COLLECTIVE PROPERTIES OF FRENKEL EXCITONS

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To analyze weakly excited states of a molecular crystal whose Hamilton operator is expressed in terms of the Pauli molecular-excitation creation and annihilation operators, it is suggested that the Pauli operators be represented in terms of Bose operators. This representation in its approximate form is identical with the Holstein—Primakoff representation[15], but does not involve the appearance of "nonphysical states." Transition to Bose operators in the crystal Hamiltonian permits separation of the kinematic-interaction operator which, together with the dynamic interaction operator, leads to exciton-exciton scattering. For the case of absence of dynamic interaction between the excitons, i.e., for an ideal gas of paulions, it is proven that condensation should be possible and the elementary excitation spectrum under condensation conditions is found. The various terms in the exciton-exciton interaction energy are estimated, and in the case of molecular crystals with weak exciton-phonon interaction a criterion is formulated for the appearance of Bose-Einstein exciton condensation. Methods for experimentally investigating the collective properties of excitons in molecular crystals are discussed.

1. INTRODUCTION

$\mathbf{I}$N the theory of Frenkel excitons[1], the zeroth-approximation wave functions are constructed by using the wave functions of the individual molecules of which the crystal is made up. Such an approach is justified if the intermolecular interaction is sufficiently weak, as is the case for the lowest excited states of a large number of molecular crystals. In these crystals, the spectrum of the lowest excited states, although possessing a large number of qualitatively new features, differs in general very little from the corresponding spectra of the individual molecules (see, for example,[2]).

Frenkel and Dabydov used the Heitler-London method for the analysis of the excited states of crystals. In accordance with this method, the wave function of the lowest excited state is a superposition of the states of the crystal, in which one of the molecules is excited and all the others are in the ground state. Then the contribution made to the wave function of the crystal by the states in which not one but two, three, etc. crystal molecules are excited, is disregarded. The correction to the crystal energy, due to these higher excited states, is of the order of $\Delta_f(V/\Delta_f)^2$, where Δ_f is the energy of the f-th excitation of the isolated molecule, and V is the magnitude of the resonance interaction between the molecules. For certain states, this correction is negligibly small. At the same time, there are also states for which this correction

leads to a noticeable shift of the terms. Thus, for example, the ratio for the second transition in anthracene is $V/\Delta_f \sim 1/3$, and the indicated correction shifts the terms of the crystal by several thousand reciprocal centimeters.

Allowance for the contribution made to the exciton energy by the aforementioned excited-states can be made by going over to the second-quantization representation, which turns out to be also convenient in the study of exciton-photon and exciton-phonon interactions, and also for the investigation of the molecular-state mixing due to the intermolecular interaction in the crystal (see[3-5]).

In the first stage of the transition to the second-quantization representation, the Hamiltonian operator of the crystal is expressed in terms of the operators of creation and annihilation of the excitations of the individual molecules. Let, for example, the index s denote a crystal-lattice site in which the molecule is located, and let the aforementioned operators be denoted by $\overset{+}{P}{}^f_s$ and P^f_s, where f is the number of the excited state of the molecule. Then, if we consider only the f-th nondegenerate excited state of the molecule, the operators $\overset{+}{P}{}^f_s$ and P^f_s satisfy the following commutation relations:

$$P_s{}^f \overset{+}{P}_s{}^f - \overset{+}{P}_s{}^f P_s{}^f = 1 - 2\overset{+}{P}_s{}^f P_s{}^f, \tag{1a}$$

$$P_s{}^f P_s{}^f = 0, \tag{1b}$$

$$P_s{}^f P_{s'}{}^f - P_{s'}{}^f P_s{}^f = 0, \tag{1c}$$

$$\overset{+}{P}_s{}^f P_{s'}{}^f - P_{s'}{}^f \overset{+}{P}_s{}^f = 0, \quad s \neq s'. \tag{1d}$$

Thus, $\overset{+f}{P_s}$ and $\overset{f}{P_s}$ are Pauli operators, since Eqs. (1a, b) and (1c, d) are combinations of the commutation relations for the Fermi operator (when s = s') and the Bose operator (s ≠ s') (see[6-8]).

The appearance of commutation relations of the same type as the relations for the Fermi operators in the case when s = s' is a reflection of the fact that the number of excitations in the molecule, that is, the eigenvalues of the operator $\overset{+f}{P_s}\overset{f}{P_s}$, can be equal either to zero (molecule in the ground state) or to unity (molecule is excited). On the other hand, the presence of Bose commutation relations when s ≠ s' is due to the fact that operators with different s act on different variables of the crystal wave function.

