THE ABSORPTION OF RADIATION BY MULTIPLY PERIODIC ORBITS, AND ITS RELATION TO THE CORRESPONDENCE PRINCIPLE AND THE RAYLEIGH-JEANS LAW.

PART I. SOME EXTENSIONS OF THE CORRESPONDENCE PRINCIPLE

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Abstract

This part deals with the quantum theory aspects of the problem. In the absence of external radiation fields the distortion in the shape of the orbit is essentially the same in both the classical and quantum theories provided in the former we retain only one particular term τ_1, τ_2, τ_3 in the multiple Fourier expansion of the force $2e^2\ddot{v}/3c^3$ on the electron due to its own radiation. The term to be retained is, of course, the combination overtone asymptotically connected to the particular quantum transition under consideration. Then the changes ΔJ_1, ΔJ_2, ΔJ_3 in the momenta J_k which fix the orbits and which in the stationary states satisfy the relations $J_k = n_k h$, are in the ratios of the integers τ_1, τ_2, τ_3 in both the classical and quantum theories, making the character of the distortion the same in both even though the speed of the alterations may differ. One particular term in the classical radiation force is thus competent to bring an orbit from one stationary state to another.

The correspondence principle is then extended so as to include absorption as well as the spontaneous emission ordinarily considered. Commencing always with a given orbit it is possible to pair together the upward and downward transitions in such a way that in each pair the upward and downward optical frequencies (determined by the $h\nu$ relation) are nearly equal for large quantum numbers (usually long wave-lengths). That is, if s denotes the initial orbit there exist levels r and t such that the ratio $(W_r - W_s)/(W_s - W_t)$ or ν_{rs}/ν_{st} approaches unity when the quantum numbers become large. We shall define as the differential absorption the excess of positive absorption due to the upward transition $s \rightarrow r$, over the negative absorption (induced emission) for the corresponding downward transition $s \rightarrow t$. It is proved that for large quantum numbers the classical theory value for the ratio of absorption to emission approaches asymptotically the quantum theory expression for the ratio of the differential absorption to the spontaneous emission. Consequently a correspondence principle which makes the numerical values of the emission in the two theories agree asymptotically, of necessity achieves a similar connection for the absorption.

The correspondence principle basis for a dispersion formula proposed by Kramers, which assumes the dispersion to be due not to the actual orbits but to Slater's "virtual" or "ghost" oscillators having the spectroscopic rather than orbital frequencies, is then presented. Kramers' formula has both positive and negative terms and the differential dispersion may be defined in a manner analogous to the differential absorption. It is shown that the quantum differential dispersion approaches asymptotically the dispersion which on the classical theory would come from the actual multiply periodic orbit found in the stationary states. This asymptotic connection for the general non-degenerate multiply periodic orbit must be regarded as an important argument for Kramers' formula.

1. INTRODUCTION

ACCORDING to the first postulate of the Bohr theory of atomic structure the electrons can move only in certain particular quantized non-radiating orbits or stationary states. In order that the quantum conditions may be applicable it is necessary for the motion to be of the so-called "multiply periodic" type, which can be represented by multiple Fourier series of the form

$$x = \Sigma_{\tau_1\tau_2\tau_3} X(\tau_1,\tau_2,\tau_3) \cos \left[2\pi(\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)t + \gamma_{\tau_1\tau_2\tau_3}{}^{(x)}\right] \qquad (1)$$

with similar expansions by y and z. The constants ω_1, ω_2, ω_3 are the intrinsic orbital frequencies, and the summation is to be extended over all possible positive and negative integral values of the integers τ_1, τ_2, τ_3 subject to the restriction that $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ be positive. For simplicity in notation we have assumed that there are only three ω's, but in general the number of such frequencies can be equal to or less than the number of degrees of freedom of the atomic system to which the electron under consideration belongs. (The slight modifications necessary to extend the results of the present paper to systems with more than three frequencies will be discussed in section 17). We shall also suppose that the system is "non-degenerate" so that the number of degrees of freedom is equal to rather than greater than the number of frequencies. This means that in the case of three ω's, the problem may be thought of as one of a single electron moving in an asymmetrical three-dimensional static force field. It will also be assumed that the orbits conform to the classical mechanics and that all solutions of the differential equations of motion can be represented by series of the form (1), thus making the complete dynamical system multiply periodic, rather than merely certain particular families of orbits.

The quantum conditions for determining the size of the stationary states consist in equating to integral multiples of h a set of orbital constants J_1, J_2, J_3 defined by the relations

$$\omega_k = \partial W/\partial J_k (k = 1,2,3)\ ; \qquad 2\overline{T} = J_1\omega_1 + J_2\omega_2 + J_3\omega_3; \qquad (2)$$

where W is the total energy and T is the average kinetic energy. We can therefore set $J_k = n_k h$ $(k = 1, 2, 3)$, where n_1, n_2, n_3 are the integers or quantum numbers characteristic of a stationary state.[1]

According to the second postulate of the Bohr theory an electron may pass from one allowed orbit to another. The frequency ν_{rs} of the quantum of light thus radiated or absorbed is determined by the familiar relation

$$h\nu_{rs} = W_r - W_s\,, \tag{3}$$

where W_τ denotes the energy of the stationary state τ (with $\tau = r$, s, etc.). In the case of emission, r is the initial state and s the final state, while for absorption the significance of these symbols is just reversed, as r represents the higher energy level.

