COLLECTIVE PROPERTIES OF EXCITONS IN SEMICONDUCTORS

L. V. KELDYSH and A. N. KOZLOV
Submitted October 10, 1967

The problem of exciton interaction in semiconductors is considered in its multi-electron formulation. Expressions are obtained, in the approximation linear in the concentration, for the ground-state energy and for the law of dispersion of elementary excitations. Conditions for the Bose condensation of excitons are investigated and it is shown that low-density system of excitons behaves like a weakly nonideal Bose-gas. Furthermore, all quantities (the chemical potential, the rate of collective excitations) that depend on the two-particle scattering amplitude in the nonideal Bose-gas case are expressed in the analysis by the same formulas through the four-fermion interaction amplitude (two electrons and two holes) which includes, apart from the two-exciton scattering amplitude, the scattering amplitudes of two and three fermions as well as the terms connected with the Pauli statistics for the electrons and holes, and resulting from the fact that excitons are compound particles. These terms yield an essential positive contribution to the exciton scattering amplitude and may in principle ensure the stability of the ground Bose-condensed state even if there is a weak attraction between the excitons.

In recent years a number of authors[1-4] indicated that excitons in crystals can reveal properties characteristic of Bose-particle systems, particularly a tendency to Bose condensation. This circumstance is quite interesting, at least because the small effective mass of the excitons can make the condensation temperature for them sufficiently high even at relatively low concentrations. Indeed, for an ideal Bose gas, as is well known[5],

\[ kT_c = 3.31hM^{-1}N^{1/3}, \]

where \( N \) is the concentration and \( M \) the mass of the particle. For large-radius excitons, and only these will be discussed here, we have \( M \approx 10^{-21} \text{ to } 10^{-26} \text{ g} \) and the condensation temperature at \( N \approx 10^{17} \text{ cm}^{-3} \) is \( T_c \approx 100K. \) Exciton concentrations of \( 10^{17} \text{ to } 10^{28} \text{ cm}^{-3} \) are presently perfectly realistic, since various methods of excitation of semiconductor lasers give apparently electron and hole concentrations of the same order of magnitude. At such densities, the interaction between the excitons (e.g., the Van der Waals interaction) becomes noticeable, i.e., they form an ideal Bose gas. The theory of a weakly-nonideal Bose gas was developed in sufficient detail[6,7],. However, the possibility of regarding the system of excitons as a weakly-nonideal gas is not obvious. The point is that excitons in semiconductors constitute a rather loosely-coupled state of two Fermi particles - an electron and a hole. The binding energy \( \epsilon_0 \) and the exciton radius \( a_0 \) are determined in the simplest case by the well known Bohr formulas for the hydrogen atom:

\[ \epsilon_0 = \frac{1}{2} \frac{e^2}{\kappa r^2} \sim 10^{-6} \text{ ev}, \quad a_0 = \frac{\hbar^2}{m_e \epsilon_0} \sim 10^{-6} \text{ cm}. \]  

(1)

where \( e \) is the electron charge, \( \kappa \) the dielectric constant (\( \kappa \approx 10 \)), and \( m \) the reduced effective mass of the electron and hole:

\[ m = m_e m_h / (m_e + m_h) \sim 10^{-8} \text{ g}. \]

At the concentrations considered above, \( N \approx 10^{17} \text{ to } 10^{28} \text{ cm}^{-3} \), the average distance between excitons \( N^{-1/3} \) is of the same order as their radius \( a_0 \). Under such conditions, an important role is assumed by the internal structure of the exciton and by the fact that the Fermi particles of which the excitons are made up obey the Pauli principle. Two electrons (or two holes) contained in different excitons cannot come close to each other if their spins are parallel. Consequently, at \( N^{-1/3} \approx a_0 \), the excitons greatly deform each other even if no account is taken of the direct dynamic interaction, merely by virtue of the Pauli principle for the electrons and the holes, and the excitons can therefore not be regarded as structureless Bose particles.

In order to clarify this problem in somewhat greater detail, we introduce the operator \( Q^p \) for the creation of an exciton with momentum \( \mathbf{p} \), and express this operator in terms of the operators for the creation of an electron, \( a^\dagger_{\mathbf{p}} / 2 \mathbf{p} \), and hole \( b^\dagger_{\mathbf{p}} / 2 \mathbf{p} \) (\( \mathbf{p} \) is the momentum of relative motion):

\[ Q^p = \sum_\mathbf{p} \psi (p) a^\dagger_{\mathbf{p}+\mathbf{p}} b^\dagger_{\mathbf{p}+\mathbf{p}}. \]  

(2)

where

\[ \psi (p) = \frac{8 \pi \hbar^2}{[1 + (p a_0 / h)^2] \hbar^2} \]  

(3)

is the normalized wave function of the exciton for the hydrogenlike exciton.