The Hamiltonian operator of the molecular crystal, expressed in terms of the operators $\overset{+f}{P_s}$ and $\overset{f}{P_s}$ (we shall henceforth omit the index f) has the following form (see[3]):

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}, \qquad (2)$$

where the operator

$$\hat{H}_0 = \sum_s \Delta \overset{+}{P}_s P_s + \frac{1}{2}\sum_{s \neq s'} V_{ss'}^{I} \overset{+}{P}_s P_{s'} + \frac{1}{2}\sum_{s \neq s'} V_{ss'}^{II}(\overset{+}{P}_s\overset{+}{P}_{s'} + P_s P_{s'}) \qquad (3)$$

is quadratic with respect to the operators P_s and $\overset{+}{P}_s$ whereas the operator $\hat{H}_{int}$ is the sum of the third and fourth order terms.

If we are interested in such states of the crystals, in which the mean value is

$$\langle \overset{+}{P}_s P_s \rangle \equiv c \ll 1, \qquad (4)$$

that is, in other words, if we consider only weakly-excited states of the crystal, in which the quantity c (dimensionless concentration of the excitations) is small, then the operator $\overset{+}{P}_s P_s$ in the right side of (1a) can be neglected. Then the operators P_s and $\overset{+}{P}_s$ become Bose operators ($P_s \equiv B_s$, $\overset{+}{P}_s \equiv \overset{+}{B}_s$). This circumstance is the basis of the second quantization method, of the main representations of which were predicted by Bloch[6,7], and which was subsequently developed by Bogolyubov and Tyablikov[8,9].

If we neglect in the zeroth approximation the scattering of excitons by excitons, then the operator $\hat{H}_{int}$ can be omitted. In this approximation, using the canonical transformation from the Bose operators B_s and $\overset{+}{B}_s$ to the Bose operators $B_{\mu k}$ and $\overset{+}{B}_{\mu k}$:

$$B_s = \frac{1}{\sqrt{M}}\sum_{\mu, k}[U_{\mu k}(s)B_{\mu k} + \overset{*}{V}_{\mu k}(s)\overset{+}{B}_{\mu k}], \qquad (5)$$

where k is the wave vector of the exciton, μ the number of the exciton band, and M the number of cells in the crystal, we obtain

$$\hat{H}_0 = \sum_{\mu k} E_\mu(k)\overset{+}{B}_{\mu k}B_{\mu k}. \qquad (6)$$

In this expression $E_\mu(k)$ are the new energies of the elementary excitations of the Coulomb excitons produced when full account is taken of the Coulomb interaction.

The delayed interaction can be taken into account by adding to the operator $\hat{H}_0$ the field operator of the transverse photons, together with the operator of the exciton-photon interaction[3,10]. If at the same time we disregard the anharmonicity as before, then the total operator of the excitons and of the field of the transverse photons turns out to be quadratic with respect to the exciton and photon Bose operators, so that the diagonalization of this Hamiltonian with the aid of a canonical transformation leads to normal electromagnetic waves in the crystal (photons in matter), which at large wavelengths can be considered also within the framework of phenomenological electrodynamics with account taken of the spatial dispersion (see[11]). The availability of powerful radiation sources has made it possible to observe in number of crystals processes in which photons collide with one another. Corresponding to these processes in the Hamiltonian of the crystal are terms of third, fourth, etc. orders with respect to the Bose operators. We shall consider below precisely the procedure for correctly separating these terms, since replacement of the Pauli operators by Bose operators gives rise, as it were, to an additional interaction between the elementary excitations, which we shall designate, just as in magnetism theory, as kinematic.

When speaking of a kinematic interaction, it should be noted that the problem of its separation in connection with the transition from Pauli operators to Bose operators is far from new. This problem arises, in particular, for the Heisenberg Hamiltonian, which corresponds, for example, to an isotropic ferromagnet with spin S = 1/2 when spin waves whose creation and annihilation operators obey Bose commutation relations are introduced. This problem was dealt with by many people, including Dyson[12], who obtained low temperature expansions for the magnetization. However, even before Dyson's paper, van Kranendonk[13] proposed to take into account the kinematic interaction by starting from a picture in which one spin wave produces an obstacle for the passage of another spin wave, since two flipped spins cannot be located at the same site (for Frenkel excitons this means that two excitations cannot be localized simultaneously on one and the same molecule). In mathematical language, such an approach means adding to the

initial Hamiltonian, in which the Pauli operators are replaced by Bose operators, a term that corresponds to the limiting strong repulsion of two bosons in one site.

