# Collective properties of molecular excitons

I. G. Kaplan and M. A. Ruvinskiĭ

*L. Ya. Karpov Physicochemical Research Institute; Ivano-Frankovsk State Pedagogical Institute*
(Submitted January 27, 1976; resubmitted July 15, 1976)
Zh. Eksp. Teor. Fiz. **71**, 2142–2157 (December 1976)

We investigate the statistical properties and obtain the spectrum of the elementary excitations of the system of Frenkel excitons in three-dimensional molecular crystals with allowance for the kinematic and dynamic interactions. The calculation is carried out with exact commutation relations for the exciton operators, so that the kinematic interaction can be taken into account automatically. The explicit form of the distribution function of the elementary excitations is obtained as a function of the concentration of the excitons; the distribution has a quasi-Bose character in the considered approximations. Expressions are obtained for the dispersion law of the elementary excitations in the Hartree-Fock approximation and in the random-phase approximation. Coherent states are introduced for a system of Frenkel excitons. The conditions for Bose condensation of excitons are investigated and the stability of the coherent state with respect to turning on the kinematic and dynamic interactions is demonstrated. The spectrum of the elementary excitations satisfies the Landau superfluidity criterion under condensation conditions, but differs from the spectrum of a weakly nonideal Bose gas, since it contains terms that depend on the exciton concentration. With increasing exciton concentration in the condensate, the energy of the elementary excitation goes through a maximum. The experimental manifestations of the collective properties are discussed.

PACS numbers: 71.80.+j, 31.70.Ks

## I. EXCITATION

Modern methods of laser excitation of crystals make it possible to obtain large molecular-excitation densities. Thus, when an anthracene crystal is excited, a free-exciton density $\sim 2\times10^{18}$ cm$^{-3}$ is reached,[1,2] corresponding to excitation of $\sim 5\times10^{-4}$ of all the molecules in a unit volume. At such densities, collective effects should appear. The collective properties of a system of molecular Frenkel excitons were investigated to a much lesser degree than those of a system of Wannier–Mott excitons in semiconductors.[3–7] The reason is that in the case of Wannier–Mott excitons the collective properties manifest themselves at a much lower concentration than in the case of Frenkel excitons. At the same time, the possibility of the appearance of a "metallic" phase[8–9] greatly limits the experimentally attainable concentration of the excitons in the semiconductors, whereas in molecular crystals a higher exciton concentration can be reached. The upper band of the molecular-exciton density is determined by the strength of the crystal and appears to be of the order of $\leqslant 10^{-19}$ cm$^{-3}$.

In the second-quantization representation, the Hamiltonian of the electronic excitation of a crystal with one molecule per unit cell, if we confine ourselves to only one excited molecular state, takes in the Heitler–London approximation the following simple form[10]:

$$H=\Delta\sum_{\nu} b_\nu^+ b_\nu+\sum_{\nu,\nu'}{}' M_{\nu-\nu'} b_\nu^+ b_{\nu'}, \tag{1}$$

where $\Delta$ is the excitation energy of the molecule in the crystal, $\nu$ numbers the lattice sites, $M_{\nu-\nu'}$ is a resonance integral characterizing the efficiency of excitation transfer from the site $\nu$ to the site $\nu'$, and the prime at the summation sign means that $\nu\neq\nu'$. The operators for the creation and annihilation of an excitation at a site are Pauli operators, i.e., the operators pertaining to a single site satisfy the fermion commutation relations pertaining to different (boson) sites:

$$\begin{aligned}&[b_\nu, b_\nu^+]_+=1, \quad b_\nu^2=(b_\nu^+)^2=0,\\ &[b_\nu, b_{\nu'}^+]_-=[b_\nu^+, b_{\nu'}^+]_-=[b_\nu, b_{\nu'}]_-=0, \quad \nu\neq\nu'.\end{aligned} \tag{2}$$

For a periodic lattice with one molecule per unit cell, the unitary transformation that diagonalizes the Hamiltonian is determined completely by the translational symmetry of the lattice

$$a_{\mathbf{k}}=\mathfrak{N}^{-1/2}\sum_{\nu} e^{-i\mathbf{k}\mathbf{r}_\nu} b_\nu, \tag{3}$$

where $\mathfrak{N}$ is the number of sites. The Hamiltonian (1) goes over into

$$H=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}}$$

and its $k$-th state energy is

$$\varepsilon=\Delta+\sum_{\nu}{}' M_{\nu-\nu'}\exp\{-i\mathbf{k}\mathbf{r}_{\nu-\nu'}\}\equiv\Delta+M_{\mathbf{k}}. \tag{4}$$

The operators $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^+$ describe molecular excitons or waves of electronic excitation in the crystal.

The exciton operators are connected with the Pauli operators by a unitary transformation. Since, however, the Pauli operators do not satisfy either the boson or fermion commutation relations, the unitary transformation is not canonical, i.e., it does not conserve the commutation relation. In fact,

$$[a_{\mathbf{k}}, a_{\mathbf{k}'}^+]_-=\delta_{\mathbf{k}\mathbf{k}'}-\frac{2}{\mathfrak{N}}\sum_{\nu}\exp\{i(\mathbf{k}'-\mathbf{k})\mathbf{r}_\nu\}\, b_\nu^+ b_\nu, \tag{5}$$

$$[a_{\mathbf{k}}, a_{\mathbf{k}'}^+]_+=\delta_{\mathbf{k}\mathbf{k}'}+\frac{2}{\mathfrak{N}}\sum_{\nu,\nu'}{}'\exp\{i(\mathbf{k}\mathbf{r}_\nu-\mathbf{k}'\mathbf{r}_{\nu'})\} b_\nu^+ b_{\nu'}. \tag{6}$$

The operators $a_k$ obtained with the aid of the unitary transformation (3) are neither Pauli nor Bose nor Fermi operators.

At low exciton concentrations, when $\langle b_\nu^+ b_\nu \rangle \equiv \langle \hat{n}_\nu \rangle \ll 1$, relations (5) go over into the usual boson relations. At large exciton concentrations, however, the corrections for the deviation from the Bose behavior become appreciable. The interaction that results from the non-Bose character of the excitons is customarily called, just as in magnetism theory, [11] kinematic to distinguish it from the interaction that has in its Hamiltonian terms that describe the so-called dynamic interaction of the excitons with one another.

The collective properties of the Frenkel excitons in three-dimensional molecular crystals at absolute zero temperature were investigated by Agranovich and Tosic[12] (see also[10], Chap. X), where the possibility of Bose–Einstein condensation was demonstrated for a gas of excitons in the absence of dynamic interaction between them, and where they obtained under condensation conditions an approximate elementary-excitation spectrum that coincides with the spectrum of a weakly nonideal Bose gas; the influence of the dynamic interaction on the results was also discussed. To take into account the kinematic interaction, an exact representation of the Pauli operators was obtained in the form of an infinite series in Bose operators. This approach was subsequently developed in a number of papers. [13–15] Vaks, Larkin, and Pikin[16] (see also[17]) have developed a diagram technique for spin systems, which makes it possible to take into account directly the kinematic and dynamic interactions without changing over to Bose operators. This technique was not applied to a system of excitons, although at temperatures above the Bose-condensation temperature it is applicable in principle also to excitons, see Sec. 3.

