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SYMMETRY RELATIONS FOR THE CROSS SUSCEPTIBILITY TENSOR

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Some general properties of the cross susceptibility with account of spatial dispersion are considered on the basis of the spectral representation. Symmetry relations which are generalizations of the reciprocity relations of Onsager for the linear susceptibility are derived from the invariance of the equations of motion with respect to time inversion. The connection between the nonlinear response and the fluctuations of quantities corresponding to dynamical variables in the unperturbed system is established in general form.

THE general method for describing transport phenomena in the case when the external field is small has been developed relatively recently.[1] With the help of this method general expressions were obtained which connect the kinetic coefficients with the correlation functions for the corresponding dynamical variables, and their general properties were investigated. This method can also be used for the calculation of higher approximations. In the calculations of the next approximations in the external field nonlinear kinetic coefficients are obtained which describe the nonlinear properties of the medium.[2,3] The nonlinear coefficients (of the cross susceptibility) are also expressed in terms of the correlation functions of the corresponding order. This results in a number of general properties for the nonlinear coefficients. The general expressions for the latter can also be used for their approximate computation on the basis of a specific model. In the present paper we consider some general properties of the nonlinear kinetic coefficients with account of spatial dispersion.

1. NONLINEAR RESPONSE AND CROSS SUSCEPTIBILITY OF AN ISOLATED SYSTEM

Let us consider a closed quantum mechanical system whose Hamiltonian is $\mathcal{H}_0$. Let us assume that a given external field $f(\mathbf{r}, t)$ acts on the system and that the interaction with the field $f^a(\mathbf{r}, t)$ is described by an operator of the form[1]

$$V = -\int x^a(\mathbf{r}) f^a(\mathbf{r}, t)\, d\mathbf{r}, \tag{1.1}$$

where $x^a(\mathbf{r})$ is the density operator of some physical quantity. The motion of the system under the action of the external field will be described by a density matrix which in the interaction representation satisfies the equation (cf. [3])

$$i\hbar \partial\rho_{\mathrm{I}} / \partial t = [V_{\mathrm{I}}(t), \rho_{\mathrm{I}}(t)]. \tag{1.2}$$

Taking account of the form of the interaction (1.1), we rewrite (1.2) in integral form:

$$\rho_{\mathrm{I}}(t) = \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{t} dt_1 \int d\mathbf{r}_1 [x^a(\mathbf{r}_1, t_1), \rho_{\mathrm{I}}(t_1)] f^a(\mathbf{r}_1, t_1), \tag{1.3}$$

where $\rho_0 = \rho(-\infty)$ is the value of the density matrix at the moment when the interaction is "switched on" and satisfies the equation $[\mathcal{H}_0, \rho_0] = 0$ (i.e., in the absence of an external field the system is in a stationary state). The external field is "switched on" adiabatically at $t = -\infty$ $[f(\mathbf{r}, -\infty) = 0]$.

To solve (1.3) we use the time dependent perturbation theory. Restricting ourselves to the n-th order of perturbation theory, we have

$$\begin{aligned} \rho_{\mathrm{I}}(t) &= \rho_0 + \rho_{\mathrm{I}}^{(1)}(t) + \ldots + \rho_{\mathrm{I}}^{(n)}(t) \\ &= \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{\infty} dt_1 \int d\mathbf{r}_1 [x^{a_1}(\mathbf{r}_1, t_1), \rho_0] \cdot \eta(t - t_1) \cdot f^{a_1}(\mathbf{r}_1, t_1) \\ &+ \ldots + \left(\frac{i}{\hbar}\right)^n \frac{P_n}{n!} \int_{-\infty}^{\infty} dt_1 \ldots \int_{-\infty}^{\infty} dt_n \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_n \cdot [x^{a_1}(\mathbf{r}_1, t_1) \\ &\times [\ldots [x^{a_n}(\mathbf{r}_n, t_n), \rho_0] \ldots]] \eta(t - t_1) \ldots \eta(t_{n-1} - t_n) \cdot \\ &\cdot f^{a_1}(\mathbf{r}_1, t_1) \ldots f^{a_n}(\mathbf{r}_n, t_n), \end{aligned} \tag{1.4}$$

where $\eta(\tau)$ is the unit step function,

$$\eta(\tau) = \begin{cases} 1, & \tau > 0 \\ 0, & \tau < 0, \end{cases}$$

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[1] In the more general case the interaction must be written in the form where

$$\begin{aligned} V &= -\int x^a(\mathbf{r}) f^a(\mathbf{r}, t)\, d\mathbf{r} + \int n(\mathbf{r}) f^a(\mathbf{r}, t) f^a(\mathbf{r}, t)\, d\mathbf{r} \\ &= -\int x_1^a(\mathbf{r}, t) f^a(\mathbf{r}, t)\, d\mathbf{r}, \end{aligned}$$