The picture postulated by van Kranendonk[13] leads molecular cross sections of a size corresponding to the "hard-sphere" approximation. Dyson calls this approach naive and criticizes it as incorrect and leading to results different from those obtained by him (see[12], end of Sec. 3). We shall show in what follows, however, on the basis of an exact representation of the Pauli operators in terms of Bose operators, that the picture described above does take place for excitons. However, this takes place only because the excitation energy Δ for excitons is large compared with the width of the exciton band. As to the spin waves, where the inequality indicated above is not satisfied, the cross section for the scattering of long-wave spin waves by each other can indeed, in agreement with Dyson, differ substantially from the value that follows from van Kranendonk's "hard sphere" approximation[13].

2. REPRESENTATION OF THE PAULI OPERATORS IN TERMS OF BOSE OPERATORS [1]

We note first that the replacement of the Pauli operators by Bose operators, which was used in Sec. 1, is approximate, since the occupation numbers for the paulions take on values from 0 to 1, whereas the occupation numbers for the bosons take on arbitrary positive integer values: 0, 1, 2, 3, etc. Therefore when the operators P_s and $\overset{+}{P}_s$ are replaced by Bose operators, uncontrollable errors are introduced in all those cases when the number of bosons exceeds unity. These errors are known in the literature as the "contribution from the unphysical states" (see, for example[14]). It is possible, however, to make more exact the transition from the Pauli operators to the Bose operators B_s and $\overset{+}{B}_s$ by stipulating that for any number of bosons the number of paulions be either 0 or 1. To this end, we rewrite the Pauli operators in the form

$$P_s = \left(\sum_{v=0}^{\infty} a_v \overset{+}{B}_s{}^v B_s{}^v \right)^{1/2} B_s, \quad \overset{+}{P}_s = \overset{+}{B}_s \left(\sum_{v=0}^{\infty} a_v \overset{+}{B}_s{}^v B_s{}^v \right)^{1/2}, \quad (7)$$

where a_v are real coefficients. We stipulate that the operators P_s and $\overset{+}{P}_s$ satisfy the condition

$$P_s \overset{+}{P}_s + \overset{+}{P}_s P_s = 1, \quad (8)$$

if B_s and $\overset{+}{B}_s$ in (7) are Bose operators. Substituting (7) in (8) and taking into account the identity $\overset{+}{B}_s{}^{v+1} B_s{}^{v+1} = (\hat{N}_s - v) \overset{+}{B}_s{}^v B_s{}^v$, where $\hat{N}_s = \overset{+}{B}_s B_s$, we find that (8) takes the form

$$P_s \overset{+}{P}_s + \overset{+}{P}_s P_s = \sum_{v=0}^{\infty} a_v [2 \overset{+}{B}_s{}^{v+1} B_s{}^{v+1} + (v+1) \overset{+}{B}_s{}^v B_s{}^v] = 1,$$

whence

$$a_v = \frac{-2}{1+v} a_{v-1}, \quad a_0 = 1,$$

or

$$a_v = (-2)^v / (1+v)! \quad (9)$$

Thus, the sought exact transformation from the Pauli operators to the Bose operators takes the form

$$P_s = \left[\sum_{v=0}^{\infty} \frac{(-2)^v}{(1+v)!} \overset{+}{B}_s{}^v B_s{}^v \right]^{1/2} B_s,$$

$$\overset{+}{P}_s = \overset{+}{B}_s \left[\sum_{v=0}^{\infty} \frac{(-2)^v}{(1+v)!} \overset{+}{B}_s{}^v B_s{}^v \right]^{1/2}. \quad (10)$$

The paulion-operator $\hat{L}_s = \overset{+}{P}_s P_s$ then is expressed in the following fashion in terms of the boson-number operator:

$$\hat{L}_s = \hat{N}_s + \sum_{v=1}^{\infty} \frac{(-2)^v}{(1+v)!} \hat{N}_s (\hat{N}_s - 1) \ldots (\hat{N}_s - v). \quad (11)$$

It is easy to verify that states with arbitrary even number of bosons corresponds to $L_s = 0$, and states with arbitrary odd number of bosons to $L_s = 1$. Thus, the transformations (10) and (11) do not give rise to boson numbers corresponding to "unphysical" paulion numbers (that is, numbers $L_s > 1$). It is also easy to verify that (10) leads to $P_s^2 = \overset{+}{P}_s{}^2 = 0$. Indeed, the operator $\left[\sum_{v=0}^{\infty} a_v \overset{+}{B}_s{}^v B_s{}^v \right]^{1/2}$ acting on a state corresponding to an odd number of bosons produces zero. Therefore, the result of the action of the operator

$$P_s^2 = \left[\sum_{v=0}^{\infty} a_v \overset{+}{B}_s{}^v B_s{}^v \right]^{1/2} B_s \left[\sum_{v=0}^{\infty} a_v \overset{+}{B}_s{}^v B_s{}^v \right]^{1/2} B_s$$

on any boson state is also equal to zero, as follows directly from the structure of the operator P_s^2. It is analogously easy to verify that $\overset{+}{P}_s{}^2 = 0$.