Using the definition (2) and the usual Fermi commutation relations for the operators \( a^\dagger \) and \( b^\dagger \), we can easily obtain the following commutation relations for the exciton creation and annihilation operators:

\[ \{Q_{\mathbf{p}}, Q_{\mathbf{p}'}\} = \delta_{\mathbf{p}+\mathbf{p}'} - \sum_{\mathbf{q}} \psi (p + q / 2) \psi (p + q / 2) (a^\dagger_{\mathbf{p}+\mathbf{q}+\mathbf{p}'} + b^\dagger_{\mathbf{p}+\mathbf{q}+\mathbf{p}'}) \]  

(4)

The second term in the right side of (4) is an operator whose matrix elements, as can be readily shown, are of the order of \( N a_0^3 \) where \( N \) is the concentration of the excitons and the holes. Thus, (4) corresponds to the commutation relations for Bose particles only accurate to terms of the order \( N a_0^3 \). The fact that a bound complex of two fermions is, strictly speaking, not a Bose particle was already indicated earlier in[8]. We note also the following circumstance, which will be of importance later. Effects connected with the deviation of
the exciton statistics from Bose statistics come into play in the same order of magnitude as the effects connected with the nonideal nature of the Bose gas. Indeed, the chemical potential of a weakly-nonideal Bose gas is

$$\mu = \frac{4\pi \hbar^2}{M a^2} N a^3, \quad (5)$$

where $a$ is the scattering length. But in our problem, involving a system of particles interacting by Coulomb's law, the only parameter with the dimension of length is $a_0$, and therefore the exciton-exciton scattering length should be of the order of $a_0$. If we take further into account the fact that the masses of the electrons and of the holes are of the same order of magnitude and therefore $M = m_e + m_h = m_e m_h / M$, then (5) is reduced to the form $\mu \sim \varepsilon_0 (N a_0^3)$. But corrections of exactly this order should arise, as we have already seen, as a result of the fact that strictly speaking the excitons do not obey the Bose statistics. Therefore the problem of an interacting system of excitons, even in the lower orders in the concentration, cannot be equated to the problem of a weakly-nonideal Bose gas. It is the aim of the present paper to examine this question consistently.

We shall show below that a system of excitons actually does have many properties similar to the properties of a weakly-nonideal Bose gas. In particular, at sufficiently low temperatures, the excitons becomes condensed in a state with momentum $\mathbf{P} = 0$; the correction to the energy of the ground state $E_0$ is quadratic in the concentration, and the correction to the chemical potential $\mu$ is linear in the exciton concentration:

$$E_0 / V = -N a_0 (1 - \frac{1}{3} N a_0^3), \quad (6)$$

$$\mu = -\varepsilon_0 + \varepsilon_0 N a_0^3, \quad (7)$$

In these formulas, $V$ is the volume of the system and $s$ is a dimensionless parameter of the order of unity, an expression for which will be given below (formula (35)). The dependence of the energy of the moving exciton on its momentum has the usual form for a Bose gas

$$\omega(P) = s \sqrt{P^2 + (P^2 / 2M)^2}, \quad (8)$$

i.e., it satisfies the Landau criterion for superfluidity, and the speed of "sound" $s$ is connected with the correction to the energy by the usual hydrodynamic relation

$$M s^2 = (\mu + \varepsilon_0) = \varepsilon_0 N a_0^3. \quad (9)$$

The essential difference, however, between formulas (6)-(9) and the corresponding formulas for a weakly-nonideal Bose gas is the fact that the coefficient $s$ (the sign of which is chosen opposite to that customarily used for the scattering amplitude in accordance with [19]) is not expressed directly in terms of the amplitude for the scattering of two free excitons by each other. Roughly speaking, the definition of $s$ includes scattering amplitudes of three different types: exciton-exciton, electron-exciton, or hole-exciton, and the corrections for the amplitudes of scattering of electrons and holes by one another, connected with the presence of the exciton condensate. The latter are connected with the fact that the presence of the excitons leads to a change in the parameters of the electrons and holes (e.g., their effective masses) and of the effective interaction between them, in the same linear order in the concentration, and this in turn gives rise to a change in the internal energy of the exciton and its binding energy, and makes a contribution to all the quantities described by formulas (6)-(9).

This circumstance is very significant, since the theory of a weakly-nonideal Bose gas shows, as is well known, that such a gas can exist at low temperatures only when the forces between the particles are on average repulsive, or, more accurately speaking, when the scattering amplitude is positive. Otherwise the gas state - state with low density - is unstable. In our case a similar criterion holds, but not for the scattering amplitude but for the quantity $s$, and the latter will be shown subsequently to differ from the amplitude of scattering of two excitons in the presence of an essentially positive and rather large term. Therefore the exciton gas can exist also in the presence of weak interaction between the excitons, provided this attraction does not lead to the formation of bound molecule-like states. This is all the more important, since at large distances between the excitons a Van der Waals attraction is certainly present. The system is stabilized in this case by the Fermi statistics of the electrons.

Similar results for the energy and for the chemical potential were already obtained by Popov [18], but for a system that differs essentially from that considered by us. Popov considered a system of Fermi particles of one kind, and to ensure its stability he proposed that the interaction forces between the particles depend essentially on the spins: attraction for one mutual orientation of the spins and repulsion for the other.

In an experimental investigation of semiconductors with large exciton density, the results presented above should become manifest in the fact that, at large concentrations, the exciton line in the optical spectrum should shift towards larger energies by an amount $\delta \mu = \varepsilon_0 N a_0^3$. The exciton binding energy decreases by an amount of the same order, i.e., the threshold of the interband transitions approaches the exciton line.