Considerable information concerning the probabilities of the various transitions between different orbits is furnished by Einstein's derivation[2] of the Planck radiation formula, $\rho(\nu) = 8\pi\nu^3 hc^{-3}/(e^{h\nu/kT} - 1)$, for the specific energy density of black body radiation. Einstein assumed:

(I) The number of atoms N_τ in the state τ is given by the statistical mechanics formula

$$N_\tau = Ne^{-W(\tau)/kT}/\ \Sigma_\tau e^{-W(\tau)/kT} \tag{4}$$

where N is the total number of atoms, and the sum is to be extended over all possible states.[3]

(II) The amount of energy emitted in a time Δt by transitions from the state r to the state s is represented by a formula of the type

$$\Delta E_{r\rightarrow s} = h\nu_{rs}\, N_r\, [A_{r\rightarrow s} + B_{r\rightarrow s}\, \rho(\nu_{rs})]\Delta t\,. \tag{5}$$

(III) The amount of energy absorbed by transitions from the state s to the state r is given by

$$\Delta E_{s\rightarrow r} = h\nu_{rs}\, N_s B_{s\rightarrow r}\, \rho(\nu_{rs})\Delta t\,. \tag{6}$$

(IV) There is to be statistical equilibrium (i.e. $\Delta E_{r\rightarrow s} = \Delta E_{s\rightarrow r}$) when the energy density has the characteristic black body distribution given by the Planck formula. Using Eqs. (3) and (4), one can verify that this equilibrium condition will be fulfilled provided the probability coefficients

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[1] The quantum conditions have been stated above in what may be termed the correspondence principle form. Some readers may be more familiar with the formulation used by Sommerfeld and others, which consists in equating certain phase or "quantum" integrals to integral multiples of h, but the two methods can readily be shown to yield the same results in non-degenerate systems. See, for instance, appendix 7 of Sommerfeld's "Atombau."

[2] Einstein, Phys. Zeit. **18**, 121 (1917)

[3] The "a priori probabilities" p_τ which ordinarily appear in front of the exponentials in Eq. (4) have been omitted, as we are concerned with non-degenerate systems where all states have the same a priori probabilities, making the p_τ's in numerator and denominator cancel.

$A_{r\rightarrow s}$, $B_{r\rightarrow s}$, and $B_{s\rightarrow r}$, which are independent of the temperature and energy density, satisfy the relations

$$B_{s\rightarrow r} = B_{r\rightarrow s} = (c^3/8\pi h\nu_{rs}{}^3)A_{r\rightarrow s} \,. \tag{7}$$

Einstein's criterion of statistical equilibrium under black body radiation thus tells us how emission and absorption vary with the density, Eqs. (5) and (6), and how they are related to each other, Eq. (7), but still leaves undetermined the magnitude of the coefficient $A_{r\rightarrow s}$ in (7). To evaluate approximately the latter it is customary to resort to the correspondence principle, as explained below.

It is well known that according to classical electrodynamics an accelerated electron radiates energy continuously and that if in particular the orbit is of the form (1) then the light thus emitted should be resolved by spectroscopes into frequencies which are combination overtones $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ of the orbital frequencies ω_1, ω_2, ω_3. According to the quantum relation (3) there is, however, no such immediate connection between the spectroscopic frequency and actual frequencies of motion, but it can easily be proved that if the quantum numbers n_1, n_2, n_3 of the states r and s differ from each other by τ_1, τ_2, τ_3 units respectively, so that $\Delta J_k=\tau_k h$, then in the region of high quantum numbers (usually also long wave-lengths) the optical frequency ν approaches asymptotically the combination overtone $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$. Since the classical and quantum mechanisms thus then give nearly the same numerical values for optical frequencies even though irreconcilably different in character, it is natural to assume that they give in the case of high quantum numbers the same numerical results for the relative intensities of different spectral lines, at least when there is no radiation field (i.e. $\rho(\nu)=0$). It is, however, to be clearly understood that the asymptotic connection of *frequencies* is a necessary mathematical consequence of the quantum conditions, and is hence, following Ehrenfest, best termed the correspondence *theorem* for frequencies.[4] On the other hand the existence of an analogous relation for the *intensities* of lines radiated when $\rho(\nu)=0$ must be regarded as an additional hypothesis, which we shall call the correspondence principle for emission. The latter is generally accepted not only because of its inherent reasonableness but also because of its excellent experimental verification in the "selection principle" and in the researches of Kramers and others on the intensities of Stark effect components.

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[4] To prove the correspondence theorem for frequencies we need simply note that $h\nu_{rs}=W_r-W_s=\Delta W$. Nearly consecutive orbits of large quantum numbers differ but little from each other in relative size and we can then without great error replace the increment ΔW of the energy by the differential $dW=\Sigma^3{}_1(\delta W/\delta J_k)\Delta J_k$. Using Eq. (2) and the relation $\Delta J_k=\tau_k h$, we thus get the result that in the limit $\nu/(\tau_1\omega_1+\tau_2\omega_2+\omega_3)=1$.

To formulate analytically the correspondence principle for emission we need simply note that from the classical expression $(2e^2/3c^3)\dot{v}^2$ for the rate of radiation from an electron having a vector acceleration , it follows that the amount of energy radiated as light of frequency $\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$ in the time interval Δt is[5]

$$\Delta E = (16\pi^4 e^2/3c^3)\,(\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)^4\,[D(\tau_1\,,\,\tau_2\,,\,\tau_3)]^2\,\Delta t \tag{8}$$

where $D^2 = X^2 + Y^2 + Z^2$. If we multiply by N_r to take into account the radiation from N_r electrons, then on comparing this classical expression with the quantum Eq. (5) for $\rho(\nu) = 0$, and using the approximation $\nu = \tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$, we see that the correspondence principle for emission requires that for high quantum numbers the probability coefficient $A_{r\to s}$ must have a value close to

$$A_{r\to s} = (16\pi^4 e^2 \nu^3_{rs}/3hc^3)\,[D^r(\tau_1\,,\,\tau_2\,,\,\tau_3)]^2\,. \tag{9}$$

where D^r denotes D evaluated for an orbit of the same size and shape as that found in the stationary state r.