If we confine ourselves in (10) to only the first term under the summation sign (with $v = 0$), we get $P_s = B_s$ and $\hat{L}_s = \hat{N}_s$, that is, we obtain exactly the approximation used in Sec. 1. If we also include the term with $v = 1$, then

$$P_s = B_s \sqrt{1 - \hat{N}_s}, \quad \overset{+}{P}_s = \overset{+}{B}_s \sqrt{1 - \hat{N}_s} \quad (12)$$

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[1] The results of this section can apparently be used also in the quantum theory of magnetism.

and we obtain the well known representation of Holstein and Primakoff[15]. With this,

$$P_s^+ P_s + \overset{+}{P}_s P_s = 1 - \hat{N}_s(\hat{N}_s - 1), \qquad (13)$$

so that the right side of (13) is equal to unity if the boson number is restricted to 0 and 1. Therefore, if the number of elementary excitations in the crystal is large, the uncontrolled errors mentioned above arise when (12) is used.

When the exact representation (10) is used, the terms with $\nu \geq 1$ under the summation sign can be regarded as small operators, the smallness of which increases with increasing ν. Indeed, for Bose operators we have

$$\overset{+}{B}_s{}^\nu B_s{}^\nu = \hat{N}_s(\hat{N}_s - 1)\ldots(\hat{N}_s - \nu + 1). \qquad (14)$$

Thus, the operator (14) vanishes identically on the class of functions corresponding to boson numbers $N_s < \nu$. On the other hand, this class of functions broadens with increasing ν. This is precisely why the square root of $\sum_\nu{}'_{\infty}$ in (10) can be represented in the form of the series $\sum_\nu b_\nu \overset{+}{B}_s{}^\nu B_s{}^\nu$.

To determine the coefficients b_ν, we make use of the fact that the relation

$$\left[\sum_{\nu=0}^{\infty} a_\nu N_s(N_s - 1)\ldots(N_s - \nu + 1) \right]^{1/2}$$

$$= \sum_{\nu=0}^{\infty} b_\nu N_s(N_s - 1)\ldots(N_s - \nu + 1)$$

should be satisfied in the representation of the boson occupation numbers for arbitrary integer $N_s \geq 0$. Putting in this relation $N_s = 0$ and using (9), we get $b_0 = 1$. Assuming $N_s = 1$, we get $b_1 = -1$; assuming $N_s = 2$, we analogously obtain $b_2 = (1/2)(1 + \sqrt{3}/3)$, etc.

Knowledge of the coefficients b_ν enables us to represent relations (10) in the form

$$P_s = \left[\sum_{\nu=0}^{\infty} b_\nu \overset{+}{B}_s{}^\nu B_s{}^\nu \right] B_s, \quad \overset{+}{P}_s = \overset{+}{B}_s \left[\sum_{\nu=0}^{\infty} b_\nu \overset{+}{B}_s{}^\nu B_s{}^\nu \right]. \qquad (10a)$$

It is interesting, that if we confine ourselves in these expansions to terms with $\nu = 0$ and $\nu = 1$, we get

$$P_s = (1 - \hat{N}_s)B_s \quad \overset{+}{P}_s = \overset{+}{B}_s(1 - \hat{N}_s), \qquad (10b)$$

which differs from the expansion of the Holstein-Primakoff relations (12) in powers of $\hat{N}$:

$$P_s = (1 - 1/2\hat{N}_s)B_s, \quad \overset{+}{P}_s = \overset{+}{B}_s(1 - 1/2\hat{N}_s).$$

The cause of the discrepancy is the inaccuracy of the latter expansion, where the discarded terms in the state $N_s = 1$ differ from 0, whereas all the discarded terms in (10b) vanish identically when $N_s = 1$.

Substituting the expansions (10a) in (2) and (3), we obtain the sought-for expansions of the Hamiltonian operators in powers of the Bose operators, with allowance of not only the dynamic but also the correct kinematic interaction. The resultant terms of the third-order anharmonicity contain no kinematic corrections. Their role in the theory of third-order nonlinear optical effects was evaluated by Ovander[16]. The fourth-order anharmonicity terms contain kinematic corrections. Their role in the theory of fourth-order nonlinear optical effects, which calls for an account of retardation, can be considered in similar fashion, and fourth-order anharmonicity terms can be separated by the approach described above[2]. We shall therefore confine ourselves only to a discussion of the possibility of Bose-Einstein condensation of Frenkel excitons.[3]

3. COLLECTIVE PROPERTIES OF AN IDEAL GAS OF PAULIONS

We shall henceforth define the paulions, for brevity, as elementary excitations whose creation and annihilation operators satisfy the commutation relations (1).

