is with a volume $v(=a^3)$ of the oscillator and 0 otherwise. We define a function S by means of the equation

$$S=\sum_{j=1}^{N}\nu(\mathbf{r}_j)$$

from which it is seen that S takes on the values $0,1,\ldots,N$. The average value of $\exp(iS\delta\omega_0 t)$ is given by

$$\langle e^{iS\delta\omega_0 t}\rangle=\prod_{j=1}^{N}\langle e^{i\nu(\mathbf{r}_j)\delta\omega_0 t}\rangle=\sum_n P(n)e^{in\delta\omega_0 t},$$

where $P(n)$ is the probability there are n molecules in v. If we neglect correlations between perturbers, $P(n)$ is given by the Poisson distribution

$$P(n)=\frac{e^{-\bar{n}}\bar{n}^n}{n!},$$

where $\bar{n}=N_\nu v/V$. As a consequence we have

$$\begin{aligned}\langle e^{iS\delta\omega_0 t}\rangle&=e^{-\bar{n}}\exp(\bar{n}e^{i\delta\omega_0 t}),\\&=\exp\left[N_\nu\frac{v}{V}(e^{i\delta\omega_0 t}-1)\right]\end{aligned}\tag{68}$$

which is seen to be of the same form as (67).

As with the Gaussian modulation we can identify two limiting cases of (67). In the statistical limit the perturbers are assumed to be stationary. We express $\delta\omega_k$ in the form $h(r)$, where $h(r)$ is the fluctuation in frequency induced by a perturber a distance r from the oscillator. We then have

$$\left\langle\exp\left[i\int_0^t\delta\omega_k(t')dt'\right]-1\right\rangle_\delta=\frac{1}{V}\int_0^\infty 4\pi r^2dr(e^{ih(n)t}-1). \tag{69}$$

In the opposite limit it is assumed that the duration of the collision is small in comparison with the reciprocal of the frequency fluctuation. The integral $\int_0^t\delta\omega_0(t')dt'$ is approximated by a phase shift which depends on the impact parameter and the relative velocity of the perturber. The resulting expression for $\phi(t)$ is obtained by averaging over velocities and impact parameters and takes the form (Anderson, 1952)

$$\phi(t)=\exp[-|t|\bar{n}\bar{u}\sigma+i\bar{n}\delta t], \tag{70}$$

where $\bar{u}$ is the average speed, σ is the optical cross section, and δ is a parameter related to the average of the sine of the phase shift. Equation (70) leads to a Lorentzian line shape centered about $\omega_0+\bar{n}\delta$ with a width equal to $\bar{n}\bar{u}\sigma$.

In connection with FM modulation there are three comments which we want to make. First, the examples of Gaussian and Poisson modulation by no means exhaust the list of physically relevant stochastic models. For instance, there can be situations where the oscillator frequency fluctuates between a number of discrete values, a situation sometimes referred to as Markovian modulation (Anderson, 1954). Second, it is important to note that the Lorentzian line shape can arise in a variety of ways and that information on the deviation of a line shape from the Lorentzian form can often provide insight into the dynamics of the modulation. Finally, it is obvious that the FM broadening is not limited to harmonic oscillators but can be a linewidth mechanism for systems characterized by multiply periodic orbits.

H. The rigid rotator as an illustrative example

The two simplest dynamical systems to examine in connection with linebreadths, etc. are the harmonic oscillator and the rigid rotator. The former was studied in detail by Van Vleck and Margenau (1949), and anyway it is clear how it is a simple case of the foregoing general analysis. However, it is less obvious how the Debye formula for the rigid rotator fits into the general formalism for multiply periodic systems and the f-sum rule.

The well known formula of Debye is

$$\chi''(\omega)=\frac{N\mu^2\omega\Delta\omega}{3kT(\omega^2+\Delta\omega^2)}, \tag{71}$$

where μ is the dipole moment of a rigid molecule buffeted by collisions.

To obtain (71) it is clear in the first place that we must use formula (54) rather than (55), as the Debye formula pertains to low frequencies, where $\chi''(\omega)$ must contain, as previously discussed, a proportionality factor ω rather than $1/\omega$. For a simple rotating dipole there is but a single value of ω_τ, which we denote by ω_1. To obtain the Debye formula, one must make the additional assumption that ω_1 is small compared to ω for all states with an appreciable Boltzmann factor. This is possible if the moment of inertia, I, is sufficiently large, for the energy $J^2/2I$ has the average value kT, and so the prevalent values of $\omega_1 = dW/dJ$ are on the order of $(kT/I)^{1/2}$. When $\omega_1 \ll \omega$ we can consider expression (53) to be simply $\Delta\omega/\pi(\omega^2+\Delta\omega^2)$, independent of the value of J. Since we are dealing with a rotator rather than a particle, ex_τ and m in (54) are replaced by μ_{1x} and I. Furthermore because of the isotropy and permanence of the dipole moment, one has on account of Eq. (10)

$$\mu^2 = 2(|\mu_{1x}|^2 + |\mu_{1y}|^2 + |\mu_{1z}|^2), \\ = 6|\mu_{1x}|^2,$$

a relation likewise independent of J. So (54) indeed reduces to (71).

It is clear that the Debye formula cannot hold as soon as ω_1 becomes comparable with ω for appreciably inhabited states, as then the resonance will begin to manifest itself over a range of values of the angular momentum. Another type of approximation is appropriate when the states for which ω_1 and $|\omega|$ are comparable are well populated, and at the same time the linewidth is fairly narrow. To display this approximation, we first observe that, for the rotator, the explicit form of (54) is

$$\chi''(\omega) = \frac{\pi N \mu^2 \omega \int_0^\infty 2J \exp[-J^2/2IkT](f(\omega_1,\omega) + f(\omega_1,-\omega))dJ}{6kT\int_0^\infty 2J\exp[-J^2/2IkT]dJ}, \tag{72}$$

since for the present problem with two degrees of freedom the triple integral in the thermal average is replaced by a double integral $\int_0^\infty \cdots dJ \int_{-J}^{J} \cdots dJ_z$. The latter reduces to $\int_0^\infty \cdots 2JdJ$ as long as the integrand is isotropic. We now assume, contrary to the Debye case, that the variation of the f function is more drastic than that of the rest of the integrand. Then only the first or second f term need be considered, depending on whether ω is positive or negative. Since $\omega_1 = dW/dJ = J/I$ the variable of integration can immediately be changed from J to ω_1. The integral in the numerator of (72) is evaluated by treating the factor multiplying f as having the value appropriate to resonance. The integral in the denominator is elementary, and so (72) becomes

$$\chi''(\omega) = \frac{\pi N \mu^2 I \omega^3}{6k^2T^2|\omega|} e^{-I\omega^2/2kT}. \tag{73}$$