$n(\mathbf{r})$ is the charge density operator.

and P_n indicates the summation over the permutations of the indices (1, 2, ..., n).[2)]

Let us find the average value of the density operator $x^a(\mathbf{r})$ in the presence of the external perturbation (1.1). [We can always choose $x^a(\mathbf{r})$ such that $x^a(\mathbf{r}) = 0$ in the absence of the external field.] Using the solution (1.4) for the density matrix and taking account of the cyclic invariance of the trace, we obtain

$$\langle x^a(\mathbf{r},t)\rangle = \operatorname{Sp}\rho_{\mathrm{I}}(t)x^a(\mathbf{r},t) = \langle x^a(\mathbf{r},t)\rangle^{(1)} + \ldots + \langle x^a(\mathbf{r},t)\rangle^{(n)} = \int_{-\infty}^{\infty} d\tau_1 \int d\mathbf{r}_1\, \varphi_{aa_1}(\tau_1,\mathbf{r},\mathbf{r}_1) f^{a_1} \times (\mathbf{r}_1, t_1-\tau_1) + \ldots + \int_{-\infty}^{\infty} d\tau_1 \ldots \int_{-\infty}^{\infty} d\tau_n \cdot \int d\mathbf{r}_1 \times \int d\mathbf{r}_n\, \varphi_{aa_1\ldots a_n}(\tau_1,\ldots,\tau_n,\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_n) f^{a_1}(\mathbf{r}_1, t-\tau_1) \ldots f^{a_n}(\mathbf{r}_n, t-\tau_n), \tag{1.5}$$

where

$$\varphi_{aa_1\ldots a_n}(\tau_1,\ldots,\tau_n,\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_n) = \left(\frac{i}{\hbar}\right)^n \frac{P_n}{n!} \operatorname{Sp}\rho_0[[\ldots[x^a(\mathbf{r}), x^{a_1}(\mathbf{r}_1,-\tau_1)]\ldots] \times x^{a_n}(\mathbf{r}_n,-\tau_n)]\cdot\eta(\tau_1)\eta(\tau_2-\tau_1)\ldots\eta(\tau_n-\tau_{n-1}) \tag{1.6}$$

is expressed only through operators and states in the absence of the external field. Following [2, 3], we shall call $\varphi_{aa_1\ldots a_n}(\tau_1, \ldots, \tau_n, \mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_n)$ the nonlinear response or reaction function.[3)]

Any external field which depends on the time and on the coordinates can be reduced to a set of monochromatic components by a Fourier expansion. We shall therefore consider in the following the reaction of the system to a monochromatic field of the form

$$f^{a_i}(\mathbf{r}_i, t-\tau_i) = f^{a_i}(\omega_i, \mathbf{k}_i)\exp\{-i[\omega_i(t-\tau_i) - \mathbf{k}_i\mathbf{r}_i]\} + \text{c.c.} \tag{1.7}$$

If the system is homogeneous in space, the reaction function will also depend only on the coordinate differences $\mathbf{R}_i = \mathbf{r} - \mathbf{r}_i$. Substituting the external field of the form (1.7) in (1.5) and expanding the left- and right-hand sides into a Fourier integral in the variables $\mathbf{r}, t$, we obtain

$$\langle x^a(\omega,\mathbf{k})\rangle^{(n)} = \chi_{aa_1\ldots a_n}(\omega_1,\mathbf{k}_1,\ldots,\omega_n,\mathbf{k}_n) f^{a_1}(\omega_1,\mathbf{k}_1) \ldots f^{a_n}(\omega_n,\mathbf{k}_n)\cdot(2\pi)^4\delta(\omega_1+\ldots+\omega_n-\omega)\,\delta(\mathbf{k}_1+\ldots+\mathbf{k}_n-\mathbf{k}), \tag{1.8}$$