In this section, using the results of Sec. 2, we consider the collective properties of an ideal paulion gas, that is, a system to which the Hamilton operator (3) corresponds, whereas the operator of dynamic interactions[4] between the elementary excitations, that is, the operator H_{int}, is equal to 0.

Substituting expressions (10) and (11) in (2) and going over from Pauli operators to Bose operators, we obtain, besides the zeroth-approximation Hamiltonian (6), also terms of two types in the operator of kinematic interaction of the excitons. The terms of the first type are those resulting from the fact, as seen from (11) that the operator $\overset{+}{P}_s P_s \neq \hat{N}_s$. These terms are proportional to the excitation energy Δ; they are of the following form:

$$H' = \Delta \sum_{\nu=1}^{\infty} \frac{(-2)^\nu}{(1 + \nu)!} \sum_s \overset{+}{B}_s{}^{\nu+1} B_s{}^{\nu+1}. \qquad (15)$$

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[2] See the paper by S. S. Toshich[17].

[3] An investigation of the collective properties of Wannier-Mott excitons was carried out by Keldysh and Kozlov [18] and by Kazarinov and Suris [19]. In earlier papers Moskalenko and Blatt et al. [20]) different aspects of Bose-Einstein condensation of excitons were also discussed.

[4] In crystals such as benzene, naphthalene, etc., made up of molecules having an inversion center, the operator H_{int} vanishes identically if one confines oneself only to allowance for the dipole-dipole interaction between the molecules. More details concerning the operator H_{int} are contained in the next section.

We shall consider in greater detail the term of (15) with $\nu = 1$, corresponding to scattering of two excitons by each other. In accordance with (15), this term has the following form:

$$H'(\nu = 1) = -\Delta \sum_{ss'} \delta_{ss'} B_s^+ B_{s'}^+ B_s B_{s'}, \qquad (15a)$$

that is, it corresponds to scattering of excitons by each other with a δ-like interaction potential

$$V_{ss'} = -2\Delta \delta_{ss'}.$$

If we go over to a coordinate frame connected with the mass center of the system consisting of the two excitons, then, in accord with (15a), the problem of determining the cross section for the scattering of the excitons by each other reduces the problem of the scattering of a quasiparticle by a potential in the form

$$V_{ss'} = -2\Delta \delta_{s0} \delta_{s'0}. \qquad (16)$$

A potential in the form (16) cannot be regarded as a weak perturbation, since this potential leads, in particular, to the appearance of local states (see[18]). The appearance of local states denotes that two bosons can be in a bound state, that is, they can form a biexciton. In this connection, let us consider the question of local states in somewhat greater detail[5].

It should be noted first that, inasmuch as the quantity 2Δ in molecular crystals is larger by more than one order of magnitude than the width of the exciton band, a local level at large depth, approximately equal to 2Δ, always appears under the influence of the potential (16). If local levels that are remote from the lowest exciton bands, at distances the order of the width of the exciton band, appear at all under these conditions (large Δ), they are always located in the intervals between the exciton bands. No shallow local levels are produced under the influence of the perturbation (16) below the lowest exciton band, which is the very band that is essential for the study of the possibilities of Bose-Einstein condensation of excitons.

However, the process of boson binding at a deep local level need not be taken into consideration if no account is taken of processes of non-radiative loss of individual excitons, whereby an energy $\sim\Delta$ goes over into phonon energy. In crystals where the quantum yield of the exciton lumin-

escence is close to unity (for example, in anthracene crystals), nonradiative electron-loss processes do not have time to occur within the exciton lifetime (otherwise we cannot regard the number of excitons in the crystal as specified).

It is clear that in crystals of this kind, the binding of two bosons at a deep local level is even less probable, since it presupposes replacement by phonons of double the energy. Therefore, in spite of the fact that states in which two bosons are situated in the same site are formally possible, their formation out of individual bosons is in practice forbidden from purely energetic considerations[6]. Thus, the potential process (16) leads only to the scattering of the bosons by each other. The effective scattering length cannot be calculated in the Born approximation.

An exact calculation of the scattering of an exciton by an impurity model, carried out by Dobovskiĭ and Konobeev[24], leads to the conclusion that in our case ($\Delta \gg$ exciton width) the length for scattering of long-wave excitons by each other is $-a/2$, so that the scattering cross section is

$$\sigma = \pi a^2 = 4\pi(a/2)^2, \qquad (17)$$

where a is the lattice constant. This result becomes obvious if we also use, for example, the results of the calculation of the length for scattering of a slow particle by a square well of depth 2Δ and of radius $a/2$ (see[25], problem No. 1 of Sec. 130) under conditions when the inequality $2\Delta \gg 4\hbar^2/m_e a^2$ is satisfied, and furthermore the quantity $(a/2\hbar)\sqrt{4m_e\Delta}$ is not close to an odd multiple of $\pi/2$ (that is, when there are no shallow levels in the well). In this case, the scattering length is equal to the radius of the well taken with the opposite sign, so that relation (17) holds, and this is precisely the result obtained if the potential well is replaced by a potential "hill" of height 2Δ. In both cases, the scattering length is negative, that is, repulsion takes place effectively at shorter distances. This repulsion is a reflection of the fact that the true electronic excitations in a molecular crystal are not bosons but paulions, so that the presence of repulsion at small distances (shorter than the lattice constant) offsets the error connected with the transition from paulions to bosons.

