NATURE OF THE PHASE TRANSITION UNDER THE CONDITIONS OF AN "EXCITONIC" INSTABILITY IN THE ELECTRONIC SPECTRUM OF A CRYSTAL

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The effect of the interband matrix elements of the electrons' Coulomb interaction on the exciton spectrum and the nature of the phase transition into the "excitonic insulator" state are investigated in a model of a semiconductor with the following features: the maximum of the valence band is located at the center of the Brillouin zone, and the conduction band minima occur at the edges of the Brillouin zone; the model is also characterized by a narrow energy gap. It is shown that if the exciton binding energy is close enough to the width of the energy gap, the system becomes thermodynamically unstable and undergoes a first-order phase transition. The two-particle excitation (exciton) spectrum in the new phase is also separated from the ground state by an energy gap.

As has been shown by a number of authors,[1-5] under certain conditions the ground state in a crystal may become unstable with respect to the formation of bound electron-hole pairs of the Mott exciton type.

Such an instability arises when the exciton binding energy becomes greater than the width of the forbidden gap. In this connection the single-particle excitation spectrum becomes restructured, a new branch of elementary excitations appears—the two-particle excitations—and, in fact, a new phase appears, which has been called an "excitonic insulator."[4] It has been shown[3] that the transition into the "excitonic insulator" state is a second order phase transition.

These results are obtained by only taking the Coulomb interaction of the electrons and holes into consideration. In terms of diagrams the Coulomb interaction of the particles simply corresponds to their scattering on each other. However, there are also other matrix elements in the total Hamiltonian describing the Coulomb interaction of the electrons; these correspond to diagrams such as those describing the scattering of a particle with the creation of an electron-hole pair, the creation from the vacuum of two electron-hole pairs with total quasimomentum equal to zero, etc.

The object of the present work is to show that the inclusion of these additional terms, which are inevitably present in the interaction Hamiltonian, leads to substantial changes in the spectrum of the elementary excitations and modifies the nature of the phase transition into the "excitonic insulator" state, namely: a region of absolute thermodynamic instability appears and the phase transition becomes a first-order transition.

Earlier we investigated[6] the simplest model having two identical parabolic bands with extrema at the point $\mathbf{k} = 0$. It was demonstrated for this model that, when the exciton binding energy becomes larger than the width of the forbidden gap, the two-particle excitation spectrum which appears has, in general, a non-acoustic nature for small momenta, and the phase transition is of first order.

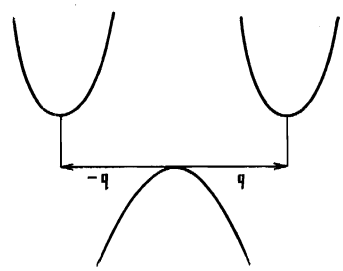

FIG. 1

In the present article we consider a more realistic model with two symmetric minima in the conduction band and a single maximum in the valence band (see Fig. 1). The minima are assumed to be located at opposite boundaries of the Brillouin zone, so that $2\mathbf{q}$ is a reciprocal lattice vector. Since these two minima are physically equivalent, it is sufficient to investigate only one of them. For simplicity the spins of the particles are not taken into consideration, and the whole investigation is carried out for the case of zero temperature.

In the representation of second quantization the Hamiltonian of the system of electrons and holes has the form

$$H=\sum_{\mathbf{p}}[\varepsilon_e(\mathbf{p})a_{\mathbf{p}}^{+}a_{\mathbf{p}}+\varepsilon_h(\mathbf{p})b_{\mathbf{p}}^{+}b_{\mathbf{p}}]+\frac{1}{2V}\sum_{\mathbf{p},\mathbf{p}',\mathbf{k}}[V_{\mathbf{k}}(a_{\mathbf{p}}^{+}a_{\mathbf{p}'}^{+}a_{\mathbf{p}'+\mathbf{k}}a_{\mathbf{p}-\mathbf{k}}$$

$$+b_{\mathbf{p}}^{+}b_{\mathbf{p}'}^{+}b_{\mathbf{p}'+\mathbf{k}}b_{\mathbf{p}-\mathbf{k}}-2a_{\mathbf{p}}^{+}b_{\mathbf{p}'}^{+}b_{\mathbf{p}'+\mathbf{k}}a_{\mathbf{p}-\mathbf{k}})+(\tilde{V}_{\mathbf{k}}a_{\mathbf{p}}a_{\mathbf{p}'}b_{\mathbf{k}-\mathbf{p}'}b_{-\mathbf{k}-\mathbf{p}}+\text{h.c.})],$$