where

$$\chi_{aa_1\ldots a_n}(\omega_1,\mathbf{k}_1,\ldots,\omega_n,\mathbf{k}_n) = \int_{-\infty}^{\infty} d\tau_1 \ldots \int_{-\infty}^{\infty} d\tau_n \int dR_1 \ldots \int dR_n \times \varphi_{ao_1\ldots a_n}(\tau_1, R_1, \ldots, \tau_n, R_n)\exp\{i(\omega_1\tau_1 - \mathbf{k}_1\mathbf{R}_1) + \ldots + i(\omega_n\tau_n - \mathbf{k}_n\mathbf{R}_n\}. \tag{1.9}$$

is the cross susceptibility of the system[3] which characterizes the nonlinear response to a monochromatic field of the form (1.7). If the system is not homogeneous in space, the response will be a function of $\mathbf{r}$ as well as of the variables $\mathbf{R}_1, \ldots \mathbf{R}_n$. An important example of such systems are the crystals.

However, taking account of the fact that $\varphi_{aa_1\ldots a_n}(\tau_1, \ldots, \tau_n, \mathbf{r}, \mathbf{R}_1, \ldots, \mathbf{R}_n)$ for a crystal is a periodic function of $\mathbf{r}$ with the period of the lattice, we expand it in a spatial Fourier series:[4]

$$\varphi_{aa_1\ldots a_n}(\tau_1,\ldots,\tau_n,\mathbf{r},\mathbf{R}_1,\ldots,\mathbf{R}_n) = \sum_{\mathbf{K}} \varphi^{\mathbf{K}}_{aa_1\ldots a_n}(\tau_1,\mathbf{R}_1,\ldots,\tau_n\mathbf{R}_n)e^{i2\pi\mathbf{K}\mathbf{r}}, \tag{1.10}$$

where $\mathbf{K} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$ are the vectors of the reciprocal lattice. Then we have instead of (1.8)

$$\langle x^a(\omega,\mathbf{k})\rangle^{(n)} = \sum_{\mathbf{K}} \chi^{\mathbf{K}}_{aa_1\ldots a_n}(\omega_1,\mathbf{k}_1,\ldots,\omega_n,\mathbf{k}_n) \times f^{a_1}(\omega_1,\mathbf{k}_1)\ldots f^{a_n}(\omega_n,\mathbf{k}_n)\cdot(2\pi)^4\delta(\omega_1+\ldots+\omega_n-\omega)\,\delta(\mathbf{k}_1+\ldots+\mathbf{k}_n-\mathbf{k}+2\pi\mathbf{K}), \tag{1.11}$$

$\chi^{\mathbf{K}}_{aa_1\ldots a_n}(\omega_1, \mathbf{k}_1, \ldots, \omega_n, \mathbf{k}_n)$ is the cross susceptibility of the crystal. In the following we shall for simplicity consider the space-homogeneous case.

2. SPECTRAL REPRESENTATION FOR THE CROSS SUSCEPTIBILITY

Let us express the cross susceptibility of the system in terms of the Fourier components of the operators $x^{a_i}(\mathbf{r}_i, t_i)$, which we define by [5]

$$x^{a_i}(\Omega_i,\mathbf{k}_i) = \frac{1}{(2\pi)^4}\int_{-\infty}^{\infty} dt_i \int d\mathbf{k}_i x^{a_i}(t_i,\mathbf{r}_i)\exp\{i(\Omega_i t_i + \mathbf{k}_i\mathbf{r}_i)\} \tag{2.1}$$

and the inverse transformation

$$x^{a_i}(t_i\mathbf{r}_i) = \int_{-\infty}^{\infty} d\Omega_i \int d\mathbf{k}_i\, x^{a_i}(\Omega_i,\mathbf{k}_i)\exp\{-i(\Omega_i t_i + \mathbf{k}_i\mathbf{r}_i)\}. \tag{2.2}$$

Substituting (2.2) in the definition of the cross susceptibility (1.9) and using the integral representation of the unit step function,[6]

$$\eta(\tau_n - \tau_{n-1}) = \frac{i}{2\pi}\int_{-\infty}^{\infty} \frac{d\Omega_n'}{\Omega_n' + i\varepsilon}\exp\{-i\Omega_n'(\tau_n - \tau_{n-1})\}, \tag{2.3}$$

[2)] We have already written a symmetrized expression for ρ_{I} $\rho_{\mathrm{I}}^{(n)}(t)$ in (1.4). The action of the permutation operator $P_n/n!$ does of course not alter $\rho_{\mathrm{I}}^{(n)}(t)$.