As shown by one of us, [18] the exciton operators satisfy trilinear commutation relations from which it follows that Frenkel excitons obey a modified parafermion statistics that admits of an $\mathfrak{N}$ fold occupation of the single-particle states. An exciton gas satisfying the parastatistics is always nonideal, since the corrections for the deviation of the operators from Bose properties introduces into the Hamiltonian corrections of the same order for the deviation from ideality. It follows therefore that at exciton concentrations at which their deviation from Bose character becomes appreciable we can no longer start with an ideal exciton gas even in the approximation of zero order in the dynamic interaction. The diagonalization of a Hamiltonian of a system with a fixed number of excitons yields new "dressed" excitons, the statistics of which depends on their concentration.

In the present study we have investigated in detail the statistical properties of a system of excitons in three-dimensional molecular crystals, taking into account both the kinematic and dynamic interactions. Since we used in all the calculations exact commutation relations for the exciton operators, the kinematic interaction was taken into account in this approach automatically. An explicit form was obtained for the distribution function as a function of the exciton concentration. In the Hartree–Fock approximation, the distribution function of the dressed excitons has a quasi-Bose character. With increasing concentration, the exciton spectrum becomes restructured and the dispersion law changes. The concentration shift of the energy spectrum of crystals with broad exciton bands can reach, at present-day pumping levels, values of several $cm^{-1}$. These effects should manifest themselves experimentally in displacements of the absorption bands and luminescence bands, and also in a decrease of the lifetime of the excited phase.

As is well known, a feature of a Bose system is the presence of a macroscopic number of condensate particles in the ground state. The proof of the stability of the condensate for a nonideal Bose gas was obtained by Belyaev, [20] who has shown in fact that the ground state of the Bose-condensed system is coherent, since the properties of the ground state obtained by Belyaev coincided with the properties of coherent states introduced later by Glauber. [21] In explicit form, the concept of coherent states was used by Keldysh to prove the stability of a condensate of Wannier–Mott excitons. In this paper we introduce coherent states for Frenkel excitons and show that the coherent condensed state of Frenkel excitons is, under certain conditions, stable with respect to turning-on the dynamic or kinematic interaction.

The presented analysis of the properties of excitons under conditions of Bose condensation will show that the spectrum of elementary excitations satisfies the Landau superfluidity criterion, but differs from the spectrum of a weakly nonideal Bose gas, since it contains concentration terms. With increasing exciton concentration in the condensate, the energy of the elementary excitations goes through a maximum. We investigate the conditions of the stability of a Bose-condensed state. Since the superfluidity condition is satisfied, the presence of an exciton condensate should manifest itself in an anomalously large exciton diffusion. Another manifestation of a condensate can be enhancement of light and sound[5,10,22] or else resonant absorption of hypersound. [23]

## 2. EXACT COMMUTATION RELATIONS FOR EXCITON OPERATORS, AND DISCUSSION OF THE STATISTICS

Relations (5) assume a simple closed form if we take a commutator from a commutation bracket. Using the commutation properties (2) of the operators $b_\nu$ and $b_\nu^+$, we can show that

$$[[a_k^+, a_{k'}]_-, a_{k''}]_- = -2\mathfrak{N}^{-1} a_{\bar{k}}, \quad \bar{k} = k' + k'' - k, \tag{7}$$

$$[[a_k^+, a_{k'}]_-, a_{k''}^+]_- = 2\mathfrak{N}^{-1} a_{\bar{k}}^+, \quad \bar{k} = k - k' + k'', \tag{8}$$

$$[a_k^+, a_{k'}^+]_- = [a_k, a_{k'}]_- = 0. \tag{9}$$

The value of the vector $\bar{k}$ in the right-hand sides of (7) and (8) is determined by the quasimomentum conservation law.

It is easily seen that the commutation relations (7) and (8) are close in their structure to the parafermion commutation relations. The latter were proposed by Green[24] and independently by Volkov,[25] who have shown that the second-quantization operators, which satisfy the causality principle, CPT invariance, and positiveness of the energy can satisfy commutation relations that are more general than the boson and fermion relations. Relations (7) at $\mathbf{k}=\mathbf{k}''$ and relations (8) at $\mathbf{k}'=\mathbf{k}''$ coincide with the parafermion relations for the normalized operators (see[26]). At different values of $\mathbf{k}$, however, the commutation relations for the excitons differ significantly from the parafermion relations in that the value of the vector $\bar{\mathbf{k}}$ in the right-hand sides of (7) and (8) is determined not by the Kronecker symbol but by the quasi-momentum conservation law.

To find the action of the operator $a_{\mathbf{k}}$ on the state of the physical vacuum $|0\rangle$, it suffices to determine the action exerted on this state by the Pauli operators

$$b_\nu|0\rangle=0, \qquad b_{\nu'}b_\nu^+|0\rangle=\delta_{\nu\nu'}|0\rangle. \tag{10}$$

From the definition (3) it follows directly that

$$a_{\mathbf{k}}|0\rangle=0, \qquad a_{\mathbf{k}'}a_{\mathbf{k}}^+|0\rangle=\delta_{\mathbf{k}\mathbf{k}'}|0\rangle. \tag{11}$$

Using the commutation relations for $b_\nu$, it is easy to show[18] that up to $\mathfrak{N}$ excitons can exist in one state, i.e.,

$$(a_{\mathbf{k}}^+)^{\mathfrak{N}}|0\rangle\neq0, \qquad (a_{\mathbf{k}}^+)^{\mathfrak{N}+1}|0\rangle=0. \tag{12}$$

Thus, the excitons described by the operators (3) satisfy a certain modification of parafermion statistics of rank $\mathfrak{N}$, characterized by the commutation relations (7)–(9).

The vector of a state containing $N$ excitons with quasimomentum $\mathbf{k}$ is defined by the usual equation

$$|N_{\mathbf{k}}\rangle=C_N(a_{\mathbf{k}}^+)^N|0\rangle \tag{13}$$

with a normalization factor that differs from that of a Bose system:

$$C_N=\left[N!\left(1-\frac{1}{\mathfrak{N}}\right)\left(1-\frac{2}{\mathfrak{N}}\right)\dots\left(1-\frac{N-1}{\mathfrak{N}}\right)\right]^{-1/2}. \tag{14}$$

The result of the action of the exciton creation and annihilation operators on the state vector (13) is[18]

$$a_{\mathbf{k}}^+|N_{\mathbf{k}}\rangle=[(N_{\mathbf{k}}+1)(1-N_{\mathbf{k}}/\mathfrak{N})]^{1/2}|N_{\mathbf{k}}+1\rangle, \tag{15}$$

$$a_{\mathbf{k}}|N_{\mathbf{k}}\rangle=[N_{\mathbf{k}}(1-(N_{\mathbf{k}}-1)/\mathfrak{N})]^{1/2}|N_{\mathbf{k}}-1\rangle. \tag{16}$$

In accordance with (12), the action of $a_{\mathbf{k}}^+$ on a state with a maximum occupation number $N_{\mathbf{k}}=\mathfrak{N}$ is equal to zero. As $\mathfrak{N}\to\infty$, relations (15) and (16) go over into the known relations for bosons.

