

Spectral density in time-dependent perturbation theory

Ad Lagendijk

Physics Department, University of Antwerp (UIA), B-2610 Wilrijk, Belgium
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The spectral density of radiation is defined within the context of the random phase approximation. This gives an expression for the radiation density in terms of the Fourier components of the field amplitudes. The result is applied to the case of a molecule in interaction with light. The approach with Fourier integrals overcomes some difficulties associated with an approach which uses a summation of discrete waves.

I. INTRODUCTION

In many physical problems one encounters the following situation: a quantum-mechanical system in interaction with a classical field. The procedure usually followed is to start with one wave of a specific frequency and examine the response of the system to this perturbation. The field induces transitions between the eigenstates of the system, and these transitions are characterized by transition probabilities. These probabilities do not show a linear dependence on time, contradicting our daily experience.¹ When we look through a colored window, we do not observe a change of light intensity as a function of time. This observation indicates that the transition probability for the light to be absorbed by the window has a linear time dependence (that is to say, the transition probability per unit time is constant). A monochromatic wave does not exist in real situations, and the field is built up with waves of different frequencies. The knowledge of the field is very incomplete, implying that the field can only be described statistically. Characteristic for a statistical description is the appearance of correlation functions. A simplifying and appealing approximation in the description of random fields is to assume that the amplitudes of waves of different frequencies are uncorrelated, an approximation known as the "random phase approximation" (RPA).² Application of the RPA results in independent contributions of the different waves to the transition probability. The summation of these contributions is replaced by an integration through the introduction of the spectral density function $I(\omega)$. The formal definition of the spectral density function is that $I(\omega) d\omega$ is the energy per unit volume associated with circular frequencies lying in the range between ω and $\omega + d\omega$. If one uses as a representation of the field a summation of discrete waves (which is not a Fourier series), it is hard to obtain an expression for the spectral density function in terms of the field amplitudes. These amplitudes should be functions of a continuous variable ω , and they are therefore difficult to calculate if the field consists of discrete waves.³ To that end one has to return to the formal definition of $I(\omega)$ and introduce the quasicontinuity of the field variables. It is more elegant and also more consistent to work with Fourier integrals right from the start.

It is the purpose of this paper to show that one can derive the Einstein coefficients in an elegant way if one uses a rigorous expression for the radiation density. In the following we will introduce the continuous description of the field. Application of the RPA² allows us to obtain a formula for the spectral density function in terms of the field amplitudes. The result will be applied to the interaction of an atom (molecule) with an electromagnetic field, leading to

induced absorption and emission represented by the Einstein coefficients.⁴ First of all, we will demonstrate the use of the RPA in a simple example.

II. RANDOM PHASE APPROXIMATION (RPA): A SIMPLE EXAMPLE

Suppose $\Psi(t)$ is a field which varies with time according to

$$\Psi(t) = A \sin(\omega t + \varphi). \quad (1)$$

The correlation function C is defined as

$$C = \langle \Psi(t)\Psi(t + \tau) \rangle. \quad (2)$$

The angular brackets mean that the enclosed quantity should be ensemble averaged.

Using expression (1) for $\Psi(t)$, and realizing that the averaging is an average over the phases φ , the correlation function C can be calculated to be

$$C = A^2 \langle \sin^2(\omega t + \varphi) \rangle \cos(\omega\tau) + (A^2/2) \langle \sin(2\omega t + 2\varphi) \rangle \sin(\omega\tau). \quad (3)$$

One expects that for a large variety of fields, such as light waves emitted by atoms of a gas or blackbody radiation, the phases φ will be completely random. Adopting the randomness of the phases for our particular example, the averaging process can be performed easily and one obtains

$$C = (A^2/2) \cos(\omega\tau). \quad (4)$$

We note that C depends only on the time difference τ . If we put τ equal to zero, we get

$$C(\tau = 0) = \langle \Psi^2(t) \rangle = A^2/2, \quad (5)$$

which is a result we expect because $C(\tau = 0)$ represents the intensity of the field.

Generalizing our results, we expect that correlation functions like $\langle \Psi(t)\Psi(t + \tau) \rangle$ depend only on the time difference τ .