Expression (73) satisfies both the Kramers–Kronig relation and the f-sum rule, which for the present model takes the form

$$\int_{-\infty}^{\infty} \omega\chi''(\omega)d\omega = \frac{2N\pi\mu^2}{3I}. \tag{74}$$

The factor 2/3 occurs in (74) but not in (29) because the rotating dipole has only two degrees of freedom, rather than three as in the particle model previously used. The occurrence of μ^2/I in place of e^2/m is also a consequence of using a dipole rather than a particle model. It is not surprising that (73) yields both the Kramers–Kronig relation and the f-sum rule, as the linebreadth has dropped out completely from (73) and we showed in Sec. I.D that both of these relations are always valid when the absorption lines are treated as infinitely sharp.

The Debye formula (71) also applies as a limiting case even if one uses a more general model of a rigid rotating molecule with three unequal moments of inertia. The description of the motion can be quite complicated, as there are in general two different frequencies in the multiple Fourier expansion analogous to (1) and in general there are harmonics, so that one no longer has the simplification $\tau = \pm 1$. However, as long as all the ω_τ associated with appreciable amplitudes are small compared to ω, our derivation of (71) is still applicable inasmuch as $2\sum_{\tau\geq 0}(|\mu_{x\tau}|^2 + |\mu_{y\tau}|^2 + |\mu_{z\tau}|^2) = \mu^2$. With the asymmetrical top model there is no simple formula for the absorption coefficient analogous to (73) for frequencies comparable to ω_τ when the lines are narrow. The reason is that the system is not a simple unifrequentic one. However, the f-sum rule is valid and takes the form[9]

$$\int_{-\infty}^{\infty} \omega\chi''(\omega)d\omega = \frac{N\pi}{3}\left[\frac{\mu_1^2}{I_1} + \frac{\mu_2^2}{I_2} + \frac{\mu_3^2}{I_3}\right], \tag{75}$$

where μ_1, μ_2, μ_3 are the components of the dipole moment along the principal axes of inertia I_1, I_2, I_3.

II. QUANTUM MECHANICAL THEORY

A. Quantum theory of emission and absorption of radiation

Beginning in 1925, the development of quantum mechanics quickly led to a quantum theory of the absorption and emission of electromagnetic radiation. In 1927 Dirac published a paper with the title of this section where he presented a theory of the interaction of an atom with a quantized electromagnetic field, which reproduced Einstein's laws for the absorption and emission of radiation. A few months prior to this paper Dirac (1926) and Slater (1927)[10] published articles, written in 1926, in which they calculated absorption by what may be called a semiclassical model, in which the atom or molecule is handled quantum-mechanically, but with the external field treated as a time-dependent classical variable, so that the

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[9] To derive (75) it is most convenient to take as the variables of integration the Eulerian angles and the three momentoids $I_1\omega_1, I_2\omega_2, I_3\omega_3$, rather than the three momenta conjugate to these angles (cf. p. 35 of Van Vleck, 1932). By using momentoids one readily establishes that each squared term in the kinetic energy $\frac{1}{2}(I_1\omega_1^2 + I_2\omega_2^2 + I_3\omega_3^2)$ has the value $\frac{1}{2}kT$, and so the proof of (75) follows essentially the same procedure as used to establish the f-sum rule in the Cartesian case in the paragraphs following Eq. (49).

[10] A "note added in proof" in Slater's paper reads, "Dirac, Proc. R. Soc. **112**, 661 (1926), in a paper the author had not seen when the present note was sent in, treats absorption by a similar method. Since he does not discuss spontaneous radiation and since the discussion seemed somewhat fuller than his, it seemed better not to withdraw the present paper."

interaction with the radiation takes the form $exE(t)$, where x is a quantum-mechanical operator. A straightforward perturbation calculation, tantamount to the use of the "golden rule" formula,[11] and essentially equivalent to the procedure of Dirac and Slater, leads to the following expression for the net rate of absorption:

$$N\left\langle\frac{dW}{dt}\right\rangle_{\text{abs}} = 4\pi^2 Ne^2\omega u(\omega)\sum_{r,s} |\langle r|x|s\rangle|^2\delta(\hbar\omega - E_r + E_s) \times (P_s - P_r)\,. \tag{76}$$

Here $\langle r|x|s\rangle$ denotes the matrix element of the dipole moment operator between atomic levels r and s, with energies E_r and E_s, respectively. As in Part I, $u(\omega)$ is the energy density of the radiation field, while $\delta(\cdots)$ is the Dirac delta function. The symbols P_r and P_s denote the occupation probabilities of the two levels. When the atom is in thermal equilibrium these take the familiar form

$$P_r = \exp[-E_r/kT]\Big/\sum_s \exp[-E_s/kT]\,.$$

Equation (76) has a simple physical interpretation: the net rate of absorption is given by the average over the levels of the difference between the rate at which the energy of the electromagnetic field is reduced by processes where a photon is destroyed and the atom is promoted from state s to state r ($E_r > E_s$) and the rate at which it is increased by the inverse process in which a photon is created and the transition is from r to s. As is to be expected, (76) is in asymptotic agreement with the classical absorption formula (14), as one sees by noting that $x^2 = \frac{1}{3}d^2$ [Eq. (8)] and that $P_s - P_r$ approaches the limit $P_s\hbar\omega_{rs}/kT$ when $\hbar\omega_{rs}/kT$ is small.

The rate of spontaneous emission can be calculated from the classical formula

$$N\left\langle-\frac{dW}{dt}\right\rangle_{\text{emis}} = \frac{2}{}\frac{Ne^2\langle\dot{v}^2\rangle}{3c^3}\,, \tag{77}$$

using the Heisenberg matrix elements of $\dot{v}$. The result is

$$N\left\langle-\frac{dW}{dt}\right\rangle_{\text{emis}} = \frac{4Ne^2\hbar\omega_{rs}^4}{c^3}\sum_{r,s} P_r|\langle r|x|s\rangle|^2\delta(\hbar\omega - E_r + E_s)\,. \tag{78}$$

This expression can be regarded as the quantum analog of the classical formula (15).