An equation of the precise form (9) can be expected to hold only asymptotically. At ordinary wave-lengths it is more probable that $A_{r\to s}$ depends not on the orbital frequencies and amplitudes evaluated for one particular stationary state but instead involves these quantities averaged in some manner or other over the continuous succession of "dis-allowed" orbits intermediate between the initial and final states. We might still have (9) valid in the limit if we assume, for instance, that a more exact expression is

$$A_{r\to s} = (16\pi^4 e^2 \nu^3/3hc^3)\left(\nu^{-m}\int_0^1 (\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3)^m [D(\tau_1,\,\tau_2,\,\tau_3)]^{\pm 2} d\lambda\right)^{\pm 1}. \tag{10}$$

Here m is some integer, while λ is an auxiliary parameter such that $J_k = (n_k + \tau_k\lambda)h$, where n_k and $n_k + \tau_k$ $(k = 1, 2, 3)$ denote respectively the quantum numbers of the states s and r. Either the + or − sign must be consistently used throughout. Ordinarily the + sign is taken, and then the special cases of $m = 0, 4$ have been studied in some detail by F. C. Hoyt.[6]

2. A Correspondence Principle for Orbital Distortions

In the review of the correspondence principle for emission given in section 1 it must be remembered that actually a classical electron radiates simultaneously all the combination overtones in the multiple Fourier

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[5] For simplicity in printing, the arguments τ_1, τ_2, τ_3 of the amplitudes X, Y, Z, D will often be omitted; also the subscripts are often dropped from ν_{rs}.

[6] F. C. Hoyt, Phil. Mag. **46**, 135 (1923); **47**, 826 (1924). Eq. (10), of course, gives by no means all the possible expressions for $A(_{r\to s})$. In fact from certain viewpoints the best arguments appear to be for a certain type of logarithmic average first introduced by Kramers (The Intensities of Spectral Lines, Dan. Acad. Memoires, 1919, p. 330) and also studied by Hoyt. **Only two out of six formulas studied by Hoyt are included in Eq. (10).**

expansion rather than just one harmonic vibration component $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$. One can, however, formally avoid this difficulty by introducing what we shall term an "abridged" radiation force obtained by retaining only the one term τ_1, τ_2, τ_3, in the multiple Fourier expansion of the complete radiation force $2e^2\ddot{v}/3c^3$. It can then be verified that the total radiation is on the average given by Eq. 8.[7] We can then imagine the emitted light in the classical theory to be monochromatic, and its frequency will approach asymptotically the optical frequency ν in the quantum theory, while an asymptotic connection of the average rates of spontaneous radiation can be secured by using some such equation as (10).

A question which naturally arises at this point is whether the abridged radiation force with only one term produces just the same distortion in the size and shape of the orbit in the classical theory as the electron experiences in the quantum theory when it passes from one stationary state to another. In the classical theory an orbit having originally the same size and shape as the initial quantized stationary state will obviously after a properly chosen lapse of time be sufficiently damped by the abridged radiation force to make the energy the same as that of the final stationary state in the quantum theory. However, we cannot immediately infer that after this interval of time has expired the classical orbit will have the same shape as the final quantized orbit unless the system has only one degree of freedom, for then only does the energy determine uniquely the shape of the orbit. In the case, for instance, of an elliptical trajectory modified by a relativity precession to make the system non-degenerate (in two dimensions) the classical and quantum orbits might have initially the same semi-major axis and eccentricity; but when the classical orbit has been sufficiently damped by the abridged radiation force to make its energy (and hence approximately the semi-major axis) the same as that of another smaller stationary state, we cannot predict off-hand that then its eccentricity will become identical with that of the latter.

The writer is not aware of any specific statement in the literature as to whether these orbital distortions are the same in the two theories, except for a brief allusion to this question in an interesting article by H. A. Senftleben, which has just appeared.[8] However, an examination

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[7] The average value of the work $-Fv\Delta t$ done in the time Δt against the abridged radiation force F has the value (8) even though the complete expansion of v (but not of $\ddot{v}$ in F) is retained, for "cross-terms" involving products of different combination overtones cancel out on the time average. For greater detail see section 16 of part II.

[8] H. A. Senftleben, Zeit. f. Phys. **22**, 127 (1924). Following Eq. (50) of his article Senftleben states the necessity of having the average time rate of change of the J's approach each other asymptotically in the two theories, and this implies an asymptotic

of this point is not difficult. In a system with 3 degrees of freedom the size and shape of the orbit are completely determined if we know the values of the expressions J_1, J_2, J_3 defined in (2), for the other arbitrary constants enter only as epoch angles. Now in the quantum theory the J's always change by integral multiples of h, and their alterations in going from one state to another are in the ratio

$$\Delta J_1 : \Delta J_2 : \Delta J_3 = \tau_1 : \tau_2 : \tau_3 \, . \tag{11}$$

On the other hand it is proved in section 16 of part II that if in the classical radiation force we keep only the term involving the combination overtone $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$, then the J's are also, in the classical theory, altered in the ratio given above for all time intervals. Therefore by including only the abridged force in the classical theory, the distortion is the same in the two theories. Another way of saying this is that one particular term in the classical radiation force damps the orbit in such a way that if at the start it coincides with a given quantized stationary state it tends to pass through a succession of stationary states of smaller energy, whose quantum numbers differ from those of the initial state by $m\tau_1$, $m\tau_2$, $m\tau_3$ units respectively, where m is an integer.

The results quoted in Eq. (11) hold even at ordinary wave-lengths (small quantum numbers) for it is shown in section 16 that according to the classical theory the J's always tend to change instantaneously in the ratio (11). Consequently the ΔJ's are in the ratio of integers even though the abridged radiation force be acting for such a long time that the alterations in the J's are of the order of magnitude of their initial values, making the radiated energy comparable with the total energy. The relations are also valid for systems with more than three J's (see section 17).