where $a_{\mathbf{p}}$ and $b_{\mathbf{p}}$ are fermion operators for the annihilation of electrons and holes; $V_{\mathbf{k}} = 4\pi e^2/\kappa\mathbf{k}^2$, κ is the dielectric constant; the dispersion law for the electrons is given by $\epsilon_e(\mathbf{p}) = (1/2)\Delta + \hbar^2(\mathbf{p}+\mathbf{q})^2/2m_e$ and the dispersion law for the holes is given by $\epsilon_h(\mathbf{p}) = (1/2)\Delta + \hbar^2\mathbf{p}^2/2m_h$, where Δ denotes the energy gap in the one-particle excitation spectrum. The form of $\tilde{V}_{\mathbf{k}}$ is not specified. It is only assumed that $\tilde{V}_{\mathbf{k}}$ is small and plays the role of a perturbation. In actual fact, we consider the case of a narrow forbidden band, and the excitons which appear are excitons of large radius. Since here all of the characteristic momenta are small

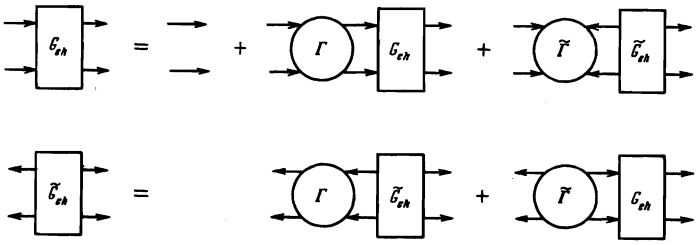

FIG. 2

(in comparison with a reciprocal lattice vector), the quantity $\tilde{V}_k$ turns out to be small due to the orthogonality of the wave functions belonging to different bands.

Not all of the interband matrix elements have been kept in the Hamiltonian (1). However, the inclusion of the remaining terms does not lead to a qualitative change in the results.

The spectrum of the excitons is determined by the poles of the two-particle Green's function $G_{eh}(P, p, p')$ with respect to the variable E, where $P = \{\mathbf{P}, E\}$ denotes the total quasimomentum and energy of the electron-hole pair, and $p = \{\mathbf{p}, \epsilon\}$ and $p' = \{\mathbf{p}', \epsilon'\}$ are the relative quasimomenta and energy of such a pair. The presence in the interaction Hamiltonian of matrix elements describing the simultaneous creation of two electron-hole pairs from the vacuum forces us to also consider the function $\tilde{G}_{eh}(P, p, p')$ in addition to the function $G_{eh}(P, p, p')$; the function $\tilde{G}_{eh}(P, p, p')$ is given by the sum of all connected diagrams describing the creation from the vacuum of two electron-hole pairs with total momentum equal to zero.

The functions $G_{eh}(P, p, p')$ and $\tilde{G}_{eh}(P, p, p')$ are determined by a system of equations[7] similar to the system of Belyaev equations,[1)] which is well-known in the theory of a Bose gas (see Fig. 2). In the present case the vortex Γ is simply the Coulomb interaction iV_k between an electron and a hole, and $\tilde{\Gamma}$ is the sum of all irreducible diagrams of first order in $\tilde{V}_k$, that is, those diagrams which cannot be divided by a vertical cut into two parts, which are joined by single electron and single hole lines running laterally. Thus, the vertex $\tilde{\Gamma}$, being of first order in $\tilde{V}_k$, contains also all possible Coulomb interactions between four particles (two electrons and two holes) to all orders; these interactions are described by diagrams that are irreducible in the sense indicated above. Since the diagrams of first order in V_k are taken into consideration in $\tilde{\Gamma}$, it is clear that the system of equations shown in Fig. 2 is approximate.

The system is solved by using the Green's function for the Coulomb problem:[7]

$$\bar{G}(E, \mathbf{p}, \mathbf{p}') = \frac{1}{(2\pi)^3} \sum_{n=1}^{\infty} \frac{\varphi_n^*(\mathbf{p}')\varphi_n(\mathbf{p})}{E - \mathscr{E}_n}, \tag{2}$$

where $\varphi_n(\mathbf{p})$ and $\mathscr{E}_n$ are the eigenfunctions and eigenvalues of the Coulomb equation:

$$\left(E - \frac{\hbar^2 \mathbf{p}^2}{2m}\right)\varphi(\mathbf{p}) + \frac{1}{(2\pi)^3}\int V_{\mathbf{p}-\mathbf{k}}\,\varphi(\mathbf{k})\,d^3k = 0. \tag{3}$$

[1)] This analogy is purely formal. Both of the functions—$G_{eh}(P, p, p')$ and $\tilde{G}_{eh}(P, p, p')$—are the usual two-particle Green's functions of the electrons, but the first is diagonal and the second is nondiagonal with respect to the band indices.