At the same time, an additional band appears in the luminescence spectrum, the upper edge of which is shifted away from the main line into the region of low frequencies by an amount equal to the binding energy of the exciton $\mu$. This band is a result of exciton collisions, in which one of the excitons recombines and the other breaks up into an electron and a hole. With further increase of the concentration, the intensity of the additional band increases, and its upper edge approaches the main line. At concentrations $N a_0^3 \approx 1$ the binding energy of the exciton tends to zero, i.e., the excitons disintegrate into a Fermi gas of electrons and holes, and the additional band merges with the region of the continuous spectrum. Strictly speaking, our analysis is not valid at such high concentrations, but the conclusion that the excitons vanish is confirmed by an analysis of the opposite limiting case $\varepsilon_0 \ll 1$, where it is shown that when $N a_0^3 \gg 1$, the gap in the electron spectrum, i.e., the effective energy of their binding with the holes, tends exponentially to zero at a perfectly isotropic dispersion law, and that it vanishes in the presence of anisotropy even at zero temperature. The
Collective properties of excitons in semiconductors

presence of a condensed state and superfluidity should apparently become manifest also in an anomalously large exciton diffusion.

We proceed now to a quantitative investigation of our problem. The Hamiltonian of the system of electrons and holes interacting in accordance with Coulomb's law has in the second-quantization representation the form

\[ \hat{H} = \sum_p [(\varepsilon_p - \mu_e) a_p^\dagger a_p + (\varepsilon_p - \mu_h) b_p^\dagger b_p] + \frac{1}{2} \sum_{p<k} [2 \varepsilon_p a_p^\dagger b_k^\dagger b_k + b_p^\dagger b_k^\dagger b_k a_k + 2\varepsilon_p b_p^\dagger b_k^\dagger b_k a_k] \]

where \( a_p \) and \( b_p \) are the Fermi operators for electron and hole annihilation, \( \varepsilon_p \) and \( \mu_p \) are the dependences of their energy on the momentum \( p \), and \( \mu_e \) and \( \mu_h \) are the chemical potentials, determined by the conditions

\[ \sum_p \langle a_p^\dagger a_p \rangle = \sum_p \langle b_p^\dagger b_p \rangle = N. \]

(10)

The symbol \( \langle ... \rangle \) denotes averaging over the ground state, and \( \epsilon \) is the dielectric constant of the semiconductor. Although it is easy to continue the analysis in rather general form, we shall confine ourselves, in order not to make the subsequent formulas too cumbersome, to the case of the simplest dispersion law

\[ \varepsilon_p = p^2 / 2m_e, \quad \varepsilon_p = p^2 / 2m_h \]

(12)

and, moreover, we put for the time being \( m_e = m_h = m \) (\( m = \text{reduced mass} \)). In addition, we disregard the spins of the electrons and the holes. The final result will be presented for the more general case \( m_e \neq m_h \), with allowance for the spin structure in all the formulas.

We note, finally, one more assumption which has already been made by choosing the Hamiltonian in the form (10). Regarding the electrons and the holes as two independent types of particles, we neglect the possibility of the transition of the electron from one band to the other, and in particular we omit from the Hamiltonian the corresponding matrix elements of the potential \( V \). This assumption however, is fully justified, for owing to the orthogonality of the wave functions of the different bands these matrix elements are small compared with those retained in (10) (their relative order is \( \epsilon_0 / \Delta \approx 10^{-2} \), where \( \Delta \) is the width of the forbidden band). Because of this we can independently reckon the energies of the electrons and holes from the edge of the corresponding band, as was done in (12); the exciton energy is reckoned in this case from the width of the forbidden band. In exactly the same manner, the momenta of the electron and of the hole are reckoned from their values at the bottom of each of the bands.

Taking the foregoing assumptions under consideration, we introduce now Coulomb measurement units, i.e., we put \( m = \hbar = e^2 / \kappa = 1 \). Then

\[ \varepsilon_p = \varepsilon_p = \hbar^2 p^2 / m, \quad \varepsilon_p = \hbar^2 p^2 / 4, \quad \mu_e = \mu_h = \mu / 2. \]

(13)

Here \( \mu = \mu_e + \mu_h \) is the chemical potential of the excitons. Finally, we introduce the dimensionless exciton concentration

\[ n = N \omega_e. \]

(14)

The quantity \( n \) is thus the only parameter; of the problem, since \( \mu \) should be expressed in terms of \( n \) with the aid of relations (11), which now take the form

\[ \sum_p \langle a_p^\dagger a_p \rangle = \frac{1}{2} \sum_p \langle b_p^\dagger b_p \rangle = n. \]

(15)

Formula (15) and all the succeeding ones are referred to a unit volume of the system.

We have already stated above that our problem corresponds to the "gas" situation, i.e., \( n \ll 1 \). In this sense, it is the opposite of the problem investigated in \(^{11} \), which was formally analogous to the problem of superconductivity, i.e., it corresponded to weak attraction of the electrons and the holes. In the case \( n \ll 1 \), the interaction energy is much larger than the kinetic energy of the ideal Fermi gas of the electrons and holes, and therefore the latter can under no consideration be used as the initial approximation for solving our problem. It is clear from physical considerations that the ground state of the system is made up of excitons, i.e., of bound electron-hole pairs. It is therefore natural to start with the Bogolyubov canonical transformation \(^{12} \), which is known from the theory of superconductivity and is described by the unitary operator

\[ S = a_p \left( \sum_p q_p (a_p + b_p^\dagger) - b_p a_p \right) \]

(16)

\[ S_h S^* = a_p^\dagger a_p + b_p^\dagger b_p \]

(17)

where

\[ u_p = \cos q_p, \quad v_p = \sin q_p, \quad u_p + v_p = 1. \]

(18)

The function \( \varphi_p \) should be determined in this case from the condition of minimum energy and of stability of the ground vacuum state of the system.