[3)] Owing to the stationary property, the reaction function depends only on the time difference $\tau_i = t - t_i$ (i = 1,2,...,n).

we obtain after simple transformations[4)]

$$\chi_{a_1 a_1 \ldots a_n}(\omega_1, \mathbf{k}_1, \ldots, \omega_n, \mathbf{k}_n) = \frac{(-1)^n P_n}{(\hbar)^n n!} \int_{-\infty}^{\infty} d\Omega_1 \ldots \int_{-\infty}^{\infty} d\Omega_n \frac{1}{\Omega_n + \omega_n + i\varepsilon}$$

$$\times \frac{1}{\Omega_n + \Omega_{n-1} + \omega_n + \omega_{n-1} + i\varepsilon} \cdots \frac{1}{\Omega + \omega + i\varepsilon}$$

$$\times I_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n), \tag{2.4}$$

where

$$I_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = \operatorname{Sp} \rho_0 [[\ldots [x^a(\Omega_0, \mathbf{k}_0),$$

$$\times x^{a_1}(\Omega_1, \mathbf{k}_1)] \ldots] x^{a_n}(\Omega_n, \mathbf{k}_n)],$$

$$\begin{aligned} \Omega &= -\Omega_0, & \Omega_0 + \Omega_1 + \ldots + \Omega_n &= 0, \\ \omega &= -\omega_0, & \omega_0 + \omega_1 + \ldots + \omega_n &= 0, \\ \mathbf{k} &= -\mathbf{k}_0, & \mathbf{k}_0 + \mathbf{k}_1 + \ldots + \mathbf{k}_n &= 0. \end{aligned} \tag{2.5}$$

Instead of $x^a(\Omega_0, \mathbf{k}_0)$ one can also write the Schrödinger operator $x^a(\mathbf{r} = 0)$ in (2.5).

The spectral representation of the type (2.4) is known in quantum field theory as the Lehmann representation.[8, 9] If we regard the operators $x^a(\mathbf{r}, t)$ in the second quantization scheme, then the response of the system (1.6) is a many-time retarded Green's function and (2.4) is its spectral representation.

Together with the Green's functions (1.6) we shall consider also the correlation functions

$$F_{aa_1 \ldots a_n}(\mathbf{r}, t, \mathbf{r}_1, t_1, \ldots, \mathbf{r}_n, t_n) = \operatorname{Sp} \rho_0 x^a(\mathbf{r}, t) x^{a_1}(\mathbf{r}_1, t_1) \ldots x^{a_n}(\mathbf{r}_n, t_n). \tag{2.6}$$

The correlation functions (2.6) characterize the fluctuations of n + 1 quantities in the unperturbed system. The spectral representations for the correlation functions (2.6) are found in analogy to (2.4):

$$S_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = \operatorname{Sp} \rho_0 x^a(\Omega_0, \mathbf{k}_0) x^{a_1}(\Omega_1, \mathbf{k}_1) \ldots x^{a_n}(\Omega_n, \mathbf{k}_n). \tag{2.7}$$

3. SYMMETRY RELATIONS FOR THE CROSS SUSCEPTIBILITY

A number of general properties follow from the definition of the cross susceptibility and its spectral representation (2.4), which are independent of the specific form of the Hamiltonian of the system (cf., for example, [3]). Let us consider some of these. From the hermiticity of the operators $x^{a_i}(\mathbf{r}_i, t_i)$ we obtain for the correlation functions (2.6) the relation

$$\operatorname{Sp} \rho_0 x^a(\mathbf{r}, t) \ldots x^{a_n}(\mathbf{r}_n, t_n) = (\operatorname{Sp} \rho_0 x^{a_n}(\mathbf{r}_n, t_n) \ldots x^a(\mathbf{r}, t))^*. \tag{3.1}$$

Then we find for the spectral representation (2.7)

$$S_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = S^*_{a_n a_{n-1} \ldots a}(-\mathbf{k}_{n-1}, -\Omega_{n-1}, \ldots, -\mathbf{k}_0, -\Omega_0). \tag{3.1$'$}$$

From the invariance of the equations of motion under time inverstion t → −t (cf. [10, 11]) we have

$$F_{aa_1 \ldots a_n}(\tau_1, \mathbf{R}_1, \ldots, \tau_n, \mathbf{R}_n) = \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} F_{aa_1 \ldots a_n}(-\tau_1, \mathbf{R}_1, \ldots, -\tau_n, \mathbf{R}_n), \tag{3.2}$$

if the operators $x^{a_i}(\mathbf{r}_i)$ $(i = 1, 2, \ldots, n)$ do not change sign under time inversion. In the general case

$$F_{aa_1 \ldots a_n}(\tau_1, \mathbf{R}_1, \ldots, \tau_n, \mathbf{R}_n) = \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} F^*_{aa_1 \ldots a_n}(-\tau_1, \mathbf{R}_1, \ldots, -\tau_n, \mathbf{R}_n), \tag{3.2$'$}$$

where ϵ^{a_i} is equal to -1 or 1, respectively, depending on whether $x^{a_i}(\mathbf{r}_i)$ changes sign or not under time inversion.