It follows from (15) and (16) that

$$a_{\mathbf{k}}^+a_{\mathbf{k}}|N_{\mathbf{k}}\rangle=N_{\mathbf{k}}(1-(N_{\mathbf{k}}-1)/\mathfrak{N})|N_{\mathbf{k}}\rangle, \tag{17}$$

i.e., the operator $a_{\mathbf{k}}^+a_{\mathbf{k}}$ is not a particle-number operator, as is the case for bosons or fermions.

The function $|N_{\mathbf{k}}\rangle$ describes $N$ non-interacting excitons with energy $\varepsilon_{\mathbf{k}}$. Not more than $\mathfrak{N}$ excitons can exist in a single state. The distribution function of an ideal gas with a maximum occupation number $\mathfrak{N}$ can be easily obtained by taking the derivative of the thermodynamic potential $\Omega_{\mathbf{k}}$ with respect to the chemical potential $\mu$ under the condition that up to $\mathfrak{N}$ quasiparticles can exist in one quantum state

$$\bar{n}_{\mathbf{k}}=-\frac{\partial\Omega_{\mathbf{k}}}{\partial\mu}=\left[\exp\left[\frac{\varepsilon_{\mathbf{k}}-\mu}{T}\right]-1\right]^{-1}-(\mathfrak{N}+1)\left\{\exp\left[\frac{(\varepsilon_{\mathbf{k}}-\mu)(\mathfrak{N}+1)}{T}\right]-1\right\}^{-1}. \tag{18}$$

Since the distribution function of an ideal gas with an arbitrary finite occupation number was first obtained by Gentile,[27] we shall call expression (18) the Gentile distribution function. The Gentile function goes over into the Bose–Einstein distribution function as $\mathfrak{N}\to\infty$ and into the Fermi–Dirac distribution function at $\mathfrak{N}=1$.

The Hamiltonian of a system of noninteracting excitons should be linear in the operators of the number of excitons in the state $\mathbf{k}$:

$$H=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}\hat{N}_{\mathbf{k}}. \tag{19}$$

However, as shown in[18], the absence of Kronecker symbols from the commutation relations (7) and (8) makes it impossible to introduce the particle-number operator $\hat{N}_{\mathbf{k}}$ for excitons. This means that in principle it is impossible to regard the exciton gas as ideal without resorting to the Bose approximation. Therefore the Gentile function does not describe a system of excitons regardless of the concentration. To find the distribution function of the excitons at concentrations at which deviation from the Bose distribution are substantial, it is necessary to take correct account of the exciton interaction. As will be shown in the next section, the obtained distribution function includes explicitly terms that depend on the concentration.

To estimate the kinematic interaction, it suffices to calculate the mean value of the Hamiltonian taken without the dynamic interaction on the functions of the noninteracting excitons $|N_{\mathbf{k}}\rangle$:

$$\bar{E}_{N_{\mathbf{k}}}=\langle N_{\mathbf{k}}|\sum_{\mathbf{k}'}\varepsilon_{\mathbf{k}'}a_{\mathbf{k}'}{}^+a_{\mathbf{k}'}|N_{\mathbf{k}}\rangle=C_N{}^2\langle0|\sum_{\mathbf{k}'}\varepsilon_{\mathbf{k}'}a_{\mathbf{k}}{}^Na_{\mathbf{k}'}{}^+a_{\mathbf{k}'}(a_{\mathbf{k}}^+)^N|0\rangle. \tag{20}$$

In the case of bosons we would have $\bar{E}_{N\mathbf{k}}=N\varepsilon_{\mathbf{k}}$. Allowance for the exact commutation relations lead to the appearance of an interaction. Using the operator equation (22) from[18], we get

$$\bar{E}_{N\mathbf{k}}=N\left\{\varepsilon_{\mathbf{k}}+\frac{N-1}{\mathfrak{N}-1}(\bar{\varepsilon}-\varepsilon_{\mathbf{k}})\right\}=N\left\{\Delta+M_{\mathbf{k}}\left(1-\frac{N-1}{\mathfrak{N}-1}\right)\right\}, \tag{21}$$

where $\bar{\varepsilon}$ denotes the average energy of the exciton band

$$\frac{1}{\mathfrak{N}}\sum_{k'}\varepsilon_{k'}.$$

It follows from (21) that the corrections for the kinematic interaction are $\sim N/\mathfrak{N}$, i.e., they are of the same order as the corrections for deviations from the Bose distribution in the commutation relations. Their absolute magnitude is larger the farther the level from the center of the exciton band.

A more accurate calculation, that takes into account both the kinematic and dynamic interaction will be presented in the next section.

## 3. ENERGY SPECTRUM AND DISTRIBUTION FUNCTION OF EXCITON SYSTEM

The total Hamiltonian for a crystal with one molecule per unit cell in the absence of interaction of the electronic states with one another and with the lattice vibrations, is given by[10,28]:

$$H=\Delta\sum_{\nu}b_{\nu}^{+}b_{\nu}+\sum_{\nu,\nu'}{}'M_{\nu-\nu'}b_{\nu}^{+}b_{\nu'}$$
$$+\sum_{\nu,\nu'}{}'Q_{\nu-\nu'}(b_{\nu}b_{\nu'}+b_{\nu}^{+}b_{\nu'}^{+})+\sum_{\nu,\nu'}{}'F_{\nu-\nu'}b_{\nu}^{+}b_{\nu'}^{+}b_{\nu}b_{\nu'}. \qquad (22)$$

The first two terms correspond to the Heitler–London approximation, the fourth characterizes the dynamic interaction between the excitons, and the third characterizes processes that lead to nonconservation of the exciton number. The Hamiltonian (22) can be regarded as semi-empirical.[29] In this case the quantities $Q_{\nu-\nu'}$ and $F_{\nu-\nu'}$ incorporate the contributions from all the processes connected with exciton collisions, including the interaction due to virtual exchange of phonons, or else exciton decay via collision with formation of an exciton of higher energy.[30]

We change over in accordance with (3) to the free-exciton operators in **k**-space. The Hamiltonian (22) becomes

$$H=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}+\sum_{\mathbf{k}}Q_{\mathbf{k}}(a_{\mathbf{k}}a_{-\mathbf{k}}+a_{-\mathbf{k}}^{+}a_{\mathbf{k}}^{+})+\frac{\mathfrak{N}}{4}\sum_{\mathbf{k}}F_{\mathbf{k}}\gamma_{\mathbf{k}}\gamma_{-\mathbf{k}}, \qquad (23)$$

where $\varepsilon_{\mathbf{k}}$ is given in (4), $Q_{\mathbf{k}}$, $F_{\mathbf{k}}$ are the Fourier components of $Q_{\nu}$, $F_{\nu}$ ($\nu\neq 0$), and the operator $\gamma_{\mathbf{k}}$ has the meaning of double the Fourier components of the dimensionless exciton density and is given by

$$\gamma_{\mathbf{k}}=\frac{2}{\mathfrak{N}}\sum_{\mathbf{t}}a_{\mathbf{k}+\mathbf{t}}^{+}a_{\mathbf{t}}. \qquad (24)$$

The transition to **k**-space provides a more convenient method than calculation in the node representation. Not only is the number of intermediate steps smaller, but in calculations with the operators $a_{\mathbf{k}}$ there is no need to look out for satisfaction of the Pauli principle (to get rid of unphysical states), since the number of excitons in one state cannot exceed the rank of the parastatistics describing the excitons; all that is necessary is to use the exact commutation relations (7) and (8).