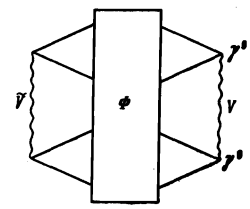

FIG. 3

The solution of the inhomogeneous equation

$$\left(E - \frac{\hbar^2 \mathbf{p}^2}{2m}\right)\varphi(\mathbf{p}) + \frac{1}{(2\pi)^3}\int V_{\mathbf{p}-\mathbf{k}}\,\varphi(\mathbf{k})\,d^3k = f(\mathbf{p})$$

is given by

$$\varphi(\mathbf{p}) = \int \bar{G}(E, \mathbf{p}, \mathbf{k}) f(\mathbf{k})\, d^3k. \tag{4}$$

Using (4), from the second equation of the system shown in Fig. 2 one can formally express $\tilde{G}_{eh}(P, p, p')$ linearly in terms of $G_{eh}(P, p, p')$ and substitute this result into the first equation; solving the latter near the lowest pole of $G_{eh}(P, p, p')$ in E, we obtain the following expression for the pole part of the function $G_{eh}(P, p, p')$:

$$G_{eh}(P, p, p') \approx A_{eh} \frac{E + \Delta + \mathscr{E}_1 + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M}{E^2 - [\Delta + \mathscr{E}_1 + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M]^2 + |\tilde{v}|^2}, \tag{5}$$

$$A_{eh} = i(2\pi)^4 \left(\mathscr{E}_1 - \frac{\hbar^2 \mathbf{p}^2}{2m}\right)\left(\mathscr{E}_1 - \frac{\hbar^2 \mathbf{p}'^2}{2m}\right)\varphi_1(\mathbf{p})\,\varphi_1(\mathbf{p}') \times G_e(p-q) G_h(-p) G_e(p'-q) G_h(-p'),$$

where $m = m_e m_h/(m_e + m_h)$, $M = m_e + m_h$, $G_e(p)$ and $G_h(p)$ denote the free Green's functions of the electrons and holes, $q = \{\mathbf{q}, 0\}$,

$$\tilde{v} = \frac{1}{(2\pi)^6}\int \varphi_1(\mathbf{p})\,(V_{\mathbf{q}}^* - V_{\mathbf{p}-\mathbf{p}'-\mathbf{q}})\,\varphi_1(\mathbf{p}')\,d^3p\,d^3p' - \frac{i}{2}\tilde{\Lambda}, \tag{6}$$

and $\tilde{\Lambda}$ is described graphically by the block diagram shown in Fig. 3. In this figure $\gamma^0_{\mathbf{p},\mathbf{p}'} = \varphi_1(\mathbf{p}) - \varphi_1(\mathbf{p}')$, and Φ is the four-particle propagator which contains all possible Coulomb interactions of the two electron-hole pairs and does not contain $\tilde{V}$.

By using Eq. (5) we obtain the following result for the pole part of $\tilde{G}_{eh}(P, p, p')$:

$$\tilde{G}_{eh}(P, p, p') \approx A_{eh}\tilde{v}^* \left[E^2 - \left(\Delta + \mathscr{E}_1 + \frac{\hbar^2(\mathbf{P}+\mathbf{q})^2}{2M}\right)^2 + |\tilde{v}|^2\right]^{-1}. \tag{7}$$

The positive pole of the function $G_{eh}(P, p, p')$ in E determines the exciton spectrum for values of p close to $-\mathbf{q}$ and for $\Delta + \mathscr{E}_1 \geq |\tilde{v}|$:

$$E(\mathbf{P}) = [(\Delta + \mathscr{E}_1 + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M)^2 - |\tilde{v}|^2]^{1/2}. \tag{8}$$

It is clear that the radicand becomes negative for $\Delta + \mathscr{E}_1 < |\tilde{v}|$ and $|\mathbf{p} + \mathbf{q}| \to 0$, and the energy of the excitations becomes imaginary. This indicates that the ground state of the system is unstable with respect to the formation of excitons with quasimomentum $-\mathbf{q}$ for $\Delta + \mathscr{E}_1 < |\tilde{v}|$. The realignment of the electron and hole wave functions which appears in this connection can be described by a canonical transformation of the basis system of the single-particle states,[7] this transformation being formally analogous to the Bogolyubov transformation, which is well-known in the theory of superconductivity. The transformation in question is generated by the unitary operator

$$S = \exp\left\{i\sum_{\mathbf{p}} [\varphi(\mathbf{p})\, a^+_{\mathbf{p}-\mathbf{q}}\, b^+_{-\mathbf{p}} - \varphi^*(\mathbf{p})\, a_{\mathbf{p}-\mathbf{q}}\, b_{-\mathbf{p}}]\right\}. \tag{9}$$

Here $\varphi(\mathbf{p})$ is an arbitrary function which must be chosen from the conditions for stability of the restructured ground state.