By equating (76) and (78) we see that a balance between absorption and emission is obtained if the equation

$$4\pi^2e^2\omega_{rs}u(\omega_{rs})(P_s - P_r) = \frac{4e^2\hbar\omega_{rs}^4}{c^3}P_r$$

is satisfied for all pairs of levels connected by nonvanishing dipole matrix elements. Thus when the atom is in thermal equilibrium we obtain the result

$$u(\omega_{rs}) = \frac{\hbar\omega_{rs}^3}{\pi^2c^3}(P_s/P_r - 1)^{-1}\,,$$

$$= \frac{\hbar\omega_{rs}^3}{\pi^2c^3}(e^{\hbar\omega_{rs}/kT} - 1)^{-1}\,, \tag{79}$$

which agrees with the Planck distribution, Eq. (18).

Rather curiously, neither Dirac in his early paper nor Slater use (77) to obtain (78) and hence the balance between absorption and emission. Instead, Dirac did not try to treat spontaneous emission and said "one cannot take spontaneous emission into account without a more elaborate theory involving the positions of the various atoms and the interference of their individual emissions." Slater tried to handle spontaneous emission, but did so the hard way—not by using the relation (77) but instead by trying to incorporate in the wave equation the force on an electron due to its own radiation. He was able to obtain equilibrium only if the classical expression for this force was transcribed into quantum theory in a highly artificial way.

It was in 1927 that Dirac published his epoch-making paper on absorption and emission. His procedure and results can be described in either of two languages, viz. that of what we call ethereal oscillators or that of bosons. In the boson approach, the vacuum is treated as a carrier of light quanta which conform to the Einstein–Bose statistics, the essence of which is that there is no "which is which" effect, i.e., two light quanta which have different frequency and polarization lose their individuality and are counted only once. With the oscillator method, the vacuum is regarded as an ensemble of oscillators whose quantized energy levels are (apart from the "zero-point" energy $\frac{1}{2}\hbar\omega$) $0, \hbar\omega, 2\hbar\omega, \ldots$ with probabilities conforming to Boltzmann statistics, whereas the boson light quanta can only have the energy $\hbar\omega$. The identity of the results with the two approaches was evident in the old quantum theory in the original 1924 paper of Bose, and Dirac in his 1927 paper showed it also was true in quantum mechanics.

We prefer the oscillator method, partly because it avoids discussion of Bose–Einstein statistics, and partly because it seems to us more physical and easier to explain, but mainly because of the rather fascinating thread of historical continuity in attempts to treat radiation as an ensemble of oscillators. It is, however, doubtful whether Dirac was influenced by, or even familiar with, the early work of Jeans, though he was obviously acquainted with Bose statistics and Einstein's 1917 paper on stimulated emission. We are not alone in preferring oscillator language, for in Fermi's classic 1932 paper on the quantum theory of radiation, which appeared in this journal, based to a large extent on Dirac's work, the word boson or name Bose never appears. We use the term "ethereal oscillators" with some

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[11] By the "golden-rule" (Fermi's terminology), the probability of transition of an atom from state s to state r per unit time is $2\pi\hbar^{2}\rho_\omega|\langle r|H'|s\rangle|^2$ when subject to a perturbation of the form $\langle r|H'|s\rangle\exp(-i\omega t)$ where $\langle r|H'|s\rangle$ is the Heisenberg matrix element of the perturbing Hamiltonian exclusive of the time factor, and ρ_ω is the density of consecutive values ω at the frequency ω_{rs} [cf., for instance, Eq. (29.12) of Schiff, 1949]. In our case we take $\langle r|H'|s\rangle = e\langle r|x|s\rangle E_0$ and identify $4E_0^2/8\pi$ with one-third the radiation energy density $u(\omega)$. The factor 4 appears here because of the fact that there are equal electric and magnetic contributions to the energy and because there is a factor of 2 involved in the mean square of a Fourier series in exponential form [cf. Eq. (10)]. The factor 1/3 disappears when one sums the contributions from the x, y, and z components. When account is taken of the fact that each transition carries an energy $\hbar\omega$, one obtains a result in agreement with (76) when one integrates out the δ function in the latter.

reservation because ether is one of the few words that is taboo these days, as it is generally associated with the outmoded idea of absolute space and time. But this need not necessarily be the case, and our terminology seems to us more colorful and descriptive than the term "normal modes of a vacuum." The situation may be likened to agnostics wanting to ban any reference to the deity, because old-fashioned fundamentalism is incompatible with evolution and other scientific facts. The terminology we use is not without precedent. In his 1909 paper Jeans called his procedure a "semi-mechanical model of the aether."

The idea of treating the ether, or if you prefer, vacuum as an ensemble of oscillators is certainly not a new one. It is found in Rayleigh's 1900 article, though not spelled out very explicitly, as the whole paper encompassed only two pages. He had the proper dependence on T and ω in Rayleigh–Jeans law, $u(\omega)=a\omega^2T$, but did not attempt to evaluate the constant of proportionality, which is $a=(k/\pi^2c^3)$ in our system of units [Eq. (18)]. He did make an attempt in 1905, but as noted by Jeans (1905), was wrong by a factor of 8. The energy density is then simply the density of modes at a given frequency multiplied by kT. Jeans obtained the Rayleigh–Jeans law with the proper proportionality factor in 1905 and presented the analysis more fully in 1909, as did Lorentz in 1908. At about that time it was natural to replace the factor kT by the mean energy of a harmonic oscillator. Then out comes the Planck radiation formula. This Debye pointed out in a 1910 paper which may be regarded as the radiation analog of his procedure for treating the specific heat of solids. As a matter of fact Planck in 1901 had a similar expression for the factor replacing kT (and also had the correct proportionality factor), but he used a somewhat different procedure in his paper. In his approach, which can be regarded as the beginning of the old quantum theory, Planck used a harmonic oscillator model for matter in equilibrium with the ether.

If one is interested only in the derivation of the Planck formula with ethereal oscillators and is not concerned with the interaction of the Planck-distributed radiation with matter, nothing substantially new has been added since 1910. The number of normal modes of course remains the same. In quantum mechanics the oscillators have a zero-point energy $\frac{1}{2}\hbar\omega$ not found in the old quantheory, but this turns out to be irrelevant, as we discuss later.