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[5] The situation under consideration is similar to that which occurs in the study of local states produced in the exciton spectrum in the presence of an impurity molecule whose excitation energy differs greatly from the excitation energy of the molecule of the main substance (see [21,22] and also [23,24]).

[6] One must not think that the local level is unphysical because the number of paulions at a given site does not become larger than unity on going to this level. To the contrary, on going to this level, the total number of paulions, which is not equal to the total number of bosons (see formula (11)) only decreases by two.

However, repulsion at short distances still does not make it possible to determine the state of the exciton system at low temperatures. Indeed, the presence of sufficiently strong attraction between the excitons at distances on the order of the lattice constant or larger can lead to the appearance of bound states, that is, to biexcitons (see, for example,[26]), after which the analysis of the system of excitons at low temperatures becomes somewhat more complicated and calls for a special approach.

In connection with the foregoing, let us calculate the remaining part of the kinematic interaction between the excitons, and let us consider first that part of the operator for the kinematic interaction between the excitons, which is not allowed for in H' (see (15)); this part, just like H', arises in (3) on going over to Bose operators, and is determined by the matrix elements $V_{s,s'}^{I,II}$. Substituting (10a) in (3) we find that the principal term in the operator that determines the kinematic interaction between two excitons not allowed for in (15) is[7]

$$H_{int}^{c} = -\frac{1}{2} \sum_{s \neq s'} V_{ss'}^{I} (\overset{+}{B}_s \overset{+}{B}_s B_s B_{s'} + \overset{+}{B}_s \overset{+}{B}_{s'} B_{s'} B_{s'}). \quad (18)$$

Let us discuss the properties of this operator in greater detail. When this operator acts on an exciton situated at the point s, it transfers it to the point s'. However, the result of the action of this operator on the corresponding wave function of the system differs from zero only if besides the exciton at the point s there exists also an exciton at the point s' or else a second exciton at the point s. Thus, the matrix element of the operator (15) differs from zero only for such pairs of states, for which both excitons "sit" on one site either in the initial state or in the final one. We now use the fact that, as shown earlier, the excitons experience strong repulsion at short distances. It is easy to show, using the results of[21-24], that the wave function corresponding to small relative distances between excitons has an absolute value $\sim V/\Delta$, where V is a quantity on the order of the width of the exciton band. Because of this circumstance, in spite of the fact that the quantity $|V_{ss'}^{I}|$ in (18) is of the order of the width of the exciton band, the corrections to the energy of interaction between the excitons, which result from the kinematic interaction (18), are proportional to the corresponding powers of the small parameter $|V^{I}|/\Delta$ in different orders of perturbation theory, and are small compared with the width of the exciton band even at a distance

on the order of the lattice constant. Inasmuch as the matrix elements $V_{ss'}^{I}$ decrease with increasing $|s - s'|$ not slower than $1/|s - s'|^{3}$, the interaction between the excitons, due to the operator (18), satisfies by virtue of the foregoing the following inequality at arbitrary distances between excitons:

$$|V_{ss'}^{c}| \ll \hbar^2/m_e |s - s'|^2, \quad s \neq s', \quad (19)$$

where m_e is the effective mass of the exciton.

In accordance with Secs. 45 and 125 of the book by Landau and Lifshitz[26], fulfillment of inequality (19) denotes that even if the interaction $V_{ss'}^{c}$ corresponds to attraction between excitons, it does not lead to the appearance of bound states, and its contribution to the scattering amplitude can be calculated in the first Born approximation. Since, as already indicated, the interaction energy $|V_{ss'}^{c}|$ is small even compared with the width of the exciton band, allowance for this interaction, which does not lead to the appearance of bound states, can only result in small corrections to the exciton-exciton scattering length, due to the energy (16). Therefore the exciton-exciton scattering length remains negative, thus pointing to the possibility of Bose-Einstein condensation of the excitons in the absence of dynamic interaction between them.