III. RANDOM PHASE APPROXIMATION (RPA): SPECTRAL DENSITY FUNCTION

Let $F(t)$ be a field amplitude of a one-dimensional real field which depends on time (the space dependence will be neglected⁵). The Fourier transform of $F(t)$ is $F(\omega)$. Consequently, the following relations hold:

$$F(t) = \int_{-\infty}^{+\infty} F(\omega) \exp(i\omega t) d\omega \quad (6)$$

and

$$F(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} F(t) \exp(-i\omega t) dt. \quad (7)$$

From (6) we note that the condition for $F(t)$ being real is

$$F(\omega) = F^*(-\omega). \quad (8)$$

The second-order wave correlation W is defined as

$$W = \langle F(\omega_1)F(\omega_2) \rangle. \quad (9)$$

W can be expressed in terms of the field amplitudes $F(t)$ with the help of Eq. (7):

$$W = (4\pi^2)^{-1} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d\tau \langle F(t)F(t+\tau) \rangle \times \exp[-i\omega_1 t - i\omega_2(t+\tau)]. \quad (10)$$

Using the RPA result that $\langle F(t)F(t+\tau) \rangle$ depends only on τ , the integration over t in Eq. (10) can be carried out, giving

$$W = (2\pi)^{-1} \delta(\omega_1 + \omega_2) \times \int_{-\infty}^{+\infty} \langle F(t)F(t+\tau) \rangle \exp(-i\omega_2 \tau) d\tau \quad (11)$$

$$\equiv \delta(\omega_1 + \omega_2) I(\omega_2). \quad (12)$$

In the derivation of Eq. (11) the δ -function representation

$$\delta(\omega) = (2\pi)^{-1} \int_{-\infty}^{+\infty} dt \exp(-i\omega t) \quad (13)$$

is used.

The integral $I(\omega)$, defined in Eq. (12), is the spectral density function. This can be seen as follows: $I(\omega)$ is proportional to the Fourier transform of $\langle F(t)F(t+\tau) \rangle$. The inverse relation of the definition of $I(\omega)$ reads

$$\langle F(t)F(t+\tau) \rangle = \int_{-\infty}^{+\infty} I(\omega) \exp(i\omega\tau) d\omega. \quad (14)$$

From this equation one gets, after setting τ equal to zero,

$$\langle F^2(t) \rangle = \int_{-\infty}^{+\infty} I(\omega) d\omega. \quad (15)$$

Equation (15) has a clear physical interpretation. $\langle F^2(t) \rangle$ is equal to the energy of the field (apart from a possible constant factor). In the right-hand side of Eq. (15) the contributions to the total energy of the different frequencies are integrated, which shows that $I(\omega) d\omega$ is equal to the energy in the interval between ω and $\omega + d\omega$ or $I(\omega)$ is the spectral density function. From Eq. (12) we have

$$I(\omega_1) \delta(\omega_1 + \omega_2) = \langle F(\omega_1)F(\omega_2) \rangle, \quad (16)$$

which is to be considered as the definition of $I(\omega)$.

The δ function in Eq. (16) is a manifestation of the RPA. In our discussion we allowed ω to be negative, implying that energy of the field will be found in that frequency range. If we want to use the spectral density function irrespective of the sign of ω , we have to divide by 2 because

$$I(\omega) = I(-\omega) = (1/2)I(|\omega|). \quad (17)$$

Equation (16) has been derived for a one-dimensional field, and evidently we need an extension to three dimensions. Suppose we have a three-dimensional vector field $\mathbf{F}(t)$ with

components $F_x(t)$, $F_y(t)$, and $F_z(t)$. The correlation functions we are interested in are

$$\langle F_k(t)F_l(t+\tau) \rangle, \quad k, l = x, y, \text{ or } z. \quad (18)$$

An additional approximation to the RPA which will be introduced is the assumption that the field will be isotropic. Any rotation of coordinate axes should leave (18) invariant. As a consequence of the isotropy, we find that

$$\langle F_x(t)F_x(t+\tau) \rangle = \langle F_y(t)F_y(t+\tau) \rangle = \langle F_z(t)F_z(t+\tau) \rangle, \quad (19)$$

and in addition we see that all other components like $\langle F_x(t)F_y(t+\tau) \rangle$ will vanish because they are not invariant under rotation of axes.

The obvious extension of Eq. (16) is now

$$(1/3)I(\omega_1)\delta(\omega_1 + \omega_2)\delta_{k,l} = \langle F_k(\omega_1)F_l(\omega_2) \rangle, \quad k, l = x, y, \text{ or } z. \quad (20)$$

Equations (16) and (20) are equations which give the spectral density in terms of the field amplitudes.