The reason that Dirac's 1927 paper was a landmark was that it was the first to bring to light the wonderful results that come out of the interaction between matter and a set of ethereal oscillators when the latter are treated quantum mechanically. The reason for this success is what we may call the $(n+1)/n$ effect, as is evident from the following. One of the most elementary results of quantum mechanics is that for a harmonic oscillator the matrix element of the amplitude connecting two states of vibrational quantum number n and $n+1$ is proportional to $(n+1)^{1/2}$. Similarly joining n and $n-1$ involves $n^{1/2}$ with the same constant of proportionality. When an atom or molecule makes a transition from a state of higher energy to one of lower energy because of interaction with radiation it must be counterbalanced by a transition of an ethereal oscillator of the upward type $n\to n+1$ rather than the downward variety $n\to n-1$, inasmuch as conservation of energy requires that a decrease in the energy of the atom must be offset by an increase in the energy of something else. By a similar argument, a transition of the atom from a state of lower to higher energy must be associated with an oscillator transition of the type $n\to n-1$. Since the transition probability is proportional to the square of the amplitude, and since the dipole factor arising from the atom itself is Hermitean, it follows that the emissive and absorptive probability coefficients associated with a given pair of states differ by a factor $(\langle n\rangle_{\text{av}}+1)/\langle n\rangle_{\text{av}}$, where $\langle n\rangle_{\text{av}}$ is the statistical average for the vibrational quantum number of the ethereal oscillator of appropriate frequency and polarization (in the boson particle picture $\langle n\rangle_{\text{av}}$ is the average number of light quanta).

The extra term $+1$ found in the emissive case is naturally interpreted as representing spontaneous emission, inasmuch as it persists at $T=0$ where the conventional energy density $u(\omega)$ vanishes [cf. Eq. (79)]. The terms proportional to $\langle n\rangle_{\text{av}}$ are the same in both directions, corresponding to the fact that the Einstein probability coefficients are the same for absorption and induced emission. For a quantum mechanical oscillator the value of $\langle n\rangle_{\text{av}}$ is $[\exp(\hbar\omega/kT)-1]^{-1}$ and so has the same dependence on temperature as the Planck formula for the energy density. In this connection it is to be noted that this density has a factor $\langle n\rangle_{\text{av}}$ rather than $(\langle n\rangle_{\text{av}}+\frac{1}{2})$ which appears in the mean energy of a quantum mechanical oscillator. In other words the zero-point energy is not involved in formula (79) for $u(\omega)$, so that the radiation energy vanishes properly at $T=0$. (It should, however, be noted that it is essentially the zero-point energy that supplies the extra coupling responsible for spontaneous emission.) If we assume that the radiation energy density is that appropriate to thermal equilibrium (i.e., Planck's law is valid) then the ratio of the induced to the spontaneous emission for a given transition from a given atomic state is $[\exp(\hbar\omega/kT)-1]^{-1}$. This is precisely the proper value, in agreement with the Einstein relation between the A and B coefficients [cf. Eq. (17a)] inasmuch as the spontaneous and stimulated emission are in general given by A and Bu. Furthermore even if the radiation field happens to be different from the ideal, blackbody case the relation between spontaneous emission and absorption or induced emission will retain the proper (now nonequilibrium) value. This happened because the spontaneous emission remains the same while the absorption and induced emission will be proportional to the average vibrational quantum number and hence to the energy density irregardless of the probability distribution associated with the levels of the ethereal oscillator.

It is almost miraculous the way spontaneous emission comes out of the $(n+1)/n$ effect, and in most of the literature its basic simplicity is obscured in the mass of general theory connected with absorption and emission. Only the most rudimentary quantum mechanics of the harmonic oscillator is needed. In fact Thomas (1925) [cf. also Reiche and Thomas (1925)] had deduced the transition probabilities for the harmonic oscillator, and hence the $(n+1)/n$ ratio, from the f-sum rule even before the appearance of Heisenberg's "breakthrough" paper into quantum mechanics. By contrast, the semiclassical treatment of spontaneous emission by use of the electrodynamic expression $2\dot{v}^2/3c^3$ for the rate of radiation implicitly involves all the apparatus of electrodynamic theory, retarded potentials, etc., as they enter in connection with the derivation of this expression. Also, with this approach, as Slater found out, there is no simple wave-mechanical transcription of the Lorentz calculation of the force on an electron due to its own radiation.

One of us remembers about fifty-five years ago how one well known American mathematical physicist told him that the Jeans enumeration of the normal modes of the ether should be regarded as sheer mathematical formalism, devoid of any physical significance. On the other hand he also recalls reading somewhere recently how Oppenheimer was in a state of almost delirious ecstasy after reading Dirac's paper based on this enumeration be it with bosons or oscillators. It is certainly obvious now which attitude was the right one.

One thing remains for us to do. We have shown that the oscillator model gives the right ratio of spontaneous emission to absorption. To complete the picture we must show that this model gives the correct absolute value of absorption. To do this we merely have to invoke the semiclassical calculation of absorption. The Fourier series used there to describe the radiation field can be regarded as simply the sum of the displacement coordinates of an ensemble of classical harmonic oscillators. The absorption contains a factor of kT if the mean energy of each oscillator is given the classical equipartition value, but this factor becomes $\hbar\omega[\exp(\hbar\omega/kT)-1]^{-1}$ if the oscillators are quantized in the 1910 fashion. In other words, in the semiclassical treatment, the coupling to the radiation field can be described by quantized classical oscillators. Substitution of the true quantum-mechanical ones introduces essentially the $(n+1)/n$ effect, and if we write off the +1 term as yielding spontaneous emission, the residue agrees with what is obtained with the semiclassical approach. Dirac (1958) expresses this thought in somewhat different language when he says "the two theories differ only in that the field quantities all commute with one another in the elementary (semiclassical) theory, and satisfy definite commutation relations in the present (quantum-mechanical) theory, and this difference becomes unimportant for strong fields (i.e., when we can neglect 1 in comparison with n in our $(n+1)/n$ effect). Thus the two theories must give the same absorption and emission when strong fields are concerned. Since both theories give the rate of absorption proportional to the intensity of the incident beam, the agreement must hold also for weak fields in the case of absorption. In the same way the stimulated part of the emission in the present theory must agree with the emission in the elementary theory."

Fermi, and also Dirac in the various editions of his book (though not in his 1927 paper), used the language of the vector potential rather than the field strength as we do. They therefore took the interaction with the radiation to be not $exE(t)$, but rather

$$\frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})+\frac{e^2}{2mc}2\mathbf{A}\cdot\mathbf{A}$$

where $\mathbf{p}$ is the momentum operator of the electron and $\mathbf{A}$ is the vector potential operator, which is related to the electric and magnetic field operators through the equations

$$\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}\,, \tag{80a}$$

$$\mathbf{H}=\nabla\times\mathbf{A}\,. \tag{80b}$$

If only linear terms in $\mathbf{A}$ are retained in the interaction, then it is readily shown that the results are the same as regards absorption and emission as are obtained by simply taking the perturbation proportional to the field strength as we did. The quadratic terms are of interest primarily in scattering, a fact nicely brought out in Fermi's article (1932).

