EXCITON-PHONON INTERACTION AND SUPERFLUID PROPERTIES OF OPTICAL EXCITATIONS

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The problem of Bose-Einstein condesation (BEC) of excitons was extensively treated recently[1,2], although more attention was paid to Wannier-Mott excitons[3].This paper is dedicated to the study of the system of Frenkel excitons, with several energy levels excited.We shall discuss some consequences of the exciton -phonon interaction under the assumption that the exciton life time is several orders of magnitude larger than the relaxation time of the system excitons + lattice.In this time interval, the exciton number can be treated as constant and the system is in the quasi-equilibrium state[2].This is well fullfiled for triplet excitons, and in some cases even for singlet excitons.

The approach we shall use will be a sort of the analogy with the superconductivity.After the investigation of the coherent states in the laser theory, it was proposed that similar ideas should apply in the theory of superconductivity and superfluidity (but this does not imply the same type of the ground state).F.W. Cummings and J.R.Johnston[4] have demonstrated that in the general case of boson quasiparticles, one can consider the quasiparticle pairing as a process which leads to the formation of the coherent ground state.As we expect BEC to occur at low temperatures, excitons can be considered as boson quasiparticles.It can be demonstrated even by simple Bogoliubov diagonalization, that the ground state energy of such a system is lowered due to the pair formation.

On the other hand, Chestnut[5] has shown that exciton-phonon interaction might be attractive, so there exists further analogy with superconductivity.In fact, the aim of this paper is to investigate whether exciton-phonon interaction can lead to BEC of excitons.

Let us consider the molecular crystal with one molecule per unit cell, having ℓ close energy levels (multilevel scheme): $\Delta\mathcal{E}_f = \mathcal{E}_f - \mathcal{E}_0$ ($f = 1, 2, \dots \ell$) where $\mathcal{E}_0$ is the ground state energy and $\mathcal{E}_f$ is the energy of level f .The exciton Hamiltonian described by exciton creation and annihilation operators $B^+_\mu(\vec{k})$ and $B_\mu(\vec{k})$, in Heitler-London approximation is given by (see[6] pp.333-337):

$$H_e = \sum_{\mu,\vec{k}} E_\mu(\vec{k}) B^+_\mu(\vec{k}) B_\mu(\vec{k}) \tag{1}$$

where $B^+_\mu(\vec{k})$ creates an exciton with energy $E_\mu(\vec{k})$ belonging to μ -th zone.

The Hamiltonian of the exciton-phonon interaction (dominated by longitudinal acoustic phonons) in the linear coupling approximation is[7,8]:

$$H_{int} = \sum_{\vec{k},\vec{q},\mu,\nu} F_{\mu\nu}(\vec{k},\vec{q}) B^+_\mu(\vec{k}-\vec{q}) B_\nu(\vec{k}) (a_{\vec{q}} + a^+_{\vec{q}}) \tag{2}$$

with

$$F_{\mu\nu}(\vec{k},\vec{q}) = i \sum_{f=1}^{\ell} (2MV\omega_{\vec{q}})^{-1/2} \Delta\varepsilon_f (\vec{q}\,\vec{e}_{\vec{q}})\, u^*_{f\mu}(\vec{k}-\vec{q})\, u_{f\nu}(\vec{k}) \tag{3}$$

where: M - is the mass of the molecule, V - the crystal volume, $\omega_{\vec{q}} = v|\vec{q}|$ - the energy of the longitudinal phonons, $\vec{e}_{\vec{q}}$ - polarization of the longitudinal mode and $a^+_{\vec{q}}$, $a_{\vec{q}}$ - phonon creation and annihilation operators. The matrix $\mathcal{U}(\vec{k}) = \{u_{\alpha\beta}\}$ diagonalizes the excitonic Hamiltonian (see[6] pp. 333-337).