It is natural to assume that the realignment is small (that is, the function $\varphi(\mathbf{p})$ is small) when $|\Delta + \mathscr{E}_1| \to |\tilde{v}|$. Therefore, one can find approximate expressions for the coefficients of the Bogolyubov transformation:

$$S^+ a_{\mathbf{p}} S = u(\mathbf{p}+\mathbf{q}) a_{\mathbf{p}} + v(\mathbf{p}+\mathbf{q}) b^+_{-\mathbf{p}-\mathbf{q}},$$
$$S^+ b_{\mathbf{p}} S = u(\mathbf{p}) b_{\mathbf{p}} - v(\mathbf{p}) a^+_{-\mathbf{p}-\mathbf{q}}, \tag{10}$$

in terms of the function $\varphi(\mathbf{p})$:

$$u(\mathbf{p}) \approx 1 - \tfrac{1}{2}|\varphi(\mathbf{p})|^2, \quad v(\mathbf{p}) \approx i(1 - \tfrac{1}{8}|\varphi(\mathbf{p})|^2)\varphi(\mathbf{p}). \tag{11}$$

As a result of the transformation the Hamiltonian (1) acquires the following structure:

$$S^+ H S = U\{\varphi(\mathbf{p})\} + \sum_{\mathbf{p}} [\mathscr{E}_e(\mathbf{p}) a^+_{\mathbf{p}} a_{\mathbf{p}} + \mathscr{E}_h(\mathbf{p}) b^+_{\mathbf{p}} b_{\mathbf{p}}] + H_i, \tag{12}$$

where $U\{\varphi(\mathbf{p})\}$ is a numerical functional of $\varphi(\mathbf{p})$,

$$\mathscr{E}_e(\mathbf{p}) = \varepsilon_e(\mathbf{p}) - |\varphi(\mathbf{p}+\mathbf{q})|^2[\varepsilon_h(-\mathbf{p}-\mathbf{q}) + \varepsilon_e(\mathbf{p})]$$
$$- \frac{1}{V}\sum_{\mathbf{p}'} V_{\mathbf{p}-\mathbf{p}'}[|\varphi(\mathbf{p}'+\mathbf{q})|^2 - 2\varphi(\mathbf{p}+\mathbf{q})\varphi^*(\mathbf{p}'+\mathbf{q})], \tag{13}$$

$$\mathscr{E}_h(\mathbf{p}) = \varepsilon_h(\mathbf{p}) - |\varphi(\mathbf{p})|^2\left(\frac{\hbar^2\mathbf{p}^2}{2m} + \Delta\right) - \frac{1}{V}\sum_{\mathbf{p}'} V_{\mathbf{p}-\mathbf{p}'}[|\varphi(\mathbf{p}')|^2 - 2\varphi(\mathbf{p})\varphi^*(\mathbf{p}')], \tag{14}$$

$$H_i = \sum_{\mathbf{p}} [M_{\mathbf{p}} a^+_{\mathbf{p}-\mathbf{q}} b^+_{-\mathbf{p}} + M^*_{\mathbf{p}} b_{-\mathbf{p}} a_{\mathbf{p}-\mathbf{q}}]$$
$$+ \frac{1}{2V}\sum_{\mathbf{p},\mathbf{p}',\mathbf{k}} \{V_{\mathbf{k}}[a^+_{\mathbf{p}} a^+_{\mathbf{p}'+\mathbf{k}} a_{\mathbf{p}'} a_{\mathbf{p}-\mathbf{k}} + b^+_{\mathbf{p}} b^+_{\mathbf{p}'+\mathbf{k}} b_{\mathbf{p}'} b_{\mathbf{p}-\mathbf{k}}$$
$$- (2 - |\gamma_{\mathbf{p},\mathbf{p}-\mathbf{k}}|^2 - |\gamma_{\mathbf{p}',\mathbf{p}'+\mathbf{k}}|^2) a^+_{\mathbf{p}-\mathbf{q}} b^+_{\mathbf{p}'} b_{\mathbf{p}'+\mathbf{k}} a_{\mathbf{p}-\mathbf{q}-\mathbf{k}}]$$
$$+ [2iV_{\mathbf{k}}(\gamma^*_{\mathbf{p}',\mathbf{k}-\mathbf{p}} b^+_{\mathbf{p}} a_{\mathbf{p}'-\mathbf{q}} b_{-\mathbf{p}'+\mathbf{k}} b_{-\mathbf{p}-\mathbf{k}} + \gamma^*_{-\mathbf{p}'-\mathbf{k},\mathbf{p}'} a^+_{-\mathbf{p}} b_{\mathbf{p}'} a_{-\mathbf{p}'-\mathbf{q}-\mathbf{k}} a_{-\mathbf{p}+\mathbf{k}})$$
$$+ (\tilde{V}_{\mathbf{k}+\mathbf{q}} - V_{\mathbf{k}}\gamma^*_{\mathbf{p}',\mathbf{k}-\mathbf{p}'}\gamma^*_{\mathbf{p},-\mathbf{p}-\mathbf{k}}) a_{\mathbf{p}-\mathbf{q}} a_{\mathbf{p}'+\mathbf{q}} b_{\mathbf{k}-\mathbf{p}'} b_{-\mathbf{k}-\mathbf{p}} + \text{h.c.}]\}, \tag{15}$$