The Hamiltonian (10) is transformed as follows:

\[ S \hat{H} S^* = U \hat{H} \]

(19)

where \( U \{ \varphi_p \} \) is a numerical (not operator) functional of \( \varphi_p \), which is separated after reducing the transformed Hamiltonian to the normal form

\[ U \{ \varphi_p \} = \sum_p (u_p - \mu) u_p^2 - \sum_p V_p (u_p v_p + v_p u_p^2 + v_p^2 u_p^2). \]

(20)

The operator \( \hat{H}_0 \) contains terms that are bilinear in the Fermi operators:

\[ \hat{H}_0 = \sum_p \left( u_p - \mu \right) u_p^2 + \sum_p \left( \varepsilon_p - \mu \right) u_p v_p + \sum_p \left( \varepsilon_p + \mu \right) v_p^2 - \varepsilon_p v_p \]

(21)

The operator \( \hat{H}_1 \) contains fourfold combinations of the Fermi operators:
\[ \mathcal{H}_I = \sum_{p,k} \left\{ V_k \left( \frac{1}{2} \bar{\gamma}_{p} \gamma_{p+k} + \bar{\gamma}_{-p-k} \gamma_{-p} \right) \right. \\
+ b_{p}^\dagger b_{p+k} b_{p-k} - 2 b_{p}^\dagger b_{p} b_{p+k} - 2 a_{p}^\dagger a_{p} b_{p+k} - 2 a_{p}^\dagger a_{p-k} a_{p-k} \right\} \\
\frac{1}{2} \bar{\gamma}_{p} \gamma_{p+k} \left( \frac{1}{2} \bar{\gamma}_{p-k} \gamma_{-p} \right) - \bar{\gamma}_{-p-k} \gamma_{-p} \left( \frac{1}{2} \bar{\gamma}_{p} \gamma_{p+k} \right) \right\} + \frac{1}{2} \bar{\gamma}_{p} \gamma_{p+k} \left\{ \gamma_{-p-k} \gamma_{-p} \right\} \right\} + \frac{1}{2} \left\{ \bar{\gamma}_{p-k} \gamma_{-p} \gamma_{p+k} \right\}.
\]

where

\[ \bar{\gamma}_{p} \gamma_{p+k} = \gamma_{p} \gamma_{p+k} = \cos (\theta) \]

\[ \bar{\gamma}_{-p-k} \gamma_{-p} = \gamma_{-p-k} \gamma_{-p} = \sin (\theta) \]

and obviously the following relation is satisfied.

\[ \gamma_{p} + \gamma_{-p} = 1. \]

The first term in the interaction Hamiltonian \( \mathcal{H}_I \) describes electron and hole scattering processes similar to those included in the initial Hamiltonian \( \mathcal{H}_0 \), except that in each vertex, where the momentum of the particle changes from \( p \) to \( q \), there appears an additional factor \( \gamma_{pq} \). A graphic representation of these matrix elements is given in Fig. 1a.

The matrix elements of the second term in \( \mathcal{H}_I \) is shown in Fig. 1b. They correspond to processes in which the Fermi particle is scattered and an electron-hole pair is created (or annihilated). The vertex at which the scattering takes place corresponds to the matrix element of the same factor \( \gamma_{pq} \) and the vertex at which creation (or annihilation) of an electron with momentum \( p \) and a hole with momentum \( -p-k \) is produced corresponds to the factor \( \gamma_{p-k,q} \). We note also that the matrix elements \( \gamma_{p} \) corresponding to creation of a pair by an electron or a hole have opposite signs.

In order not to write out the indices \( e \) and \( h \) on the diagrams, we propose henceforth that if creation (or annihilation) of an electron-hole pair occurs at any one vertex, the upper of the lines drawn from this vertex corresponds to the electron and the lower to the hole.

Finally, the last term in \( \mathcal{H}_I \) corresponds to processes in which two pairs are produced (or annihilated), or else one pair is produced from vacuum and the other is annihilated. A graphic representation of these processes is shown in Figs. 1c, d. To each vertex on these diagrams there corresponds a factor \( \gamma \).

