

GREEN'S FUNCTIONS IN QUANTUM STATISTICAL PHYSICS – CONDENSED MATTER PHYSICS

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Abstract: One of the very powerful and reliable theoretical methods of research in quantum statistical physics or solid-state physics is the method of Green's functions. This method represents a completely closed formalism in the framework of which the problem of particle and quasiparticle systems is completely solved, i.e. the energies and lifetimes of elementary excitations are found, as well as the statistical mean values of the corresponding physical quantities. In this paper, the general –definition procedure of introduction to the theory of Green's functions and the way of manipulating it in order to calculate the properties of the observed physical system will be presented. In the second part, this procedure will be demonstrated on the determination of the temperature dependence of magnetization in ferromagnetic materials and on the analysis of the optical properties of molecular crystals.

Keywords: Quantum statistical physics, Green's functions, correlation functions, Pauli operators, magnetization, kinematic excitations

1. INTRODUCTION

The Green functions (GF) represent statistical mean values of time-ordered products of two complexes of Heisenberg operators [1–7]. One of the complexes depends on the spatial variable x and acts in moment of time t , while the other depends on x' in another moment of time t' . Since the following described (time-editing operation and statistical averaging operation) are independent, the order of these operations is arbitrary.

It is most important that described form of GF appear when calculating the mean values of the physical characteristics of the system affected by external, time-dependent fields. [5–7]. A typical example of this is the placing of metals in external electric fields that direct the chaotic movement of their free electrons, i.e. convert it into electric current. In the process of analyzing the influence of external fields on material environments, it appears through important phenomenological characteristics of materials such as transport coefficients (coefficient of electrical and thermal conductivity, diffusion coefficient, etc.), dielectric permittivity, magnetic permeability, electrical resistance and many others [1–4].

The operator complexes are composed of operators of creation and annihilation of elementary excitations that occur in the middle. Therefore, GF depends on the energy of elementary excitations of the medium, and through it on the micro-characteristics of the medium, such as electronic or other states of atoms or molecules, intermolecular forces, local fields of elementary cells – if it is a crystalline medium. In this way, GF is a bridge that connects the macroscopic characteristics of the environment with its micro-characteristics [1–4]. Once this connection is known, the material can be improved in order to make their macroscopic characteristics better and more effective in direct (practical) application or to explain and learn the mechanisms that lead to changes in macroscopic faces of large samples [9–13]. All of the above is the reason why the properties of GF and the ways of their calculation have been studied and improved for decades.

It should be noted here that contemporary calculations use method of quantum two-time and temperature dependent (Q2TT) GF when calculating time-bound statistical mean values of operator products, using Heisenberg equations of motion, and therefore, further exposition will refer to this method.

2. BASIC DEFINITION OF Q2TT GF

We will here introduce the properties of the commutator GF (kGF), which represents the time-ordered statistical mean value of the commutator of two operator complexes operating at two different points in time [5,6,8]. In this form kGF appears when calculating the mean values of the physical characteristics of the system, when it is affected by an external, time-dependent field.¹

Therefore, Q2TTkGF is defined as follows [4–6]:

$$G(x, x', t, t') = \Theta(t - t') \text{Sp}\{[A(x, t), B(x', t')]\hat{Q}\}, \quad (2.1)$$

where $\Theta(t - t')$ is the Heaviside step function, and \hat{Q} is the statistical operator of the canonical ensemble:

$$\hat{Q} = e^{(\hat{F} - \hat{H})/\theta}, \quad (2.2)$$

¹In addition to commutator GFs, there are also anticommutator GFs (as the mean values of two anticommutator complexes) that are suitable for the analysis of fermion systems and causal GFs (as mean values of the products of two operator complexes). The results of the analysis of commutator functions are very easily transferred to anticommutator and causal functions, so it is not necessary to examine these separately.

while the operator complexes $A(x, t)$ and $B(x', t')$ are given in Heisenberg's form:

$$A(x, t) = e^{i\hat{H}t/\hbar} A(x) e^{-i\hat{H}t/\hbar}; \quad B(x', t') = e^{i\hat{H}t'/\hbar} B(x') e^{-i\hat{H}t'/\hbar}. \quad (2.3)$$

In expression (2.2) F denotes free energy, and \hat{H} is the Hamiltonian of the system. The quantity $\theta = k_B T$ characterizes the energy exchange between the system and the thermostat.