If we form a three-dimensional space for plotting values of J_1, J_2, J_3, the deformations of the orbit produced by one particular term in the classical radiation force may be represented by a straight line (neglecting small periodic fluctuations which cancel out on the average). The equations of these lines may be written $J_k = J_k^{\circ} + \lambda\tau_k h$, where λ is a parameter.

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connection of the orbital distortions. No detailed proof of this, however, is contained in part I of Senftleben's article (the only part available at time of writing) but an indication is given of how it might be obtained from an asymptotic connection of the rates of radiation of angular momentum and energy in the two theories provided the system has only one electron. Both the method of proof and interpretation of the result (reached independently) in the present paper differ in many respects from the above, especially the ability to generalize the results to atoms with more than one electron (section 17), and the emphasis on the validity of the relation $\Delta J_1 : \Delta J_2 : \Delta J = \tau_1 : \tau_2 : \tau_3$ at ordinary wave-lengths.

Consequently the present considerations give a semi-theoretical basis for determining the probability coefficient $A_{r\rightarrow s}$ by averaging some function of the amplitudes and orbital combination frequencies along a straight line in the three dimensional space connecting the points corresponding to the initial and final states. This procedure, illustrated in Eq. (10), was adopted by Kramers and by Hoyt, but it is not apparent from the articles of these investigators whether they realized they were actually averaging along a path which would be traversed by the orbit under the influence of the abridged radiation forces. The various methods which have been suggested for determining $A_{r\rightarrow s}$ by averaging over the straight line path mentioned above are such as to make the mean free time in the initial state different from the actual time of transit between the two states under the influence of the abridged radiation force, except, of course, for an asymptotic connection of the two times for high quantum numbers. Neglecting higher powers of $1/c^2$, the quantum mean free time and the classical time of transit can be shown to be identical at ordinary wave-lengths or small quantum numbers provided in Eq. (10) we take the $-$ sign in both exponents and take the integer $m=-3$.[9] This result seems worth noting, but it is questionable how much significance should be attached to this method of procedure for there is no obvious reason why the two times should be exactly equal rather than asymptotically connected.[10]

3. INSUFFICIENCY OF A CORRESPONDENCE PRINCIPLE RELATING ONLY TO EMISSION

The correspondence principle for emission reviewed in section 1, cannot in a certain sense be regarded as entirely adequate because it establishes (or rather postulates) an asymptotic numerical connection of the classical

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[9] To get the result quoted we need simply integrate Eq. (8) between $\lambda=0$ and $\lambda=1$, noting that $dE=(\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3)hd\lambda$ by Eq. (2). This gives the classical transit time. The quantum mean free time is on the other hand simply the reciprocal of $A_{r\rightarrow s}$.

[10] It is interesting to note that the classical time of transit from a 3_3 to a 2_2 orbit in hydrogen works out as 1.04×10^{-8} sec. Wien's canal ray experiments indicate a mean free time for Hα of 1.85×10^{-8} sec. (Ann. der Phys. **73**, 485, 1924). The latter, Wien shows, is almost exactly the reciprocal (1.87×10^{-8} sec.) of the logarithmic decrement for a linear oscillator of frequency ν (not an actual orbit), but this very close agreement is probably only a coincidence. On the other hand the value 1.04×10^{-8} sec. must be corrected to allow for the transitions $3_2\rightarrow2_1$, $3_1\rightarrow2_2$, which also contribute to Hα and have longer mean free times than $3_3\rightarrow2_2$,—the 3_1 state is, in fact, almost metastable—thus making the effective mean free time much larger. The agreement is as good as can be expected, for the correct formula for $A_{r\rightarrow s}$ probably does not make the quantum mean free time exactly equal to the classical time of transit, but instead involves a different kind of average of amplitudes and frequencies than that obtained by putting $m=-3$ in Eq. (10).

and quantum theory for intensity only in the special case that there is no radiation field (i.e. $\rho(\nu)=0$). The term present in Eq. (5) when $\rho(\nu)=0$ we shall call the spontaneous emission (Einstein's "Ausstrahlung"), while the second or remaining term proportional to the energy density we shall call the induced emission, although it is sometimes called the "negative absorption" in distinction from the true or positive absorption given by Eq. (6). The correspondence principle for emission correlates quantum theory spontaneous emission with classical theory emission due to the radiation force $2e^2\ddot{v}/3c^3$. On the other hand an electron can according to the classical theory absorb energy from a radiation field, and there must be some kind of an asymptotic connection between this absorption in the classical electrodynamics and the induced emission and absorption in the quantum theory. This will be discussed in sections 4 and 5. There can be no question of a correlation of the classical and positive quantum absorptions alone, as this would leave the induced emission unexplained. The existence of the induced emission term in the quantum theory may at first sight appear strange, but it is well known that this is qualitatively explained in that with the proper phase relations a classical electric wave may receive energy from an atomic system although on the average (i.e. integrating over all possible phase relations) it contributes more than it receives in exchange. It is therefore the excess of positive absorption over the induced emission which one must expect to find asymptotically connected to the net absorption in the classical theory.

4. CORRESPONDENCE PRINCIPLE FOR ABSORPTION FOR A LINEAR OSCILLATOR

Before seeking to develop a correspondence principle for absorption for the general case of an arbitrary multiply periodic orbit, we shall first for simplicity and clarity confine our attention to a one-dimensional linear oscillator. Here the multiple Fourier expansion reduces to

$$x = D\cos(2\pi\omega t + \gamma)\,, \quad (y = z = 0).$$

As there is only one degree of freedom, there is just one quantum number n, and this can by the correspondence principle only change by one unit, as there are no harmonics of the fundamental frequency ω in the Fourier expansion. Now the energy W of a linear oscillator of amplitude D, mass m, and frequency ω is in general $2\pi^2\omega^2 mD^2$. Furthermore it is well known that for a linear oscillator the quantum conditions require that the energy W_n of a state of quantum number n have the value $nh\omega$. Therefore the amplitude D_n of an orbit of quantum number n is given by

