THE TIME CORRELATION FUNCTION TECHNIQUE AND ITS APPLICATION TO THE THEORY OF THE SHIFT AND DEFORMATION OF THE MÖSSBAUER LINE

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The interactions of arbitrary radiations (particles, light quanta) with complex systems (molecules, liquids, etc) are discussed to see what information about the structure and dynamics of a complex system can be gotten from an analysis of data concerning its interaction with the probe system, and conversely what characteristics of the complex system must be known in order to predict the results of such an interaction. It is shown that the time correlation function (TCF) is a convenient formalism for this purpose; in the special case where the interaction of the radiation and the system can be treated in the Born approximation, the results agree with those of Van Hove.[1]

We consider the basic properties of the TCF's corresponding to different types of probe particles and their interaction with the system. In particular it is shown that the TCF is generally complex and becomes real only when one neglects "recoil" of the system, which is equivalent to going over to the classical limit ($\hbar \to 0$). If the system is in thermal equilibrium, the real and imaginary parts of the TCF are connected by relations which are a consequence of the Nyquist fluctuation dissipation theorem. The formalism is generalized to the case where effects of damping in the initial state are important. As an example, we treat the shift and distortion of lines for recoilless resonant absorption or emission of γ quanta which result from the difference in the Hamiltonians for the atomic motion in the ground and excited states of the Mössbauer nucleus. Integral relations connecting the Mössbauer probability (as a function of temperature) with the shape of the Mössbauer line are obtained. It is shown that when there are discrete degrees of freedom the Mössbauer line will not only shift but will also be markedly distorted.

1. INTRODUCTION

The experimental study of complex atomic systems (molecules, crystals, liquids) and other quantum mechanical systems with a large number of degrees of freedom is done as a rule by studying their interaction with simpler objects, whose states are relatively easily distinguished experimentally: for example, by studying the scattering, absorption and emission of light quanta, electrons, slow neutrons, etc. The system under investigation is frequently a statistical ensemble (in particular it may be in thermal equilibrium at temperature T). The question arises: what is the maximal information about the investigated system that can be gotten from such experiments if we assume that the states of the directly measured object (the "probing radiation") before and after interaction can be determined to arbitrary accuracy? Another aspect of the problem is: what properties of the system "under investigation" must one know in order to predict the result of its interaction with the "probe particles"?

In the particular case of scattering, for the case where the Born approximation is applicable, this question was discussed by Van Hove.[1] In the Born approximation, except for a trivial factor the differential scattering cross section $\partial^2\sigma/\partial E\,\partial\Omega$ depends only on four independent variables: the energy transfer ΔE and the momentum transfer Δp. Van Hove showed that it can be related uniquely to the pair correlation function in space and time of the particles constituting the scattering system. For example, if scattering occurs only from one of the nuclei of the system,

$$\frac{\partial^2\sigma}{\partial E\,\partial\Omega} \sim \int_{-\infty}^{\infty} \exp\left(-\frac{i}{\hbar}t\Delta E\right) K(t)\,dt, \qquad (1.1)$$

where K(t) is the statistical and quantum mechanical average of the operator $\hat{T}^+(t)\,\hat{T}(0)$, where $\hat{T}(t) = \exp(i\Delta p \cdot \hat{R}(t)/\hbar)$, where $\hat{R}(t)$ is the Heisen-

berg operator for the coordinate of the scattering particle. Van Hove's approach proved to be extremely fruitful in describing and interpreting the potential scattering of neutrons (and also the Mössbauer effect) in complex atomic systems.

Earlier[2] the Van Hove formalism was generalized to the case of resonance scattering of neutrons and γ quanta by atomic systems. In the present work we show that formula (1.1) is entirely general: different types of probe particles and their interaction with the system under study are distinguished only by the particular type of operator $\hat{T}(t)$ (i.e., by its dependence on the parameters of the probe radiation). Each such operator can be regarded as a sort of dynamic variable characterizing the system under investigation. The corresponding function K(t) is the time correlation function (TCF) of this dynamical variable. The form of the operator $\hat{T}(t)$ for various special cases is discussed. As an example we consider the question of the shift and deformation of the Mössbauer line because of the difference in the Hamiltonians for the atomic motion when the Mössbauer nucleus is in the ground state and in the excited state. This question has been considered previously only in special cases, in connection with the so-called isomer or chemical shift[3] and the temperature or Doppler[4-6] shift.

2. DERIVATION OF GENERAL FORMULAS

We denote the sets of variables, the quantum numbers and the energy of the system by R, ρ and E^{ρ}, respectively; similarly, for the probe particles, we use the symbols Z, ζ and ϵ^{ζ}. The final states will be marked by a subscript f and the initial states by i. The set of quantities characterizing the system includes indices giving the type of particle (which may change in the course of the interaction).

We also introduce the operator $\hat{T}$, the scattering matrix,[7] which coincides in first order perturbation theory with the operator for the energy of interaction of the systems; the matrix elements of $\hat{T}$ are related to those of the $\hat{S}$ matrix by

$$(\rho_f\zeta_f|\hat{S}-1|\zeta_i\rho_i) = -2\pi i\delta(E_f^{\rho}+\varepsilon_f^{\zeta}-E_i^{\rho}-\varepsilon_i^{\zeta}) \times(\rho_f\zeta_f|\hat{T}(Z,R)|\zeta_i\rho_i). \quad (2.1)$$

In addition we introduce the notation $F(\zeta_f)d\zeta_f$ for the number of final states of the probe particle in the interval of quantum numbers $d\zeta_f$, g_i^{ρ} for the statistical weight of the state $|\rho_i)$ of the system under investigation, with $\Sigma_i g_i\rho = 1$. The probability for transition into unit interval of the quantum numbers of the probe system per unit time is

$$W(\zeta_f,\zeta_i) = \frac{2\pi}{\hbar}\sum_{\rho_f}\sum_{\rho_i} g_i^{\rho}|(\rho_f|\hat{T}_{fi}^{\zeta}(R)|\rho_i)|^2 F(\zeta_f) \times\delta(E_f^{\rho}-E_i^{\rho}+\hbar\omega_{fi});$$

$$\hat{T}_{fi}^{\zeta}(R) = (\zeta_f|\hat{T}(Z,R)|\zeta_i), \qquad \hbar\omega_{fi} = \varepsilon_f^{\zeta}-\varepsilon_i^{\zeta}. \quad (2.2)$$