The Hamiltonian of the system excitons+phonons has the form:

$$H = \sum_{\vec{k},\mu} E_\mu(\vec{k}) B^+_\mu(\vec{k}) B_\mu(\vec{k}) + \sum_{\vec{q}} \omega_{\vec{q}}\, a^+_{\vec{q}} a_{\vec{q}} + H_{int} \tag{4}$$

Next step is to perform a unitary transformation analogous to Frölich transformation in theory of supercondutivity. After averaging the resulting effective Hamiltonian over the phonon vacuum, we introduce the idea of the creation of exciton drops (biexcitons) formed from the pair of excitons with opposite momenta (following the above reasoning).

In order to apply such an approach we must verify whether these bound states can really exist. In previous papers[9,10] the expression for the energy of these bound states (biexcitons) was derived. By studying this expression, it can be seen that the formation of bound state is possible under the following conditions: a) exciton-exciton interaction must be attractive and b) the magnitude of exciton-exciton interaction must be larger than the bandwidth of corresponding exciton zone. It turns out that this is possible for very narrow exciton zones with the bandwidth of order 10^{-21} J or smaller.

In our case, the effective exciton-exciton interaction is of the form

$$H^{eff}_{int} = \sum_{\vec{k},\vec{q},\mu,\nu} W_{\mu\nu}(\vec{k},\vec{q}) B^+_\mu(\vec{k}) B_\mu(-\vec{k}) B_\nu(-\vec{q}) B_\nu(\vec{q}) \tag{5a}$$

with
$$W_{\mu\nu}(\vec{k},\vec{q}) = \frac{F^{*}_{\mu\nu}(\vec{k},\vec{k}+\vec{q})F_{\mu\nu}(\vec{q},\vec{k}+\vec{q})\ \omega_{\vec{k}+\vec{q}}}{[E_{\mu}(\vec{k})-E_{\nu}(\vec{q})]^{2} - \omega^{2}_{\vec{k}+\vec{q}}} \tag{5b}$$

The condition a)($W<0$) is fulfilled when the phonon energy $\omega_{\vec{k}+\vec{q}}$ exceeds Bethe splitting of the exciton zones $\beta_{\mu\nu} = E_{\mu}(\vec{k}) - E_{\nu}(\vec{q})$ If we estimate phonon energies from the Debye temperature ($k_B T_D \sim 10^{-21} J$ for the molecular crystals) and $\beta_{\mu\nu} \lesssim 10^{-22} J$ (for triplet excitons, see Ref. 6, Chap.XII), we see that this condition is satisfied. From (3) and (5) we estimate $|W| \sim (\Delta\mathcal{E}_f)^2 (2Mv^2)^{-1} \lesssim 10^{-20} J$, so we see that the condition b) is also fulfilled.

The spectrum of elementary excitations of the Hamiltonian
$$H_{eq} = H_e + H^{eff}_{int} \tag{6}$$
will be determined by the application of Zubarev's Green's function (GF) method[11]. Taking into account the possibility of both processes: creation and annihilation of exciton drops, we shall introduce two types of GF:
$$G_{\mu\nu}(\vec{k},E) = \langle\langle B_{\mu}(\vec{k}) | B^{+}_{\nu}(\vec{k}) \rangle\rangle; \qquad D_{\mu\nu}(\vec{k},E) = \langle\langle B^{+}_{\mu}(-\vec{k}) | B^{+}_{\nu}(\vec{k}) \rangle\rangle \tag{7}$$
which are the Fourier-transforms of double-time, temperature dependent retarded commutator GF[11].