According to this definition, Q2TT kGF depends on four variable arguments: x, x', t, t' . The calculation of such Q2TT kGFs is very complicated, and therefore we made a certain idealization. It is considered that the environment is spatially homogeneous and unbounded and that the operator complexes \hat{A} and \hat{B} are explicitly independent of time. Then GF depends on two "combined" variables $x - x'$ and $t - t'$, therefore instead of the more general expression (2.1), we use:

$$G(x - x', t - t') = \Theta(t - t') \text{Sp}\{[A(x, t), B(x', t')]\hat{Q}\}. \quad (2.4)$$

In this expression, the statistical values of operator products appear:

$$J_{AB}(x - x', t - t') = \text{Sp}\{A(x, t), B(x', t')\hat{Q}\}; \quad J_{BA}(x - x', t - t') = \text{Sp}\{B(x', t'), A(x, t)\hat{Q}\}. \quad (2.5)$$

which are called Correlation Functions (CF) [4–6,8]. Based on this definition, expression (2.4) for Q2TT GF turns into:

$$G(x - x', t - t') = \Theta(t - t') [J_{AB}(x - x', t - t') - J_{BA}(x - x', t - t')], \quad (2.6)$$

so the analysis of CF can be used to draw some important conclusions that also apply to GF. The spur, in expression (2.4), i.e. (2.6), is taken according to the Eigen-functions of the Hamiltonian system \hat{H} :

$$\hat{H}|k\rangle = E_k|k\rangle, \quad (2.7)$$

where E_k are the energies of the system in the quantum state $|k\rangle$. With respect to this, the expression for CF $J_{BA}(x - x', t - t') \equiv J_{BA}(x - x', \tau)$, $\tau = t - t'$, can be transformed:

$$\begin{aligned} J_{BA}(x - x', \tau) &= \text{Sp}\{B(x', t') A(x, t)\hat{Q}\} \equiv e^{F/\theta} \text{Sp}\{B(x', t') A(x, t) e^{-\hat{H}/\theta}\} = \\ &= e^{F/\theta} \sum_{k,l} \langle k|B(x')|l\rangle \langle l|A(x)|k\rangle e^{-\frac{E_k}{\theta}} e^{-i(E_k - E_l)\tau/\hbar}. \end{aligned} \quad (2.8)$$

After multiplication by $e^{i\omega\tau}$ and integration by $\tau \in (-\infty, +\infty)$, it becomes:

$$\begin{aligned} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} J_{BA}(x - x', \tau) &= \\ &= e^{F/\theta} \sum_{k,l} \langle k|B(x')|l\rangle \langle l|A(x)|k\rangle e^{-E_k/\theta} \int_{-\infty}^{+\infty} d\tau e^{-i[\omega - (E_k - E_l)/\hbar]\tau}. \end{aligned} \quad (2.9)$$

The direct Fourier transform of $J_{BA}(x - x', \tau)$ and their inverse $J_{BA}(x - x', \omega)$, in relation to the time-frequency transformation, is defined as:

$$\begin{aligned} J_{BA}(x - x', \omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} J_{BA}(x - x', \tau); \\ J_{BA}(x - x', \tau) &= \int_{-\infty}^{+\infty} d\omega e^{-i\omega\tau} J_{BA}(x - x', \omega). \end{aligned} \quad (2.10)$$

If it is taken into account that: $\int_{-\infty}^{+\infty} d\tau e^{-i(\omega - \omega_{kl})\tau} = 2\pi\delta\left(\omega - \frac{E_k - E_l}{\hbar}\right) = 2\pi\hbar\delta(E - E_{kl})$, where: $\omega_{kl} = E_{kl}/\hbar, E_{kl} = E_k - E_l$ and $E = \hbar\omega$, relation (2.10) will be reduced to:

$$\begin{aligned} J_{BA}(x - x', \omega) &= e^{F/\theta} \sum_{k,l} \langle k|B(x')|l\rangle \langle l|A(x)|k\rangle e^{-F/\theta} \delta(\omega - \omega_{kl}) = \\ &= \hbar e^{F/\theta} \sum_{k,l} \langle k|B(x')|l\rangle \langle l|A(x)|k\rangle e^{-E_k/\theta} \delta(E - E_{kl}). \end{aligned} \quad (2.11)$$

Dirac's delta function is a singular function [1,2], so it can be concluded that the Fourier transform of CF $J_{BA}(x - x', \omega)$ has singularity for $\hbar\omega \equiv E = E_k - E_l$. Therefore, the quantity E in (2.11) must be treated as complex. The term E_{kl} represents the change in energy of the system during the transition from the initial $|k\rangle$ into the final state $|l\rangle$. This difference represents energy of elementary excitation of the system during the transition $|k\rangle \rightarrow |l\rangle$, which has final time of life. For these the value $E_k - E_l$ have an imaginary correction, which is far smaller than the real part. The following conclusion is: singularities CF $J_{BA}(x - x', \omega) \equiv J_{BA}(x - x', E/\hbar)$ (and both GF) in a complex E -plane determine the energies (real part) and lifetimes (imaginary part) of the elementary excitations of the system.