$$M_{\mathbf{p}} = i\left(\frac{\hbar^2\mathbf{p}^2}{2m} + \Delta\right)\left(1 - \frac{2}{3}|\varphi(\mathbf{p})|^2\right)\varphi(\mathbf{p})$$
$$- \frac{i}{V}\sum_{\mathbf{p}'} V_{\mathbf{p}-\mathbf{p}'}\left\{\left[1 - 2|\varphi(\mathbf{p})|^2 - \frac{2}{3}|\varphi(\mathbf{p}')|^2\right]\varphi(\mathbf{p}') + 2\varphi(\mathbf{p})|\varphi(\mathbf{p}')|^2\right\}$$
$$+ \frac{i}{V}\sum_{\mathbf{p}'} (\tilde{V}^*_{\mathbf{p}-\mathbf{p}'-\mathbf{q}} - \tilde{V}^*_{\mathbf{q}})\varphi^*(\mathbf{p}'), \tag{16}$$
$$\gamma_{\mathbf{p},\mathbf{p}'} = \varphi(\mathbf{p}) - \varphi(\mathbf{p}').$$

The transformation of the Hamiltonian has been carried out approximately. Terms giving corrections $\sim\varphi^2$ to the single-particle spectrum, and to Γ and $\tilde{\Gamma}$, have been kept, and also the terms enabling us to obtain the equation of "compensation" (see below) correct to terms of order φ^3 inclusively.

In order to obtain the equation which determines the function $\varphi(\mathbf{p})$, it is necessary to take the following fact into consideration. The Hamiltonian (12) allows the creation from vacuum of electron-hole pairs with total quasimomentum equal to $-\mathbf{q}$. The corresponding matrix elements are contained in the bilinear part of H_i, and can also be obtained in higher orders of perturbation theory from the parts of H_i which are quartic in the operators. For example, in second-order perturbation theory one can construct the matrix element corresponding to the creation (from the vacuum) of an electron-hole pair with total quasimomentum $-\mathbf{q}$ from the terms of H_i which describe the creation (from the vacuum) of two electron-hole pairs and a scattering of

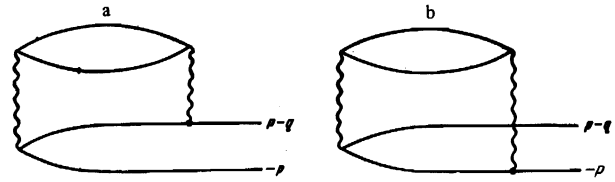

FIG. 4

the particles involving the annihilation of one electron-hole pair (see Fig. 4).

The appearance in the diagrams of the perturbation-theoretic series of parts, which are connected to the remaining part by single electron and single hole lines moving laterally, with total quasimomentum $-\mathbf{q}$, is an indication that the ground state is unstable with respect to the formation of such pairs in the vicinity of the point $\Delta + \mathscr{E}_1 = |\tilde{v}|$; this has already been mentioned above in connection with the investigation of the exciton spectrum in the restructured state.

However, we may express the arbitrary function $\varphi(\mathbf{p})$ in such a way as to compensate for such "dangerous" diagrams and thereby make the ground state stable.[7] In order to do this we introduce the function

$$F(\mathbf{p}, t_1 - t_2) = -i\langle T\tilde{a}_{\mathbf{p}-\mathbf{q}}(t_1)\tilde{b}_{-\mathbf{p}}(t_2)\rangle. \tag{17}$$

Here $\tilde{a}_{\mathbf{p}}(t)$ and $\tilde{b}_{\mathbf{p}}(t)$ denote the operators in the Heisenberg representation, and the average is taken with respect to the ground state of the Hamiltonian (12).