We introduce the Heisenberg operators

$$\hat{T}_{fi}^{\zeta}(R,t) = \exp(i\hat{H}t/\hbar)\hat{T}_{fi}^{\zeta}(R)\exp(-i\hat{H}t/\hbar), \quad (2.3)$$

where H is the Hamiltonian for the investigated system alone. To do this we write the δ function in the energy as a Fourier integral and carry out the summation over ρ_f. The result is

$$W(\zeta_f,\zeta_i) = \hbar^{-2}F(\zeta_f)\int_{-\infty}^{\infty} dt\exp(-i\omega_{fi}t) \times\langle(\hat{T}_{if}^{\zeta+}(R,t)\,\hat{T}_{fi}^{\zeta}(R,0))\rangle, \quad (2.4)$$

where the angular brackets denote an average over the initial states of the investigated system:

$$\langle(\ldots)\rangle = \sum_i g_i^{\rho}(\rho_i|\ldots|\rho_i).$$

Thus the transition probability is the time Fourier component of the function $K_{fi}^{\zeta}(t) \equiv K_{fi}^{\zeta}(t,0)$, where

$$K_{fi}^{\zeta}(t,t') \equiv \langle(\hat{T}_{if}^{\zeta+}(R,t)\hat{T}_{fi}^{\zeta}(R,t'))\rangle, \quad (2.5)$$

i.e., knowing $K_{fi}^{\zeta}(t)$ as a function of t, one can uniquely determine $W(\zeta_f,\zeta_i)$.

The problem of reconstructing $K_{fi}^{\zeta}(t)$ from data on $W(\zeta_f,\zeta_i)$ is more complicated, since the inverse formula

$$K_{fi}^{\zeta}(t) = \frac{\hbar^2}{2\pi}\int_{-\infty}^{\infty} d\omega_{fi}\exp(i\omega_{fi}t)\,W(\zeta_f,\zeta_i)/F(\zeta_f)$$

is meaningless, since ζ_f and ζ_i are a complete set of variables and ω_{fi} is a single valued function of ζ_f and ζ_i. Thus to solve this problem one must go over from the variables ζ_f and ζ_i to a set of new variables η_{fi} and ω_{fi} (each of which, in general, depends on the parameters of the probing system in both the initial and final states), including ω_{fi} as an independent variable. In the case of scattering such variables might be the energy transfer $\Delta E = \hbar\omega_{fi}$ and the momentum transfer $\Delta p = \eta_{fi}$; for emission (absorption) they might be the energy transfer and the angle of emergence, etc.

It may happen that the operator $\hat{T}_{fi}^{\zeta}(R)$ when expressed in terms of the new variables ($\hat{T}_{fi}^{\eta\omega}(R)$) is independent of ω_{fi}. Then obviously K(t) must also be independent of ω_{fi}, i.e., it is a function only of η_{fi} and t, and the problem of reconstructing K(t) from W is solved using the formula

$$K_{fi}^{\eta}(t)=\frac{\hbar^2}{2\pi}\int_{-\infty}^{\infty}d\omega_{fi}\exp(i\omega_{fi}t)\,\widetilde{W}(\eta_{fi},\omega_{fi})\,\widetilde{F}^{-1}(\eta_{fi},\omega_{fi});$$

$$\widetilde{F}(\eta_{fi},\omega_{fi})\equiv F(\zeta_f),\qquad \widetilde{W}(\eta_{fi},\omega_{fi})\equiv W(\zeta_f,\zeta_i). \tag{2.6}$$

The operator $\hat{T}_{fi}^{\eta\omega}(R)$ does not depend on ω_{fi} in the case of scattering if the Born approximation is applicable. If this operator can be written as $\tau(\eta_{fi},\omega_{fi})\,\hat{T}_{fi}^{0\eta}(R)$, where $\tau(\eta_{fi},\omega_{fi})$ does not contain the variables R, while the operator $\hat{T}_{fi}^{0\eta}(R)$ does not depend on ω_{fi}, the function

$$K_{fi}^{0\eta}(t)\equiv K_{fi}^{\eta\omega}(t)/\tau^*(\eta_{if},\omega_{if})\tau(\eta_{fi},\omega_{fi})$$

satisfies the relation

$$K_{fi}^{0\eta}(t)=\frac{\hbar^2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_{fi}\widetilde{W}(\eta_{fi},\omega_{fi})\exp(i\omega_{fi}t)}{\widetilde{F}(\eta_{fi},\omega_{fi})\tau^*(\eta_{if},\omega_{if})\tau(\eta_{fi},\omega_{fi})}\cdot \tag{2.7}$$

This case occurs when the particles (or light quanta) are emitted (absorbed) within an energy interval small compared to their energy, for example in the case of interaction of visible or harder radiation with atomic systems. One may hope that the range of problems where the dependence on ω_{fi} of the operator $\hat{T}(R)$, and consequently also of K(t), is weak will be quite extensive.

Thus the answer to the question: what information about the system can be obtained from analysis of its interaction with the probe particles and what data are needed to predict the result of such an interaction, is closely related to the question of the properties of $K_{fi}^{\zeta}(t)$, which will also be the main object of our further investigation. This function, as we see from its definition, is the TCF of the dynamical variable corresponding to the operator $\hat{T}_{fi}^{\zeta}(R)$ (which acts on the state vector of the system and contains the quantum numbers of the probe system as parameters).

In certain cases the function $K_{fi}^{\zeta}(t)$ can be related to the usual two particle Green's functions for the investigated system. Thus if the system is an ensemble of N identical particles and the operator $\hat{T}_{fi}^{\zeta}(R)$ is additive over these particles,

$$\hat{T}_{fi}^{\zeta}(R)=\sum_{j=1}^{N}\hat{T}_{fi}^{j\zeta}(R_j), \tag{2.8}$$

where $\hat{T}_{fi}^{j\zeta}(R)$ is an operator acting only on the variables R_j of the j-th particle, then in the second quantization representation (under conditions where the number of particles of the investigated system is conserved),

$$\hat{T}_{fi}^{\zeta}(R)=\sum_{kk'}\mathcal{T}_{fi}^{\zeta}(k,k')\,\hat{a}_k^{+}\hat{a}_{k'},$$

$$\mathcal{T}_{fi}^{\zeta}(k,k')=(k|\hat{T}_{fi}^{j\zeta}(R_j)|k'); \tag{2.9}$$

$$K_{fi}^{\zeta}(t)=\sum_{k,k',k'',k'''}\mathcal{T}_{if}^{\zeta*}(k,k')\,\mathcal{T}_{fi}^{\zeta}(k''',k'')$$

$$\times\langle\hat{a}_k^{+}(t)\,\hat{a}_{k'}(t)\,\hat{a}_{k'''}^{+}(0)\,\hat{a}_{k''}(0)\rangle, \tag{2.10}$$

where $\hat{a}_k^{+}$ and $\hat{a}_k$ are the creation and annihilation operators for particles in state |k). Formula (2.10) means that in this case the TCF is a linear combination of the standard two-particle, two-time correlation functions, which are closely related to the Green's functions (cf., for example, [8]).