Thus, following the transformation (19), our problem becomes in some respects similar to the problem of a weakly-nonideal Bose gas in the Belyaev analysis \(^{[7]} \); the perturbation-theory diagrams include, besides the processes describing the particle scattering, also vertices in which creation of particles from the vacuum (condensate) takes place, or else their annihilation (falling into the condensate). This analogy even closer if account is taken of the fact that \( \gamma \sim \sqrt{n} \), as will be shown below; consequently, \( \gamma \) in our case plays the same role as the operators of creation and annihilation of condensate particles in Belyaev's technique. To verify this, we perform the transformation (16) also in the normalization condition (15). Then, adding both equations of (13), we get

\[ \sum_{p} \{ v_{p}^{2} + (1/2)(v_{p}^{2}) (a_{p}^\dagger a_{p} + b_{p}^\dagger b_{p}) \]

\[ + v_{p} a_{p}^\dagger b_{p} + b_{p}^\dagger a_{p} \} = n. \]

However, as is clear from physical considerations (and will be confirmed by the subsequent analysis), the mean values \( \langle a_{p}^\dagger a_{p} \rangle \) and \( \langle b_{p}^\dagger b_{p} \rangle \) should vanish. Indeed, all the levels of the single-particle Fermi excitations should lie at energies close to zero (bottom of the band) and higher energies, and the chemical potentials of the electrons and holes are essentially negative \( \mu_{e} = \mu_{H} = \mu/2 = -\gamma n \), inasmuch as the chemical potential of the excitons \( \mu \) should obviously be somewhere near the level of the free exciton. But then all the levels of the single-particle Fermi excitations will be empty, as stated above.

To avoid misunderstanding, we emphasize that although we use as before the terms electron and hole, in fact, following the transformation (17), \( a_{p} \) and \( b_{p} \), are operators of certain new Fermi quasiparticles corresponding to elementary excitations in the system under consideration, and going over into ordinary electrons and holes only when \( n \to 0 \).

The last term in (25) must also be set equal to zero, i.e.,

\[ \langle a_{p}^\dagger b_{-p} \rangle = \langle b_{p}^\dagger a_{-p} \rangle = 0. \]

Condition (26) is not satisfied, of course, automatically, but we can use the leeway we still possess in the choice of the function \( \varphi_{pq} \) in (16), in order to ensure satisfaction of (26). Moreover, we shall verify below that condition (26) is necessary to ensure stability of the ground (vacuum) state of the system chosen by us. In other words, (26) should be regarded as an equation defining \( \varphi_{pq} \) with the normalization obtained simultaneously from (25):

\[ \sum_{p} v_{p}^{2} = \sum_{p} \sin^{2} \varphi_{p} = n. \]

It follows directly from (27) that \( \varphi_{p} \sim \sqrt{n} \), and then from (18) we get \( u_{p} = 1 - O(n) \). Using these estimates and the definitions (23), we get \( \gamma \sim \sqrt{n} \) and \( \gamma \sim 1 - O(n) \). Thus, the scattering of the quasiparticles by one another is renormalized by the transformation (16) only in order \( n \); on the other hand, the appearing new processes of creation and annihilation of particle pairs contain factors of order \( \sqrt{n} \), as do the processes connected with the emergence of the particles from the condensate in Belyaev's technique.

We now proceed to obtain the explicit form of (26), and to prove that it is a necessary condition for the stability of the ground state. To this end, we note first that the transformed Hamiltonian \( \mathcal{H} \) admits of creation of single electron-hole pairs with a total momentum equal to zero from vacuum. The corresponding matrix elements are contained in \( \mathcal{H}_{0} \), and can also be obtained
in higher orders of perturbation theory from \( \mathcal{F}_3 \). For example, the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from the matrix elements of Figs. 1b, c. The somewhat more complicated diagram of Fig. 2c can be obtained by making Fig. 2a more complicated by introducing in it a block \( \Phi \), that describes all possible processes of scattering of two electrons and two holes by one another. It is easy to see that the diagrams of Figs. 2a and 2c are of the same order, since the quasi-particle scattering processes are of zero order in the concentration. Both these diagrams are of order \( n^{3/2} \), since they contain each three vertices \( \gamma \). If we confine ourselves to this order, as we shall do in what follows, then the block \( \Phi \) must be replaced by \( \Phi_{32} \), which describes the interaction of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.

We now call attention to the fact that addition, to the diagrams of the perturbation-theory series, of parts connected with the remaining part of the diagram by only one pair of lines - electron and hole - with zero total momentum, leads immediately to divergences. Indeed, taking into account the interaction, such a pair, what more complicated diagram of Fig. 2c can be obtained in higher orders of perturbation theory from \( \mathcal{F}_3 \), the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from vacuum. The only possibility of eliminating this process of scattering of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.

We now call attention to the fact that addition, to the diagrams of the perturbation-theory series, of parts connected with the remaining part of the diagram by only one pair of lines - electron and hole - with zero total momentum, leads immediately to divergences. Indeed, taking into account the interaction, such a pair, what more complicated diagram of Fig. 2c can be obtained in higher orders of perturbation theory from \( \mathcal{F}_3 \), the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from vacuum. The only possibility of eliminating this process of scattering of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.

We now call attention to the fact that addition, to the diagrams of the perturbation-theory series, of parts connected with the remaining part of the diagram by only one pair of lines - electron and hole - with zero total momentum, leads immediately to divergences. Indeed, taking into account the interaction, such a pair, what more complicated diagram of Fig. 2c can be obtained in higher orders of perturbation theory from \( \mathcal{F}_3 \), the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from vacuum. The only possibility of eliminating this process of scattering of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.

We now call attention to the fact that addition, to the diagrams of the perturbation-theory series, of parts connected with the remaining part of the diagram by only one pair of lines - electron and hole - with zero total momentum, leads immediately to divergences. Indeed, taking into account the interaction, such a pair, what more complicated diagram of Fig. 2c can be obtained in higher orders of perturbation theory from \( \mathcal{F}_3 \), the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from vacuum. The only possibility of eliminating this process of scattering of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.