The compensation of the "dangerous" diagrams lies in the fact that the function $\varphi(\mathbf{p})$ is determined from the condition[7]

$$F(\mathbf{p}, 0) = 0. \tag{18}$$

This condition is simultaneously the condition that the ground state energy be a minimum, and from this point of view it ensures the best choice for the basis of single-particle states.

Taking the smallness of the function $\varphi(\mathbf{p})$ into consideration, let us carry out the compensation to terms of order $\varphi^3(\mathbf{p})$ inclusively, and in this approximation Eq. (18) takes the form

$$M_{\mathbf{p}} - \left(\frac{\hbar^2\mathbf{p}^2}{2m} + \Delta\right)\int_{-\infty}^{\infty} [\tilde{\Lambda}(\mathbf{p}, \varepsilon) - \Lambda(\mathbf{p}, \varepsilon)]\frac{d\varepsilon}{2\pi} = 0. \tag{19}$$

$\tilde{\Lambda}(\mathbf{p}, \epsilon)$ denotes the sum of the diagrams shown in Figs. 5a and 5b, and $\Lambda(\mathbf{p}, \epsilon)$ denotes the sum of the diagrams shown in Figs. 5c and 5d.

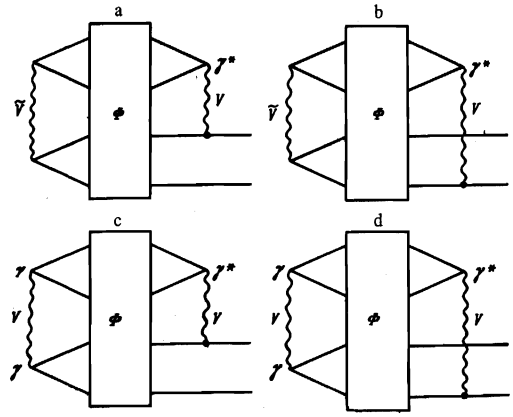

FIG. 5

To the first approximation in $\varphi(\mathbf{p})$ and to zero-order in $\tilde{V}$, Eq. (19) reduces to the Coulomb equation (3) in which Δ plays the role of the energy. Its solution is given by $\varphi(\mathbf{p}) = ce^{i\alpha}\varphi_1(\mathbf{p})$ for $\Delta = -\mathscr{E}_1$. Here c is a real positive coefficient, $\alpha \equiv \arg \varphi(\mathbf{p})$, and $\varphi_1(\mathbf{p})$ and $\mathscr{E}_1$ denote the eigenfunction and the eigenvalue of the hydrogen-like ground state.

Now substituting the value of $\varphi(\mathbf{p})$ into Eq. (19), we obtain an equation for the determination of the coefficient c, and by solving this we find

$$c = \begin{cases} f\sqrt{-\Delta - \mathscr{E}_1 + |\tilde{v}|} & \text{for } \Delta + \mathscr{E}_1 < |\tilde{v}|, \\ 0 & \text{for } \Delta + \mathscr{E}_1 > |\tilde{v}|, \end{cases} \qquad \alpha = {}^1/_2 \arg \tilde{v}.$$

The quantity $\tilde{v}$ was defined earlier by Eq. (6), and f is a real, positive constant:

$$f = \Big[\frac{2}{(2\pi)^3}\int \Big(\frac{\hbar^2\mathbf{p}^2}{2m} - \mathscr{E}_1\Big)\varphi_1^4(\mathbf{p})\,d^3p - \frac{2}{(2\pi)^6}\int \varphi_1^2(\mathbf{p})\,V_{\mathbf{p}-\mathbf{p}'}\,\varphi_1^2(\mathbf{p}')\,d^3p\,d^3p' - \frac{i}{2}\Lambda\Big]^{-1/2} = \Big[2\frac{13\pi}{3}a_1^3|\mathscr{E}_1| - \frac{i}{2}\Lambda\Big]^{-1/2},$$

where $a_1 = \kappa\hbar^2/me^2$, and Λ is described graphically by a block diagram similar to the one shown in Fig. 3 with, however, the difference that in the present case V_k appears instead of $\tilde{V}_k$ and the vertices on the left part also contain γ^0.

The equations for $G_{eh}(P, p, p')$ and $\tilde{G}_{eh}(P, p, p')$, defined in terms of the new operators, have the same structure as the equations shown in Fig. 2; however, Γ and $\tilde{\Gamma}$ now contain corrections of order φ^2, and $G_e(p)$ and $G_h(p)$ are the free Green's functions of particles whose dispersion laws are given by $\mathscr{E}_e(\mathbf{p})$ and $\mathscr{E}_h(\mathbf{p})$, respectively.