The approximation (2.8) is unsatisfactory in many cases; further improvement is possible in two directions:

1. By including in the expression for the operator $\hat{T}_{fi}^{\zeta}(R)$ the contribution of binary operators and terms of higher order. In place of (2.8) we then get

$$\hat{T}_{fi}^{\zeta}(R)=\sum_{j=1}^{N}\hat{T}_{fi}^{j\zeta}(R_j)+\frac{1}{2}\sum_{j\neq j'}^{N}\hat{T}_{fi}^{jj'\zeta}(R_j,R_{j'})+\ldots.$$

In the second quantization formulation the correlation function $K_{fi}^{\zeta}(t)$ takes the form

$$K_{fi}^{\zeta}(t)=\sum_{l=1}^{\infty}K_{fi}^{l\zeta}(t),$$

where $K_{fi}^{l\zeta}(t)$ is a linear combination of $2l$-particle two-time correlation functions of the creation and annihilation operators, where $K_{fi}^{l\zeta}(t)$ is given by (2.10).

2. By using the distorted wave approximation, which is more suited for the inclusion of many-body effects. According to this approximation, the effect of the operator $\hat{T}$ on the plane waves of the probe particles is equivalent to the action of an additive operator of the type (2.8) on the Hartree-Fock functions of the probe particles in the effective potential (generally complex) produced by all the particles of the system.

To conclude this section we discuss the specific form of the operator $\hat{T}_{fi}^{\zeta}(R)$ in various cases of practical interest. If the probing radiation is a current of slow neutrons or light quanta, the interaction has a δ-function character, and as a rule it is permissible to use the Born approximation

$$\hat{T}_{fi}^{\zeta}(R)=\sum_{j=1}^{N}C_{fi}^{j\zeta}\exp\left[\frac{i}{\hbar}\mathbf{R}_j(\mathbf{p}_i-\mathbf{p}_f)\right], \tag{2.11}$$

where p is the momentum of the probe particle, while C is an energy-independent constant characterizing the interaction with the j-th particle of the investigated system. Near resonances, where there is a significant formation of an intermediate state, (2.11) should be replaced [2] by

$$\hat{T}_{fi}^{\zeta}(R) = \sum_{j=1}^{N} \exp\left(-i\mathbf{R}_j\mathbf{p}_f/\hbar\right)\left[C_{fi}^{j\zeta} + c_{fi}^{j\zeta}/(\hat{H} - E_i^0 - \varepsilon_i^{\zeta})\right]$$

$$\times \exp\left(i\mathbf{R}_j\mathbf{p}_i/\hbar\right), \qquad (2.11')$$

where the c's are also constants. In addition, near resonances it may sometimes be necessary to include the distortion of the wave function of the probe particle (method of distorted waves).

The Born approximation is also applicable to the description of the scattering of fast electrons and muons in matter. The scattering of slow electrons and muons far from resonances is satisfactorily described by the method of distorted waves. Near resonances, formula (2.11') or its modification to include distortion of the plane waves is applicable.

The interaction of heavy charged particles and of ions and atoms with atomic systems is more complicated. But on the other hand such particles, in passing through matter, produce strong perturbations, and are poorly suited to the investigation of the dynamics of electrons and nuclei in atomic systems.

The TCF formalism is also applicable to nuclei. In particular, the scattering of electrons by nuclei was treated using the TCF method by Czyz and Gottfried.[9] The above remarks also apply to the interaction of mesons, hyperons and light quanta with atomic nuclei. The question of the applicability of the TCF method to the analysis of the interaction of nucleons with nuclei requires a special examination, since we have not considered the effects of antisymmetry of the probe system and the system under study. In addition it should be emphasized that the distorted wave approximation seems to be effective only for the description of direct processes and does not permit the inclusion of effects caused by the formation of a compound nucleus.

3. GENERAL PROPERTIES OF THE TIME CORRELATION FUNCTION

1. According to the definition (2.5), $K_{fi}^{\zeta}(t, t')$ depends only on the difference $t - t'$:

$$K_{fi}^{\zeta}(t, t') = K_{fi}^{\zeta}(t - t'). \qquad (3.1)$$

2. In general the TCF is complex. From the reality of the transition probability $W(\zeta_f, \zeta_i)$ it follows immediately that

$$K_{fi}^{\zeta *}(t) = K_{fi}^{\zeta}(-t) \qquad (3.2)$$

or

$$\mathrm{Re}\, K_{fi}^{\zeta}(t) = \mathrm{Re}\, K_{fi}^{\zeta}(-t), \quad \mathrm{Im}\, K_{fi}^{\zeta}(t) = -\mathrm{Im}\, K_{fi}^{\zeta}(-t). \qquad (3.2')$$

3. From the unitarity of the $\hat{S}$ matrix, using (2.1), it follows that

$$\frac{i}{\hbar}\int F(\zeta_f)\, d\zeta_f \int_{-\infty}^{\infty} K_{fi}^{\zeta}(t) \exp\left(-i\omega_{fi} t\right) dt$$

$$= \langle(\hat{T}_{ii}^{\zeta +}(R) - \hat{T}_{ii}^{\zeta}(R))\rangle. \qquad (3.3)$$

This relation is the content of the so-called "optical theorem."

