F I Z I K A VOLUME 10 SUPPLEMENT 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics of Condensed Matter, Kruševac, September, 18-22, 1978

# The Exciton and Polariton Kinematical Levels

M. Pirić
Institute of Physics, University of Sarajevo

A possibility of the appearance of new excitations, being the result of the interaction between Frenkel excitons, will be analysed here. It will be shown that these new excitations appear as the result of kinematical interaction of the initial excitations. They have a finite lifetime which is of the order of $10^{-14}$ sec and it is plausible to assume that they are responsible for the large broadening of absorption lines experimentaly found in optical systems.

The exciton Hamiltonian, corresponding to two level scheme of molecular excitation will be analysed. This Hamiltonian is of the form:

$$\hat{H} = \sum_{\vec{n}} \Delta P^{+}_{\vec{n}} P_{\vec{n}} + \frac{1}{2} \sum_{\vec{n}\vec{m}}{}' \alpha_{\vec{n}\vec{m}} P_{\vec{n}} P_{\vec{m}} + \frac{1}{2} \sum_{\vec{n},\vec{m}}{}' \beta_{\vec{n}\vec{m}} P^{+}_{\vec{n}} P_{\vec{n}} P^{+}_{\vec{m}} P_{\vec{m}} , \qquad (1)$$

where P and $P^{+}$ are the Pauli-operators. The details about $\Delta$ , $\alpha$ and $\beta$ can be found in the reference [1].

The properties of the system with Hamiltonian (1) will be analysed with help of the Green's function $\Gamma_{\vec{f}\vec{g}} = \langle\langle P_{\vec{f}}(t) | P^{+}_{\vec{g}}(0) \rangle\rangle$. Using the standard procedure of the Green's fuction method we obtain

$$i \frac{d}{dt} \Gamma_{\vec{f}\vec{g}}(t) = i(1 - 2 \langle P^{+}_{\vec{f}} P_{\vec{f}} \rangle) \delta_{\vec{f}\vec{g}} \delta(t) + \langle\langle \Omega_{\vec{f}}(t) | P^{+}_{\vec{g}}(0) \rangle\rangle , \qquad (2)$$

where

$$\Omega_{\vec{f}} = \Delta P_{\vec{f}} + \frac{1}{2} \sum_{\vec{m}} \alpha_{\vec{f}\vec{m}} P_{\vec{m}} - \sum_{\vec{m}} \alpha_{\vec{f}\vec{m}} P^{+}_{\vec{f}} P_{\vec{f}} P_{\vec{m}} + \sum_{\vec{m}} \beta_{\vec{f}\vec{m}} P^{+}_{\vec{m}} P_{\vec{m}} P_{\vec{f}} . \qquad (3)$$

The further procedure consists of: overgoing from Pauli-operators P to Bose-operators B, according to the approximate formula $P = B - B^{+}B\,B$, and decoupling the higher order boson Green's functions with the strict use of the

**Wick's theorem. So we obtain the following equation for the Fourier component $G_{\vec{k}}(E)$ of the boson Green's function:**

$$G_{\vec{k}}(E) = \frac{i}{2\pi} \frac{1+2C_0}{E - \mathcal{E}_{\vec{k}} + M_{\vec{k}}} \times \tag{4}$$
$$\times \left\{ 1 + \frac{1}{2N^2} \sum_{\vec{q}_1 \vec{q}_2} \left[ \rho_{\vec{q}_1 \vec{q}_2} - i\pi \varphi_{\vec{q}_1 \vec{q}_2} \delta(E - \mathcal{E}_{\vec{q}_1} + \mathcal{E}_{\vec{q}_2} - \mathcal{E}_{\vec{k}-\vec{q}_1+\vec{q}_2}) \right] \right\}^{-1},$$

**where**

$$\mathcal{E}_{\vec{k}} = \Delta + \frac{1}{2}\alpha_{\vec{k}}, \qquad M_{\vec{k}} = \frac{1}{N}\sum_{\vec{q}} (\alpha_{\vec{k}} + \alpha_{\vec{q}} - \beta_0 - \beta_{\vec{k}-\vec{q}}) < B^+_{\vec{q}} B_{\vec{q}} >_0,$$

$$f_{\vec{k}} = \sum_{\vec{n}} f_{0\vec{n}} e^{i\vec{k}\vec{n}}, \qquad < B^+_{\vec{q}} B_{\vec{q}} >_0 = \left(e^{\frac{\mathcal{E}_{\vec{q}}}{kT}} - 1\right)^{-1}, \tag{5}$$

$$\rho_{\vec{q}_1 \vec{q}_2} = \frac{E - \mathcal{E}_{\vec{k}} - \alpha_{\vec{k}-\vec{q}_1+\vec{q}_2} + \beta_{\vec{q}_1-\vec{q}_2}}{E - \mathcal{E}_{\vec{q}_1} + \mathcal{E}_{\vec{q}_2} - \mathcal{E}_{\vec{k}-\vec{q}_1+\vec{q}_2}}, \qquad \varphi_{\vec{q}_1 \vec{q}_2} = E - \mathcal{E}_{\vec{k}} - \alpha_{\vec{k}-\vec{q}_1+\vec{q}_2} + \beta_{\vec{q}_1-\vec{q}_2},$$