The method based on field strength which we employed is somewhat simpler, at least superficially, than that utilizing the vector potential, but lacks the latter's elegance and completeness. In particular, introduction of the vector potential enables one to handle the electric and magnetic fields simultaneously. Maxwell's equations show that there cannot be a time-dependent electric field without there being a magnetic one, and vice versa. Our presentation has been on the basis that there is only an electric field, which is tantamount to assuming that the external magnetic forces on the electron are negligible compared with the electric ones. With minor modifications, our calculations can be adapted to the other limiting case where the external magnetic field is more important than the electric one, so that one is dealing with a magnetic rather than an electric susceptibility. It should be pointed out that we tacitly assumed $E=H$ in the relations connecting field strength and energy density. The procedure with the vector potential enabled Fermi to write down an oscillator-type Hamiltonian function for the radiation fields in which the electric field energy is the kinetic term and the magnetic the potential term (or vice versa—the procedure is such a formal one that there is no real way of deciding which is which). However it is not really necessary to invoke the vector potential, as it was not employed in Jeans' 1909 "semimechanical model of the aether," which had essentially this type of Hamiltonian function.

In terminating the present section it should be mentioned that despite its many successes, the quantum theory of radiation is not without its Achilles heel, viz. the infinite self-energy which results from the interaction of an electron with the radiation field, be it oscillators or bosons. Such a difficulty was first pointed out by Weisskopf and Wigner in 1930. This infinity, which must be written off the books, like the energy of the sea of states of negative energy of the Dirac electron, must be regarded as one of the imperfections or mysteries of present day physics.

B. Correlation functions and the fluctuation-dissipation theorem

In the equations presented in the preceding section the symbols $r, s, \ldots$ referred to levels of the isolated atom or molecule. However the equations are equally valid for atoms perturbed by collisions, provided the levels are interpreted as states of the coupled system of the atom and its perturbers. Because the eigenstates of the coupled system are not usually known, Eqs. (76) and (78), while exact, are not particularly illuminating or useful. When collisions are important the equations for the absorption and emission are much more easily handled when written in terms of correlation functions analogous to those introduced in the classical calculations in Sec. I.E. The changeover to a description involving correlation functions takes several steps. We illustrate them using spontaneous emission as an example. Since $\langle r|x|s\rangle = \langle s|x|r\rangle^*$ (x is a Hermitian operator) we have

$$\sum_{r,s} P_r\,|\langle r|x|s\rangle|^2\delta(\hbar\omega - E_r + E_s) = \sum_{r,s} P_r\langle r|x|s\rangle\langle s|x|r\rangle \times(\hbar\,\omega - E_r + E_s)\,.$$

Using the integral representation of the delta function

$$\delta(y) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-iyt}\,dt\,,$$

we can rewrite the right-hand side of the above equation in the form

$$\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\,e^{-i\omega t}\sum_{r,s} P_r\,\langle r|\,e^{iE_r t/\hbar}\,x e^{-iE_s t/\hbar}\,|s\rangle\langle s|x|r\rangle = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\,e^{-i\omega t}\sum_{r,s} P_r\langle r|\,x(t)|\,s\rangle\langle s|x|r\rangle\,.$$

Here $x(t)$ denotes the dipole operator in the Heisenberg picture

$$x(t) = \exp(i\mathcal{H}t/\hbar)x\exp(-i\mathcal{H}t/\hbar)\,,$$

where $\mathcal{H}$ is the Hamiltonian operator. By making use of the symbolic identity

$$\sum_r |r\rangle\langle r| = 1\,,$$

where the sum is over a complete set of states, we finally obtain the equation

$$\sum_{r,s} P_r|\langle r|x|s\rangle|^2\delta(\hbar\omega - E_r + E_s) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dte^{-i\omega t}\langle x(t)x(0)\rangle\,.$$

In this expression the symbol $\langle\theta'\rangle$ refers to the average

$$\langle O\rangle = \sum_r P_r\langle r|O\,|r\rangle\,, \qquad = \mathrm{Tr}(e^{-\mathcal{H}/kT}O)/\mathrm{Tr}e^{-\mathcal{H}/kT}\,,$$

where Tr signifies the trace operation.

When written in terms of correlation functions the expression for the absorption becomes

$$N\langle dW/dt\rangle_{\mathrm{abs}} = \frac{2\pi Ne^2\omega}{\hbar}u(\omega)\int_{-\infty}^{\infty} dte^{-i\omega t}[\langle x(0)x(t)\rangle - \langle x(t)x(0)\rangle]\,, \tag{81}$$

where $\langle x(0)x(t)\rangle$ and $\langle x(t)x(0)\rangle$ correspond to the terms with P_s and P_r, respectively, in Eq. (76). Likewise for the emission we have

$$N\langle -dW/dt\rangle_{\mathrm{emis}} = \frac{2Ne^2\omega^4}{\pi c^3}\int_{-\infty}^{\infty} dte^{-i\omega t}\langle x(t)x(0)\rangle\,. \tag{82}$$

Although in general we cannot equate $\langle x(t)x(0)\rangle$ and $\langle x(0)x(t)\rangle$ there is an important relation between the Fourier transforms of the two correlation functions, which is sometimes referred to as the fluctuation–dissipation theorem (Callen and Welton, 1951; Kubo, 1957). As shown in the appendix to our previous paper (1966) we have

$$\int_{-\infty}^{\infty} dt\,e^{-i\omega t}\langle x(0)x(t)\rangle = \exp[\hbar\omega/kT]\int_{-\infty}^{\infty} dt\,e^{-i\omega t}\langle x(t)x(0)\rangle\,. \tag{83}$$

With the help of (83) it is possible to express both the absorption and the emission in terms of the Fourier transform of the symmetrized correlation function $\langle x(0)x(t) + x(t)x(0)\rangle$, which we write as

$$\mathcal{R}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\,e^{-i\omega t}\langle x(0)x(t) + x(t)x(0)\rangle\,. \tag{84}$$

Using (83) and (84) in (81) and (82) we obtain the results

$$N\langle dW/dt\rangle_{\mathrm{abs}} = 4\pi^2Ne^2\hbar^{-1}\omega u(\omega)\tanh(\hbar\omega/2kT)\mathcal{R}(\omega)\,, \tag{85}$$

$$N\langle -dW/dt\rangle_{\mathrm{emis}} = 4Ne^2\omega^4c^{-3}(e^{\hbar\omega/kT} + 1)^{-1}\mathcal{R}(\omega)\,, \tag{86}$$

which lead directly to the equality between absorption and emission when the radiation field is in thermal equilibrium.