4. If the degenerate states of the system appear in the statistical ensemble with equal weights, then in the absence of a magnetic field

$$K_{fi}^{\zeta}(t) = K_{ij}^{\zeta}(t). \qquad (3.4)$$

5. The behavior of the TCF at small times is conveniently investigated using relations that are obtained immediately by differentiating (2.5) with respect to t ($t' = 0$):

$$K_{fi}^{\zeta}(t) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{it}{\hbar}\right)^n \Big\langle\Big(\Big[\underbrace{\hat{H}, [\hat{H}, \ldots [\hat{H}}_{n}, \hat{T}_{ij}^{\zeta +}(R, 0)]\ldots]\Big]$$

$$\hat{T}_{fi}^{\zeta}(R, 0)\Big)\Big\rangle. \qquad (3.5)$$

The coefficients in this expansion are closely related to the moments of the transferred energy $\hbar^n\langle(\omega_{fi}^n)\rangle$. To show this property we again go over from the variables ζ_f, ζ_i to η_{fi}, ω_{fi}, where ω_{fi} is an independent variable, just as we did in deriving formula (2.6). Then by definition

$$\langle\omega_{fi}^n\rangle_{\eta} = \langle\omega_{fi}^0\rangle_{\eta}^{-1} \int_{-\infty}^{\infty} d\omega_{fi} \tilde{W}(\eta_{fi}, \omega_{fi})\, \omega_{fi}^n, \quad n \neq 0;$$

$$\langle\omega_{fi}^0\rangle_{\eta} = \int_{-\infty}^{\infty} d\omega_{fi} \tilde{W}(\eta_{fi}, \omega_{fi}). \qquad (3.6)$$

The index η emphasizes that the moments are calculated for fixed values of η_{fi} and not for a given initial state. For example, in the case of scattering (3.6) gives the moments of the energy transfer for fixed momentum transfer.

If on changing to the new variables the operators $\hat{T}_{fi}^{\eta\omega}(R)$ (and also $\tilde{F}(\eta_{fi}, \omega_{fi})$ actually do not depend on ω_{fi}, then it is easily verified that

$$\langle\omega_{fi}^n\rangle_{\eta} = [K_{fi}^{\eta}(0)]^{-1}(-i)^n \partial^n K_{fi}^{\eta} / \partial t^n|_{t=0}, \quad n \neq 0; \qquad (3.7)$$

$$\langle\omega_{fi}^0\rangle_{\eta} = 2\pi\hbar^{-2} F(\eta_{fi}) K_{fi}^{\eta}(0). \qquad (3.8)$$

These formulas are also valid when the static approximation is applicable. In the latter case they actually determine the moments of the energy transfer for a given initial state.

From formula (3.7) it follows that in general the

function $K_{fi}^{\zeta}(t)$ must be asymmetric in t, since otherwise all the odd moments of the energy transfer would be zero.[1)] But according to (3.2), this in turn means that the TCF has a nonzero imaginary part. The classical analog of this function is symmetric in t, since the transition to classical mechanics implies that we neglect the non-commutativity of the operators $\hat{T}_{fi}^{\zeta}(R, t)$ at different times.

6. The behavior of the TCF at large times is related to interaction processes accompanied by small energy changes. In particular it follows that with increasing t the domain of applicability of the static approximation increases. It is also obvious that, as t increases, in actual systems the time correlations for any physical quantity should wash out, so that the noncommutativity of the operators $\hat{T}_{if}^{\zeta+}(R, t)$ and $\hat{T}_{fi}^{\zeta}(R, 0)$ disappears, i.e., the imaginary part of the TCF should go to zero.

The asymptotic behavior[2)] of K_{fi}^{ζ} with t corresponds to "elastic" interaction, i.e., to interaction in which there is no exchange of energy between the systems. The asymptotic form of $K_{fi}^{\zeta}(t)$ is

$$K_{fi}^{\zeta}(\infty) = \sum_{\rho_f \rho_i} g_i^{\rho} \delta(E_i^{\rho} - E_f^{\rho}) |(\rho_f | \hat{T}_{fi}^{\zeta}(R) | \rho_i)|^2. \quad (3.9)$$

7. In the important special case where the system is in thermal equilibrium at temperature T, so that it can be described by the Gibbs canonical ensemble, according to (2.5) the function $K_{fi}^{\zeta}(t)$ can be written in the form

$$K_{fi}^{\zeta}(t) = \Big\{\sum_{\rho_i} (\rho_i | \exp(-\beta\hat{H}) | \rho_i)\Big\}^{-1} \times \sum_{\rho_i} (\rho_i | \exp(-\beta\hat{H} + i\hat{H}t/\hbar) \times \hat{T}_{if}^{\zeta+}(R) \exp(-i\hat{H}t/\hbar) \hat{T}_{fi}^{\zeta}(R) | \rho_i). \quad (3.10)$$

(where $\beta = 1/k_B T$, and k_B is the Boltzmann constant). Using (3.2) and (3.4), we easily get the relations

$$K_{fi}^{\zeta}(t - i\hbar\beta) = K_{fi}^{\zeta}(-t) = K_{fi}^{\zeta *}(t); \quad (3.11)$$

$$\mathrm{Im} K_{fi}^{\zeta}(t) = (K_{fi}^{\zeta}(t) - K_{fi}^{\zeta}(t - i\hbar\beta)) / 2i,$$

$$\mathrm{Re} K_{fi}^{\zeta}(t) = (K_{fi}^{\zeta}(t) + K_{fi}^{\zeta}(t - i\hbar\beta)) / 2. \quad (3.11')$$

We note that in the case of high temperatures ($\beta \to 0$), we get from (3.11) $K_{fi}^{\zeta}(t) = K_{fi}^{\zeta *}(t)$, i.e., in the high temperature region, where the motion of the atoms of the system can be treated by the methods of classical physics, the TCF is real.

The function $K_{fi}^{\zeta}(t - i\beta\hbar/2)$ is of interest. It is easily seen that it is real and symmetric under the replacement of t by −t. In the special case of the Born approximation this was pointed out by Schofield.[10]

From (2.4), (2.5), and (3.11), we immediately get the principle of detailed balancing for the transition probability

$$W(\zeta_f, \zeta_i) \exp(\beta\hbar\omega_{fi}) F(\zeta_i) / F(\zeta_f) = W(\zeta_i, \zeta_f). \quad (3.12)$$