IV. APPLICATION

We will demonstrate the application of Eq. (20) to a molecule in interaction with an electromagnetic field. The energy density (= energy per volume) U can be written as a function of the electric field⁶ \mathbf{E} :

$$U = (4\pi)^{-1} \langle E^2 \rangle. \quad (21)$$

The spectral density function $\rho(\omega)$ (conventional notation), the radiation density, is then given by

$$\langle E_k(\omega_1)E_l(\omega_2) \rangle = (4\pi/3)\rho(\omega_1)\delta(\omega_1 + \omega_2)\delta_{k,l}. \quad (22)$$

To calculate the influence of the field on the molecular system, the variation-of-the-constants method is used. The wave functions of the molecule perturbed by the electromagnetic field will be developed in the unperturbed set $\{\Psi_j^0\}$:

$$\Psi_m = \sum_k C_k \Psi_k^0. \quad (23)$$

If initially only the state Ψ_m^0 was occupied, the product $\langle C_n C_n^* \rangle$ will give the transition probability of the transition $\Psi_m^0 \rightarrow \Psi_n^0$. After substitution of expression (23) in the time-dependent Schrödinger equation, one obtains the following differential equation for the coefficients⁷ C_n :

$$\frac{dC_n}{dt} = \frac{\omega_{nm}}{c\hbar} \int_{-\infty}^{+\infty} \mu_{mn} \cdot \mathbf{A}(\omega) \exp[i(\omega - \omega_{nm})t] d\omega, \quad (24)$$

where the vector potential of the electromagnetic field has been written in its Fourier representation. In Eq. (24) ω_{nm} is the energy difference between Ψ_n^0 and Ψ_m^0 in circular-frequency units and μ_{mn} in the transition dipole moment associated with the transition $\Psi_m^0 \rightarrow \Psi_n^0$. Integration of Eq. (24) with respect to time yields

$$C_n = \frac{\omega_{nm}}{c\hbar} \int_{-\infty}^{+\infty} \mu_{mn} \cdot \mathbf{A}(\omega) f(\omega, t) d\omega. \quad (25)$$

For typographical reasons we have introduced the function $f(\omega, t)$ defined by

$$f(\omega, t) = \frac{\exp[i(\omega - \omega_{nm})t] - 1}{i(\omega - \omega_{nm})}. \quad (26)$$

The probability that the molecule will be in the state Ψ_n^0 at time t will be given by the statistical average of $C_n C_n^*$:

$$\langle C_n C_n^* \rangle = \frac{\omega_{nm}^2}{c^2 \hbar^2} \int \int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \times \langle \mu_{mn} \cdot A(\omega_1) \mu_{mn}^* \cdot A(-\omega_2) \rangle f(\omega_1, t) f^*(\omega_2, t). \quad (27)$$

There remains the problem of finding the relation between $E(\omega)$ and $A(\omega)$. Employing $E = (-1/c)\partial A/\partial t$, we find⁸

$$E(\omega) = -i(\omega/c)A(\omega). \quad (28)$$

When Eq. (28) is substituted in Eq. (27), using Eq. (22), we arrive at

$$\langle C_n C_n^* \rangle = \frac{4\pi\omega_{nm}^2 \mu_{mn}^2}{3\hbar^2} \int \int_{-\infty}^{+\infty} d\omega_1 d\omega_2 \times \frac{\rho(\omega_1)\delta(\omega_1 - \omega_2)f(\omega_1, t)f^*(\omega_2, t)}{\omega_1\omega_2}. \quad (29)$$

Using the definition of the δ function, the double integral is transformed into a single one (RPA!):

$$\langle C_n C_n^* \rangle = \frac{4\pi\omega_{nm}^2 \mu_{mn}^2}{3\hbar^2} \int_{-\infty}^{+\infty} d\omega_1 \rho(\omega_1) \times \frac{\sin^2[(\omega_1 - \omega_{nm})t/2]}{\omega_1^2[(\omega_1 - \omega_{nm})/2]^2}. \quad (30)$$

The time-dependent function

$$\frac{\sin^2[(\omega_1 - \omega_{nm})t/2]}{[(\omega_1 - \omega_{nm})/2]^2}$$

is strongly peaked around $\omega_1 = \omega_{nm}$. We expect that $\rho(\omega_1)/\omega_1^2$ is a slowly varying function in the neighborhood of $\omega_1 = \omega_{nm}$. For sufficiently long times⁹ we can replace $\rho(\omega_1)/\omega_1^2$ by $\rho(\omega_{nm})/\omega_{nm}^2$ because the contribution of $\omega_1 \approx \omega_{nm}$ is strongly dominant to the integral of Eq. (30):

$$\langle C_n C_n^* \rangle = \frac{8\pi\rho(\omega_{nm})\mu_{mn}^2 t}{3\hbar^2} \int_{-\infty}^{+\infty} \frac{\sin^2[(\omega - \omega_{nm})t/2]}{[(\omega - \omega_{nm})t/2]^2} d\left(\frac{\omega - \omega_{nm}}{2}\right). \quad (31)$$