We shall investigate the system of equations characterized by the Hamiltonian (23) by the method of equal-time retarded Green's functions, defined in accordance with[31]

$$\ll a_{\mathbf{k}}(t)\,|\,a_{\mathbf{k}}^{+}(t')\gg\equiv\theta(t-t')\langle[a_{\mathbf{k}}(t),\,a_{\mathbf{k}}^{+}(t')]_{-}\rangle,$$
$$\ll a_{-\mathbf{k}}^{+}(t)\,|\,a_{\mathbf{k}}^{+}(t')\gg\equiv\theta(t-t')\langle[a_{-\mathbf{k}}^{+}(t),\,a_{\mathbf{k}}^{+}(t')]_{-}\rangle, \qquad (25)$$

where

$$\theta(x)=\begin{cases}1 & x>0\\ 0 & x<0\end{cases}.$$

Changing over to the energy representation with $\hbar=1$

$$\ll A(t)\,|\,B(t')\gg=\frac{1}{2\pi}\int_{-\infty}^{\infty}\ll A|B\gg_{E}e^{-iE(t-t')}\,dE,$$

we obtain, using the exact commutation relations (7) and (8), the following chain of equations:

$$(E-\varepsilon_{\mathbf{k}})\ll a_{\mathbf{k}}|a_{\mathbf{k}}^{+}\gg_{E}=\frac{i}{2\pi}\left(1-\frac{2\bar{N}}{\mathfrak{N}}\right)+2Q_{\mathbf{k}}\ll a_{-\mathbf{k}}^{+}|a_{\mathbf{k}}^{+}\gg_{E}$$
$$-\sum_{\mathbf{q}}Q_{\mathbf{q}}\ll a_{-\mathbf{q}}^{+}\gamma_{\mathbf{q}-\mathbf{k}}+\gamma_{\mathbf{q}-\mathbf{k}}a_{-\mathbf{q}}^{+}|a_{\mathbf{k}}^{+}\gg_{E}-\sum_{\mathbf{q}}(\varepsilon_{\mathbf{q}}-F_{\mathbf{q}-\mathbf{k}})\ll\gamma_{\mathbf{q}-\mathbf{k}}a_{\mathbf{q}}|a_{\mathbf{k}}^{+}\gg_{E}$$
$$-\frac{1}{2}\sum_{\mathbf{q},\mathbf{t}}F_{\mathbf{t}-\mathbf{q}}\ll\gamma_{\mathbf{t}-\mathbf{k}}\gamma_{\mathbf{q}-\mathbf{t}}a_{\mathbf{q}}|a_{\mathbf{k}}^{+}\gg_{E}; \qquad (26)$$

$$(E+\varepsilon_{\mathbf{k}})\ll a_{-\mathbf{k}}^{+}|a_{\mathbf{k}}^{+}\gg_{E}=-2Q_{\mathbf{k}}\ll a_{\mathbf{k}}|a_{\mathbf{k}}^{+}\gg_{E}+\sum_{\mathbf{q}}Q_{\mathbf{q}}\ll a_{\mathbf{q}}\gamma_{\mathbf{q}-\mathbf{k}}+\gamma_{\mathbf{q}-\mathbf{k}}a_{\mathbf{q}}|a_{\mathbf{k}}^{+}\gg_{E}$$
$$+\sum_{\mathbf{q}}(\varepsilon_{\mathbf{q}}-F_{\mathbf{k}-\mathbf{q}})\ll a_{-\mathbf{q}}^{+}\gamma_{\mathbf{q}-\mathbf{k}}|a_{\mathbf{k}}^{+}\gg_{E}+\frac{1}{2}\sum_{\mathbf{q},\mathbf{t}}F_{\mathbf{q}-\mathbf{t}}\ll a_{-\mathbf{q}}^{+}\gamma_{\mathbf{q}-\mathbf{t}}\gamma_{\mathbf{t}-\mathbf{k}}|a_{\mathbf{k}}^{+}\gg_{E}. \qquad (27)$$

We shall close the chain of equations (26) and (27) in two approximations, expressing the higher Green's functions in terms of single-particle ones.

### A. The Hartree-Fock approximation

In this approximation we use approximate functions of the type

$$G_{\mathbf{qtk}}(E)\equiv\ll a_{\mathbf{q}-\mathbf{k}+\mathbf{t}}^{+}a_{\mathbf{t}}a_{\mathbf{q}}|a_{\mathbf{k}}^{+}\gg_{E}\cong\left(\bar{n}_{\mathbf{t}}\delta_{\mathbf{kq}}+\bar{n}_{\mathbf{q}}\delta_{\mathbf{kt}}-\frac{2}{\mathfrak{N}}\bar{n}_{\mathbf{q}-\mathbf{k}+\mathbf{t}}\right)\ll a_{\mathbf{k}}|a_{\mathbf{k}}^{+}\gg_{E}$$
$$+\bar{m}_{\mathbf{q}}\delta_{\mathbf{q},-\mathbf{t}}\ll a_{-\mathbf{k}}^{+}|a_{\mathbf{k}}^{+}\gg_{E}, \qquad (28)$$

where $\bar{n}_{\mathbf{t}}\equiv\langle a_{\mathbf{t}}^{+}a_{\mathbf{t}}\rangle$ is the "true" mean value of the operator $a_{\mathbf{t}}^{+}a_{\mathbf{t}}$ (for a system with Hamiltonian (23)), and $\bar{m}_{\mathbf{q}}\equiv\langle a_{\mathbf{q}}a_{-\mathbf{q}}\rangle$ is the "anomalous" mean value. In addition to the obvious equality $\sum_{\mathbf{t}}\bar{n}_{\mathbf{t}}=\bar{N}$, the exact commutation relations lead to $\sum_{\mathbf{q}}\bar{m}_{\mathbf{q}}=0$. It is easy to show that

$$G_{\mathbf{qtk}}=G_{\mathbf{tqk}},\qquad\sum_{\mathbf{q},\mathbf{t}}G_{\mathbf{qtk}}=0, \qquad (29)$$

and these relations are satisfied also by the approximate expression (28).[1)]

We consider the case of a fixed number of excitons. Formally this corresponds to $Q_{\mathbf{k}}=0$ in (26) and (27).