CF $J_{AB}(x - x', t - t')$ can be transformed in a similar way as the function J_{BA} . Therefore we quote here only the final result for the Fourier transform $J_{AB}(x - x', \tau)$ and inverse transform:

$$\begin{aligned} J_{AB}(x - x', \omega) &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} J_{AB}(x - x', \tau); \\ J_{AB}(x - x', \tau) &= \int_{-\infty}^{+\infty} d\omega e^{-i\omega\tau} J_{AB}(x - x', \omega). \end{aligned} \quad (2.12)$$

By comparing expressions (2.10) and (2.12), a connection between these CFs is obtained:

$$J_{AB}(x - x', \omega) = e^{E/\theta} J_{BA}(x - x', \omega); \quad E = \hbar\omega. \quad (2.13)$$

From here, it is easy to state that these two CF have the same singularities in the complex E -plane.

Now it is necessary to find relationship between these CFs and adequate GF. After substituting $t - t' = \tau$ (2.6), we get:

$$G(x - x', \tau) = \Theta(\tau)[J_{AB}(x - x', \tau) - J_{BA}(x - x', \tau)]. \quad (2.14)$$

Heaviside's step function is an integral of Dirac's delta function [2]:

$$\Theta(\tau) = \int d\tau \delta(\tau) = \frac{1}{2\pi} \int d\tau \int_{-\infty}^{+\infty} d\omega'' e^{-i\omega''\tau} = \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega'' \frac{e^{-i\omega''\tau}}{\omega'' \pm i\delta}.$$

If performed the Fourier transforms [2] of GF and CF:

$$G(x - x', \tau) = \int_{-\infty}^{+\infty} d\omega' e^{-i\omega'\tau} G(x - x', \omega');$$

$$J_{AB}^{BA}(x - x', \tau) = \int_{-\infty}^{+\infty} d\omega' e^{-i\omega'\tau} J_{AB}^{BA}(x - x', \omega'),$$

when replace it all in (2.14), we get:

$$\lim_{\delta \rightarrow +0} \int_{-\infty}^{+\infty} d\omega' e^{-i\omega'\tau} G(x - x', \omega' \pm i\delta) =$$

$$= \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' d\omega'' e^{-i(\omega' + \omega'')\tau} \frac{(e^{\frac{\omega'}{\theta}} - 1) J_{BA}(x - x', \omega')}{\omega'' \pm i\delta}. \quad (2.15)$$

After multiplying last equation by $e^{i\omega'\tau}$ and integrating in infinite limits by τ , the result follows:

$$\lim_{\delta \rightarrow +0} G(x - x', \omega \pm i\delta) = \frac{i}{2\pi i} \int_{-\infty}^{+\infty} d\omega' \frac{(e^{\frac{\hbar\omega'}{\theta}} - 1) J_{BA}(x - x', \omega')}{\omega' - \omega \mp i\delta}. \quad (2.16)$$

With respect to [2], $\lim_{\delta \rightarrow +0} \frac{1}{\omega' - \omega \mp i\delta} = P \frac{1}{\omega' - \omega} \pm i\pi\delta(\omega' - \omega)$, replacing in (2.16), follows:

$$\lim_{\delta \rightarrow +0} G(x - x', \omega' \pm i\delta) = \frac{P}{2\pi i} \int_{-\infty}^{+\infty} d\omega' \frac{(e^{\frac{\hbar\omega'}{\theta}} - 1) J_{BA}(x - x', \omega')}{\omega' - \omega} \pm \frac{e^{\frac{\hbar\omega'/\theta} - 1}}{2} J_{BA}(x - x', \omega'). \quad (2.17)$$

After subtracting: $G_- - G_+$, the required connection between the Fourier transforms CF and GF is obtained:

$$J_{BA}(x - x', \omega) = \frac{G(x - x', \omega + i\delta) - G(x - x', \omega - i\delta)}{e^{\frac{\hbar\omega'}{\theta}} - 1}. \quad (2.18)$$

With similar procedure, we obtain:

$$J_{AB}(x - x', \omega) = \frac{G(x - x', \omega + i\delta) - G(x - x', \omega - i\delta)}{1 - e^{\frac{\hbar\omega'}{\theta}}}, \quad (2.19)$$