**$E_N(\vec{k}) = \mathcal{E}_{\vec{k}} - M_{\vec{k}}$ are the exciton energies. The energies of the additional levels of the system are obtained by letting the bracketed expression in (4) to tend to infinity, and they are given as follows**

$$E^{(1)}_{I,II} = \frac{1}{2}\left\{ E_0 + E_3 \pm \left(\frac{\sqrt{A^2+B^2}+A}{2}\right)^{1/2} + i\left[E_5 \pm \left(\frac{\sqrt{A^2+B^2}-A}{2}\right)^{1/2}\right]\right\} \tag{6}$$

$$E^{(2)}_{I,II} = \frac{E_S^2 E_4 + E_T^2 E_3}{E_S^2 + E_T^2} \pm i \frac{E_S E_T |E_4 - E_3|}{E_S^2 + E_T^2} \tag{7}$$

**The expression (6) is obtained in the small wave vectors approximation and the expression (7) corresponds to the high wave vectors, close to the end of the first Brillouin's zone. The notations used in the last two formulae are:**

$$E_0 = \Delta + 3\alpha, \quad E_S = \frac{4\hbar^2 \mu_0 k}{\pi m}, \quad E_T = \frac{\hbar^2 \mu_0^2}{2m}, \quad E_j = E_0 + \lambda_j; \quad j = 1,2,3,4$$

$$\lambda_1 = -\frac{\hbar^2 k^2}{2m}, \quad \lambda_2 = 2(\alpha-\beta) - \frac{\hbar^2 k^2}{2m} - \frac{2(1-\xi)}{5}\frac{\hbar^2 \mu_0^2}{2m},$$

$$\lambda_3 = -6(\alpha-\beta) + \frac{\hbar^2 k^2}{2m} - \xi\frac{\hbar^2 \mu_0^2}{2m},$$

$$\lambda_4 = 6(\alpha-\beta) + \frac{28\xi - 36}{15}\frac{\hbar^2 \mu_0^2}{2m} + (2\xi - 3)\frac{\hbar^2 k^2}{2m}; \quad \xi = \frac{\beta}{\alpha},$$

$$A = (E_0 - E_3)^2 - E_S^2, \qquad B = 4E_S(E_0 + E_3 - E_2),$$

where $m = \frac{\hbar^2}{\alpha a^2}$ is the effective mass of excitons, a is the lattice constant and $\mu_0$ is the boundary vector of the first Brillouin's zone. As we see from (7), the additional kinematical excitations have the finite life-time

$$\frac{\hbar (E_s^2 + E_T^2)}{E_s E_T |E_4 - E_3|} \sim 10^{-14} s \qquad (10)$$

Now the kinematical levels arising in the polariton system will be analysed. The polaritons are a "mixture" of excitons and vacuum photons which arise due to the retarded interaction of electrons in electromagnetic field:

$$-\frac{e}{mc} \sum_{\vec{n}} \vec{p}_{\vec{n}} \cdot \vec{A}_{\vec{n}} \ . \qquad (10)$$

The electron momentum operator $\vec{p}$ can be expressed in terms of exciton operators, corresponding to three kinds of excitons: the usual ones and two kinds of kinematical excitons. Going over from the momentum operator to the operator of the electric dipole, we obtain the interaction (10) in the following form:

$$\hat{H}_{INT} = -\frac{e}{mc} \sum_{\vec{n},\nu} \vec{P}^{(\nu)}_{\vec{n}\nu} \cdot \vec{A}_{\vec{n}} = -\frac{i}{\hbar c} \sum_{\vec{n},\nu} [\vec{d}^{(\nu)}_{\vec{n}}, \hat{H}_{EX}] \cdot \vec{A}_{\vec{n}} \ , \qquad (11)$$
$$\nu \in (N, I, II)$$

and after expressing $\vec{d}$ in terms of exciton operators (11) and vector potential in terms of photon-operators we finaly find:

$$\hat{H}_{INT} = \sum_{\vec{k} j \nu} [W_{\vec{k}}(\nu,j) B_{-\vec{k}\nu}(b_{\vec{k}j} + b^{+}_{-\vec{k}j}) - W^{*}_{\vec{k}}(\nu j) B^{+}_{\vec{k}\nu}(b_{\vec{k}j} + b^{+}_{-\vec{k}j})] \qquad (12)$$

where

$$W_{\vec{k}}(\nu,j) = -i\left(\frac{2\pi N}{V\hbar c k}\right)^{1/2} [u_j(\vec{k}) + v_j(\vec{k})] (\vec{D}_{0\nu} \vec{l}_{\vec{k}j}) E_\nu(\vec{k}) \ . \qquad (13)$$

The functions u and v figuring in W are due to the diagonalization of the vacuum photons Hamiltonian and a part of the retarded interaction proportional to the square of vector potential. The explicit form of u and v can be found in [3].