These functions, calculated from the equations of motion using the linear decoupling procedure, are given by
$$G_{\mu\nu}(\vec{k},E) = G_{\mu}(\vec{k},E)\delta_{\mu\nu} = \frac{i}{2\pi}\ \frac{E + \tilde{E}_{\mu}(\vec{k})}{E^{2} - \mathcal{E}^{2}_{\mu}(\vec{k})}\ \delta_{\mu\nu}$$
$$D_{\mu\nu}(\vec{k},E) = D_{\mu}(\vec{k},E)\delta_{\mu\nu} = -\frac{i}{2\pi}\ \frac{\Delta^{*}_{\mu}(\vec{k})}{E^{2} - \mathcal{E}^{2}_{\mu}(\vec{k})}\ \delta_{\mu\nu} \tag{8}$$
The energy of the elementary excitations is
$$\mathcal{E}_{\mu}(\vec{k}) = \left\{ [E_{\mu}(\vec{k}) - E_{\mu}(0) + |\Delta_{\mu}(0)|]^{2} - |\Delta_{\mu}(\vec{k})|^{2} \right\}^{1/2} \tag{9}$$
where we have introduced, following Evans and Imry[12], the "coherence parameter"
$$\Delta_{\mu}(\vec{k}) = \sum_{\vec{q},\mu} W_{\mu\nu}(\vec{k},\vec{q})\ \langle B_{\nu}(-q) B_{\nu}(\vec{q}) \rangle =$$
$$= \sum_{\vec{q},\nu} W(\vec{k},\vec{q})\ \frac{\Delta_{\nu}(\vec{q})}{2\,\mathcal{E}_{\nu}(\vec{q})}\ \coth\frac{\mathcal{E}_{\nu}(\vec{q})}{2k_B T}\ , \quad \mu = 1,2,\dots \ell \tag{10}$$
and the chemical potential μ_e by: $\mu_e = E_{\mu}(\vec{k}) - \tilde{E}_{\mu}(\vec{k})$,
which was determined from the condition that the energy $\mathcal{E}_{\mu}(\vec{k})$

has no gap, i.e. $\mathcal{E}_\mu(0) = 0$, which is equivalent to measuring the energy from the bottom of the exciton zone.
In the effective mass approximation $E_\mu(\vec{k}) - E_\mu(0) = \frac{k^2}{2m_\mu}$ so

$$\mathcal{E}_\mu(\vec{k}) = \left\{ \left[\frac{k^2}{2m_\mu} + |\Delta_\mu(0)| \right]^2 - |\Delta_\mu(\vec{k})|^2 \right\}^{1/2}; \quad (\hbar = 1). \tag{11}$$

In the small wave vector limit, we obtain the "phonon" spectrum as in the case of superfluid Bose gas:

$$\mathcal{E}_\mu(\vec{k})_{k \to 0} \approx \sqrt{\frac{|\Delta_\mu(0)|}{m_\mu}}\, |\vec{k}| = v_\mu |\vec{k}|. \tag{12}$$

v_μ is the sound velocity in the system of elementary excitations. We did not attempt to analyse the roton part of the spectrum due to the rather complicated form of equations (10).

We shall analyse also the optical properties of this system using the tensors of dielectric susceptibility $\tilde{\chi}_{ij}$ or dielectric permeability $\tilde{\mathcal{E}}_{ij}$, which relate the crystal polarization $\vec{P}$ and the electric field $\vec{\mathcal{E}}$ of the incoming electromagnetic wave

$$\vec{P}(\vec{k},\omega) = \tilde{\mathcal{E}}_0\, \tilde{\chi}(\vec{k},\omega)\, \vec{\mathcal{E}}(\vec{k},\omega) = \tilde{\mathcal{E}}_0 \left[\tilde{\mathcal{E}}(\vec{k},\omega) - 1 \right] \vec{\mathcal{E}}(\vec{k},\omega) \tag{13}$$

Our main interest will be the imaginary part of $\tilde{\chi}$ which is proportional to the absorption coefficient.
The vector potential of this field is given by

$$\vec{A}(\vec{r},t) = \vec{\ell} A_0 e^{i\vec{Q}\vec{r} - i\Omega t} + \text{c.c.} \tag{14}$$

where $\vec{\ell}$ - is the unit vector of the polarization, satisfying $\vec{\ell}\cdot\vec{Q} = 0$, and Ω is the frequency of the transverse electromagnetic field.