If (2.18) and (2.19) are replaced in (2.12) and the replacement $\tau = t - t'$ is returned, we obtained formulas that are fundamental for determining the statistical mean values of the products of two operator complexes²:

$$J_{BA}(x - x', t - t') \equiv \langle B(x', t') A(x, t) \rangle = \int_{-\infty}^{+\infty} d\omega e^{-i\omega(t-t')} \frac{G(x - x', \omega + i\delta) - G(x - x', \omega - i\delta)}{e^{\frac{\hbar\omega'}{\theta}} - 1}. \quad (2.19)$$

$$J_{AB}(x - x', t - t') \equiv \langle A(x', t') B(x, t) \rangle = \int_{-\infty}^{+\infty} d\omega e^{-i\omega(t-t')} \frac{G(x - x', \omega + i\delta) - G(x - x', \omega - i\delta)}{1 - e^{\frac{\hbar\omega'}{\theta}}}. \quad (2.20)$$

It is shown here how finding Q2TT kGF allows finding expressions for CFs and they are included in the definition of many physical quantities.

3. EXAMPLES OF APPLICATION OF GF METHODS

This section will present characteristic examples of the application of the presented GF method in the theory of the condensed state of matter.

— Magnetization at low temperatures

Here it will be shown how, by applying the GF method to testing the behavior of ferromagnetics with spin $S = 1/2$, the well-known Dyson result for magnetization is very easily obtained [1–4, 13–16], if the Pauli operators, which satisfy the commutation relations:

$$[P_{\bar{n}}, P_{\bar{m}}^+] = (1 - 2P_{\bar{n}}^+ P_{\bar{n}}) \delta_{\bar{n}\bar{m}}; \quad \langle P_{\bar{n}}^+ P_{\bar{n}} \rangle \approx 0, 1;$$

$$[P_{\bar{n}}, P_{\bar{m}}] = [P_{\bar{n}}^+, P_{\bar{m}}^+] = 0; \quad P_{\bar{n}}^2 = P_{\bar{n}} = 0, \quad (3.1)$$

introduce exactly through the Bose operator according to the formula [20–22]:

$$P = \left[\sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} B^{+\nu} B^\nu \right]^{1/2}; \quad B; \quad P^+ = B^+ \left[\sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} B^{+\nu} B^\nu \right]^{1/2};$$

$$P^+ P = \left[\sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} B^{+(\nu+1)} B^{\nu+1} \right]^{1/2}. \quad (3.2)$$

In the fifties of the last century, intensive work was done to explain the mechanism of low-temperature magnetization. The problem itself is of more methodological – than practical importance, and in 1956 Dyson

²In this term, the use of a "more economical" way of writing statistical averages - instead of the symbol $\langle \dots \rangle$ the symbol $\langle \langle \dots \rangle \rangle$ was used. In further text will be used this symbolic writing.

found the correct expression for magnetization [1–4,17], but with very complex calculations of spin statistical sums.

In order to obtain a more elegant Dyson result, Tyablikov used the Q2TT GF method [2,3,18] for a ferromagnetic model with spin $S = 1/2$, but with an approximate expression where he changed the Pauli operator representation with the boson operators:

$$P_{\vec{n}} = B_{\vec{n}} - B_{\vec{n}}^{\dagger} B_{\vec{n}} B_{\vec{n}}; P_{\vec{n}}^{\dagger} = B_{\vec{n}}^{\dagger}; P_{\vec{n}}^{\dagger} P_{\vec{n}} = B_{\vec{n}}^{\dagger} B_{\vec{n}}.$$

This method was tempting, because – in addition to the energies of elementary excitations, it also gave expressions for the mean values of physical characteristics, and therefore magnetization itself. However, with this approach, Tyablikov failed to reproduce Dyson's result – in the expression for magnetization, a member proportional to the third degree of temperature appeared, which entered the literature called "spur error". Here we will show that the GF method gives the correct result for magnetization, but only when the Pauli operators are correctly replaced by boson ones:

$$P_{\vec{n}} = B_{\vec{n}} - B_{\vec{n}}^{\dagger} B_{\vec{n}} B_{\vec{n}}; P_{\vec{n}}^{\dagger} = B_{\vec{n}}^{\dagger} - B_{\vec{n}}^{\dagger} B_{\vec{n}} B_{\vec{n}}. \quad (3.3)$$