The use of correlation functions to characterize the absorption and emission in both the quantum and the classical analyses suggests an alternative statement of the correspondence principle which we write as

$$\tfrac{1}{2}\langle x_{\mathrm{op}}(t)x_{\mathrm{op}}(0) + x_{\mathrm{op}}(0)x_{\mathrm{op}}(t)\rangle \to \langle x(0)x(t)\rangle\,, \tag{87}$$

where the subscript op has been added to emphasize that the left-hand side of (87) is a correlation function associated with the operator x, whereas on the right-hand side x denotes the classical variable.

C. Susceptibility and sum rules

By making use of Eq. (23), which connects the absorption with the imaginary part of the susceptibility, and the expression for $\langle dW/dt\rangle_{\mathrm{abs}}$ given in Eq. (81) we obtain the equation

$$\chi''(\omega) = \frac{Ne^2}{2\hbar}\int_{-\infty}^{\infty} dt\,e^{-i\omega t}[\langle x(0)x(t)\rangle - \langle x(t)x(0)\rangle]\,. \tag{88}$$

Because of the fluctuation–dissipation theorem we can rewrite (88) in the form

$$\chi''(\omega) = \frac{Ne^2\pi}{\hbar}\tanh(\hbar\omega/2kT)\mathcal{R}(\omega)\,, \tag{89}$$

where $\mathcal{R}(\omega)$, the Fourier transform of the symmetrized correlation function, is given by Eq. (84). Equations (88) and (89) are the quantum-mechanical counterparts of the classical expression for the susceptibility obtained in Part I. The derivation of $\chi''(\omega)$ given here was based on a calculation of the net rate of absorption from the field, and is to be contrasted with an alternative derivation, given in Appendix A of our earlier paper (1966). In the latter approach an expression for the susceptibility was obtained by calculating the first-order change in polarization arising from a time-dependent external field. The two derivations lead to the same expression for $\chi''(\omega)$ [cf. Eq. (A10) of the 1966 paper]; however, the calculation based on an analysis of the polarization gives the real part of the susceptibility as well.

We now turn to a discussion of the sum rules for $\chi''(\omega)$. Of the two mentioned in Part I the easiest to establish is the f-sum rule. From (88) we obtain the result

$$\int_{-\infty}^{\infty}\omega\chi''(\omega)d\omega = \frac{Ne^2}{2\hbar}\int_{-\infty}^{\infty}\omega d\omega\int_{-\infty}^{\infty} dt\,e^{-i\omega t}[\langle x(0)x(t)\rangle - \langle x(t)x(0)\rangle]\,, = \frac{-iN\pi e^2}{\hbar}\left\langle x\left(\frac{dx}{dt}\right) - \left(\frac{dx}{dt}\right)x\right\rangle. \tag{90a}$$

In the Heisenberg picture $dx/dt = (i/\hbar)[\mathcal{H}, x] = p/m$ for a particle of mass m. Thus (90) reduces to

$$\int_{-\infty}^{\infty} \omega\chi''(\omega)d\omega = \frac{-iN\pi e^2}{m\hbar}\langle xp - px\rangle = \frac{N\pi e^2}{m} . \tag{90b}$$

From (90b) it is evident that just as in the classical theory the f-sum rule is nonstatistical in nature. Because of the fundamental commutation relations the expression appearing inside the brackets in (90b) has the value $i\hbar$ independent of the levels involved in the thermodynamic averaging.

In the analysis of the Kramers–Kronig relations presented in Part I it was tacitly assumed that the static limit of $\chi'(\omega)$ could be identified with the isothermal susceptibility χ_T. While this is the case for all practical purposes there are so-called non-ergodic model systems where $\chi'(0) \neq \chi_T$ (Falk, 1968). As shown in the appendix to our earlier paper [1966, Eq. (A11)], the analysis of the induced polarization leads directly to an expression for $\chi'(\omega)$ which satisfies the Kramers–Kronig relations. As a result we can express $\chi'(\omega)$ in terms of $\chi''(\omega)$ by means of the integral

$$\chi'(\omega) = \frac{\mathcal{P}}{\pi}\int_{-\infty}^{\infty} d\omega \frac{\chi''(\omega)}{\omega' - \omega} , \tag{91}$$

where $\mathcal{P}$ denotes the principal value, and $\chi''(\omega)$ is given by Eq. (89).

We identify the $\omega = 0$ limit of (91) with the isothermal response to a static field. A general expression for the low field limit of the isothermal susceptibility is obtained by adding to the Hamiltonian a term $-exE$ and calculating the resulting polarization $N\langle ex\rangle$ to first order in E. The result takes the form (Van Vleck, 1927)

$$\chi_T = \frac{e^2}{ZkT}\left\{\sum_R e^{-E_R/kT}|\langle R|X|R\rangle|^2 + \sum_{\substack{R\neq S\\ E_R = E_S}} e^{-E_R/kT}|\langle R|X|S\rangle|^2 - 2kT\sum_{\substack{R\neq S\\ E_R \neq E_S}} e^{-E_R/kT}\frac{|\langle R|X|S\rangle|^2}{(E_R - E_S)}\right\} , \tag{92}$$

provided there is no spontaneous polarization. Here Z denotes the partition function and $eX = e\sum_i x_i$ is the total dipole moment operator of the ensemble of N molecules whose energy levels we denote by R and S. The restrictions on the summations, $E_R = E_S$ and $E_R \neq E_S$, refer to exactly degenerate and nondegenerate levels, respectively. Strictly speaking, $\chi'(0)$, which is often referred to as the isolated susceptibility, is given by the third term in the above expression (Falk, 1968; Morita and Katsura, 1969). However, in real systems the interactions between the molecules and with stray fields will remove virtually all of the degeneracies. When this happens in a system made up of a large number of molecules the contributions from the first and second terms in (92) are negligible in comparison with that from the third, so that $\chi'(0)$ and χ_T are essentially equal.[12] Moreover when $\chi_T(0) \neq \chi'(0)$ it is not clear how χ_T could ever be measured experimentally. All measurements of the isothermal susceptibility are carried out over finite intervals of time and thus involve in effect time-dependent fields, albeit of very low frequencies.