We now call attention to the fact that addition, to the diagrams of the perturbation-theory series, of parts connected with the remaining part of the diagram by only one pair of lines - electron and hole - with zero total momentum, leads immediately to divergences. Indeed, taking into account the interaction, such a pair, what more complicated diagram of Fig. 2c can be obtained in higher orders of perturbation theory from \( \mathcal{F}_3 \), the diagrams shown in Figs. 2a, b, which describe the creation of one pair, can be constructed from vacuum. The only possibility of eliminating this process of scattering of two electrons and two holes in the absence of other particles, and which is obtained from \( \Phi \) by replacing all the scattering vertices \( \gamma \) by unity.
were omitted from (31), the zeroth approximation for $\nu p$ from (32) and we regard them as a small perturbation. After simple calculations we obtain (in Coulomb units)

$$\mu - \nu_0 = \frac{13\pi}{3} n + \frac{4}{n} \Lambda = \left( \frac{13\pi}{3} + \lambda \right) n,$$

(33)

where

$$\Lambda = \int \Lambda(p, \epsilon) \nu p (\mu_0 - \epsilon_p) \frac{\nu p}{(2\pi)^3} = n\lambda.$$

(34)

We shall show that the quantity $\Lambda$, defined by formula (34), is described by the graphic block shown in Fig. 4a. To this end we draw in greater detail, for example, the diagram of Fig. 2c, drawing in it a vertical section corresponding to the instant of time of the last interaction on the $G_2(-p)$ line. One of the corresponding diagrams is shown in Fig. 4b. Since the interaction $V_k$ does not depend on the transferred frequency, the entire left part of this diagram does not depend on $\epsilon$.

In its right side, the functions that depend on $\nu_0$ are $G_0(p)$, $G_0(-p)$, and the three-particle propagation function for which $\nu_0$ is the summary energy. The singularities of the last two functions with respect to $\nu_0$ lie at $\epsilon_0 > 0$ (i.e., in the lower half-plane), and the singularities of $G_0(-p)$ lie at $\epsilon_0 < 0$ (i.e., in the upper half-plane). We note now that the product $(\mu_0 - \nu_0) G_0(p) G_0(-p)$ simply equals $G_0(p) + G_0(-p)$. Then, taking into account the forgetting, the only term making a contribution is that containing $G_0(-p)$, but not $G_0(p)$. Therefore when integrating the contribution from diagram 2c in (34), we leave out the product $(\mu_0 - \nu_0) G_0(p)$.

Repeating this reasoning for the contribution from diagram 2d, we can readily verify that $\Lambda$ is given by the diagram of Fig. 4a, in accordance with the statement made above, and is a dimensionless constant of the order of unity. From a comparison of formulas (7) and (33) it follows that

$$\lambda = 13\pi / 3 + \lambda,$$

(35)

where

$$\lambda = \left[ \int \left[ \nu_0 \left( \frac{k}{2} - p \right) - \nu_0 \left( \frac{k}{2} + p \right) \right] \nu_0 \left[ \frac{k}{2} - q \right] - \nu_0 \left[ \frac{k}{2} + q \right] \right] \nu_0 \left[ \frac{k}{2} - p' \right] - \nu_0 \left[ \frac{k}{2} + p' \right] \left[ \nu_0 \left( \frac{k'}{2} - q' \right) \right.

- \nu_0 \left( \frac{k'}{2} + q' \right) \left(2\pi \right)^3 \delta(p' - p) \delta(q' - q) \delta(k' - k) \delta(p'),$$

(36)

$\Phi$ is the complete single-time propagation function of two electrons and two holes with total momentum equal to zero and with total energy equal to $-2\epsilon_0$.

We emphasize now that in obtaining these results we actually used the assumption that two excitons cannot form a bound state. Indeed, if such a state were to exist, then the quantity $\Lambda(p, \epsilon)$, regarded as a function of $\mu_0$, would have a pole at $\mu_0 = -\epsilon_0$. In the vicinity of this pole, neither the perturbation theory used by us to solve (30), nor this equation itself, which is obtained by choosing the principal diagrams with respect to the powers of the concentration, would be valid. The validity of the assumption that there are no bound states of two excitons will be discussed later.

We now proceed to consider the spectrum of elementary excitations in the exciton system. Obviously, one-particle excitations (band states of electrons and holes) will be separated from the ground state by a gap having a width approximately equal to $\epsilon_0$. The lowest excited states should be the two-particle states corresponding, in the limit as $n \to 0$, to the motion of the individual exciton as a whole. They are determined by the poles of the two-particle Green's function $G_2(p, p')$ where $P = \{p, E\}$ is the summary momentum and frequency of the electron-hole pair, and $p = \{p, \epsilon\}$ and $p' = \{p', \epsilon'\}$ are the relative momentum and frequency of the electron-hole pair. The presence of an exciton condensate makes it necessary to introduce into consideration, besides the ordinary pair function $G_2$, also the function $G_2(p, p')$, which is the sum of all the connected diagrams describing creation of two electron-hole pairs from vacuum. A diagram of this function is shown in Fig. 5a. The equivalent diagram shown in Fig. 5b is more convenient for tracing out the diagrams, and therefore will also be used later.