In ferromagnetics with spin $S = 1/2$, spin operators can be represented by the Pauli operator: $S^+ = P, S^- = P^{\dagger}$ and $S^z = 1/2 - P^{\dagger}P$, so the Hamiltonian of that ferromagnetics has the form [1–4,9]:

$$H = \frac{1}{2} J_0 \sum_{\vec{n}} P_{\vec{n}}^{\dagger} P_{\vec{n}} - \frac{1}{2} \sum_{\vec{n}, \vec{m}} I_{\vec{n}\vec{m}} P_{\vec{n}}^{\dagger} P_{\vec{m}} - \frac{1}{2} \sum_{\vec{n}, \vec{m}} I_{\vec{n}\vec{m}} P_{\vec{n}}^{\dagger} P_{\vec{m}} P_{\vec{m}}^{\dagger} P_{\vec{m}}; \quad (3.4)$$

$$J_0 = \sum_{\vec{m}} I_{0\vec{m}}; I_{\vec{n}\vec{m}} = I_{\vec{m}\vec{n}}; I_{\vec{n}\vec{n}} = 0; \quad I_{\vec{n}\vec{m}} \equiv I_{\vec{n}-\vec{m}}.$$

The analysis of a system with this Hamiltonian starts from the Paulian GF:

$$\Gamma_{\vec{a}\vec{b}}(t) = \Theta(t) \langle [P_{\vec{a}}(t), P_{\vec{b}}(0)] \rangle \equiv \langle \langle P_{\vec{a}}(t) | P_{\vec{b}}(0) \rangle \rangle, \quad (3.5)$$

where \vec{a} and \vec{b} are the vectors of the crystal lattice nodes and $\Theta(t)$ is the Heaviside step function. If this expression is differentiated by time and the Heisenberg equations of motion are used, we get:

$$i\hbar \frac{d}{dt} \Gamma_{\vec{a}\vec{b}}(t) = i\hbar \delta(t) \delta_{\vec{a}\vec{b}} (1 - 2\langle P^{\dagger}P \rangle) - \frac{1}{2} J_0 \Gamma_{\vec{a}\vec{b}}(t) - \frac{1}{2} \sum_{\vec{m}} I_{\vec{a}\vec{m}} \Gamma_{\vec{m}\vec{b}}(t) + \quad (3.6)$$

$$+ \sum_{\vec{m}} I_{\vec{a}\vec{m}} \langle \langle P_{\vec{a}}(t)^{\dagger} P_{\vec{a}}(t) P_{\vec{m}}(t) | P_{\vec{m}}^{\dagger}(t) \rangle \rangle - \sum_{\vec{m}} I_{\vec{a}\vec{m}} \langle \langle P_{\vec{m}}(t)^{\dagger} P_{\vec{m}}(t) P_{\vec{a}}(t) | P_{\vec{a}}^{\dagger}(0) \rangle \rangle.$$

Using the representation: $P \rightarrow B$, given in (3.3), from the Paulian ones, we switch to the bosonic GFs. On this occasion, Wick's theorem for Bose operators [19] is used, and the following connections are obtained:

$$\Gamma_{\vec{a}\vec{b}}(t) \approx (1 - 4\langle B^{\dagger}B \rangle) G_{\vec{a}\vec{b}}(t);$$

$$\langle \langle P_{\vec{a}}(t)^{\dagger} P_{\vec{b}}(t) P_{\vec{c}}(t) | P_{\vec{d}}^{\dagger}(0) \rangle \rangle \approx \langle \langle B_{\vec{a}}^{\dagger}(t)^{\dagger} B_{\vec{b}}(t) B_{\vec{c}}(t) | B_{\vec{d}}^{\dagger}(0) \rangle \rangle = \langle B_{\vec{a}}^{\dagger} B_{\vec{b}} \rangle G_{\vec{c}\vec{d}}(t) + \langle B_{\vec{a}}^{\dagger} B_{\vec{c}} \rangle G_{\vec{b}\vec{d}}(t). \quad (3.7)$$

If we take $\langle P^{\dagger}P \rangle = \langle B^{\dagger}B \rangle$ (which is valid in the zero approximation), after replacing (3.7) in (3.6) and the corresponding Fourier transforms, we get:

$$G_{\vec{k}}(\omega) = \frac{i}{2\pi} \frac{1+2\langle B_{\vec{a}}^{\dagger} B_{\vec{b}} \rangle}{\omega - \omega_{\vec{k}}^{(1)}}, \quad (3.8)$$

from where it follows:

$$\langle B_{\vec{a}}^{\dagger} B_{\vec{b}} \rangle = (1 + 2\langle B_{\vec{a}}^{\dagger} B_{\vec{b}} \rangle) \frac{1}{N} \sum_{\vec{k}} \left(e^{\frac{E_{\vec{k}}^{(1)}}{\theta}} - 1 \right)^{-1}. \quad (3.9)$$