8. It was shown earlier in various papers[10-12] that in the Born approximation the TCF satisfies certain integral relations connecting its real and imaginary parts ("dispersion relations"). When the operators $\hat{T}_{fi}^{\zeta}$ do not depend on ω_{fi}, certain analogous formulas can also be obtained for the function $K_{fi}^{\zeta}(t)$ in more general cases. Thus, if the system is in thermal equilibrium one can find from formulas (2.4), (2.5), (3.11), and (3.12) that

$$\mathrm{Im} K_{fi}^{\zeta}(t) = -\frac{1}{\hbar\beta} P \int_{-\infty}^{\infty} d\tau \, \mathrm{Re} K_{fi}^{\zeta}(\tau) \, \mathrm{sh}^{-1}\left(\pi \frac{t - \tau}{\hbar\beta}\right), \quad (3.13)^*$$

$$\mathrm{Re} K_{fi}^{\zeta}(t) = K_{fi}^{\zeta}(0) + \frac{1}{\hbar\beta} P \int_{-\infty}^{\infty} d\tau \, \mathrm{Im} K_{fi}^{\zeta}(\tau) \times \left[\mathrm{cth}\left(\pi \frac{t - \tau}{\hbar\beta}\right) + \mathrm{cth} \frac{\pi\tau}{\hbar\beta}\right]. \quad (3.14)^{\dagger}$$

These formulas are equivalent to the operator relation

$$\mathrm{Im} K_{fi}^{\zeta}(t) = \mathrm{tg}\left(\frac{\beta\hbar}{2} \frac{\partial}{\partial t}\right) \mathrm{Re} K_{fi}^{\zeta}(t). \quad (3.15)^{\ddagger}$$

Formulas (3.13)—(3.15) are an expression of the well known Nyquist theorem, relating the equilibrium fluctuations of the system (Re $K_{fi}^{\zeta}(t)$) to the reaction of the system to an external perturbation (Im $K_{fi}^{\zeta}(t)$).

In certain cases the function $K_{fi}^{\zeta}(t)$ can be calculated by the methods of classical physics: the quantity obtained then coincides with Re $K_{fi}^{\zeta}(t)$ except for terms $\sim \hbar^2$. Therefore, using formulas (3.13) and (3.15), from the classical expression for the TCF one can calculate the first quantum correction ($\sim \hbar$).

[1)] In particular the average energy transfer would be zero, which corresponds to neglecting recoil effects.

[2)] If the function $K_{fi}^{\zeta}(t)$ does not approach a limit as $t \to \infty$, as occurs for example for a system of a finite number of undamped oscillators, by the asymptotic form of $K_{fi}^{\zeta}(t)$ we mean the average over t of the value of $K_{fi}^{\zeta}(t)$ for $t \to \infty$:

$$\overline{K_{fi}^{\zeta}(\infty)} = \lim_{t_0 \to \infty} \frac{1}{t_0} \int_0^{t_0} K_{fi}^{\zeta}(t) \, dt.$$

*sh = sinh.

†cth = coth.

‡tg = tan.

4. INCLUSION OF DAMPING EFFECTS IN THE INITIAL STATE

The formalism developed in Sec. 2 is applicable to those cases where the interaction of the probe radiation with the system is characterized by a transition probability per unit time. But in certain cases, for example the decay of quasistationary systems, this interaction is characterized by the probability distribution of the various final states in the course of a long time interval:[13]

$$W(\rho_f\zeta_f;\ \rho_i\zeta_i) = |(\rho_f\zeta_f|\hat{S}|\zeta_i\rho_i)|^2, \tag{4.1}$$

where the $\hat{S}$ matrix element is

$$(\rho_f\zeta_f|\hat{S}|\zeta_i\rho_i) = \frac{(\rho_f\zeta_f|\hat{T}|\zeta_i\rho_i)}{E_f^{\rho} + \varepsilon_f^{\zeta} - E_i^{\rho} - \varepsilon_i^{\zeta} + i\hbar\Gamma(E_f^{\rho} + \varepsilon_f^{\zeta})/2}. \tag{4.2}$$

In cases of practical interest the level width Γ is real:

$$\Gamma(E) = \mathrm{Re}\,\Gamma(E) = \frac{2\pi}{\hbar}\sum_f |(\rho_f\zeta_f|\hat{T}|\zeta_i\rho_i)|^2\,\delta(E - E_f^{\rho} - \varepsilon_f^{\zeta}) \tag{4.3}$$

and is independent of the energy E. Following a procedure similar to that of Sec. 2, we then find for the probability of transition into unit interval of the quantum numbers of the probe system, averaged over initial and summed over final states of the system under study, the following expression:

$$W(\zeta_f,\ \zeta_i) = \frac{2}{\hbar^2\Gamma}F(\zeta_f)\,\mathrm{Re}\int_0^{\infty} dt\exp(-i\omega_{fi} - \Gamma t/2)\,K_{fi}^{\zeta}(t). \tag{4.4}$$

In many cases the energy spectrum of the system consists of a set of bands well separated in energy; the transition from one band to another corresponds to excitation of stiff (ballistic) degrees of freedom, so that the changes of the coordinates of the other degrees of freedom can be treated in the adiabatic approximation (for example, in treating the Mössbauer effect the motion of the centers of gravity of the nuclei is adiabatic relative to the internal nuclear motion). An interesting case occurs when the probe system interacts directly only with the ballistic degrees of freedom; the excited levels for these degrees of freedom can as a rule be distinguished uniquely, i.e., there is no need to average the probability (2.1) over the initial states and sum over the final states corresponding to these degrees of freedom. Obviously one should still take account of the fact that the Hamiltonian describing the adiabatic motion may be different for the different states of excitation of the ballistic degrees of freedom.

We shall denote by $\chi, \eta\ (\rho \equiv (\chi, \eta))$ the set of quantum numbers characterizing respectively the motion in the ballistic and adiabatic degrees of freedom, and by $\hat{T}_{fi}^{\zeta}(r, \chi_f, \chi_i)$ the matrix element of the operator $\hat{T}_{fi}^{\zeta}(R)$ between states $|\chi_f)$ and $|\chi_i)$ of rapid motion; r is the set of coordinates which change adiabatically (the wave functions $|\chi)$ contain the r as parameters). Then the matrix elements of the operator $\hat{T}_{fi}^{\zeta}(R, t)$ between the states $|\chi_f)$ and $|\chi_i)$ have the form

$$(\chi_f|\exp(i\hat{H}t/\hbar)\,\hat{T}_{fi}^{\zeta}(R, 0)\exp(-i\hat{H}t/\hbar)\,|\chi_i) = \exp\{i(E_f^{\chi} - E_i^{\chi})t/\hbar\}\,T_{fi}^{\zeta\chi}(r, t), \tag{4.5}$$