$$D_n{}^2 = nh\,/\,(2\pi^2\nu m). \tag{12}$$

In writing (12) we have utilized the familiar fact that for a linear oscillator $\nu = \omega$, as here the spectroscopic and orbital frequencies are identical.[11] We can now apply the correspondence principle for emission, as embodied in Eq. (9), to determine the approximate value of the probability coefficient $A_{r\rightarrow s}$. Using the fact that in the present notation $D^n(\tau_1,\tau_2,\tau_3)$ is nothing but D_n, while $\nu_{\tau s}$ is simply ν, and taking r as an n quantum state, s as an $(n-1)$ quantum state, we thus get $A_{r\rightarrow s} = 8\pi^2 e^2 \nu^2 n/(3c^3 m)$. From (7) it then follows that

$$B_{n\rightarrow(n-1)} = B_{(n-1)\rightarrow n} = n\pi e^2 / (3hm\nu). \tag{12a}$$

Hence by Eq. (6) we see that in a time Δt the energy which is removed from a radiation field of density $\rho(\nu)$ by the positive absorption of quanta by N oscillators all in $(n-1)$ quantum states is

$$\Delta E_{(n-1)\rightarrow n} = \tfrac{1}{3}n\pi e^2 m^{-1}\, N\rho(\nu)\Delta t\ . \tag{13}$$

On the other hand it is well known that according to the classical theory the average rate at which a linear oscillator absorbs energy in a field of radiation is independent of the amplitude and is given[12] by $\frac{1}{3}\pi e^2 m^{-1}\rho(\nu)$. Consequently in the interval Δt, N oscillators should absorb the energy

$$\Delta E_{abs} = \tfrac{1}{3}\pi e^2 m^{-1}\, N\rho(\nu)\Delta t\ . \tag{14}$$

Because of the presence of the factor n, the quantum theory expression (13) for the positive absorption differs increasingly from (14) as the quantum number becomes larger. This discrepancy is not surprising, for we have not taken into account the fact that oscillators in the state $(n-1)$ may in the presence of a radiation field be induced to emit energy and pass to the state $(n-2)$ at a more rapid rate than when $\rho(\nu)=0$ and there are only spontaneous transitions.[13] Each of these excess or induced transitions may be thought of as returning to the ether or light wave the energy $h\nu_{st}$, a sort of regenerative effect. Hence we can take as the *net* absorption of energy in the time Δt by N oscillators in the state $(n-1)$ the expression

$$\Delta F = [B_{(n-1)\rightarrow n} - B_{(n-1)\rightarrow(n-2)}]\ h\nu\ N\rho(\nu)\ \Delta t\ .$$

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[11] The result $\nu = \omega$ is obvious from an inspection of Eq. (3), as in the present case $W_n = nh\omega$, $\Delta n = \pm 1$.

[12] Cf. Planck, Wärmestrahlung, 4th Ed., Eqs. (260) and (159)

[13] If the electrons are in the orbit of lowest quantum number there can be only positive absorption because there are no still lower energy levels to which induced emission may take place. This case has been considered by Ladenburg (Zeit. f. Phys. **4**, 451, 1921); also by Ladenburg and Reiche (Naturwissenschaften, **27**, 584, 1923). These writers note the necessity of having the factor n in comparing the classical and positive quantum absorption.

This way of measuring absorption we shall term the differential rate of absorption in contrast to the true positive rate given by Eq. (13). Now by (12a) we have, on lowering the integer n by one unit, the result $B_{(n-1)\rightarrow(n-2)} = (n-1)\pi e^2/(3mh\nu)$, and hence $\Delta F = \Delta E_{abs}$. We thus see that in the limiting case of large quantum numbers, where Eq. (12a) is valid, the classical value (14) for the rate of absorption of energy is nothing but the differential rate of absorption in the quantum theory. This connection of the classical and quantum differential absorption we shall term the correspondence principle for absorption; it is a purely mathematical consequence of the correspondence principle for emission, which was used in deriving (12a). Another way of stating the results is that because of Eqs. (9) and (12a) the ratio $(B_{(n-1)\rightarrow n} - B_{(n-1)\rightarrow(n-2)})\,\rho(\nu)/A_{(n-1\rightarrow(n-2)}$ of the differential absorption to the spontaneous emission for any given orbit has for large n very nearly the classical value $c^3\rho(\nu)/(16\pi^3 m D_n{}^2\nu^4)$ for the ratio of absorption to emission.[14]

5. GENERALIZATION OF THE CORRESPONDENCE PRINCIPLE FOR ABSORPTION TO AN ARBITRARY NON-DEGENERATE MULTIPLY PERIODIC SYSTEM

We must now seek to examine whether an analogous correspondence principle for absorption holds for an arbitrary non-degenerate multiply periodic system, whose orbits are given by Eq. (1) and which represent essentially the most general type of motion amenable to present quantum theory methods. Here we can no longer enjoy such simplifications as the existence of a single quantum number and the results $\Delta n = \pm 1$, $\nu = \omega$ characteristic of a linear oscillator.

Let us consider a state s of quantum numbers n_1, n_2, n_3.[15] Then when a quantum of energy is absorbed by an orbit of this type the electron will pass to some other state of quantum numbers $n_1+\tau_1$, $n_2+\tau_2$, $n_3+\tau_3$.[16] Starting with the state s (not r) there is no emissive transition to a state t such that the frequency ν_{st} of the light thus emitted is just equal to the frequency ν_{rs} of that absorbed on passage to the state r. (This amounts

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[14] Reference should be made while on the present subject to the discussion in section 158 of Planck's "Wärmestrahlung" (4th Ed.) ,which establishes an asymptotic connection between the classical and quantum formulas for statistical equilibrium. A correspondence principle for absorption could doubtless be derived from such considerations, but no explicit mention is made of the asymptotic connection of the classical absorption and the differential absorption for a single orbit (where thermodynamic equilibrium need not be assumed) which is the primary concern of the present paper.