For the spectral representation (2.7) we obtain from (3.2′)

$$S_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} S^*_{aa_1 \cdots a_n}(-\mathbf{k}_1, \Omega_1, \ldots, -\mathbf{k}_n, \Omega_n). \tag{3.3}$$

In particular, (3.3′) implies that for media without spatial dispersion or with inversion symmetry, $S_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n)$ is purely real or imaginary depending on the sign of the product $\epsilon^a \epsilon^{a_1} \ldots \epsilon^{a_n}$. In this case the cross susceptibility without absorption will be purely real if $\epsilon^a \epsilon^{a_1} \ldots \epsilon^{a_n} = 1$, and purely imaginary if $\epsilon^a \epsilon^{a_1} \ldots \epsilon^{a_n} = -1$.

Comparing (3.1′) with (3.3), we find

$$S_{aa_1 \ldots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} S_{a_n a_{n-1} \ldots a}(-\Omega_{n-1}, \mathbf{k}_{n-1}, \ldots, -\Omega_0, \mathbf{k}_0), \tag{3.4}$$

which leads to

$$I_{aa_1, \ldots, a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n) = (-1)^n \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} I_{aa_1 \ldots a_n}(-\Omega_1, \mathbf{k}_1, \ldots, -\Omega_n, \mathbf{k}_n). \tag{3.5}$$

We note that for the linear susceptibility we ob-

[4)] We assume that $I_{aa_1 \ldots a_n}(\Omega_1, k_1, \ldots, \Omega_n, k_n)$ tends to zero as $\Omega_i \to \infty$ $(i = 1, 2, \ldots, n)$. Otherwise one must introduce subtractions (cf. the book Bololyubov and Shirkov [7]).

tain at once from (3.5) the known Onsager reciprocity relation[5)][12, 1]

$$\chi_{aa_1}(\omega, \mathbf{k}) = \varepsilon^a \varepsilon^{a_1} \chi_{a_1 a}(\omega, -\mathbf{k}). \qquad (3.6)$$

For the cross susceptibility (2.4) we obtain

$$\chi_{aa_1\cdots a_n}(\omega_1, \mathbf{k}_1, \ldots, \omega_n, \mathbf{k}_n)$$
$$= \frac{(-1)^n P_n}{(\hbar)^n n!} \int_{-\infty}^{\infty} d\Omega_1 \ldots \int_{-\infty}^{\infty} d\Omega_n \frac{\varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n}}{\Omega_n - \omega_n - i\varepsilon} \cdots$$
$$\cdots \frac{1}{\Omega - \omega - i\varepsilon} I_{aa_1\cdots a_n}(\Omega_1, \mathbf{k}_1, \ldots, \Omega_n, \mathbf{k}_n), \qquad (3.7)$$

i.e., apart from the sign function $\epsilon^{a} \epsilon^{a_1} \ldots \epsilon^{a_n}$ the Fourier transform of the advanced Green's function is equal to the Fourier transform of the retarded one when the signs of the frequencies ω_i ($i = 1, 2, \ldots, n$) are reversed.

Let us assume further that the frequencies $\omega_2, \ldots, \omega_n$ and their combinations are far away from the eigen-frequencies of the system (no resonance). Then the cross susceptibility (2.4) satisfies the symmetry relation

$$\chi_{aa_1\cdots a_n}(\omega_1, \mathbf{k}_1, \ldots, \omega_n, \mathbf{k}_n)$$
$$= \varepsilon^a \varepsilon^{a_1} \ldots \varepsilon^{a_n} \chi_{a_1 a \ldots a_n}(\omega, \mathbf{k}_0, \ldots, -\omega_n, \mathbf{k}_n). \qquad (3.8)$$