$$\hat{T}_{fi}^{\zeta\chi}(r, t) = \exp\{i\hat{H}_f^{\chi}t/\hbar\}\,T_{fi}^{\zeta}(r;\ \chi_f,\ \chi_i)\exp\{-i\hat{H}_i^{\chi}t/\hbar\}$$
$$\equiv \exp(i\hat{H}t/\hbar)\,\hat{T}_{fi}^{\zeta}(r;\ \chi_f,\ \chi_i)\exp(-i\hat{H}t/\hbar)$$
$$\times\,\mathrm{T}\exp\left\{-\frac{i}{\hbar}\int_0^t \exp(i\hat{H}t'/\hbar)\,\Delta\hat{H}\exp(-i\hat{H}t'/\hbar)\,dt'\right\},$$

where the symbol T denotes the chronological product; $\Delta\hat{H} = \hat{H}_i\chi - \hat{H}_f\chi$, $\hat{H} = \hat{H}_f\chi$; $\hat{H}\chi$ is the Hamiltonian describing the adiabatic motion when the state for the fast motion is characterized by the quantum numbers χ; E^{χ} is the position of the lowest level of the χ-th band. Then according to (4.4) the transition probability (with a change of quantum numbers of the fast motion from χ_i to χ_f) is

$$W(\zeta_f\chi_f;\ \zeta_i\chi_i) = \frac{2}{\hbar^2\Gamma}F(\zeta_f)\,\mathrm{Re}\int_0^{\infty} dt\exp\left(-i\Omega_{fi}t - \frac{\Gamma t}{2}\right)K_{fi}^{\zeta\chi}(t),$$
$$K_{fi}^{\zeta\chi}(t) = \langle\hat{T}_{if}^{\zeta\chi+}(r, t)\,\hat{T}_{fi}^{\zeta\chi}(r, 0)\rangle,$$
$$\Omega_{fi} = \omega_{fi} + (E_f^{\chi} - E_i^{\chi})/\hbar. \tag{4.6}$$

5. APPLICATION TO THE THEORY OF THE SHIFT AND DEFORMATION OF THE MÖSSBAUER LINE

The TCF technique formulated above allows one to describe for an arbitrary system the shift and deformation of the Mössbauer line caused by the difference between the Hamiltonians for the atomic motion in the ground and excited nuclear states. The Mössbauer effect is a typical case where one must include the damping of the initial state; the atomic motion can be regarded as adiabatic compared to the nuclear motion. Thus the results of the preceding section are applicable.

To be specific, let us consider the case of recoilless emission of a γ quantum. Then $|\chi_i)$ and $|\chi_f)$ are the wave functions for the internal motion of the Mössbauer nucleus in the excited and ground states, respectively; $E_i^{\chi} - E_f^{\chi} = E_0$ is the position of the resonance level of the nucleus. The transi-

tion operator corresponding to the emission of a γ quantum with momentum $\mathbf{p}$ (so that the wave function $|\xi_f\rangle$ is a plane wave while $|\xi_i\rangle$ corresponds to the absence of quanta) has the form

$$\hat{T}_{fi}^{\xi}(r; \chi_f, \chi_i) = T_0 \exp(-i\,\mathbf{pr}/\hbar), \qquad (5.1)$$

where $\mathbf{r}$ is the center of mass coordinate of the radiating nucleus, while T_0 is the nuclear matrix element. As a result, from formula (4.6) we find for the probability of emission of a γ quantum with momentum $\mathbf{p}$ (energy E_p) per unit solid angle and energy ($F(\xi_f) = E_0^2/c^3$) the following expression:[3)]

$$W(\Omega, \mathbf{e}) = \gamma\,\mathrm{Re}\int_0^\infty dt\, e^{-\Gamma t/2} e^{-it\Omega} \times \left\langle \left(\left[\mathrm{T}\exp\left\{ -\frac{i}{\hbar}\int_0^t \Delta\hat{H}(t')\,dt' \right\} \right]^+ \exp\left\{ \frac{i\mathbf{pr}(t)}{\hbar} \right\} \times \exp\left\{ -\frac{i\mathbf{pr}(0)}{\hbar} \right\} \right) \right\rangle, \qquad (5.2)$$

$$\Omega = (E_p - E_0)/\hbar, \qquad \mathbf{e} = \mathbf{p}/p, \qquad \gamma = 1/4\pi^2\hbar.$$

The probability for recoilless radiation of a γ quantum corresponds to very small values of $\Omega(\sim\Gamma)$, i.e., to very large t, much larger than the effective periods of the atomic motion. Thus the part of $W(\Omega, \mathbf{e})$ that corresponds to recoilless emission is given by the expression

$$W_{\mathrm{n.r}}(\Omega, \mathbf{e}) = \gamma\,\mathrm{Re}\int_0^\infty dt\, K_{\mathrm{as}}(t, \beta)\exp\left(-i\Omega t - \frac{\Gamma t}{2}\right), \qquad (5.3)$$

$$K_{\mathrm{as}}(t, \beta) = \lim_{t\to\infty} \mathrm{Sp}\left\{ \exp(\beta(\Psi - \hat{H})) \times \left[\mathrm{T}\exp\left(-\frac{i}{\hbar}\int_0^t \Delta\hat{H}(t')\,dt' \right) \right]^+ \times \exp\left(\frac{i\mathbf{pr}(t)}{\hbar} \right) \exp\left(\frac{-i\mathbf{pr}(0)}{\hbar} \right) \right\}, \qquad (5.4)$$

where $\Psi(\beta)$ is the free energy of the system (the limit for $t\to\infty$ imposes no restrictions on the order of magnitude of $t\Delta\hat{H}(t)/\hbar$, which can be greater than, less than, or of the order of unity). In the limit of large t, the exponential under the T-product becomes a diagonal operator (in general a function of the Hamiltonian), since the nondiagonal terms correspond to very rapid oscillations of the integrand in (5.3) and give a negligible contribution, of order $\beta\langle(\hat{H})\rangle$.[4)] As a result we get

$$K_{\mathrm{as}}(t, \beta) = \lim_{t\to\infty} \mathrm{Sp}\{\exp(\beta(\Psi - \hat{H}))\exp(i\varphi(\hat{H})t) \times \exp(i\mathbf{pr}(t)/\hbar)\exp[-i\mathbf{pr}(0)/\hbar]\} = \sum_\eta g'_\eta(t)\,|(\eta|\,e^{i\mathbf{pr}/\hbar}\,|\eta)|^2, \qquad (5.5)$$