It is easy to verify that the functions $G_2$ and $G_2$ are determined by the system of equations of Fig. 6, which is analogous in some respect to Belyaev's system of equations \cite{2} for a non-ideal Bose gas. In the equations of Fig. 6 we have grouped together the terms in such a way that $G_2$ denotes not the two-particle Green's function itself, but only that part corresponding to the connected diagrams. The main difference between these equations and the purely algebraic equations of Belyaev lies in the fact that the equations of Fig. 6 are integral with respect to the momenta of the relative motion of the electron and the hole, and therefore describe both the motion of the exciton and its internal structure. Near the poles corresponding to the exciton-gas density oscillations, the main contribution to the functions $G_2$ and $G_2$ is made by diagrams that break up into two parts connected by a single electron line and a single hole line, directed to one side, i.e., homogeneously...
ous terms with respect to $G_2$ and $G_2$ in the right sides of the equations of Fig. 6. The inhomogeneous terms contain the vertices $\Gamma(P, p, p')$ and $\tilde{\Gamma}(P; p, p')$, which have no pole character and constitute sums of diagrams that ar irreducible in the indicated sense. Accurate to terms linear in $n$ we have

$$\Gamma(P; p, p) = - V_{p-p'}^{a} \delta_{p-p'}^a + V_{p-p'}^{a} \delta_{p-p'}^a + \gamma(P; p, p'), \tag{37}$$

where the first term corresponds to Fig. 1a, and the second is the sum of the diagrams of Fig. 7a-d. The block $\Phi$ in these diagrams, just as in Fig. 2, contains all possible scatterings of two electrons and two holes by one another in the concentration, while the block $\Phi'$ in the diagrams of Figs. 7a,d differs from $\Phi$ only in that it does not contain the diagrams shown in Figs. 8a, b, since they are included in the self-energy corrections to the functions $G_2$ and $G_0$. If we join these corrections to the diagrams of Fig. 7, then the block $\Phi'$ is completed to form the block $\Phi$.

In order not to complicate the derivations that follow, we shall proceed in this fashion, i.e., we shall assume that the function $\gamma'(P; p, p')$ is determined by the diagrams of Fig. 7, in which $\Phi'$ is replaced by $\Phi$, and the single-particle Green's functions $G_0$ and $G_H$ are taken throughout without the self-energy corrections of second and higher orders in the interaction, i.e., in accordance with (21), also in an approximation that is linear in $n$

$$G_s(p) = G_s(p) = \left\{ e - \frac{p^2}{2} - \int V_{p-p'}(v_{p+p'}) dp' + \phi \right\}. \tag{38}$$

In analogy with formula (37), the vertex part of $\tilde{\Gamma}$ is the sum of all the diagrams describing the creation of two pairs from vacuum and of internal lines that are irreducible in terms of the pair and go to one side. In the approximation linear in $n$ we have

$$\tilde{\Gamma}(P; p, p) = V_{p-p'}^{a} \delta_{p-p'}^a + \gamma(P; p, p'). \tag{39}$$

The first of the terms in (39) corresponds to the matrix element of Fig. 1c, and the second to the sum of the diagrams of Figs. 9a-d. The diagrams of Fig. 9 have the general property that the outermost interaction occurs on them between one of the particles of the first electron-hole pair and the particle from the second pair. This property reflects the requirement that the diagrams entering in $\tilde{\Gamma}$ be irreducible with respect to each of the particle pairs.

As seen from (37) and (39), $\Gamma = V_{p-p'}^{a} + O(n)$, and $\tilde{\Gamma} \sim n$. Consequently, the system of Fig. 6 can be solved with the aid of perturbation theory, putting in the zeroth order $\Gamma = V_{p-p'}^{a}$ and $\tilde{\Gamma} = 0$. We shall assume also that the summary frequency $E$ and the kinetic energy $P^2/2M$ of the exciton are small compared with unity, and employing perturbation theory, we confine ourselves to terms of the first order in all three parameters $n, E$, and $P^2/2M$. It can be readily seen that accordingly we must put $P = 0$ in (37) and (39).

We now write out, using the assumed approximation, the equations of Fig. 6 in analytic form

$$G_2(P; p, p') = - G_s(p + P/2) G_s(-p + P/2) \int \frac{d^3p_1}{(2\pi)^3} V_{p-p'}^{a} G_s(p_1; p, p')$$

$$+ G_s(p) G_s(-p) \int \frac{d^3p_1}{(2\pi)^3} V_{p-p'}^{a} G_s(p_1; p, p') \tag{40}$$

$$+ G_s(p) G_s(-p) \int \frac{d^3p_1}{(2\pi)^3} V_{p-p'}^{a} G_s(p_1; p, p') \tag{40}$$

$$+ G_s(p + P/2) G_s(-p + P/2) \Gamma(p; p') G_s(p; p') G_s(p; p') \tag{40}$$

$$+ G_s(p + P/2) G_s(-p + P/2) \Gamma(p; p') G_s(p'; p') \tag{40}$$

$$+ G_s(p) G_s(-p) \tilde{\Gamma}(p; p') G_s(p; p') \tag{40}$$

In the zeroth order in the perturbation, the pole part of the functions $G_2$ and $G_2$ is determined by the first terms in the right sides of (40) and (41). We see therefore that

$$G_2(P; p, p') = G_s(p) G_s(-p) A(P; p, p') G_s(p; p') \tag{42}$$

$$G_2(P; p, p') = G_s(p) G_s(-p) A(P; p, p') G_s(p; p') \tag{42}$$

Substituting (42) in those terms of (40) and (41) which pertain to the perturbation, and integrating with respect to $\epsilon$, we obtain a system in which the integration takes place already over the three-dimensional momentum $p$, and in the zeroth order the homogeneous parts of both equations reduce to a Coulomb equation of the type (31). The solution can be obtained in standard fashion with the aid of the Green's function of the Schrödinger equation with Coulomb potential. This procedure is straightforward but quite laborious, and we therefore confine ourselves to presenting the final results.