[15] The generalization to cases of more than three quantum numbers is given in section 17.

[16] Not all the integers τ_1, τ_2, τ_3 need be positive but the state r must have a greater energy than s.

virtually to saying that in general energy levels are not evenly spaced, except, of course, for such an ideal case as the linear oscillator). However, if the state t has quantum numbers $n_1-\tau_1$, $n_2-\tau_2$, $n_3-\tau_3$, then for large values of n_1, n_2, n_3 the ratio ν_{rs}/ν_{st} approaches unity, for both these spectroscopic frequencies approach asymptotically the combination overtone $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ of the orbital frequencies. Hence it is natural to define as the differential rate of absorption the excess of light absorbed by transitions from the state s to the state r over the energy returned to the ether by induced emissive transitions from the state s to the state t, where, as mentioned above, the differences between the quantum numbers for the states s and t are the same as the corresponding differences for the states r and s.

With this definition it follows that in the time Δt the differential absorption of light energy of frequency approximately $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ by N atoms in the state s amounts to

$$\Delta F = \left[h\nu_{rs}\rho(\nu_{rs})B_{s\rightarrow r} - h\nu_{st}\rho(\nu_{st})B_{s\rightarrow t}\right] N\Delta t. \qquad (15)$$

If we admit the validity of the correspondence principle for emission then Eqs. (7) and (9) show that for large quantum numbers this expression becomes approximately

$$\Delta F = \tfrac{2}{3}\pi^3 e^2 h^{-1} \left[\nu_{rs}\rho(\nu_{rs})\, D_r^2 - \nu_{st}\rho(\nu_{st})\, D_s^2\right] N\Delta t$$

where for brevity we have written D_r for D^r (τ_1, τ_2, τ_3), etc. Also for large quantum numbers the discrete succession of quantum orbits becomes so nearly consecutive that differences may be replaced by differentials, just as is done in the derivation of the correspondence theorem for frequencies.[4] Consequently

$$\Delta F = \tfrac{2}{3}\pi^3 e^2 h^{-1}\left\{\rho(\nu)D_s^2(\nu_{rs}-\nu_{st})+\nu_{st}\left(\frac{\partial\rho}{\partial\nu}\right)D_s^2(\nu_{rs}-\nu_{st})+\nu_{st}\rho(\nu_{st})\delta D^2\right\}N\Delta t$$

where δ denotes the difference between an expression evaluated for the states s and t. It is, of course, to be understood that $\rho(\nu)$ and $\partial\rho/\partial\nu$ are to be evaluated with ν approximately equal to ν_{st} (or ν_{rs}). Now since we are dealing with the large quantum number limit, the correspondence theorem for frequencies tells us that ν_{st} may without sensible error be replaced by the combination overtone $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ of the orbital frequencies, and similarly $\nu_{rs}-\nu_{st}$ is to the desired approximation equal to $\delta(\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3)$. Now since the system is non-degenerate, the amplitude D as well as the ω's and the energy W, is a function of the constants J_1, J_2, J_3 which according to the quantum conditions are equated to integral multiples of h, and consequently

$$\delta\omega_1 = \frac{\partial\omega_1}{\partial J_1}\delta J_1+\frac{\partial\omega_1}{\partial J_2}\delta J_2+\frac{\partial\omega_1}{\partial J_3}\delta J_3 = h\left(\tau_1\frac{\partial}{\partial J_1}+\tau_2\frac{\partial}{\partial J_2}+\tau_3\frac{\partial}{\partial J_3}\right)\omega_1, \text{ as } \delta J_k=\tau_k h\ .$$

Similar relations hold for $\delta\omega_2$, $\delta\omega_3$, and δD^2. The expression for the differential absorption therefore becomes

$$\Delta F = \tfrac{2}{3}\pi^3 e^2 \left[\rho(\omega_\tau) \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_2} + \tau_3 \frac{\partial}{\partial J_3} \right) G_\tau + \frac{\partial \rho}{\partial \nu} G_\tau \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_2} + \tau_3 \frac{\partial}{\partial J_3} \right) \omega_\tau \right] N \Delta t \qquad (16)$$

where we have written ω_τ for $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$ and G for $\omega_\tau[D(\tau_1, \tau_2, \tau_3)]^2$.

It is shown in part II of the present paper that Eq. (16) also gives the amount of energy which according to purely classical mechanics is absorbed in a time Δt by N systems, each with a multiply periodic orbit similar to the state s, when exposed to a radiation field of vanishing intensity except for frequencies in the vicinity of $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$. That is to say Eq. (16) also gives the part of the classical absorption due to resonance of the impressed waves with the combination overtone τ_1, τ_2, τ_3. The total classical absorption is, of course, the sum of resonance effects for all possible overtones.

We may therefore conclude that the correspondence principle for absorption holds even for an arbitrary multiply periodic orbit; i. e. assuming the validity of the correspondence principle for emission, the differential quantum absorption by a particular orbit approaches at high quantum numbers (usually long wave-lengths) the classical absorption of light of asymptotically corresponding frequency.[17]

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[17] It is clearly to be understood that although in deriving (16) we have apparently utilized Eq. (9), the proof of (16) can be readily shown to be equally valid if (9) holds asymptotically, so that at ordinary wave-lengths $A_{r\rightarrow s}$ might, for instance, be determined by averaging the frequencies and amplitudes in the manner given in Eq. (10). In this connection it is interesting to note that it is not difficult to prove that for the special case of a linear oscillator the differential quantum absorption and the classical absorption are exactly equal to each other even for low quantum numbers provided $A_{r\rightarrow s}$ is determined by taking the + signs in (10), with the integer m arbitrary. On the other hand it was found in section 2 that to make the mean free time of spontaneous emission in the quantum theory just equal the classical time of transit from one state to another in the absence of external radiation (i.e $\rho(\nu)=0$), it is necessary to take the − signs in (10) and $m=-3$.