For simplicity we restrict ourselves to the proof of (3.8) for the third rank tensor $\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2)$. We rewrite the spectral representation (2.4) using the operator identity

$$\frac{1}{\omega + \Omega + i\varepsilon} = \frac{P}{\omega + \Omega} - i\pi\delta(\omega + \Omega) \qquad (3.8')$$

and replacing $(\omega_2 + \Omega_2 + i\epsilon)^{-1}$ by $P(\omega_2 + \Omega_2)^{-1}$:

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2)$$
$$= \frac{P_2}{\hbar^2 2!} \int_{-\infty}^{\infty} d\Omega_1 \int_{-\infty}^{\infty} \frac{d\Omega_2}{\Omega_2 + \omega_2} \frac{1}{\Omega + \omega} I_{aa_1a_2}(\Omega_1, \mathbf{k}_1, \Omega_2, \mathbf{k}_2)$$
$$- \frac{i\pi P_2}{\hbar^2 2!} \int_{-\infty}^{\infty} \frac{d\Omega_2}{\Omega_2 + \omega_2} I_{aa_1a_2}(\omega_0 - \Omega_2, \mathbf{k}_1, \Omega_2, \mathbf{k}_2)$$
$$- \frac{i\pi}{\hbar^2 2!} \int_{-\infty}^{\infty} \frac{d\Omega_2}{\Omega_2 + \omega_2} I_{aa_2a_1}(\Omega_2, \mathbf{k}_2, -\omega_1, \mathbf{k}_1). \qquad (3.9)$$

The integrals in (3.9) are taken in the sense of the principal value. The first term on the right-hand side of (3.9) has the same form as the cross susceptibility in the absence of absorption and has the symmetry[6)]

$$\overset{(1)}{\chi}_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \overset{(1)}{\chi}_{a_1a_2a}(\omega_2, \mathbf{k}_2, \omega_0, \mathbf{k}_0)$$
$$= \overset{(1)}{\chi}_{a_2aa_1}(\omega_0, \mathbf{k}_0, \omega_1, \mathbf{k}_1). \qquad (3.10)$$

Using (3.7) we can rewrite the first equation (3.10) as

$$\overset{(1)}{\chi}_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \varepsilon^a \varepsilon^{a_1} \varepsilon^{a_2} \overset{(1)}{\chi}_{a_1aa_2}(\omega_1 + \omega_2, \mathbf{k}_0, -\omega_2, \mathbf{k}_2). \qquad (3.10')$$

Applying a dispersion relation in ω_1 for fixed ω_2 to (3.10′),[7)] we obtain the symmetry relation

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \varepsilon^a \varepsilon^{a_1} \varepsilon^{a_2} \chi_{a_1aa_2}(\omega_1 + \omega_2, \mathbf{k}_0, -\omega_2, \mathbf{k}_2).$$

In the general case the proof of (3.8) is analogous. If the frequencies $\omega_2, \ldots, \omega_n$ are zero, (3.8) leads to the Onsager reciprocity relations for a system in a constant external field:

$$\chi_{aa_1}(\omega, \mathbf{k}, \mathbf{E}) = \varepsilon^a \varepsilon^{a_1} \chi_{a_1a}(\omega, -\mathbf{k}, \mathbf{E}),$$
$$\chi_{aa_1}(\omega, \mathbf{k}, \mathbf{H}) = \varepsilon^a \varepsilon^{a_1} \chi_{a_1a}(\omega, -\mathbf{k}, -\mathbf{H}), \qquad (3.11)$$

where **E** is the electric field and **H** the magnetic field. The symmetry relations (3.8) can also be regarded as the generalization of the reciprocity relations (3.11) for the case when the system is in a variable external field.

Let us obtain the symmetry relations corresponding to the replacement $a_2, \omega_2, \mathbf{k}_2 \rightleftarrows a, \omega_0, \mathbf{k}_0$ (there is no resonance at the frequency ω_2). To this end we also write down the explicit form of $\chi_{a_2a_1a}(\omega_1, \mathbf{k}_1, \omega_0, \mathbf{k}_0)$ replacing $(\omega_2 + \Omega_2 + i\epsilon)^{-1}$ by $P(\omega_2 + \Omega_2)^{-1}$:

$$\chi_{a_2a_1a}(\omega_1, \mathbf{k}_1, \omega_0, \mathbf{k}_0) = \overset{(1)}{\chi}_{a_2a_1a}(\omega_1, \mathbf{k}_1, \omega_0, \mathbf{k}_0) + \frac{i\pi}{\hbar^2 2!} \int_{-\infty}^{\infty} \frac{d\Omega_2}{\Omega_2 + \omega_2}$$
$$\times [I_{a_2a_1a}(\omega - \Omega_2, \mathbf{k}_1, \omega, \mathbf{k}_0) + I_{a_2aa_1}(\omega_1 - \Omega_2, \mathbf{k}_0, -\omega_1, \mathbf{k}_1) \qquad (3.12)$$