So, the total Hamiltonian of the system, including excitons ( the usual as well as the kinematical ones ), photons and their interactions can be written in the form

$$\hat{H} = \sum_{\vec{k}\nu} E_\nu(\vec{k}) B^+_{\vec{k}\nu} B_{\vec{k}\nu} + \sum_{\vec{k}j} \varepsilon_j(\vec{k}) b^+_{\vec{k}j} b_{\vec{k}j} + \\ + \sum_{\vec{k}\nu j} [W_{\vec{k}}(\nu,j) B_{-\vec{k}\nu} - W^*_{\vec{k}}(\nu,j) B^+_{\vec{k}\nu}](b_{\vec{k}j} + b^+_{-\vec{k}j}) . \tag{14}$$

After the canonical transformation

$$B_{\vec{k}\nu} = \sum_{\rho} [u_{\vec{k}\nu}(\rho) \eta_{\vec{k}\rho} + v^*_{-\vec{k}\nu}(\rho) \eta^+_{-\vec{k}\rho}]$$

$$b_{\vec{k}j} = \sum_{\rho} [u_{\vec{k}j}(\rho) \eta_{\vec{k}\rho} + v^*_{-\vec{k}j}(\rho) \eta^+_{-\vec{k}\rho}] ,$$

the Hamiltonian (14) reduces to

$$\hat{H} = \mathcal{E}_0 + \sum_{\vec{k}\rho} \mathcal{E}_\rho(\vec{k}) \eta^+_{\vec{k}\rho} \eta_{\vec{k}\rho} , \quad ; \quad \rho = 1, 2, 3, 4, 5 .$$

The functions u and v as well as the energies $\mathcal{E}_\rho(\vec{k})$ are defined by the system of equations

$$[\mathcal{E}_\rho(\vec{k}) - E_\nu(\vec{k})] u_{\vec{k}\nu}(\rho) - \sum_j W^*_{\vec{k}}(\nu,j)[u_{\vec{k}j}(\rho) + v^*_{-\vec{k}j}(\rho)] = 0$$

$$[\mathcal{E}_\rho(\vec{k}) + E_\nu(\vec{k})] v_{\vec{k}\nu}(\rho) - \sum_j W^*_{\vec{k}}(\nu j)[u^*_{-\vec{k}j}(\rho) + v_{\vec{k}j}(\rho)] = 0 \tag{17}$$

$$[\mathcal{E}_\rho(\vec{k}) - \varepsilon_j(\vec{k})] u_{\vec{k}j}(\rho) - \sum_\nu [W_{\vec{k}}(\nu,j) u_{\vec{k}\nu}(\rho) + W^*_{-\vec{k}}(\nu,j) v^*_{-\vec{k}\nu}(\rho)] = 0$$

$$[\mathcal{E}_\rho(\vec{k}) + \varepsilon_j(\vec{k})] v_{\vec{k}j}(\rho) - \sum_\nu [W^*_{-\vec{k}}(\nu j) u^*_{\vec{k}\nu}(\rho) - W_{-\vec{k}}(\nu,j) v_{\vec{k}\nu}(\rho)] = 0$$

$$\nu \in (N, I, II) \; ; \quad j \in (1, 2) \; , \quad \rho \in (1, 2, 3, 4, 5).$$

The secular equation of the system (17) requires the numerical calculations, but independently, one can easily conclude that all energies $\mathcal{E}_\rho(\vec{k})$ have imaginary parts, and consequently, all excitations of the system have finite life-time. This is a very important conclusion which leads to the idea that the large broadening of optical excitations lines ( about 300 $cm^{-1}$) is due to the presence of kinematical levels. Such a large broadening could not be theoretically explained as an effect of exciton-phonon interaction.

ACKNOWLEDGMENT

The author would like to express her gratitude to Prof. B.S.Tošić for having suggested this problem and numerous discussions and suggestions.

REFERENCES:

1 V.M.Agranovič, ŽETP 37, 430 (1959)

2 D.Hadžiahmetović, M.Pirić and B.S.Tošić, Phys.Stat. Sol. (b) 83, 479 (1977)

3 M.M.Marinković, I.Maksimov, Ž.Škrbić, Physica 80 c. 585 (1975)