Using the scattering length obtained above, and also the results of[27,28], we find that if k = 0 corresponds to the minimum energy in the exciton band, then the spectrum of an ideal paulion gas is of the form

$$\varepsilon(k) = \left[\left(\frac{\hbar^2 k^2}{2m_e} \right)^2 + \frac{4\pi n_0 \hbar^2 a}{m_e} \left(\frac{\hbar^2 k^2}{2m_e} \right) \right]^{1/2}, \quad (20)$$

where n_0 is the excitation concentration, $n_0 \ll a^{-3}$, that is, it coincides with the spectrum of a weak non-ideal Bose gas with repulsion between particles. The use of the transition from the Pauli operator to the Bose operators has enabled us here to separate the kinematic interaction between the excitons, to determine the scattering length involved in (20), and to use the well known results of the theory of a weakly non-ideal Bose gas.

As follows from (20), when $|k| \ll \sqrt{an_0/2}$ the quasiparticles have acoustic dispersion, and when $|k| \gg \sqrt{an_0/2}$ they go over into "almost free particles" with

$$\varepsilon(k) = \frac{\hbar^2 k^2}{2m_e} + \frac{2\pi \hbar^2 a n_0}{m_e}.$$

At a concentration $n_0 \lesssim 10^{18}$ exciton/cm^3 and at $a_0 \approx 5 \times 10^{-8}$ cm, we have for the wave vector $\sqrt{an_0/2} \lesssim 10^5$ cm^{-1}, i.e., on the order of optical. The energy shift for $|k| \gg an_0/2$ is equal to $2\pi \hbar^2 an_0/m_e \lesssim 2 \times 10^{-4}$ eV.

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[7]For a reason which will explained in the next section, we have left out from (18) the terms which do not leave the number of excitons unchanged.

We note that the deduction that condensation of elementary excitations of a system with Hamiltonian (3) is possible in momentum space agrees with the result of Bocchieri and Seneci[29], who also discuss the possibility of condensation of an ideal paulion gas in a crystal lattice. They, however, did not obtain the spectrum of the elementary excitations of the system under the condensation conditions.

In concluding this section, we note that the terms of the kinematic interaction in (15) with $\nu > 1$, which were not taken into account above, are negligible because of the proposed smallness of the exciton concentration (the concentration of the excitons produced by a laser apparently does not exceed 10^{-4}). If we recognize that the operator of the kinematic interaction $H'(\nu = 1)$ causes the state of the excitons in the presence of condensate to be stable (owing to the predominant repulsion), it is easy to show, using for example the Bogolyubov method[27], that the unaccounted for terms in (15) add under these conditions only negligible corrections both to the energy of the ground state and to the energy of the elementary excitations; these are proportional to higher powers of the exciton concentration.

4. COLLECTIVE PROPERTIES OF FRENKEL EXCITONS WITH ALLOWANCE FOR THE DYNAMIC INTERACTION BETWEEN THEM

The operator H_{int} in (2) contains, generally speaking, third- and fourth-order terms in the operators P_s and P_s^+. The third-order terms in the operators P_s and P_s^+ in H_{int} always lead only to very weak interaction between the excitons. Since the width of the exciton band in the crystals under consideration is much smaller than the energy of exciton production, the third-order terms, which do not conserve the number of excitons, make a contribution of their own to the energy of interaction between the excitons only in even orders of perturbation theory. If $V_{ss'}^{III}$ is the matrix element that enters in the cubic terms, then, for example, the second-order correction to the energy of this interaction is $\approx |V_{ss'}^{III}|^2/\Delta$, that is, it is negligibly small compared with the width of the exciton band even if $|V_{ss'}^{III}|$ is of the order of this width. Inasmuch $|V_{ss'}^{III}|$ decreases more rapidly than $|s - s'|^{-3}$ with increasing $|s - s'|$, it can be assumed that an inequality such as (19) is always satisfied for this energy of interaction between the excitons. As to the fourth-order terms, they are significant and we shall consider them in greater detail.

Using formula (15) of[3], we find that the exciton-exciton interaction operator is

$$H_{int}^{IV} = \frac{1}{2} \sum_{s \neq s'} V_{ss'}^{IV} \hat{P}_s^+ \hat{P}_{s'}^+ P_s P_{s'}, \qquad (21)$$

where, in the notation of[3],

$$V_{ss'}^{IV} = V_{ss'}(ff, ff) + V_{ss'}(00, 00) - 2V_{ss'}(0f, 0f). \quad (22)$$

The first term in (22) is equal to the interaction energy of the molecules s and s' in the f-th excited state, the second equals the interaction energy of the same molecules under conditions when both molecules are in the ground state. As to the third term, it is determined by the energy of interaction between the molecules s and s' in the case when only one of them is in the excited state f. The quantities contained in (22) can be obtained if one knows the wave functions of the isolated molecule in the ground and in the f-th excited states.