where $\varphi(\hat{H}) = \overline{\Delta\hat{H}(t)/\hbar}$ is the time-averaged operator, and

$$g'_\eta(t) = \exp\{\beta(\Psi - E_\eta) + it\varphi(E_\eta)\}. \qquad (5.6)$$

In completely analogous fashion one can get the expression for the probability of recoilless absorption of a γ quantum, which can easily be shown to coincide in our approximation with (5.3) and (5.5). The quantity $K_{\mathrm{as}}(0, \beta) \equiv f$ is the "standard" probability for recoilless emission of a γ quantum. Knowing $K_{\mathrm{as}}(0, \beta)$ as a function of β from experiment (and of course knowing $\varphi(E)$), one can in principle extend K_{as} analytically into the region of values of t, if different from zero. For example, if one finds an analytic continuation of $K_{\mathrm{as}}(0, \beta)$ to complex values of β, then $K_{\mathrm{as}}(t, \beta)$ can be reconstructed using the formula which gives the general connection between the Mössbauer probability f and the deformation of the Mössbauer line:

$$K_{\mathrm{as}}(t, \beta) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} K_{\mathrm{as}}(0, \beta')\,d\beta' \int_0^\infty dE \exp[E(\beta' - \beta) + \beta\Psi(\beta) - \beta'\Psi(\beta') + it\varphi(E)]. \qquad (5.7)$$

This formula follows directly from (5.6). But in practice such a problem requires the measurement of $K_{\mathrm{as}}(0, \beta)$ as a function of β to a sufficiently high degree of accuracy, and therefore in each specific case one must find some way to simplify it.[5)] In particular in certain cases it may be extremely useful to compute the coefficients in the expansion of $\ln K_{\mathrm{as}}(t, \beta)$ in powers of it, since the linear term in such an expansion determines the shift (the first moment of the Mössbauer line), the quadratic term

[3)] Strictly speaking, what is intended in (5.2) is an averaging over states of the Hamiltonian H_i^χ. But practically the results of averaging over the states of the Hamiltonians H_i^χ and H_f^χ coincide to a high degree of accuracy; the error is of order $\beta\langle(\Delta H)\rangle$. We shall therefore neglect this effect.

[4)] For simplicity, we neglect effects related to degeneracy of the states of atomic motion. These effects may be sizable in the case of degeneracy of the isolated degrees of freedom.[14] We note that since the atomic systems considered here have a quasicontinuous spectrum, dropping nondiagonal matrix elements also means neglecting effects of second order in $\Delta M/M$, the ratio of the difference in mass of the nucleus in its excited and ground states to its total mass. These effects are important only in the case of anomalously narrow Mössbauer lines.[15]

[5)] The situation is complicated even more by the fact that the function $\varphi(E)$, being actually a function of the set of variables η, can have a very complex dependence on E.

gives the broadening (the second moment), while the higher terms affect only the finer features of the line shape.

Actually, as one sees from (5.3) and (3.7), the expansion of $K_{as}(t, \beta)$ in powers of it corresponds to the asymptotic expansion of $W_{nr}(\Omega, \mathbf{e})$ for large Ω:

$$W_{n.r.}(\Omega, \mathbf{e}) = \gamma \sum_{n=0}^{\infty} \mathrm{Re}\left[\left(\frac{\Gamma}{2} + i\Omega\right)^{-n-1} \frac{\partial^n K_{as}(t, \beta)}{\partial t^n}\Big|_{t=0}\right]. \tag{5.8}$$

We also note that in certain cases it is convenient, in calculating $K_{as}(t, \beta)$, to write it as a product

$$K_{as}(t, \beta) = K_1(t, \beta) K_2(t, \beta); \tag{5.9}$$

$$K_1(t, \beta) = \sum_{\eta} g_{\eta}''(t) |(\eta | e^{ipr/\hbar} | \eta)|^2, \tag{5.10}$$

$$g_{\eta}''(t) = \exp[-\beta E_{\eta} + it\varphi(E_{\eta})] / \mathrm{Sp}\{\exp[-\beta\hat{H} + it\varphi(\hat{H})]\}; \tag{5.11}$$

$$K_2(t, \beta) = \mathrm{Sp}\{\exp[\beta(\Psi - \hat{H}) + it\varphi(\hat{H})]\} \equiv \langle(\exp[it\varphi(\hat{H})])\rangle. \tag{5.12}$$

The function $K_1(t, \beta)$ differs from (5.5) in that the quantity g_{η}'', unlike g_{η}', is normalized to unity ($\Sigma g_{\eta}'' = 1$). Thus the function $K_1(t, \beta)$ is a kind of "average over initial states" of the radiation probability.

In the case of a large number N of degrees of freedom of the system, (and in the absence of local degrees of freedom [16]) the result of averaging in (5.10) should usually be very little different from the result of the usual statistical averaging (with weight $g_{\eta}''(0)$). One may therefore hope that for a quite extensive class of physically interesting cases the function $K_1(t, \beta)$ varies slowly with t and has a small effect on the shape and position of the Mössbauer line, i.e., one can approximately set $K_1(t, \beta) = K_1(0, \beta)$. Furthermore, as is easily verified, to terms of order N^{-1},

$$\langle(\exp[i\varphi(\hat{H})t])\rangle = \exp[it\langle(\varphi(\hat{H}))\rangle].$$

Finally we get

$$W_{n.r.}(\Omega, \mathbf{e}) = \gamma K_{as}(0, \beta)(\Gamma/2) \times [\Gamma^2/4 + (\Omega - \langle(\varphi(\hat{H}))\rangle)^2]^{-1}, \tag{5.13}$$

i.e., in agreement with well known results, [3,4] in the case of large systems without local degrees of freedom the difference in the Hamiltonians for the atomic motion in the ground and excited states of the Mössbauer nucleus leads only to a shift of the line but does not change its shape.