The quantity $\langle P^{\dagger}P \rangle$ can be calculated in the approximation:

$$\langle P^{\dagger}P \rangle = \langle B^{\dagger}B \rangle - \langle B^{\dagger} B^2 \rangle \approx \langle B^{\dagger}B \rangle - 2(\langle B^{\dagger}B \rangle)^2. \quad (3.10)$$

If (3.9) is included in this, it follows:

$$\langle P^{\dagger}P \rangle = \frac{1}{N} \sum_{\vec{k}} \frac{1}{e^{\frac{E_{\vec{k}}^{(1)}}{\theta}} - 1} + 2\langle B^{\dagger}B \rangle \frac{1}{N} \sum_{\vec{k}} \frac{1}{e^{\frac{E_{\vec{k}}^{(1)}}{\theta}} - 1} - 2(\langle B^{\dagger}B \rangle)^2 = \frac{1}{N} \sum_{\vec{k}} \frac{1}{e^{\frac{E_{\vec{k}}^{(1)}}{\theta}} - 1} + O(\tau^2), \quad (3.11)$$

where: $E_{\vec{k}}^{(1)} \equiv \hbar \omega_{\vec{k}}^{(1)} = \frac{J_0 - J_{\vec{k}}}{2}$.

The correct expression for magnetization: $\sigma = 1 - 2\langle P^{\dagger}P \rangle$, with the calculated sums from (3.11), has the form which Dyson obtained:

$$\sigma = 1 - 2\zeta_{3/2} \tau^{3/2} - \frac{3\pi}{2} \zeta_{5/2} \tau^{5/2} - \frac{33\pi^2}{16} \zeta_{7/2} \tau^{7/2} - 6\pi \zeta_{3/2} \zeta_{5/2} \tau^4 + O(\tau^{9/2}), \quad (3.12)$$

where: $\zeta_p \equiv \sum_{n=1}^{\infty} n^{-p}$ – is the Riemann zeta-function, $\tau \equiv \frac{\theta}{2\pi I}$ and I is the integral of the spin change for the nearest neighbors.

— Kinematic excitations in the system of optical excitations

Optical excitations occur in crystals under the influence of incident light [11–16]. A photon transfers an electron from the ground state to an excited state, thus creating an electron-hole pair, called exciton. In semiconductors appear Wannier–Mott excitons and they have a large radius (the hole is in the valence band and the electron is

in the conduction band), while in molecular crystals appear Frenkel excitons, which have a small radius because they are localized on the same molecule.

The system of Frenkel excitons will be analyzed here. In order to simplify the calculations, we will consider the case when the incident light quanta translate the electron into only one type of excited state (the so-called two-level scheme). Then the operators of creation and annihilation of excitons are Pauli operators and satisfy the already given commutation relations (3.1).

The formation of excitons as a collective crystal excitation is physically represented in the following way [20]: a quantum of light excites one molecule and this excitation propagates in the form of waves through the crystal due to the interaction between molecules. The intermolecular interactions are of the dipole-dipole type with 0.01 eV order of magnitude of energy. The excitation energy of an isolated molecule is much higher, up to several eV, depending on how much energy the incident quantum of light possesses.

Concentrations of excitons produced by classical light sources were of the order of $10^{-10} - 10^{-7}$. With use of the laser, the concentrations of the optical excitation reached a value of 10^{-3} and then the interaction between these excitations could not be neglected. One type of interaction is of the dynamic type and represents the scattering of optical excitations at the intermolecular potential. The second type of interaction is of the kinematic type and comes from the difference in the commutation rules between Pauli and the Bose operator. The point is that, in the case of low concentrations, Pauli operators were simply replaced by Bose operators and this approximation was completely satisfactory. At higher concentrations this procedure is not enough and gives not accurate results.

The Pauli operators are represented by the Bose operator, and the exact boson representation Agranovich-Toshich [15], of the already mentioned form (3.2), will be used here. In this representation, the Pauli operators are represented by infinite bosonic series, which in other words means that the processes between Pauli excitations can be described by multi-bosonic processes. The case of fusion of two excitons into one and its corresponding decay will be considered here. In the second part of the process, new excitations arise in relation to the original "normal" excitons, which are short-lived and are called kinematic excitations in the literature.

The Hamiltonian of such an exciton system has the following form [13-16]:

$$H = \Delta \sum_{\vec{n}} P_{\vec{n}}^+ P_{\vec{n}} + \sum_{\vec{n}\vec{m}} T_{\vec{n}\vec{m}} P_{\vec{n}}^+ P_{\vec{m}} + \sum_{\vec{n}\vec{m}} \tilde{D}_{\vec{n}\vec{m}} P_{\vec{n}}^+ P_{\vec{m}} P_{\vec{m}}^+ P_{\vec{n}}, \quad (3.13)$$

where Δ – is the excitation energy of the isolated molecule and is 3 – 5 eV, $T_{\vec{n}\vec{m}}$ characterizes the transfer of excitons from the node \vec{n} to node \vec{m} , and $\tilde{D}_{\vec{n}\vec{m}}$ – their scattering. Both of these quantities are of the order of 0.1 eV and less.