After obtaining the explicit form of the single-particle Green's function, we get the energy and the distribution function,[31,32] of the elementary excitations of the system of excitons:

$$E_k=\Delta+M_k-\frac{2}{\mathfrak{N}}\Big[N(M_k-F_0)+\sum_q (M_q-F_{q-k})\bar{n}_q\Big]$$
$$-\frac{2}{\mathfrak{N}^2}\Big[\sum_{q,t} F_{q-t}\bar{n}_t\bar{n}_q+N\sum_q F_{q-k}\bar{n}_q\Big], \quad (30)$$

$$\bar{n}_k=\frac{1-2N/\mathfrak{N}}{\exp\{\beta(E_k-\mu)\}-1}, \quad (31)$$

and $\mu$ is the chemical potential of the excitons, determined from the condition

$$\sum_k \bar{n}_k=N. \quad (32)$$

In the considered case of a fixed number of excitons, the number of elementary excitations is equal to the number of the initial excitons, and the ground state for the elementary excitations is the same as for the initial excitons, i.e., the mean value of the Hamiltonian (23) is equal to

$$\bar{H}=\sum_k E_k\bar{n}_k. \quad (33)$$

By the same token, the obtained elementary excitations can be regarded as "dressed" (on account of the kinematic and dynamic interaction) excitons with energy $E_k$ (30). The distribution function of an ideal gas of dressed excitons coincides in the case of a fixed number of excitons with a distribution function of interacting "bare" excitons and has according to (31) a quasi-Bose character.

If we confine ourselves to corrections that the quadratic in the concentration for the unperturbed spectrum $E_k^0=\varepsilon_k=\Delta+M_k$, then we must substitute in (30) the Bose distribution function

$$\bar{n}_k^0=[\exp\{\beta(E_k^0-\mu_0)\}-1]^{-1} \quad (34)$$

with the chemical potential $\mu_0$ of an ideal exciton gas in the Bose approximation.[28]2) The expression for the chemical potential in approximation quadratic in the concentration is obtained from (31) and (32) and is quite cumbersome. We present the expressions for the corrections to $E_k^0$ and $\mu_0$ in the approximation linear in the concentration:

$$\delta E_k\equiv E_k-E_k^0=-\frac{2}{\mathfrak{N}}\Big[N(M_k-F_0)+\sum_q (M_q-F_{q-k})\bar{n}_q^0\Big], \quad (35)$$

$$\delta\mu\equiv\mu-\mu_0=-\frac{2N}{\mathfrak{N}}\Big[\bar{M}+\frac{1}{N}\sum_q M_q\bar{n}_q^0-F_0-\bar{F}-(\beta D)^{-1}\Big]. \quad (36)$$

In (36), we have used $D$ and the mean values $\bar{M}$ and $\bar{F}$ to denote

$$D=\frac{1}{N}\sum_q \bar{n}_q^0(1+\bar{n}_q^0),\quad \bar{M}=(DN)^{-1}\sum_q M_q\bar{n}_q^0(1+\bar{n}_q^0),$$

$$\bar{F}=(N^2D)^{-1}\sum_{k,q} F_{q-k}\bar{n}_q^0\bar{n}_k^0(1+\bar{n}_k^0). \quad (37)$$

We note that $\bar{n}_q^0(1+\bar{n}_q^0)=(\overline{\delta n_q^0})^2$ is the mean squared fluctuation of the number of single-particle states in an ideal Bose gas.

The shifts $\delta E_k$ and $\delta\mu$ are directly proportional to the relative concentration of the excitons $N/\mathfrak{N}$ and depend substantially on the signs and absolute values of $M_k$ and $F_k$. At $M_k<0$ (positive exciton effective mass) and $F_k>0$ (repulsion between excitons), the energy and the chemical potential of the excitons shift to the short-wave region of the spectrum with increasing concentration. Shifts to the long-wave region are possible in other cases.

The energy shift due only to the kinematic interaction is, according to (35),

$$\delta E_k=-\frac{2N}{\mathfrak{N}}M_k-\frac{2}{\mathfrak{N}}\sum_q M_q\bar{n}_q^0. \quad (38)$$

For $M_k<0$, the corrections to the spectrum are positive and the kinematic interaction is equivalent to the effective repulsion between the excitons. Since the factor $2N/\mathfrak{N}$ enters in the expression for the shift of any level $E_k$ of the exciton band, the kinematic interaction leads to a narrowing of the band. If we denote the width of the elementary-excitation band (dressed electrons) by $V$, and the width of the band of the initial excitations (bare excitons) by $V_0$, then as a result of the kinematic interaction we have

$$V=V_0(1-2N/\mathfrak{N}). \quad (39)$$

For crystals with exciton-band width $\sim 10^3$ cm$^{-1}$ and exciton concentration $N/\mathfrak{N}\sim 10^{-3}$, the kinematic interaction leads to a narrowing of the excitation band by several cm$^{-1}$.

### B. Random-phase approximation

It is of interest to consider the spectrum of the excitons in the random-phase approximation,[33,11] which is valid at sufficiently high exciton concentrations. We use the customary approximations of this approach

$$\langle\langle\gamma_{q-k}a_q|a_k^+\rangle\rangle_E\cong\langle\gamma_{q-k}\rangle\langle\langle a_q|a_k^+\rangle\rangle_E$$
$$=2\bar{N}\mathfrak{N}^{-1}\delta_{kq}\langle\langle a_k|a_k^+\rangle\rangle_E. \quad (40)$$

Leaving out the intermediate steps, we present the final results for a system of excitons described by a total Hamiltonian (23). The number of excitons is not fixed. The energy of the elementary excitations of the exciton system is given by

$$E_k=(\alpha_k^2-\delta_k^2)^{1/2}, \quad (41)$$

$$\alpha_k=\Delta+M_k(1-2\bar{N}/\mathfrak{N})+2\bar{N}F_0/\mathfrak{N}, \quad (42)$$

$$\delta_k=2Q_k(1-2\bar{N}/\mathfrak{N}). \quad (43)$$

The distribution function of the elementary excitation is

$$\bar{n}_{\mathbf{k}}=\frac{1-2\bar{N}/\mathfrak{N}}{\exp\{\beta\tilde{E}_{\mathbf{k}}\}-1}, \tag{44}$$

where $\bar{N}$ is the average number of the excitons, $\bar{N}=\sum_{\mathbf{k}}\bar{n}_{\mathbf{k}}$, and the mean occupation number is $n_{\mathbf{k}}$ (or the distribution function of the interacting excitons) are determined from the equation

$$\bar{n}_{\mathbf{k}}\equiv\langle a_{\mathbf{k}}^{+}a_{\mathbf{k}}\rangle=\left(\frac{1}{2}-\frac{\bar{N}}{\mathfrak{N}}\right)\left(\frac{\alpha_{\mathbf{k}}}{\tilde{E}_{\mathbf{k}}}\operatorname{cth}\frac{\beta\tilde{E}}{2}-1\right). \tag{45}$$

The average number of elementary excitations $\tilde{N}=\sum_{\mathbf{k}}\tilde{n}_{\mathbf{k}}$ is always less than the average number of excitons $\bar{N}$. The ground state, from which the energy of the elementary excitations $\tilde{E}_{\mathbf{k}}$ is reckoned, does not coincide in this case with the state from which the exciton energy is reckoned. In place of (33) we now have

$$\bar{H}=\Delta E_0+\sum_{\mathbf{k}}\tilde{E}_{\mathbf{k}}\tilde{n}_{\mathbf{k}},\quad \Delta E_0<0. \tag{46}$$

Therefore, in contrast to the case considered above with a fixed number of excitons, in the present case the elementary excitations cannot be regarded as dressed excitons, and the functions $\tilde{n}_{\mathbf{k}}$ and $\bar{n}_{\mathbf{k}}$ are not equal.