In the approach taken in this review we treat the molecules as independent subsystems (apart from perturbations associated with the linewidth). In this approximation the susceptibility is equal to N times the susceptibility of a single subsystem, i.e.,

$$\chi_T = \frac{Ne^2}{ZkT}\left\{\sum_r e^{-E_r/kT}|\langle r|x|r\rangle|^2 + \sum_{\substack{r\neq s\\ E_r = E_s}} e^{-E_r/kT}|\langle r|x|s\rangle|^2 - 2kT\sum_{\substack{r\neq s\\ E_r \neq E_s}} e^{-E_r/kT}\frac{|\langle r|x|s\rangle|^2}{(E_r - E_s)}\right\} , \tag{93}$$

where r and s refer to levels of the unperturbed molecule. It is interesting to note that the formal equivalence of χ_T and $\chi'(0)$ cannot be established from (93). It is necessary to base the analysis on (92), which involves the exact eigenstates of the coupled system of N molecules and their perturbers.

In addition to the f-sum rule and the Kramers–Kronig relation there is another sum rule which is connected with the fluctuation-dissipation theorem. If we multiply the expression for $\chi''(\omega)$ given in Eq. (89) by $\coth(\hbar\omega/2kT)$ and integrate from $-\infty$ to $+\infty$ we obtain the result

$$\frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\omega \coth(\hbar\omega/2kT)\chi''(\omega) = Ne^2\langle x^2\rangle , \tag{94}$$

which can be regarded as a generalization of the Nyquist relation connecting the resistivity with the fluctuations in the current (Nyquist, 1928; Callen and Welton, 1951).[13] The distinction between (94) and the static limit of (91) appears only in the quantum-mechanical regime. In the classical limit, $\hbar \to 0$, $\coth(\hbar\omega/2kT) \to (2kT/\hbar\omega)$, the Kramers–Kronig relation and the generalized Nyquist theorem are equivalent since

$$\chi_T = Ne^2\frac{\langle x^2\rangle}{kT} ,$$

for unpolarized classical electrons.

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[12] When the system is polarized either spontaneously or by a biasing field it is necessary to distinguish between the adiabatic and isothermal susceptibilities. If the thermal relaxation time characterizing the interaction between the molecules and the bath, T_1, is long in comparison with the relaxation time associated with intermolecular interactions, $T_2, \chi'(\omega)$ will be equal to χ_T in the region $0 \ll \omega \ll 1/T_1$. On the other hand, in the region $1/T_1 \ll \omega \ll 1/T_2, \chi'(\omega)$ will be approximately the same as the adiabatic susceptibility (Gorter, 1947).

[13] The validity of the generalized Nyquist relation has been studied by one of us recently (Huber, 1977) with the conclusion that the precise statement of the relation takes the form

$$\left(\frac{\hbar}{2\pi}\right)\int_{-\infty}^{\infty} d\omega \coth(\hbar\omega/2kT)\chi''(\omega) = Ne^2(\langle x^2\rangle - \langle x\rangle^2) + kT(\chi'(0) - \chi_T) ,$$

which reduces to (94) when the electrons are unpolarized and $\chi'(0) = \chi_T$.

D. Quantum mechanical theory of the rotating dipole

In this section we apply the general theory developed in the preceding sections to the rotating dipole. The Hamiltonian for the unperturbed dipole is written

$$\mathcal{H}=\frac{\hbar^2\mathbf{J}^2}{2I}\,, \tag{95}$$

where $\mathbf{J}$ is the angular momentum operator, and I is the moment of inertia. The energy levels of the system are given by

$$E_J=(\hbar^2/2I)J(J+1)\,,\quad J=0,1,2,\ldots \tag{96}$$

and are $2J+1$-fold degenerate. The corresponding state vectors are denoted by $|JM_J\rangle$ with $-J\leqslant M_J\leqslant J$.

Before analyzing the dynamics we calculate the isothermal susceptibility from Eq. (92). We take the axis of quantization to be in the x direction and identify ex with $\mu\cos\theta$, where θ is the angle between the axis of the dipole and the x direction, and μ is the dipole moment. Because of parity and angular momentum selection rules only matrix elements of the type $\langle M_J J\pm 1|\cos\theta|JM_J\rangle$ are nonvanishing. After an elementary calculation we obtain the result (Van Vleck, 1932)

$$\chi_T=\frac{2NI\mu^2}{3\hbar^2Z}\,, \tag{97}$$

where the partition function is given by

$$Z=\sum_{J=0}^{\infty}(2J+1)e^{-E_J/kT}\,. \tag{98}$$

In the high-temperature limit, $Z=2IkT/\hbar^2$ so that $\chi_T=N\mu^2/3kT$, the familiar classical value. In the opposite limit, $Z=1$ so that χ_T has the limiting value $2NI\mu^2/3\hbar^2$ at zero temperature.

The calculation of the dynamic susceptibility in the absence of perturbing interactions is also straightforward. From Eqs. (84) and (89) we obtain the exact result

$$\begin{aligned}\chi''(\omega)=&\frac{N\pi I\mu^2}{3\hbar^2Z}\tanh(\hbar\omega/2kT)\\&\times\sum_{J=0}^{\infty}(e^{-E_J/kT}+e^{-E_{J+1}/kT})(E_{J+1}-E_J)\\&\times[\delta(E_{J+1}-E_J-\hbar\omega)+\delta(E_{J+1}-E_J+\hbar\omega)]\,.\end{aligned} \tag{99}$$

Equation (99) is seen to be an infinite series of delta functions at frequencies corresponding to the energy differences between adjacent rotational levels. In the high-temperature limit we can approximate the sum over angular momentum states by a corresponding integral, i.e.,

$$\sum_{J=0}^{\infty}(2J+1)\to 2\int_0^{\infty}J\,dJ\,,$$

so that $\chi''(\omega)$ reduces to

$$\chi''(\omega)=\frac{N\pi I\mu^2\omega^3}{6k^2T^2|\omega|}\,e^{-I\omega^2/2kT}\,, \tag{100}$$

which is identical to the expression given in Eq. (73).