The starting point of the calculation will be the Hamiltonian of the interaction of the radiation with the crystal in the dipole approximation (see[6] pp. 356-358).In the linear response theory for the frequency region of exciton photon resonance $\Omega \sim E_\mu(0)$, we obtain

$$\vec{P}(\vec{Q},\Omega) = i \sum_{\mu=1}^{\ell} \vec{d}_\mu(\vec{Q}) L_\mu(\vec{Q})\, G_\mu(\vec{Q},\Omega) \tag{15}$$

where $\vec{d}_\mu(\vec{k})$ represent the molecular dipole moment which corresponds to the transition from the ground state to the exciton state $|\mu\vec{k}\rangle$ and $L_\mu(\vec{Q})$ is the exciton-phonon coupling constant.

In order to simplify the analysis of $Jm\{\tilde{\chi}_{ij}\}$ let us discuss the case of one excited level ($f=1$; $\mu=1$) in the molecule (the other excited levels are rather separated). Then, in the vicinity of T=0 K using (15),(13) and (8) we obtain ($\mathcal{E}_\mu(\vec{k})\to\mathcal{E}(\vec{k})$ etc):

$$Jm\{\tilde{\chi}_{ij}(\vec{Q},\Omega)\}=\frac{E(0)\,d_i d_j}{\tilde{\mathcal{E}}_0 V_0 \Omega}\{(\bar{n}_{\vec{Q}}+1)\,\delta[\Omega-E(0)-\mathcal{E}(\vec{Q})]-$$
$$-\bar{n}_{\vec{Q}}\,\delta[\Omega-E(0)+\mathcal{E}(\vec{Q})]\};\quad i,j=x,y, \qquad (16)$$

$\bar{n}_{\vec{Q}}=\langle B^+(\vec{Q})B(\vec{Q})\rangle_{T=0}$; $\qquad V_0$ – unit cell volume;

$\vec{d}=\langle f|\sum_\alpha e_\alpha \vec{r}_\alpha|0\rangle$ – is the vector matrix element of the transition dipole moment.

(In (8) we performed the change $E\to\Omega-E(0)$, because here the excitation energy must be calculated from the ground state of molecule and not from the bottom of the exciton zone.)

From the equation (16) we see that the (positive) light absorption proportional to $\bar{n}_{\vec{Q}}+1$ (exciton creation) occurs at the frequency

$$\Omega_1=E(0)+\mathcal{E}(\vec{Q}) \qquad (17)$$

and the negative absorption (i.e. stimulated emission) proportional to $\bar{n}_{\vec{Q}}$, occurs at the frequency

$$\Omega_2=E(0)-\mathcal{E}(\vec{Q}) \qquad (18)$$

This result can be explained in the following way: the incoming photon interacting with the exciton drop with the momentum $\vec{k}_0=0$ and energy $E_0\sim 2E(0)$ creates two excitons with the energies Ω_1 and Ω_2 (renormalized due to the interaction with phonons). The other exciton (with the energy Ω_2) is being emited as the photon of the energy Ω_2 (stimulated emission). We see that there appears the shift of absorption and emission line for the magnitude $\Omega_1-\Omega_2=2\mathcal{E}(\vec{Q})$ which could be used as an experimental test of this theory.

The results obtained can be summarized as follows. Effective exciton-exciton interaction, due to the exchange of virtual phonons, leads to the creation of the metastable bound exciton state: exciton drop with the momentum $\vec{k}_0=0$. Elementary excitations created by the decay of the drops have the dispersion law $\mathcal{E}_\mu(\vec{k})$ satisfying the superfluidity condition. In this case, the quasi-particle mean free path is governed by the critical velocity v_μ and the life-time and not by the quasi-particle colisions, which might lead to the superfluid energy transfer on large distances, which might be experimentally tested. The explanation why kinetic effects do not influence these result in a great measure, can follow the lines given in the paper[13].

The repulsion in the system of excitons was not considered for two reasons: a) at small exciton concentrations exciton-phonon interaction is dominant and b) the repulsion in the system of Frenkel excitons becomes important at the distances of order $10^{-9}-10^{-10}m$ (hard core repulsion), while it can be shown that the radius of exciton drops is of order $10^{-7}m$[14].

R e f e r e n c e s

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