[5)] We use the commutator property.

$$I_{aa_1}(\Omega, \mathbf{k}) = -I_{a_1a}(-\Omega, -\mathbf{k}).$$

[6)] The symmetry relations (3.10) follow from the spectral representation (2.4) if we replace $(\omega + \Omega + i\epsilon)^{-1}$ by $P(\omega + \Omega)^{-1}$. The symmetry relations (3.10) have been proved phenomenologically by Bloembergen [13] using the condition that there be no absorption, and by Fain and Khanin [3] from the form of the tensor. When the frequency disperion and the spatial dispersion are neglected, (3.10) goes over into the symmetry relations of Kleinman. man. [14]

[7)] The dispersion relations are obtained from the spectral representation (2.4) by using the analytic properties of the cross susceptibility as a function of the complex variables $\omega_1, \ldots, \omega_n$ (cf. [7,15,16]):

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{\chi_{aa_1a_2}(\omega_1', \mathbf{k}_1, \omega_2, \mathbf{k}_2)}{\omega_1' - \omega_1} d\omega_1'.$$

We note that if there is a resonance at $\omega_1 \neq 0$, then there is no resonance at $\omega = \omega_1 + \omega_2$, and vice versa. Depending on this circumstance, we obtain different symmetry relations.

If there is no resonance at the frequency ω, then we find, using the Jacobi identity (3.16) and (3.3),

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \chi_{a_2a_1a}(\omega_1, \mathbf{k}_1, \omega_0, \mathbf{k}_0). \tag{3.13}$$

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = \varepsilon^{\alpha}\varepsilon^{\alpha_1}\varepsilon^{\alpha_2}\chi^{*}{}_{a_2a_1a}(\omega_1, -\mathbf{k}_1, \omega_0, -\mathbf{k}_0). \tag{3.14}$$

The relations (3.13) and (3.14) can be proved for tensors of higher rank (assuming that there is no resonance at the frequencies $\omega_2, \ldots, \omega_n$).

Let us assume there is a resonance at the frequencies ω_1 and ω_2. Then there is also a resonance at the frequency $\omega = \omega_1 + \omega_2$. If we discard the nonresonance term, we have the relation

$$\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) + \chi_{a_1a_2a}(\omega_2, \mathbf{k}_2, \omega_0, \mathbf{k}_0) + \chi_{a_2aa_1}(\omega_0, \mathbf{k}_0, \omega_1, \mathbf{k}_1) = 0. \tag{3.15}$$

Relation (3.15) is a consequence of the Jacobi identity

$$I_{aa_1a_2}(\Omega_1, \mathbf{k}_1, \Omega_2, \mathbf{k}_2) + I_{a_1a_2a}(\Omega_2, \mathbf{k}_2, \Omega_0, \mathbf{k}_0) + I_{a_2aa_1}(\Omega_0, \mathbf{k}_0, \Omega_1, \mathbf{k}_1) = 0. \tag{3.16}$$

The relations (3.8), (3.13), (3.14), and (3.15) completely characterize the symmetry of the cross susceptibility $\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2)$ under the replacement

$$a,\ \omega_0,\ \mathbf{k}_0 \rightleftarrows a_1,\ \mathbf{k}_1,\ \omega_1; \quad a_2,\ \omega_2,\ \mathbf{k}_2.$$

4. FLUCTUATION-DISSIPATION THEOREM

Let us assume that the unperturbed system is in a state of thermodynamic equilibrium. In this case we extract significant information merely from the cyclic invariance of the trace and the formal similarity between the evolution operator of the system, $e^{-i\mathscr{H}t}$, and the density matrix for the Gibbs distribution $\rho_0 = e^{-\beta\mathscr{H}}$ (cf. [6]). Indeed, for imaginary values of the time $t = -i\beta$ the two quantities coincide. Using this fact we can write

$$x^{a}(\mathbf{r}, t)\, e^{-\beta\mathscr{H}} = e^{-\beta}\, x^{a}(\mathbf{r}, t - i\beta). \tag{4.1}$$