Equation (99) is an exact result. As a consequence $\chi''(\omega)$ satsifies the various sum rules discussed in II.C. Thus we have

$$\begin{aligned}\chi'(0)&=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\chi''(\omega)}{\omega}\,d\omega\,,\\&=\frac{2NI\mu^2}{3\hbar^2Z}=\chi_T\,.\end{aligned} \tag{101}$$

The f-rule also has a simple form. From (90) we have

$$\int_{\infty}^{\infty}d\omega\,\omega\chi''(\omega)=\frac{-iN\pi}{\hbar}\left\langle\mu_x\left(\frac{d\mu_x}{dt}\right)-\left(\frac{d\mu_x}{dt}\right)\mu_x\right\rangle\,.$$

By making use of the equation of motion for μ_x, $d\mu_x/dt=(i\hbar)[\mathcal{H},\mu_x]$, and the commutation relations between $\mathbf{J}$ and $\boldsymbol{\mu}$, which can be expressed as (Landau and Lifshitz, 1958)

$$\mathbf{J}\times\boldsymbol{\mu}=i\boldsymbol{\mu}\,, \tag{102}$$

we obtain the result

$$\int_{-\infty}^{\infty}d\omega\,\omega\chi''(\omega)=\frac{N\pi}{\hbar^2}\left\langle\frac{\hbar^2}{I}\,(\mu_y^2+\mu_z^2)\right\rangle\,. \tag{103}$$

Because of the isotropy of the thermal averages and the fixed magnitude of the dipole moment Eq. (103) reduces to

$$\int_{-\infty}^{\infty}d\omega\,\omega\chi''(\omega)=\frac{2N\pi\mu^2}{3I}\,, \tag{104}$$

which agrees with the classical value given by Eq. (74). In addition, we note that the generalized Nyquist relation is equally simply in form. From Eq. (94) we have

$$\frac{\hbar}{2\pi}\int_{\infty}^{\infty}d\omega\coth\left(\frac{\hbar\omega}{2kT}\right)\chi''(\omega)=\frac{N\mu^2}{3}\,, \tag{105}$$

as can be verified from (99).

As might be anticipated from the classical analysis in Sec. I, the delta functions characterizing the susceptibility of the unperturbed dipoles are broadened by "collisions" with perturbers. Just as in the classical case the effects of collisions can frequently be simulated by stochastic models similar to those discussed in Sec. I.F and I.G. In the case of the dipole, a particularly simple model of collision broadening is obtained by adding to the Hamiltonian a time-dependent perturbation of the form

$$\mathcal{H}'(t)=J_xA_x(t)+J_yA_y(t)+J_zA_z(t)\,, \tag{106}$$

where the functions $A_k(t)$ satisfy the conditions

$$\langle A_k(t)\rangle_A=0\,, \tag{107a}$$

$$\langle A_j(t)A_k(t')\rangle_A=\delta_{jk}\,g(|t-t'|)\,, \tag{107b}$$

in which $\langle\cdots\rangle_A$ denotes an average over the fluctuations. Since the unperturbed Hamiltonian commutes with $\mathcal{H}'$, the perturbations bring about random reorientations of the dipole without changing its rotational energy. Thus the model is suitable only for characterizing elastic collisions.

To obtain an approximate expression for $\chi''(\omega)$ we make use of the representation in terms of the Fourier transform of the symmetrized correlation function [Eq. (89)]. The expansion of the correlation function leads to terms of the form

$$\langle M_J J|\mu_x|J'M_{J'}\rangle\langle M_{J'}J'|e^{i\mathcal{H}t/\hbar}\left\langle\exp\left[(i/\hbar)\int_0^t\mathcal{H}'(t')dt'\right]\mu_x\exp\left[-(i/\hbar)\int_0^t\mathcal{H}'(t')dt'\right]\right\rangle_A e^{-i\mathcal{H}t/\hbar}|JM_J\rangle,$$

where we have made use of the property that $\mathcal{H}$ and $\mathcal{H}'$ commute in order to factor the exponential. At this point we specialize to Gaussian modulation. In the Gaussian approximation we keep only terms up to order $(\mathcal{H}')^2$ in the expansion of the logarithm of the expression in angular brackets. We have

$$\ln\left\langle\exp\left[(i/\hbar)\int_0^t\mathcal{H}'(t')dt'\right]\mu_x\exp\left[-(i/\hbar)\int_0^t\mathcal{H}'(t')dt'\right]\right\rangle_A$$

$$=\ln\mu_x+(i/\hbar)\int_0^t dt'\,\langle\mathcal{H}'(t)\mu_x-\mu_x\mathcal{H}'(t')\rangle_A/\mu_x$$

$$-\tfrac{1}{2}\int_0^t dt'\int_0^t dt''[\langle\mathcal{H}'(t')\mathcal{H}'(t'')\mu_x\rangle_A+\langle\mu_x\mathcal{H}'(t'')\mathcal{H}'(t')\rangle_A-2\langle\mathcal{H}'(t')\mu_x\mathcal{H}'(t'')\rangle_A]/\mu_x$$

$$+\tfrac{1}{2}\left(\int_0^t dt'\langle\mathcal{H}'(t')\mu_x-\mu_x\mathcal{H}'(t')\rangle_A/\mu_x\right)^2+\cdots,$$

By making use of the commutation relations between $\boldsymbol{\mu}$ and $\mathbf{J}$ and the statistical properties of the fluctuations displayed in Eq. (107), it can be shown that the above expression reduces to

$$\ln\mu_x-2\int_0^t(t-\tau)g(\tau)dt.$$

As a consequence, the result of averaging the correlation function over the perturbations is to modulate the unperturbed dipole moment correlation function by the overall factor $\exp[-2\int_0^t(t-\tau)g(\tau)d\tau]$. Thus in place of the delta functions in (99) we have the functions $(1/\hbar)f((E_{J+1}-E_J)/\hbar,\pm\omega)$, which are given by

$$f(x,x_0)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{it(x-x_0)}\exp\left[-2\int_0^t(t-\tau)g(\tau)d\tau\right],\tag{108}$$

a result similar to that following from Eqs. (62) and (64) of Sec. I.G.

There are two features of our stochastic model which deserve further comment. First, the modulation factor we derive is independent of the angular momentum states involved in the transition. Second, by working with the symmetrized correlation function we obtain an approximate expression for $\chi''(\omega)$ which rigorously satisfies the generalized Nyquist relation [Eq. (105)]. However the Kramers–Kronig relation (101) and the f- sum rule (104) are only approximately satisfied.

For other attempts to treat the rigid rotators inclusive of both inertial and collisional effects, the reader is referred to a paper by Calderwood *et al.* (1976) and references included therein; see also Gross (1955b).

ACKNOWLEDGMENT

We are indebted to Professor Paul C. Martin for helpful discussions.

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