Another way of formulating the correspondence principle for absorption is as follows. The quantity $h\nu A_{r\rightarrow s}$ plays in the quantum theory the rôle of a coefficient of emission, and may be denoted by α. Using arguments similar to those employed in the derivation of (16), it is easy to show that the differential absorption has for large quantum numbers very approximately the value

$$\Delta F = (c^3/8\pi) \left[\rho(\omega_\tau) \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_2} + \tau_3 \frac{\partial}{\partial J_3} \right) (\alpha\omega_\tau^{-3}) + \alpha\omega_\tau^{-3} \frac{\partial \rho}{\partial \nu} \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_2} + \tau_3 \frac{\partial}{\partial J_3} \right) \omega_\tau \right] N \Delta t\,.$$

In the present paper we have proved the correspondence principle for absorption after assuming the validity of the ordinary correspondence principle for emission. The procedure could equally well have been reversed. That is to say, assuming an asymptotic connection of the differential absorption in the quantum theory with the corresponding absorption in the classical mechanism we could show that the spontaneous emission in the quantum theory must approach equality with the classical formula (8) for the spontaneous radiation of energy.

The classical formula (8) for spontaneous emission involves rather more electrodynamics than the analogous classical formula for absorption, given in Eq. (16), for the derivation of the former is based on retarded potentials and the validity of the field equations, while the latter requires simply that there be a certain incoherence in the radiation field and that the change in the energy be equal to the scalar product of the impressed force and the velocity of the particle, a very broad mechanical principle. As pointed out in the preceding paragraph, the asymptotic values of the probability coefficients $A_{r\rightarrow s}$, $B_{r\rightarrow s}$, etc., can be derived from the absorption instead of the emission viewpoint. Because of this alternative the correspondence principle for evaluating these coefficients is in a certain sense less electrodynamical and more purely mechanical in nature than it has sometimes been considered to be. From this standpoint the connection between the quantum theory and classical electrodynamics comes through the assumption of Wien's law in obtaining Eq. (7), for in Einstein's derivation of the Planck radiation formula considerations of statistical equilibrium without resorting to Wien's law do not suffice to determine $B_{r\rightarrow s}/A_{r\rightarrow s}$. If we assumed both the correspondence principle for emission and that for absorption it would be possible to dispense with the need of assuming (rather than proving) Wien's law. Virtually this procedure was adopted by Planck, who studied the special cases of the linear oscillator and rotating dipole.[18] As pointed out to the writer by Prof. Ehrenfest, the content of the present paper may be regarded as placing such a procedure on a more general basis.[19]

This is, however, nothing but the classical theory formula for the coefficient of absorption in terms of the coefficient of emission as can be seen from (8) and (16). This way of stating the correspondence principle for absorption does not utilize (9) even asymptotically.

[18] Wärmestrahlung, 4th Ed., section 158. Cf. footnote [14].

[19] The writer has just learned (Sept. 1924) that in unpublished computations made at Copenhagen, J. C. Slater has independently derived an absorption formula similar to Eq. (16) and has also noted the asymtotic connection of the classical and quantum absorption discussed in sections 4 and 5.

6. THE GENERAL CORRESPONDENCE PRINCIPLE BASIS FOR KRAMERS' DISPERSION FORMULA

In a recent note[20] H. A. Kramers has proposed a formula for dispersion which is a modification of an equation previously developed by Ladenburg and Reiche,[21] and which must be regarded as a distinct advance in the problem of reconciling dispersion with quantum phenomena. The physical principle underlying Kramer's formula is that of "virtual" or "ghost" resonators, first suggested by Slater[22] and elaborated by Bohr, Kramers, and Slater.[23] According to this viewpoint the dispersion is not to be calculated by considering the actual orbit (stationary state) as reacting classically to the impressed waves. Instead, the stationary states appear to be unaffected except for occasional quantum leaps, but the dispersion is to be computed as due to a set of hypothetical linear oscillators whose frequencies are the spectroscopic ones rather than those of the orbits. The introduction of these virtual resonators is, to be sure, in some ways very artificial, but is nevertheless apparently the most satisfactory way of combining the elements of truth in both the classical and quantum theories. In particular this avoids the otherwise almost insuperable difficulty that it is the spectroscopic rather than the orbital frequencies, i.e. ν rather than $\tau_1\omega_1+\tau_2\omega_2+\tau_3\omega_3$, which figure in dispersion.[24]

Kramer's formula for the polarization due to N_s electrons in the state s is[25]

$$P_s = \frac{c^3}{32\pi^4}\left[\sum_r \frac{A_{r\to s}}{\nu_{rs}^2(\nu_{rs}^2-\nu^2)} - \sum_t \frac{A_{s\to t}}{\nu_{st}^2(\nu_{st}^2-\nu^2)}\right] N_s\mathcal{E} \qquad (17)$$

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[20] H. A. Kramers Nature, May 10, 1924, p. 673; Aug. 30, 1924, p. 310.

[21] Ladenburg and Reiche, Naturwissenschaften **27**, 584 (July 6, 1923). Ladenburg and Reiche's formula differs from that of Kramers, given in (17), principally in that the negative terms are not included.

[22] Slater, Nature, Mar. 1, 1924, p. 307

[23] Bohr, Kramers and Slater, Phil. Mag. **47**, 785 (1924)

[24] Reference should, however, be made to the alternative explanation proposed by Darwin (Proc. Nat. Acad. **9**, 25, 1923).