The pole terms of the two-particle Green's functions are of the form (42), with

$$A(P; p, p') = \left( \epsilon_p + \frac{p^2}{2m^2} \right) \psi_p(P; p) \phi_p(p') \tag{43}$$

$$A(P; p, p') = \left( \epsilon_p + \frac{p^2}{2m^2} \right) \psi_p(P; p') \phi_p(p') \tag{43}$$

$$A(P; p, p') = \left( \epsilon_p + \frac{p^2}{2m^2} \right) \psi_p(P; p) \phi_p(p') \tag{43}$$

$$A(P; p, p') = \left( \epsilon_p + \frac{p^2}{2m^2} \right) \psi_p(P; p) \phi_p(p') \tag{43}$$
Indeed, if a bound state with radius $a_1$ is produced, where $\rho_1$ is the density of the hydrogen-molecule type.
The principle of interaction of two hydrogen atoms.
The energy of the exciton motion to the total energy of the system increases strongly. In this case the problem of the interaction of two excitons does not differ in principle from the excitons should be, by virtue of the uncertainty principle, $\hbar^2/(m_e + m_h) a_1^2$. When $m_e/m_h \ll 1$, this quantity is small compared with the interaction energy, the order of which is $\epsilon_0 \sim \hbar^2/m_e a_0^2$. But when $m_e/m_h \sim 1$, these two energies are of the same order, if $a_1 \sim a_0$, which should prevent formation of a bound state or, at any rate, should decrease noticeably its binding energy $\epsilon_1$ and increase the radius $a_1$.

The limiting case $m_e = m_h$ was considered by Hylleras and Ore (1944) (bound state of two positrons). The binding energy obtained in this case $\epsilon_1 \approx 10^{-4} \epsilon_0$ corresponds in our problem to $\epsilon_1 \approx 10^{-4} \epsilon_0$ and can be disregarded, since at temperatures $T \gtrsim 1 \text{K}$ this bound state no longer exists. It vanishes apparently also at zero temperature, if the exciton density is such that $n_1 \gg 1$, where $a_1 \sim \hbar \sqrt{\epsilon_1} a_0$, i.e., if the average distance between excitons is smaller than the radius $a_1$, but still much larger than $a_0$. In this case the results obtained by us for $T = 0$ are valid in the region of intermediate concentrations $a_1^2 \ll n < a_0^3$.

According to (43)–(47), the factors $\beta_1(P)$ and $\beta_2(P)$ of the two-particle Green’s functions $G_2$ and $G_2$, which depend on the summary 4-momentum of the electron-hole pair $P$, coincide in form with the single-particle Green’s function for a weakly non-ideal Bose gas, and the energy of the elementary excitations $E(P)$ and the occupation numbers of the excitons $N_P$ are connected in the usual manner with the correction to the chemical potential $\mu - \mu_0$. In formulas (43) $m^*$ denotes the reduced mass of the electron of the hole (without the previous limitation $m_h = m_h$). It can be shown, in addition, that allowance for the spin variables does not change any of the final formulas.

Let us make one more remark explaining formulas (44)–(47). The correction to the chemical potential $\mu - \mu_0$, which enters in these formulas, is due to such terms of the Eqs. (40) and (41), which contain the quantities $v(P; p, p')$ and $\tilde{v}(P; p, p')$. During the course of the solution, as can be readily seen, operations are performed on these functions, corresponding the closing of the diagrams of Figs. 7–9, as a result of which they reduce to the already known blocks of type shown in Fig. 4a.

We now discuss the results from the point of view of the possibility of their experimental observation. We have already mentioned that our analysis, strictly speaking, is not valid if the excitons form a bound state of the hydrogen-molecule type. Such a state apparently arises unavoidably in those cases when the mass of one of the particles (usually a hole) is much larger than that of the other, i.e., for example, in the majority of semiconductors of the type $Al\bar{I}V$, where $m_e + m_h \sim 0.1$, inasmuch as in this case the problem of the interaction of two excitons does not differ in principle from the problem of interaction of two hydrogen atoms. The situation changes radically, however, if the masses of the electron and hole are of the same order. In this case the relative contribution made by the kinetic energy of the exciton motion to the total energy of the system increases strongly (the analog of zero-point oscillations of the atoms in the hydrogen molecule). Indeed, if a bound state with radius $a_1$ is produced, then the average kinetic energy of relative motion of the excitons should be, by virtue of the uncertainty principle, $\hbar^2/(m_e + m_h) a_1^2$. When $m_e/m_h \ll 1$, this