The system of equations is solved in exactly the same way as before the realignment, and as a result we obtain the following expressions for the pole parts of the Green's functions:

$$G_{eh}(P, p, p') \approx A_{eh}\frac{E - \Delta - \mathscr{E}_1 + 2|\tilde{v}| + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M}{E^2 - [-\Delta - \mathscr{E}_1 + 2|\tilde{v}| + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M]^2 + (\Delta + \mathscr{E}_1)^2}, \tag{20}$$

$$\tilde{G}_{eh}(P, p, p') \approx A_{eh}\frac{(\Delta + \mathscr{E}_1)e^{-i2\alpha}}{E^2 - [-\Delta - \mathscr{E}_1 + 2|\tilde{v}| + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M]^2 + (\Delta + \mathscr{E}_1)^2} \tag{21}$$

After the realignment ($\Delta + \mathscr{E}_1 < |\tilde{v}|$) the spectrum of the "excitons" has the following form:

$$E(\mathbf{P}) = [(2|\tilde{v}| - \Delta - \mathscr{E}_1 + \hbar^2(\mathbf{P}+\mathbf{q})^2/2M)^2 - (\Delta + \mathscr{E}_1)^2]^{1/2}. \tag{22}$$

For $\mathbf{P}$ close to $-\mathbf{q}$ the spectrum has a slotted character with a gap $\delta = 2[|\tilde{v}|(|\tilde{v}| - \Delta - \mathscr{E}_1)]^{1/2}$ which vanishes simultaneously with the realignment at the point $\Delta + \mathscr{E}_1 = |\tilde{v}|$. It is only in this case that the spectrum is acoustic, with the velocity of sound given by $s = (|\tilde{v}|/M)^{1/2}$.

Thus, taking account of the terms proportional to $\tilde{V}$ in the Hamiltonian (1) eliminates the analogy, which has been repeatedly discussed earlier, of an "excitonic insulator" with a superfluid condensate of Bose particles or Cooper pairs. These terms play the role of a "source of excitons" and they remove the degeneracy of the ground state of the system with respect to the phase of the function $\varphi(\mathbf{p})$. The conditions for the validity of the Goldstone theorem are thereby violated, and there is no reason to expect the spectrum of the collective excitations to be acoustic.

In order to clarify the nature of the phase transition it is necessary to investigate the behavior of the ground state energy in the neighborhood of the realignment point. Let us calculate the contribution to the energy coming from the interaction $\tilde{V}$, since the remaining part of the energy does not contain any singularities.

As is well known,[8] the change in the energy of the ground state originating from the interaction $\tilde{H}$ is given by the formula

$$\delta\mathscr{E} = \int_0^1 \langle \tilde{H}(g)\rangle \frac{dg}{g}, \tag{23}$$

where g denotes the coupling constant of the interaction contained in $\tilde{H}$. Let us calculate this change of the energy as a function of the volume, first in the absence of the realignment ($\Delta + \mathscr{E}_1 > |\tilde{v}|$), and then with the realignment ($\Delta + \mathscr{E}_1 < |\tilde{v}|$) taken into consideration.

1) $\Delta + \mathscr{E}_1 > |\tilde{v}|$.

In this case the average $\langle \tilde{H} \rangle$ is expressed in terms of $\tilde{G}_{eh}(P, p, p')$ in the following manner:

$$\langle \tilde{H}\rangle = \frac{1}{2}\frac{V}{(2\pi)^{16}}\mathrm{Re}\Big\{\int (\tilde{V}_{\mathbf{p}} - \tilde{V}_{\mathbf{p}'-\mathbf{p}-\mathbf{q}})\tilde{G}_{eh}(P, p, p')\,d^4p\,d^4p'\,d^4P\Big\}. \tag{24}$$

This equation is approximate in the same sense that the system of equations shown in Fig. 2 is approximate for the functions $G_{eh}(P, p, p')$ and $\tilde{G}_{eh}(P, p, p')$. Substituting expression (7) for $\tilde{G}_{eh}(P, p, p')$ into (24) and integrating over the four-dimensional momenta p and p', and also integrating over E, we obtain

$$\langle \tilde{H}\rangle = -\frac{1}{4}\frac{V}{(2\pi)^3}\mathrm{Re}\Big\{\tilde{v}^*\int \frac{\tilde{V}^*(\mathbf{P}+\mathbf{q})}{[(\Delta + \mathscr{E}_1 + \hbar^2\mathbf{P}^2/2M)^2 - |\tilde{v}|^2]^{1/2}}\,d^3P\Big\}, \tag{25}$$

where

$$\tilde{V}(\mathbf{P}) \equiv \frac{1}{(2\pi)^6}\int \varphi_1(\mathbf{p})[\tilde{V}_{\mathbf{p}} - \tilde{V}_{\mathbf{p}'-\mathbf{p}-\mathbf{q}}]\varphi_1(\mathbf{p}')\,d^3p\,d^3p'.$$