The system will be analyzed, as in (3.5), via a commutator two-time Pauli GF:

$$\Gamma_{\vec{a}\vec{b}}(t) \equiv \langle\langle P_{\vec{a}}(t) | P_{\vec{b}}^+(0) \rangle\rangle = \Theta(t) \langle [P_{\vec{a}}(t), P_{\vec{b}}^+(0)] \rangle. \quad (3.14)$$

This equation is differentiated by time and together with Heisenberg's equations, follows:

$$i\hbar \frac{d}{dt} \langle\langle P_{\vec{a}}(t) | P_{\vec{b}}^+(0) \rangle\rangle = i\hbar \delta(t) \langle [P_{\vec{a}}(0), P_{\vec{b}}^+(0)] \rangle + \Delta \langle [P_{\vec{a}}(t), P_{\vec{b}}^+(0)] \rangle + \sum_{\vec{m}} T_{\vec{a}\vec{m}} \langle\langle P_{\vec{a}}(t) | P_{\vec{b}}^+(0) \rangle\rangle - 2 \sum_{\vec{a}\vec{m}} T_{\vec{a}\vec{m}} \langle\langle P_{\vec{a}}^+(t) P_{\vec{a}}(t) P_{\vec{m}}(t) | P_{\vec{b}}^+(0) \rangle\rangle + 2 \sum_{\vec{m}} \tilde{D}_{\vec{n}\vec{m}} \langle\langle P_{\vec{m}}^+(t) P_{\vec{m}}(t) P_{\vec{a}}(t) | P_{\vec{b}}^+(0) \rangle\rangle \quad (3.15)$$

Now the Pauli GFs from (3.15) are replaced by bosonic GFs, where the exact boson representation (3.2) is used in the following approximation:

$$P \approx B - B^+ B B; P^+ \approx B^+ - B^+ B^+ B.$$

After replacing this in all Pauli GFs from (3.14), the mean values of the Bose operator up to six operators are retained. The mean products of the Bose operator are broken down into the sums of the mean products of the pairs of operators, according to Wick's theorem [19]. Pauli GFs, which are expressed in the described way through bosonic ones, are replaced by expression (3.15). The resulting equation, which now contains only bosonic GFs, is translated into algebraic equations by their Fourier transformations. On this occasion, all contributions proportional to the square or higher degree of the bosonic concentration are neglected. In this way, the following result is obtained (details in [16]):

$$G_{\vec{k}}^-(\omega) = \frac{i}{2\pi} \frac{1+2\bar{N}}{\omega - \Omega_{\vec{k}} + M_{\vec{k}} Q_{\vec{k}}(\omega)}; \bar{N} \equiv \langle B_{\vec{k}}^+ B_{\vec{k}} \rangle = \frac{1}{N} \sum_{\vec{k}} N. \quad (3.16)$$

The function $M_{\vec{k}}$, which appears in (3.16), is given by:

$$M_{\vec{k}} = \frac{2}{N} \sum_{\vec{q}} \left(\Omega_{\vec{k}} + \Omega_{\vec{q}} - \omega_{\vec{k}} - \omega_{\vec{k}-\vec{q}} \bar{N} \right); \quad \Omega_{\vec{k}} = \Omega_{\Delta} + \Omega_{T_{\vec{k}}}; \Omega_{\Delta} = \hbar^{-1} \Delta; \omega_{\vec{k}} = \hbar D_{\vec{k}}; D_{\vec{k}} = \sum_{\vec{m}} D_{\vec{m}} e^{i\vec{k}\vec{m}} \quad (3.17)$$

and represents the correction of the harmonic exciton frequency $\Omega_{\vec{k}}$ which originates from nonlinear effects. Based on this, the frequencies of normal exciton levels are given by the expression:

$$\omega_n(\vec{k}) = \Omega_{\vec{k}} - M_{\vec{k}}. \quad (3.18)$$

As follows from the poles GF (3.16), the function $Q_{\vec{k}}(\omega)$ is given by:

$$Q_{\vec{k}}(\omega) = 1 + \frac{3}{2N^2} \sum_{\vec{q}_1, \vec{q}_2} \left[\omega - \Omega_{\vec{k}} - \Phi_{(\vec{k}\vec{q}_1\vec{q}_2)} \right] \Lambda(\vec{k}\vec{q}_1\vec{q}_2; \omega) \bar{N}_{\vec{q}_1}; \quad (3.19)$$