[25] This equation differs by a factor 1/3 from the formula in Kramer's note to Nature, as (17) is written for the case where all orientations of the atom are equally probable, while Kramers' original equation is for the case that the atoms are always so oriented that their free vibrations are parallel to the impressed electric field. The assumption that all orientations are equally probable may appear at first sight contrary to the assumption that the system is non-degenerate, as all three intrinsic frequencies (the criterion for non-degeneracy) can appear only when the atomic force field does not have a spacial symmetry, and with such a dissymmetry the quantum conditions allow only certain particular orientations. However, we may imagine the asymmetrical internal atomic force fields to have all possible orientations in the different atoms. This artifice,

where $\mathscr{E}$ is the electric intensity and ν is the frequency of the impressed wave. The summation with respect to r is to be taken over all states of energy content higher than s, while that for t over all orbits of lower energy content than s. Each term in this equation represents the dispersion due to a "virtual oscillator" and corresponds to a particular quantum transition starting from the state s. Each oscillator in the t summation gives a negative dispersion, corresponding to Einstein's negative absorption, mentioned in section 3.

Kramers states that (17) merges asymptotically for large quantum numbers into the classical formula for the polarization. It is our purpose to show that this is true not just when the quantized system is a linear oscillator, but also when it is the most general type of non-degenerate multiply periodic orbit.[26] Just as in section 5, the upward transitions $(s \rightarrow r)$ and the downward ones $(s \rightarrow t)$ may be mated together in such a way that in each pair ν_{rs}/ν_{st} converges to unity for large quantum numbers. This is accomplished, just as before, by making the differences in quantum numbers between the states r and s the same as those between the states s and t, and we shall denote these differences by τ_1, τ_2, τ_3. Each pair contributes a positive and a negative term in (17) and their net effect is a "differential dispersion" very analogous to the differential absorption mentioned in sections 4 and 5. In precisely the same way that (16) is

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introduced for simplicity, enables one to have a random spacial distribution of orbits without having degenerate systems.

In this connection it is interesting to note that if the axes of the asymmetrical atomic force fields had the same orientations in all atoms, as is the case when the dissymetry is due to a constant external magnetic or electric field, then we should expect the virtual resonators to have only certain particular orientations, as only a few quantized spacial positions can be assumed by the atoms. By analogy with the classical theory results mentioned after Eq. (41) in section 15 of part II, there might then be possible a polarization in the y and z directions even though the electric intensity coincides with the x axis. The polarization and electric vectors would then have different directions, as in a crystal. Therefore the application of a weak constant external field would cause an abrupt dissymmetry in the index of refraction just as it creates an abrupt outstanding polarization of the spontaneously radiated light (cf. N. Bohr, the Fundamental Postulates of the Quantum Theory, Supplement of Proc. Cambr. Phil. Soc., p. 27). These sudden discontinuities are not found in the classical theory because the spacial distributions are continuous rather than quantized.

[26] In his first note Kramers did not give his proof of the desired asymptotic connection. Inasmuch as the formula for the dispersion by an arbitrary multiply periodic orbit, to be developed in section 15 of part II, did not appear to have previously been given and was not mentioned in Kramers' note, the writer supposed that Kramers' prior demonstration was somewhat less general than that of the present paper. Since writing this paper, the author has learned, however, that Kramers' unpublished computations are of the same scope and generality as those in § 15. Cf. Kramers' second note[20].

derived from (15) we find that for very large quantum numbers the contribution of one particular pair to the polarization becomes

$$P_s = \frac{1}{6}e^2 \left[\frac{1}{(\omega_\tau{}^2 - \nu^2)} \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_2} + \tau_3 \frac{\partial}{\partial J_3} \right) G_\tau - \frac{2\omega_\tau G_\tau}{(\omega_\tau{}^2 - \nu^2)^2} \left(\tau_1 \frac{\partial}{\partial J_1} + \tau_2 \frac{\partial}{\partial J_1} + \tau_3 \frac{\partial}{\partial J_2} \right) \omega_\tau \right] N_s \mathscr{E} \quad (18)$$

where G_τ and ω_τ are defined as in Eq. (16).

It is proved in section 15 that (18) also gives the polarization which according to the classical theory would be produced by resonance between the impressed frequency and the combination overtone ω_τ in a multiply periodic orbit of the same size and shape as the state s. The differential dispersion in Kramers' theory therefore approaches asymptotically the classical dispersion for the actual orbit. The asymptotic connection is thus very similar to that previously encountered in the correspondence principle for absorption.

It is particularly interesting to note that although both the positive and negative terms in the differential dispersion taken separately represent a type of dispersion characteristic of a linear oscillator (except that oscillators with negative dispersion correspond to no ordinary physical reality, as they would have to possess a negative mass) the difference of the two terms approaches asymptotically a more complicated type of dispersion appropriate to the general multiply periodic orbit. For Eq. (18) contains a term in $(\omega_\tau{}^2 - \nu^2)^{-2}$ as well as the familiar term in $(\omega_\tau{}^2 - \nu^2)^{-1}$ characteristic of the ideal resonator. The fact that the dispersion for the simple virtual oscillators thus merges asymptotically into the more complex classical dispersion for the actual orbits must be regarded as an important argument for the virtual resonator viewpoint, as such a connection is not an obvious outcome of the theory. Especially does this asymptotic connection increase our faith in the particular form of virtual oscillator theory embodied in Kramers' dispersion formula, and makes it easier to accept the rather artificial negative dispersion terms thus involved.[27]

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[27] It is to be noted that if $A_{r \to s}$ is determined in accordance with Eq. (10), the + signs being taken, then the differential dispersion in the Kramers' formula is for the special case of a quantized linear oscillator easily proved identical even at low quantum numbers with the classical dispersion. It was pointed out in footnote [17] that this kind of formula also makes the differential and classical absorption identical for the ideal oscillator without passing to the high quantum number limit. These facts taken together furnish a limited amount of evidence for the use of the average of the form (10) (with + signs) rather than the alternative logarithmic average which Hoyt has shown explains observed intensities equally well in the instances studied by him.[6]