In order to find $\delta\mathscr{E}$, it is necessary to explicitly introduce the coupling constant g into Eq. (25), substitute $\langle \tilde{H}(g)\rangle$ into Eq. (23) and integrate with respect to g. Thus, we find

$$\delta\mathscr{E} = \frac{1}{4}\frac{V}{(2\pi)^3}\mathrm{Re}\Big\{\frac{1}{\tilde{v}}\int\Big[\sqrt{\Big(\Delta + \mathscr{E}_1 + \frac{\hbar^2\mathbf{P}^2}{2M}\Big)^2 - |\tilde{v}|^2} - \Big(\Delta + \mathscr{E}_1 + \frac{\hbar^2\mathbf{P}^2}{2M}\Big)\Big]\tilde{V}^*(\mathbf{P}+\mathbf{q})\,d^3P\Big\}. \tag{26}$$

It is clear from Eq. (26) that the second derivative of $\delta\mathscr{E}$ with respect to the volume (Δ is assumed to be a monotonic function of the volume), evaluated at the point $\Delta + \mathscr{E}_1 = |\tilde{v}|$, contains an integral which diverges at zero. Isolating the part of $\delta\mathscr{E}$ which gives this singularity, we have

$$\delta\mathscr{E}_{\mathrm{sing}} = \frac{V_0|\tilde{v}|^{1/2}M^{3/2}}{8(2\pi)^2\hbar^3}\mathrm{Re}\Big\{\frac{\tilde{V}^*(\mathbf{q})}{\tilde{v}}\Big\}(\Delta + \mathscr{E}_1 - |\tilde{v}|)^2\ln\frac{\Delta + \mathscr{E}_1 - |\tilde{v}|}{|\tilde{v}|}, \tag{27}$$

where V_0 denotes the volume at which $\Delta + \mathscr{E}_1 = |\tilde{v}|$.

2) $\Delta + \mathscr{E}_1 = |\tilde{v}|$.

With the realignment taken into consideration, the average $\langle \tilde{H}\rangle$ is expressed in terms of the Green's function $\tilde{G}_{eh}(P, p, p')$ by a formula analogous to Eq. (24); now the Green's function is already defined in terms of the transformed operators. Using expression (21) for $\tilde{G}_{eh}(P, p, p')$ and isolating the part of $\delta\mathscr{E}$ which gives the singularity in the second derivative with respect to the volume (in the same way as before the realignment), we obtain

$$\delta\mathscr{E}_{sing} = -\frac{V_0|\tilde{v}|^{1/2}M^{3/2}}{4(2\pi)^2\hbar^3}\mathrm{Re}\left\{\frac{\tilde{V}^*(q)}{\tilde{v}}\right\}(|\tilde{v}|-\Delta-\mathscr{E}_1)^2\ln\frac{|\tilde{v}|-\Delta-\mathscr{E}_1}{|\tilde{v}|}. \quad (28)$$

From Eqs. (27) and (28) it is seen that near the realignment point a region exists in which the pressure of the system, $P = -\partial\mathscr{E}/\partial V$, is an increasing function of the volume, and furthermore, depending on the sign of the quantity $\mathrm{Re}\{\tilde{V}^*(q)/\tilde{v}\}$, this region will be to the left or to the right of the point $\Delta + \mathscr{E}_1 = |\tilde{v}|$ corresponding to realignment of the spectrum.

The presence of a region of absolute thermodynamic instability leads to the result that, associated with changes of the volume including the point $\Delta + \mathscr{E}_1 = |\tilde{v}|$, the system undergoes a phase transition of the first kind, and moreover this point itself always falls in the region of the thermodynamically unstable states and therefore cannot be reached. The transition under consideration may correspond to a discontinuous change of not only the volume but also of any other parameter which the energy gap significantly depends on (uniaxial deformation, restructuring of the elementary crystal cell, etc.). In addition, the reason for a transition of the first kind may be the interelectron interaction itself,[5] if it leads to the result that attractive forces act between the excitons which are large enough so that the exciton system has a tendency to "liquefy," that is, if its energy for a given total number of excitons were to have a minimum at a certain nonzero value of the exciton density.

Thus, the transition into the "excitonic insulator" state is always a transition of the first kind, and this state itself does not possess any properties which might distinguish it from ordinary dielectrics.

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