In crystals with inversion centers, the quantity $V_{ss'}^{IV}$ decreases like $|s - s|^{-5}$ or faster with increasing $|s - s'|$, and consequently at large $|s - s'|$ an inequality of the type of (19) is always satisfied for the quantity $|V_{ss'}^{IV}|$. Of greatest significance for the solution of the question of the possibility of formation of a biexciton is therefore the sign and magnitude of the interaction $V_{ss'}^{IV}$ in the case when the molecules s and s' are nearest neighbors.[8] If the quantity $V_{ss'}^{IV}$ is positive or negative in this case, but its absolute value is small compared with the width of the exciton band, then the dynamic interaction, just as the kinematic interaction considered in the preceding section, does not lead to formation of bound state of two electrons, so that the Bose-Einstein condensation of the excitons is possible in this case.

Inasmuch as the Bose-Einstein condensation of the excitons is accompanied by the appearance of a spectrum (20) satisfying the Landau superfluidity criterion, this condensation could apparently be detected by observing the contribution of the superfluid component to the energy transfer from the main substance to the exciton detector, in experiments similar to those of Simpson[30]. The energy transfer of the super-condensate excitons can be estimated, as before, with the aid of the diffusion equation. As to the motion of the condensate, it can be initiated by the concentration gradient of the excitons which are produced in connection with the fact that their concentration is small on the surface of the exciton-capturing detector.

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[8]If a biexciton is produced, the quantity V_{ss}^{IV} might be estimated from the shift of the term of the biexciton relative to double the energy of the exciton. Unfortunately, there are no corresponding experimental data at present.

We note that in the opposite limiting case, that of very narrow exciton bands, when the interaction (21) leads to the "sticking" of the excitons in pairs, triads, and larger exciton "drops" [9], the transition used above from the Pauli operators to the Bose operators makes it necessary to take into account the terms with $\nu > 1$ in the operator (15), since the distribution of the excitations of the crystal ceases to be homogeneous in this case, and the small parameter (4) of the theory disappears. In this situation, it is more correct to describe the system of excitations in terms of excitons (paulions) that are "localized" at the lattice sites and diffuse in the lattice, so that the process of coagulation of the excitons can be described by the well known method of colloidal statistics [31].

We note in this connection that the character of the distribution of the "exciton drops" by sizes depends on the lifetime of the exciton, and also on its mobility, and should be considered separately in each concrete case. If, however, the formation of "exciton drops" does take place, then the crystal becomes optically inhomogeneous, since the polarizability of the excited molecules differs from the polarizability of molecules in the ground state. This circumstance can lead to an additional scattering of light and to other analogous effects. As to the energy transfer from the main substance to the impurity or to the exciton detector, this transfer should decrease rapidly as a result of the small mobility of the "drops" compared with the mobility of the individual excitons, It is possible that this is precisely the simplest way of investigating the states of the exciton system.

In the foregoing discussion of the properties of the exciton systems we disregarded the possibility of exciton decay by collision, accompanied by formation of free carriers or of higher-energy exciton states. This process is particularly important in the case when the exciton system has a tendency to produce drops, since it prevents the formation of sufficiently large coagulations of excitons. On the other hand, if repulsion between exciton predominates in the system, then the process of exciton decay by collision is apparently not very significant under realistic concentrations.

If n is the concentration of the excitons, then the number of decays per unit time is equal to γn^2, where γ is the corresponding kinetic parameter.

At the same time, the number of exciton decays with emission of a photon is equal to n/τ, where τ is the exciton lifetime. Thus, decays resulting from the collision are perfectly insignificant if $n \lesssim 1/\gamma\tau$. For singlet excitons in anthracene [32] $\tau \approx 10^{-8}$ sec and $\gamma \approx 10^{-12}$ cm^3/sec, so that when $n \leq 10^{20}$ cm^{-3} the collision-induced decays are insignificant in this case. The situation is somewhat different in anthracene with triplet excitons. Here $\tau \approx 2 \times 10^{-3}$ sec and $\gamma \approx 10^{-11}$ sec, so that decays occurring during the collision can be regarded as inessential only during a time on the order of $10^{-6}-10^{-8}$ sec. This time, however, is much larger longer than the time of establishment of thermodynamic equilibrium of the excitons with the lattice, and nevertheless sufficient for a noticeable migration of the exciton [10].

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[9] If the interaction (22) corresponds to attraction, with the modulus of the energy (22) large compared with the width of the exciton band for arbitrary nearest neighbors, then the character of the interaction (attraction) remains the same for arbitrary excitation groups.

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[10] In anthracene, the length of the diffusion displacement of the triplet exciton within a time 10^{-6} sec has an order of magnitude of 0.1 μ (see [33]).

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