By analogy with ferromagnetism theory,[31,17] we can introduce the order parameters[34]:

$$\sigma=\frac{1}{2}-\frac{\bar{N}}{\mathfrak{N}}=\frac{1}{2}-\frac{1}{\mathfrak{N}}\sum_{\mathbf{k}}\bar{n}_{\mathbf{k}}, \tag{47}$$

which characterizes the degree of excitation of the system at a given level of optical pumping and temperature $\beta^{-1}$. Small values of $\sigma$ correspond to large degrees of excitation of the system and to a possibility of a transition into the so-called superradiant state.[34,35] It can be shown that $\sigma$ satisfies a relation

$$\frac{1}{2\sigma}=\frac{1}{\mathfrak{N}}\sum_{\mathbf{k}}\frac{\alpha_{\mathbf{k}}}{\tilde{E}_{\mathbf{k}}}\operatorname{cth}\frac{\beta\tilde{E}_{\mathbf{k}}}{2}, \tag{48}$$

that generalizes the corresponding relation from ferromagnetism theory.[31]

If $|Q_{\mathbf{k}}/\Delta|\ll 1$, we obtain for $\tilde{E}_{\mathbf{k}}$

$$\tilde{E}_{\mathbf{k}}=\Delta+F_0+2\sigma\left[M_{\mathbf{k}}-F_0-\frac{4\sigma Q_{\mathbf{k}}^{2}}{\Delta+F_0+2\sigma(M_{\mathbf{k}}-F_0)}\right]. \tag{49}$$

To obtain the energy spectrum of excitons in the random-phase approximations, Marinkovic[15] used the procedure of[14] to exclude from the Hamiltonian the terms that do not conserve the number of electrons, followed by expansion of the exciton operators in Bose operators. Our expression (49) agrees with expression (21) obtained in[15] under the same conditions only at $Q_{\mathbf{k}}=0$. The discrepancy is apparently caused by the inaccuracy, due to the cumbersome procedure used by Marinkovic, of expression (21) of[15].

## 4. BOSE CONDENSATION

As shown above, when the interaction between excitons is taken into account, they are subject to the quasi-Bose statistics (31). This means that there are no statistical hindrances to Bose condensation of excitons. The condensation temperature $T_{\mathrm{cr}}$ of an ideal gas of quasiparticles with a distribution function (31) is estimated at

$$T_{\mathrm{cr}}=\frac{T_{\mathrm{cr}}^{0}}{(1-2N/\mathfrak{N})^{1/3}}, \tag{50}$$

where $T_{\mathrm{cr}}^{0}$ is the condensation temperature of an ideal Bose gas. $T_{\mathrm{cr}}$ is always higher than $T_{\mathrm{cr}}^{0}$, although this excess is insignificant because $N/\mathfrak{N}$ is small.

The expressions obtained in the preceding section for the energy spectrum of a system of excitons are valid at $T>T_{\mathrm{cr}}$. In the present section we investigate the ground state and obtain the spectrum of elementary excitations under conditions of Bose condensation at $T<T_{\mathrm{cr}}$. The initial Hamiltonian can be written in the form

$$H=\sum_{\mathbf{k}}(\Delta+M_{\mathbf{k}})a_{\mathbf{k}}^{+}a_{\mathbf{k}}+\frac{1}{2}\sum_{\mathbf{k},\mathbf{t}}F_{\mathbf{k}-\mathbf{t}}a_{\mathbf{k}}^{+}\gamma_{\mathbf{t}-\mathbf{k}}a_{\mathbf{t}}, \tag{51}$$

where $\gamma_{\mathbf{t}-\mathbf{k}}$ is given by (24). The terms with $Q$ have been left out of the Hamiltonian (23), since the number of excitons is assumed to be fixed.

As already mentioned in the Introduction, it followed from Belyaev's work[20] on the stability of a Bose condensate that the ground state is coherent in this case. Coherent states were subsequently resorted to in a number of studies for the investigation of the phenomena of superfluidity and superconductivity, see[36]. The concept of coherent states was used by Keldysh[4] to prove the stability of a Bose condensate of Wannier–Mott excitons. We shall use a similar approach here to demonstrate the stability of a Bose condensate of Frankel excitons.

The Bose-condensed state of the Frenkel exciton is a coherent (with definite phase) wave of electronic excitation of a finite amplitude but not of the order of $1/\mathfrak{N}$. As a result of the allowance for the deviations of the exciton statistics from Bose statistics, the coherent states of one mode are determined for operators $\tilde{a}_{\mathbf{k}}$ that differ from the operators $a_{\mathbf{k}}$ and depend on the exciton-wave amplitude $\alpha_{\mathbf{k}}$:

$$\tilde{a}_{\mathbf{k}}|\alpha_{\mathbf{k}}\rangle=\tilde{\alpha}_{\mathbf{k}}|\alpha_{\mathbf{k}}\rangle, \tag{52}$$

where

$$\tilde{a}_{\mathbf{k}}=a_{\mathbf{k}}+\tilde{\alpha}_{\mathbf{k}}{}^{2}a_{\mathbf{k}}{}^{+}/\mathfrak{N}. \tag{53}$$

$$\tilde{\alpha}_{\mathbf{k}}=\alpha_{\mathbf{k}}(\mathfrak{N}^{1/2}/|\alpha_{\mathbf{k}}|)\operatorname{tg}(|\alpha_{\mathbf{k}}|/\mathfrak{N}^{1/2}).$$

The commutation relations for the new operators $\tilde{a}_{\mathbf{k}}$ at $\mathbf{k}=\mathbf{k}'$ differ from the commutation relations for the operators $a_{\mathbf{k}}$ only by a $c$-number:

$$[\tilde{a}_{\mathbf{k}},\ \tilde{a}_{\mathbf{k}}{}^{+}]_{-}=(1-|\tilde{\alpha}_{\mathbf{k}}|^{4}/\mathfrak{N}^{2})[a_{\mathbf{k}},\ a_{\mathbf{k}}{}^{+}]_{-}. \tag{54}$$

The coherent state is defined by

$$\begin{aligned}|\alpha_{\mathbf{k}}\rangle&=\exp\{(1-|\tilde{\alpha}_{\mathbf{k}}|^{2}/\mathfrak{N})^{-1}(\alpha_{\mathbf{k}}\tilde{a}_{\mathbf{k}}{}^{+}e^{-i\omega t/\hbar}\\&\quad-\alpha_{\mathbf{k}}{}^{*}\tilde{a}_{\mathbf{k}}e^{i\omega t/\hbar})\}|0\rangle\\&\equiv\exp\{\alpha_{\mathbf{k}}a_{\mathbf{k}}{}^{+}e^{-i\omega t/\hbar}-\alpha_{\mathbf{k}}{}^{*}a_{\mathbf{k}}e^{i\omega t/\hbar}\}|0\rangle,\end{aligned} \tag{55}$$

where $\mu$ is the chemical potential of the system.