Now let us consider a radiating system with (for simplicity) one local degree of freedom. Then the function $K_{as}(t, \beta)$ can be written as a product

$$K_{as}(t, \beta) = K_l(t, \beta) K_n(t, \beta),$$

where $K_n(t, \beta)$ denotes expressions of the kind treated above for nonlocal degrees of freedom, while $K_l(t, \beta)$ describes the effect of the local degrees of freedom alone. In general the problem of the line shape is very complicated. We shall therefore limit ourselves to the special assumption that φ depends linearly on the energy of the local degree of freedom, i.e., [6] $\varphi(E) = A + BE$. Then $K_l(t, \beta)$ is obtained from the Mössbauer probability $K_l(0, \beta) = K_{as}(0, \beta) = f(\beta)$ by analytic continuation to complex temperatures, $K_l(t, \beta) = K_{as}(0, \beta - it\beta)$, while

$$K_2(t, \beta) = \exp\{\beta\Psi(\beta) - (\beta - itB)\Psi(\beta - itB) + iAt\}.$$

As a result we get ($z(\beta) \equiv -\ln f(\beta)$)

$$q(t, \beta) \equiv -\ln K_{as}(t, \beta) = z(\beta - itB) + (\beta - itB) \times \Psi(\beta - itB) - \beta\Psi(\beta) - itA.$$

To study the shift and broadening of the line, we expand $q(t, \beta)$ in powers of it:

$$q(t, \beta) = z(\beta) - it\Delta - t^2\delta; \quad \Delta = B(U(\beta) + dz/d\beta) + A,$$
$$\delta = \tfrac{1}{2}B^2(d^2z/d\beta^2 + dU/d\beta) \tag{5.14}$$

($U(\beta) = d(\beta\Psi)/d\beta$ is the internal energy of the system). Substituting (5.14) in (5.3), we get the final expression

$$W_{n.r.}(\Omega, \mathbf{e}) = \gamma e^{-z(\beta)} \mathrm{Re} \int_0^{\infty} dt \exp\left\{-\frac{\Gamma t}{2} + \frac{t^2B^2}{2}\left(\frac{d^2z}{d\beta^2} + \frac{dU}{d\beta}\right) + it[E_p - E_0 + B(U + dz/d\beta) + A]\right\}. \tag{5.15}$$

Thus when there are isolated degrees of freedom, the Mössbauer line is both shifted and broadened, and the shift does not coincide with the value of $\varphi(E)$ which is equal to A + BU. (We recall that the possibility of broadening of the line in this case was pointed out by Snyder and Wick [5].)

Our results, obtained from expansion of $K_{as}(t, \beta)$ in powers of it, are strictly speaking valid only when $\varphi(E)/\Gamma \lesssim 1$. In this case the deformation of the line reduces essentially to a shift and a possible broadening. If, however, $\varphi(E)/\Gamma \gg 1$, the line may acquire a complex, irregular shape. This is easily seen from the simple example of a single harmonic oscillator of frequency ω_0, if we assume for simplicity that the momentum of the quantum is zero, i.e., for $K_1(t, \beta) = 1$ and $\varphi(E) = BE$. Then

[6] This occurs, for example, for the isomer shift (φ = const) and for the temperature shift in the case of the harmonic oscillator ($\Delta H = (\Delta M/M)P^2/2M$).

$$K_2(t, \beta) = [1 - \exp(-\beta\hbar\omega_0)]$$
$$\times [1 - \exp(-\beta\hbar\omega_0 + itB\hbar\omega_0)]^{-1}.$$

We then have, from (5.3),

$$W_{n.r.}(\Omega, \mathbf{e}) = \gamma [1 - \exp(-\beta\hbar\omega_0)] \sum_{n=0}^{\infty} \frac{\Gamma \exp(-n\beta\hbar\omega_0)}{2}$$
$$\times \left[(\Omega + nB\hbar\omega_0)^2 + \frac{\Gamma^2}{4} \right]^{-1}. \quad (5.16)$$

Thus in this case there is an infinite set of equidistant lines, starting from the undisplaced line. We note that the fraction in the shifted lines is the greater the higher the temperature, and that for infinite temperature ($\beta \to 0$) the unshifted line is absent; conversely, in the case of zero temperature ($\beta \to \infty$) only the unshifted line remains. Such a situation can be interpreted as a sort of "microscopic" Mössbauer effect within the Mössbauer line itself. The analogous effect is well known in optics.[17] As already mentioned, when $B\hbar\omega_0/\Gamma \lesssim 1$ the line will be deformed moderately. With increasing $B\hbar\omega_0/\Gamma$, marked irregularities of the line shape begin to appear and finally, for very large values of $B\hbar\omega_0/\Gamma$, the unshifted line again appears near $\Omega = 0$.

The presence of the unshifted line means that as $t \to \infty$, the function $K_{as}(t, \beta)$ in (5.6) has a nonzero component that is independent of t. In the opposite case, as occurs for large systems, the unshifted line should be absent. The most favorable conditions for the appearance of the unshifted line are low temperature and a large difference between the Hamiltonians for the atomic motion in the ground and excited states of the Mössbauer nucleus.

6. CONCLUSION

In the present paper a general formalism is developed which makes it possible in general to express the probability of interaction of probes with the system in terms of certain time correlation functions (TCF). These are time correlations of definite physical quantities characterizing the system under investigation and depending on the type and the parameters of the probing radiation in the initial and final states. The interpretation from the single viewpoint of the TCF of data obtained from experiments with different types of probes considerably extends the possibilities for carrying out the complicated investigation of complex systems. Thus the analysis of experiments on scattering of neutrons in liquids by the correlation function method would enable one to understand many interesting regularities.

The TCF method for describing the interaction of different kinds of radiation with complex systems is also convenient for another reason. As a quantum mechanical system becomes more complex (more degrees of freedom), its description using wave functions becomes inordinately more complicated and is practically impossible. At the same time fewer and fewer details of the wave functions of the system really determine its action on the probe radiation. All the information about the system that is needed for predicting this result is contained precisely in the TCF, i.e., the TCF formalism is the best suited for this problem.

In many cases the TCF of a complicated system can be calculated more or less accurately by the methods of quantum statistics, or at least one can find its most important properties. The recently developed Green's function technique may be useful for this analysis. A considerable simplification of the computation and interpretation of the TCF is possible if the system under study is quasiclassical, as is quite often the case for complex atomic systems. This is related to the fact that the TCF's are expressed in terms of Heisenberg operators, for which the transition to the classical limit is especially simple and clear. The "dispersion relations" (3.13)—(3.15) enable one to calculate the first quantum correction. Summarizing, we may conclude that to describe those properties of complex systems which can be observed by probing the system with radiations of different types (i.e., practically all the physically observable characteristics of a complex system) one of the most convenient techniques is to use the TCF.

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