$$\Phi_{(\vec{k}\vec{q}_1\vec{q}_2)} = \Omega_{\vec{k}-\vec{q}_1+\vec{q}_2} + \Omega_{\vec{q}_2} - \omega_{\vec{q}_1-\vec{q}_2} - \omega_{\vec{k}-\vec{q}_2};$$

$$\Lambda(\vec{k}\vec{q}_1\vec{q}_2; \omega) = \frac{1}{\omega + \Omega_{\vec{q}_1} - \Omega_{\vec{q}_2} - \Omega_{\vec{k}-\vec{q}_1+\vec{q}_2} + \frac{\delta}{3}}$$

$$= \frac{1}{\omega + \Omega_{\vec{q}_1} - \Omega_{\vec{q}_2} - \Omega_{\vec{k}-\vec{q}_1+\vec{q}_2}} - \frac{i\pi}{3} \delta(\omega + \Omega_{\vec{q}_1} - \Omega_{\vec{q}_2} - \Omega_{\vec{k}-\vec{q}_1+\vec{q}_2}).$$

Equation

$$Q_{\vec{k}}(\omega) = 0, \quad (3.20)$$

gives the complementary poles GF $G_{\vec{k}}(\omega)$ with respect to the pole $\omega_n(\vec{k})$. The solutions of equation (3.20) represent the frequencies of kinematic excitations that occur in three-particle boson processes.

In the general case, the frequencies that satisfy equation (3.20) are complex quantities. This means that kinematic excitations are muted and have a finite lifetime. Equation (3.20) will be solved approximately, because it cannot be solved analytically exactly, but only numerically. If we neglect the spatial dispersion, i.e. $\Omega_{\vec{k}} \rightarrow \Omega_0$, $\omega_{\vec{k}} \rightarrow \omega_0$ and assume that $\omega \neq \Omega_0$, equation (3.20) reduces to the form:

$$1 + \frac{3}{2} \bar{N} - \frac{3\Omega_0(1-\eta)\bar{N}}{\omega - \omega_0} = 0, \quad (3.21)$$

therefore, after neglecting the square of the exciton concentrations, we get:

$$\omega_0 = \Omega_{\Delta} + \Omega_0 + 3\Omega_0(1-\eta)\bar{N}; \eta = \frac{\omega_0}{\Omega_0}. \quad (3.22)$$

If the same approximation is used in (3.17) then, based on (3.18), the energies of normal exciton levels are obtained:

$$\omega_n = \Omega_{\Delta} + \Omega_0 - 2\Omega_0(1-\eta)\bar{N}. \quad (3.23)$$

In the indicated approximation, the bosonic GF (3.16) reduces to the following form:

$$G_0 = \frac{i}{2\pi} \frac{(1+1/2\bar{N})(\omega - \Omega_{\Delta} - \Omega_0)}{(\omega - \omega_n)(\omega - \omega_0)}. \quad (3.24)$$

Comparing (3.22) with (3.23), it can be concluded that the kinematic and normal exciton levels are energetically very close to each other due to the fact that the maximum exciton concentrations are of the order of $10^{-3} - 10^{-2}$.

Finally, it must be noted that the use of kinematic excitations explains Urbach's rule [20] for light absorption, according to which the absorption decrement does not depend on the crystal structure and is approximately equal to unity.

4. CONCLUSION

The paper presents one of the very popular, powerful and reliable theoretical research methods in quantum statistical physics or solid state physics – the GF method. This method is a completely closed formalism in the framework of which the problem of particle and quasiparticle systems is completely solved, i.e. the energy spectra and lifetimes of elementary excitations are found. In addition, its great advantage over some other theoretical methods is that GF theory offers the calculation of statistical averages of relevant physical quantities. All this makes it one of the most efficient instruments of theoretical analysis of phenomena in condensed matter physics.

This paper briefly presents the general definitions and essence of the method of application of quantum two-time GFs, as well as the procedure of GF calculation through CF, and the way of manipulating them to calculate the features of the observed physical system.

We have demonstrated the application of this procedure to the determination of the low-temperature dependence of magnetization in ferromagnetic and to the analysis of the optical properties of molecular crystals. From the results of these calculations, already known results have been confirmed: Dyson's law of low-temperature behavior of relative magnetization of ferromagnets: $\sim T^{i/2}$, $i = 3, 5, 7, 8$ and Urbach's fold of light absorption in molecular crystals, according to which the absorption decrement does not depend on the crystal structure and is approximately equal to one.

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