The probability that $N_{\mathbf{k}}$ quasiparticles are in a state $|\alpha_{\mathbf{k}}\rangle$ is equal to

$$P_{\alpha_{\mathbf{k}}}(N_{\mathbf{k}})=\frac{|\tilde{\alpha}_{\mathbf{k}}|^{2N_{\mathbf{k}}}}{N_{\mathbf{k}}!}\left(1+\frac{|\tilde{\alpha}_{\mathbf{k}}|^2}{\mathfrak{N}}\right)^{-\mathfrak{N}}\left(1-\frac{1}{\mathfrak{N}}\right)\left(1-\frac{2}{\mathfrak{N}}\right)\ldots\left(1-\frac{N_{\mathbf{k}}-1}{\mathfrak{N}}\right). \tag{56}$$

At $N_{\mathbf{k}}>\mathfrak{N}$ we have $P_{\alpha_{\mathbf{k}}}(N_{\mathbf{k}})\equiv 0$ in accordance with the character of the modified parastatistics for the excitons (see (12)). The average occupation number is

$$\bar{N}_{\mathbf{k}}=\sum_{n=0}^{\mathfrak{N}} nP_{\alpha_{\mathbf{k}}}(n)=\frac{|\tilde{\alpha}_{\mathbf{k}}|^2}{1+|\alpha_{\mathbf{k}}|^2/\mathfrak{N}}. \tag{57}$$

As $\mathfrak{N}\to\infty$ we obtain from (56) and (57) the known relations for bosons: $P_{\alpha_{\mathbf{k}}}(N_{\mathbf{k}})$ goes over into the Poisson distribution,[21] and $\bar{N}_{\mathbf{k}}\to|\alpha_{\mathbf{k}}|^2$.

If a Bose condensation takes place in a state with quasimomentum $\mathbf{k}=0$ and with an average number $\bar{N}_0$ excitons in the condensate, then it follows from (57) that the amplitude of the coherent wave in the state (55) is equal to

$$|\tilde{\alpha}_0|=\left(\frac{\bar{N}_0}{1-\bar{N}_0/\mathfrak{N}}\right)^{1/2}. \tag{58}$$

The value of $\mu$ in (55) should be determined from the Schrödinger equation for the interacting excitons:

$$\left(i\hbar\frac{\partial}{\partial t}-H\right)|\alpha_{\mathbf{k}}\rangle=0. \tag{59}$$

The coherent state of the type (55) satisfy Eq. (59) only in the self-consistent approximation. Following Keldysh,[4] we confine ourselves to this approximation and to the case of relatively small excitation densities $N/\mathfrak{N}\ll 1$, corresponding to macroscopic occupation of the mode with $\mathbf{k}=0$. From (59) we find that the dominant term in the expression for the chemical potential, which takes into account only the contribution of the exciton condensate (in the absence of formation of excitonic molecules), is of the form

$$\mu_0=\Delta+M_0+\frac{2\bar{N}_0}{\mathfrak{N}}\left(1-\frac{\bar{N}_0}{\mathfrak{N}}\right)(F_0+|M_0|), \tag{60}$$

where $\bar{N}_0$ is the average number of excitons in the condensate.

The stationary coherent (Bose-condensed) state of a system of interacting excitons, obtained by solving (59), is at $T=0$ the ground state of the system and is stable under the condition

$$F_0+|M_0|>0, \tag{61}$$

i.e., a condensate of Frenkel excitons does not vanish when the kinematic or dynamic condensation is turned on. We note that the conclusion that the Bose condensation of Frenkel excitons is possible pertains only to the case of three-dimensional crystals. The transition to one-dimensional and two-dimensional crystals leads, independently of the statistical difficulties[37] (see also also[38]), to the appearance of a large number of fundamental factors that prevent Bose condensation of the excitons.[10]

To find the spectrum of the elementary excitations, we take into account the presence, under Bose-condensation conditions, of a macroscopic number of excitons $N_0$ with quasimomentum $\mathbf{k}=0$, by using the transformation wherein the operators $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^+$ are shifted by a $c$-number[39,19]:

$$a_{\mathbf{k}}=(N_0^*)^{1/2}\delta_{\mathbf{k}0}+\alpha_{\mathbf{k}},\quad \alpha_0\equiv 0, \tag{62}$$

where $N_0$ is replaced by $N_0^*$ because of the non-Bose statistics of the excitons (see relation (17)):

$$N_0^*=N_0\left(1-\frac{N_0-1}{\mathfrak{N}}\right)\cong N_0\left(1-\frac{N_0}{\mathfrak{N}}\right). \tag{63}$$

The condition for the Bose condensation of the excitons is, besides $N_0\gg 1$, also $N_0^*\gg 1$, thus imposing an upper bound on $N_0$.

The operators $\alpha_{\mathbf{k}}$, $\alpha_{\mathbf{k}}^+$ satisfy the following commutation relations:

$$[\alpha_{\mathbf{k}},\alpha_{\mathbf{k}'}^+]_-=\delta_{\mathbf{k}\mathbf{k}'}\left(1-\frac{2N_0^*}{\mathfrak{N}}\right)-\frac{2(N_0^*)^{1/2}}{\mathfrak{N}}(\alpha_{\mathbf{k}-\mathbf{k}'}+\alpha_{\mathbf{k}'-\mathbf{k}}^+)-\beta(\mathbf{q}'-\mathbf{q}), \tag{64}$$

$$[\alpha_{\mathbf{k}},\alpha_{\mathbf{k}'}]_-=[\alpha_{\mathbf{k}}^+,\alpha_{\mathbf{k}'}^+]_-=0,$$

where

$$\beta(\mathbf{q}'-\mathbf{q})=\frac{2}{\mathfrak{N}}\sum_{\mathbf{t}}\alpha_{\mathbf{q}'-\mathbf{q}+\mathbf{t}}^+\alpha_{\mathbf{t}}.$$

Setting up next a chain of equations for the Fourier components of the single-particle temperature Green's functions

$$\langle\langle\alpha_{\mathbf{k}}(t)\,|\,\alpha_{\mathbf{k}}^+(t')\rangle\rangle,\quad \langle\langle\alpha_{-\mathbf{k}}^+(t)\,|\,\alpha_{\mathbf{k}}^+(t')\rangle\rangle,\quad \mathbf{k}\neq 0,$$

in an approximation corresponding to the Bogolyubov approximation[39] for a weakly nonideal Bose gas, we obtain for condensation into a state with $k=0$ the following energy spectrum of elementary excitations in excess of the condensate:

$$E_{\mathbf{k}}=\Big[(M_{\mathbf{k}}-M_0)^2\left(1-\frac{2N_0^*}{\mathfrak{N}}\right)^2+\frac{4N_0^*}{\mathfrak{N}}\left(1-\frac{2N_0^*}{\mathfrak{N}}\right)\times(M_{\mathbf{k}}-M_0)(F_{\mathbf{k}}-M_0)\Big]^{1/2}. \tag{65}$$

The obtained spectrum is valid under the condition

$$N-N_0^*\ll N_0^*. \tag{66}$$

Substituting in (66) the expression (63) for $N_0^*$ and recognizing that $N_0\sim N$, we find that the condition (66) is equivalent to the condition $N_0/\mathfrak{N}\ll 1$. The spectrum (65) contains characteristic differences from the spectrum of a weakly nonideal Bose gas, owing to the non-Bose distribution of the excitons.