The analyticity of the trace of operators $x^{a_i}(\mathbf{r}_i, t_i)$ for complex values of the time arguments introduced according to (4.1) follows from the condition of the existence of the correlation functions (2.7). Applying a Fourier transformation to both sides of (4.1), we have

$$x^{a}(\mathbf{k}, \Omega)\, e^{-\beta\mathscr{H}} = e^{-\beta\mathscr{H}}\, x^{a}(\mathbf{k}, \Omega)\, e^{-\beta\Omega}. \tag{4.2}$$

Using the cyclic invariance of the trace and the property (4.2), we can easily express the cross susceptibility of the system through the spectral correlation function (2.7). For simplicity we restrict ourselves to the case of a third-rank tensor. Using also (3.7), we obtain

$$\begin{aligned}\chi_{aa_1a_2}(\omega_1, \mathbf{k}_1, \omega_2, \mathbf{k}_2) = {} & \frac{1}{\hbar^2 2!}\int_{-\infty}^{\infty} d\Omega_1 \\ & \times \int_{-\infty}^{\infty} d\Omega_2 \Big[\frac{1}{f(\Omega_1+\Omega_2)}\Big(\frac{1}{\Omega_1+\omega_1+i\varepsilon} \\ & \times \frac{1}{\Omega+\omega+i\varepsilon} + \frac{\varepsilon^{a}\,\varepsilon^{a_1}\,\varepsilon^{a_2}}{(\omega_1-\Omega_1+i\varepsilon)\,(\omega-\Omega+i\varepsilon)}\Big) \\ & - \frac{1}{f(\Omega_2)}\Big(\frac{1}{\omega_2+\Omega_2+i\varepsilon}\cdot\frac{1}{\omega+\Omega+i\varepsilon} \\ & + \frac{\varepsilon^{a}\,\varepsilon^{a_1}\,\varepsilon^{a_2}}{(\omega_2-\Omega_2+i\varepsilon)\,(\omega-\Omega+i\varepsilon)}\Big)\Big]\, S_{aa_1a_2}(\Omega_1, \mathbf{k}_1, \Omega_2, \mathbf{k}_2),\end{aligned} \tag{4.3}$$

where the function $f(\Omega) = (e^{\beta\Omega} - 1)^{-1}$ has the meaning of an average value of the occupation number for energy Ω and temperature $T = 1/k\beta$.

The relation (4.3) establishes a connection between the nonlinear response of the system to an external perturbation and the fluctuation of three quantities in a state of thermodynamic equilibrium. The relation between the linear susceptibility and the fluctuations in an unperturbed system has been considered by many authors and bears the name of the Callen-Welton theorem or fluctuation-dissipation theorem.[17,1]

We also note that the fluctuations in a system in the presence of external fields can also be expressed in terms of the correlation functions (2.7).

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[1] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[2] W. Bernard and H. B. Callen, Revs. Modern Phys. **31**, 1017 (1959).

[3] V. M. Faĭn and Ya. I. Khanin, Kvantovaya radiofizika (Quantum Radiophysics), Sov. Radio (1965).

[4] V. M. Agranovich and V. L. Ginzburg, Kristallooptika s uchetom prostranstvennoĭ dispersii (Crystal Optics with Account of Spatial Dispersion), Nauka (1965).

[5] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Fizmatgiz (1964), Engl. Transl. Pergamon Press, London (1958).

[6] P. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

[7] N. N. Bogolyubov and D. V. Shirkov, Vvedenie v teoriyu kvantovannykh poleĭ (Introduction to the Theory of Quantized Fields) Gostekhizdat (1957), Engl. Transl. Interscience Publishers, Inc., N. Y. (1959).

[8] H. Lehmann, Nuovo Cimento **11**, 342 (1954).

[9] Y. Nambu, Phys. Rev. **100**, 394 (1955).

[10] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat (1957), Engl. Transl. Pergamon Press, London (1960).

[11] A. S. Davydov, Kvantovaya Mekhanika (Quantum Mechanics), Fizmatgiz (1963), Engl. Transl. Pergamon Press, London (1965).

[12] L. Onsager, Phys. Rev. **37**, 405 (1931) and **38**, 2265 (1931).

[13] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[14] D. A. Kleinman, Phys. Rev. **126**, 1977 (1962).

[15] F. V. Bunkin, Izv. VUZov, Radiofizika **5**, 687 (1962).

[16] Sh. M. Kogan, JETP **43**, 304 (1962), Soviet Phys. JETP **16**, 217 (1963).

[17] N. V. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

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