The integral in Eq. (31) is standard and equal to π , so that

$$\langle C_n C_n^* \rangle = 8\pi^2 \mu_{mn}^2 \rho(\omega_{nm}) t / 3\hbar^2 = (4\pi^2 / 3\hbar^2) \mu_{mn}^2 \rho(|\omega_{nm}|) t = (2\pi / 3\hbar^2) \mu_{mn}^2 \rho(|\nu_{nm}|) t. \quad (32)$$

The transition probability for the transition $\Psi_m^0 \rightarrow \Psi_n^0$ is proportional to the exposure time. With some minor changes of notation we could use the same calculation for the transition $\Psi_n^0 \rightarrow \Psi_m^0$ and we would have gotten the same result. In general, this means that the induced transition probability per unit time for the transition $\Psi_k^0 \rightarrow \Psi_l^0$ is equal to

$$(2\pi / 3\hbar^2) \mu_{kl}^2 \rho(|\nu_{lk}|) \equiv B_{kl} \rho(|\nu_{lk}|), \quad (33)$$

where the B_{kl} are the Einstein coefficients for induced absorption and emission.

In many, more conventional derivations of the Einstein coefficients an extra approximation is made.¹⁰ The field is

described as a monochromatic wave, and one finds that

$$C_n \propto \frac{\exp[i(\omega_{nm} - \omega)t] - 1}{\omega_{nm} - \omega} + \frac{\exp[i(\omega_{nm} + \omega)t] - 1}{\omega_{nm} + \omega}, \quad (34)$$

and one argues that the second nonresonance term can be neglected when $\omega \approx \omega_{nm}$. This argument is wrong because afterwards the frequency is integrated from $-\infty$ to $+\infty$, and neglecting the second term when $\omega \approx -\omega_{nm}$ seems difficult to justify. The truth is that none of the terms can be neglected. Both terms give an equal contribution to the absorption if ω_{nm} is positive and to the emission if ω_{nm} is negative. Interference of the two terms of Eq. (34) when calculating $\langle C_n C_n^* \rangle$ does not occur because of the RPA. Combination of Eqs. (8) and (16) shows that the Fourier component of the field with frequency ω is statistically independent of the complex conjugate of the Fourier component with frequency $-\omega$.

The advantage of the derivation given here of the Einstein coefficients is that we know precisely what is meant by the RPA. The radiation density can be given in terms of the Fourier components of the field amplitudes, an expression which cannot be obtained if one uses as a description of the field a summation of discrete waves. In addition, it has been proved here that the separation in resonance and nonresonance terms is unnecessary and false if the light is chaotic.

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¹In the limit $t \rightarrow \infty$ a linear dependence on time is found. The present approach will put a much weaker and more realistic restriction on the exposure time. See also Ref. 9.

²B. B. Kadomtsev, *Plasma Turbulence* (Academic, London, 1965), pp. 19 and 32.

³This difficulty is reflected in the fact that various textbooks give expressions for the spectral density function that are wrong. For instance: (i) H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944), p. 113; (ii) L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935), International Student Edition, p. 302; (iii) J. C. Davis, Jr., *Advanced Physical Chemistry* (Ronald, New York, 1965), p. 252; (iv) G. M. Barrow, *Introduction to Molecular Spectroscopy* (McGraw-Hill, New York, 1962), p. 32.

⁴G. Herzberg, *Atomic Spectra and Structure* (Dover, New York, 1944), p. 152.

⁵This implies that the wavelength of the radiation should be much larger than the dimensions of the molecule. See, for instance, Ref. 7.

⁶L. Landau and E. Lifchitz, *Electrodynamique des Milieux Continus* (MIR, Moscow, 1969), pp. 333 and 346.

⁷D. Bohm, *Quantum Theory* (Prentice-Hall, Englewood Cliffs, NJ, 1951), pp. 416 and 427.

⁸Reference 6, p. 453.

⁹This is allowed if the inverse of the exposure time is smaller than the bandwidth of the light source, a condition usually fulfilled in actual experimental situations.

¹⁰See, for instance, the textbooks mentioned in Ref. 3.