The condition for the stability of the Bose-condensed state is

$$\frac{1}{4}\frac{\Re}{N_0^*}(M_k-M_0)+\frac{1}{2}|M_k+M_0|>-F_k. \quad (67)$$

In the case of repulsion between excitons ($F_k>0$) this condition is always satisfied. For the Bose-condensed state to be stable in the case of attraction between excitons ($F_k<0$), besides satisfying condition (67), it is necessary also that no bound states (of the biexciton type) be produced. At $\mathbf{k}=0$ expression (67) coincides with the condition (61) obtained above by the method of coherent states.

In the absence of dynamic interaction ($F_k=0$), for a primitive cubic lattice with constant $d=(V/\Re)^{1/2}$, expression (65) goes over in the effective-mass approximation $m^*=\hbar^2/2|M|d^2$ into

$$E_k=\left[\left(\frac{\hbar^2k^2}{2m^*}\right)^2(1-2n_0^*d^3)^2+\frac{12n_0^*\hbar^2d}{m^*}(1-2n_0^*d^3)\frac{\hbar^2k^2}{2m^*}\right]^{1/2}. \quad (68)$$

$$n_0^*=n_0(1-n_0d^3),\ n_0=N/V. \quad (69)$$

The Bose-condensed state, in view of the assumed smallness of $n_0d^3$, is stable; the kinematic interaction manifests itself as an effective repulsion, similar to the case of a lattice gas.[40] If $2n_0^*d^3$ is neglected in comparison with unity, formula (68) coincides, apart from a numerical factor of little importance, with the result of Agranovich and Tosic.[12,10] If the minimum of the energy in the exciton band corresponds to a state with $\mathbf{k}_0\neq 0$ and the condensation takes place in the state $\mathbf{k}_0$, the formulas (65)–(67) derived above remain valid subject to the substitution $M_0\to M_{k_0}$.

The spectrum (65), at small values of the quasimomentum $p$

$$p=\hbar k\ll\left\{\frac{8m^*N_0^*}{\Re}\frac{|M_0|+F_0}{1-2N_0^*/\Re}\right\}^{1/2}, \quad (70)$$

has an acoustic dispersion $E_p=sp$ with a speed of sound

$$s=\left\{\frac{2N_0^*}{\Re}\left(1-\frac{2N_0^*}{\Re}\right)\frac{1}{m^*}(|M_0|+F_0)\right\}^{1/2}. \quad (71)$$

It is interesting to note that extrapolation of the results leads to the conclusion that with increasing exciton concentration in the condensate, the energy of the elementary excitations $E_k$, just as the speed of sound $s$, goes through a maximum.

The distribution function of elementary excitations with energy $E_k$ (65) has a quasi-Bose character:

$$\bar{n}=\frac{1-2N_0^*/\Re}{e^{\beta E_k}-1}. \quad (72)$$

From the spectral representation of the Green's function for the average of the operator $\alpha_k^+\alpha_k$ of the excitons in excess of the condensate excitons we obtain

$$\langle\alpha_k^+\alpha_k\rangle=\left(\frac{1}{2}-\frac{N_0^*}{\Re}\right)\left(\frac{\xi_k}{E_k}\operatorname{cth}\frac{\beta E_k}{2}-1\right), \quad (73)$$

$$\xi_k=M_k-M_0-\frac{2N_0^*}{\Re}(M_k-F_k). \quad (74)$$

We emphasize that the operator $\alpha_k^+\alpha_k$ does not have the meaning of the operator of the number of excitons in the state $\mathbf{k}$, for no such operator can be introduced at all.[18] However, since the operator of the total number of excitons is

$$\hat{N}=\sum_k a_k^+a_k, \quad (75)$$

it follows from (62) that

$$N=N_0^*+\sum_{k\neq 0}\langle\alpha_k^+\alpha_k\rangle. \quad (76)$$

The average number of excitons in excess of the condensate is

$$\bar{N}'=N-N_0=\sum_{k\neq 0}\langle\alpha_k^+\alpha_k\rangle-\frac{N_0^2}{\Re}. \quad (77)$$

We now derive an explicit expression for the number of excitons in excess of the condensate at $T=0$. We carry out the calculation in the effective-mass approximation and neglect the dependence of the dynamic interaction on $\mathbf{k}$. To this end we introduce the effective scattering length $a$ in accordance with the equality

$$2l^3(|M_0|+F_0)=4\pi\hbar^2a/m^*. \quad (78)$$

At $T=0$ we have

$$\langle\alpha_k^+\alpha_k\rangle=\left(\frac{1}{2}-\frac{N_0^*}{\Re}\right)\left(\frac{\xi_k}{E_k}-1\right). \quad (79)$$

Substituting (78) in (79) and integrating with respect to $\mathbf{k}$ in the effective-mass approximation, we get

$$\bar{N}'=\frac{8N_0^*}{3\pi^{1/2}}\left(\frac{n_0^*a^3}{1-2n_0^*d^3}\right)^{1/2}-N_0(n_0d^3). \quad (80)$$

For the number of excitons in excess of the condensate to be small in comparison with the number of excitons in the condensate, it is necessary to satisfy two conditions:

$$n_0^*d^3\ll 1 \text{ and } n_0^*a^3\ll 1. \quad (81)$$

If we set the dynamic-interaction constant $F_0$ equal to zero, then it follows from (78) that $a=3d/2\pi\approx\frac{1}{2}d$.

Inasmuch as the excitation spectrum has no energy gap in the case of Bose condensation and satisfies the Landau superfluidity criterion, one can expect the appearance of a superfluid component for Frenkel excitons just as for Wannier–Mott excitons.[3,5,41] The appearance of the condensate can be accompanied by light and sound amplification effects.[5,10,12] We point out also the possibility of resonant absorption of hypersound[23] by an exciton condensate, and this can serve as a method of observing the condensate.

In conclusion, the authors thank V. M. Agranovich, V. A. Benderskiĭ, V. L. Bonch-Bruevich, M. A. Kozhushner, V. I. Man'ko, L. P. Pitaevskiĭ, and G. I. Salistra for useful discussions of a number of questions touched upon in the present paper.

[1)]It can be shown that when applied to the theory of the Heisenberg ferromagnet, the uncoupling method described here corresponds, in the limiting case of low temperatures, to the "improved" self-consistent field approximation,[16,17] when the correct temperature dependence of the magnon spectrum $\alpha T^{5/2}$ is obtained; when better allowance was made for the kinematics, the Dyson term in the magnetization $\alpha T^4$ is obtained.

[2)]A similar result for the energy spectrum of the exciton is obtained also when the calculations are made by the diagram method[16] in the self-consistent field approximation.


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Translated by J. G. Adashko