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DAVYDOV SPLITTING AND KINEMATICAL INTERACTION OF EXCITONS

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Abstract. The molecular crystal with the complex lattice was analysed at the low as well as at the high exciton concentrations.It was shown that apart from normal exciton levels the same number of kinematical levels exist in the system, and they have the same splitting.The ordering parameter of the system at the high concentrations was determined, too.

The influence of the kinematical interaction of excitons on the Davydov splitting of exciton zones will be analysed.The analysis of the high concentration effects in a molecular crystal with σ sublattices will be carried out, too.For this purpose the symbolical, matrix method of analysis of crystals with the complex lattice will be developed.

The Hamiltonian of the crystal (in the case of two level exciton scheme) can be written as follows:

$$\hat{H} = H_0 + \sum_{\vec{n}\theta} \Delta_\theta P_\theta^+(\vec{n}) P_\theta(\vec{n}) + \sum_{\vec{n}\vec{m}\theta\omega} X_{\theta\omega}(\vec{n}-\vec{m}) P_\theta^+(\vec{n}) P_\omega(\vec{m}) + \sum_{\vec{n}\vec{m}\theta\omega} Y_{\theta\omega}(\vec{n}-\vec{m}) P_\theta^+(\vec{n}) P_\theta(\vec{n}) P_\omega^+(\vec{m}) P_\omega(\vec{m}), \quad \theta,\omega \in (1,2,\dots\sigma). \qquad (1)$$

The operators $P_\theta^+(\vec{n})$ and $P_\theta(\vec{n})$ create and annihilate the excitation at the molecule placed at $\vec{n} + \vec{S}_\theta(\vec{n})$ and they satisfy the Pauli commutation relations.The meaning of the other notations in the formula (1) are given in the monograph[1].

The system of excitons will be analysed with help of the Green's function $\Gamma_{\alpha\beta}(\vec{a},\vec{b},t)=\langle\langle P_\alpha(\vec{a}t)|P^+_\beta(\vec{b}0)\rangle\rangle$. According to the general theory of two-time temperature Green's functions[2], the equation for the function Γ is the following:

$$i\frac{d}{dt}\Gamma_{\alpha\beta}(\vec{a},\vec{b},t)=i\,\delta(t)\,\delta_{\vec{a}\vec{b}}\,\delta_{\alpha\beta}\,(1-2\mathcal{L}_{\alpha\alpha})\;+$$
$$+\sum_{\vec{m}\omega}Z_{\alpha\omega}(\vec{a}-\vec{m})\,\Gamma_{\omega\beta}(\vec{m},\vec{b},t)\;-$$
$$-2\sum_{\vec{m}\omega}\Big[X_{\alpha\omega}(\vec{a}-\vec{m})\langle\langle P^+_\alpha(\vec{a}t)P_\alpha(\vec{a}t)P_\omega(\vec{m}t)|P^+_\beta(\vec{b}0)\rangle\rangle\;-$$
$$-Y_{\alpha\omega}(\vec{a}-\vec{m})\langle\langle P^+_\omega(\vec{m}t)P_\omega(\vec{m}t)P_\alpha(\vec{a}t)|P_\beta(\vec{b}0)\rangle\rangle\Big],\qquad(2)$$

where $Z_{\alpha\beta}(\vec{a}-\vec{b})=\Delta_\alpha\delta_{\alpha\beta}\delta_{\vec{a}\vec{b}}+X_{\alpha\beta}(\vec{a}-\vec{b})$ and $\mathcal{L}_{\alpha\alpha}=\langle P^+_\alpha(\vec{a}t)P_\alpha(\vec{a}t)\rangle$ does not depend on $\vec{a}$ and t. Further analysis will be carried out in terms of Bose operators B and B^+, because kinematical effects are already and most adequately included into calculations by the Bose representation of Pauli operators. According to the formulae from[3] we shall take approximately

$$P_\alpha(\vec{a}t)=B_\alpha(\vec{a}t)-B^+_\alpha(\vec{a}t)B_\alpha(\vec{a}t)B_\alpha(\vec{a}t)$$
$$P^+_\beta(\vec{a}0)=B^+_\beta(\vec{a}0)-B^+_\beta(\vec{a}0)B^+_\beta(\vec{a}0)B_\beta(\vec{a}0).\qquad(3)$$

Using the Wick's theorem for Bose operators the paulion Green's functions will be decoupled in the following way:

$$\Gamma_{\alpha\beta}(\vec{a},\vec{b},t)=G_{\alpha\beta}(\vec{a},\vec{b},t)-2N_{\beta\beta}\,G_{\alpha\beta}(\vec{a},\vec{b},t)-2N_{\alpha\alpha}\,G_{\alpha\beta}(\vec{a},\vec{b},t)\;+$$
$$+\;2D_{\beta\alpha}(\vec{b},\vec{a},t)\,G^2_{\alpha\beta}(\vec{a},\vec{b},t)+O\big[N^2_{\alpha\beta}(\vec{a},\vec{b})\big],$$

$$\langle\langle P^+_\alpha(\vec{a}t) P_\alpha(\vec{a}t) P_\omega(\vec{m}t) | P^+_\beta(\vec{b}0)\rangle\rangle =$$

$$= N_{\alpha\alpha} G_{\omega\beta}(\vec{m},\vec{b},t) + N_{\omega\alpha}(\vec{m},\vec{a}) G_{\alpha\beta}(\vec{a},\vec{b},t) -$$

$$- 2 D_{\alpha\beta}(\vec{b},\vec{a},t) G_{\alpha\beta}(\vec{a},\vec{b},t) G_{\omega\beta}(\vec{m},\vec{b},t) +$$

$$+ O[N^2_{\alpha\beta}(\vec{a},\vec{b})], \qquad (4)$$

where $D_{\alpha\beta}(\vec{a},\vec{b},t) = \langle\langle B^+_\beta(\vec{b}t) | B_\alpha(\vec{a}0)\rangle\rangle$,

$$G_{\alpha\beta}(\vec{a},\vec{b},t) = \langle\langle B_\alpha(\vec{a}t) | B^+_\beta(\vec{b}0)\rangle\rangle, \quad N_{\alpha\beta}(\vec{a},\vec{b}) = \langle B^+_\beta(\vec{b}t) B_\alpha(\vec{a}t)\rangle,$$

$$N_{\alpha\alpha} = \langle B^+_\alpha(\vec{a}t) B_\alpha(\vec{a}t)\rangle, \quad N_{\alpha\alpha} \approx \mathcal{L}_{\alpha\alpha}. \qquad (5)$$

After going over to the Fourier components

$$A_{\alpha\beta}(\vec{a},\vec{b},t) = \frac{1}{N}\sum_{\vec{k}} \int_{-\infty}^{+\infty} dE\, A_{\alpha\beta}(\vec{k},E)\, e^{i\vec{k}(\vec{a}-\vec{b}) - iEt}$$

$$C_{\alpha\beta}(\vec{a},\vec{b}) = \frac{1}{N}\sum_{\vec{k}} C_{\alpha\beta}(\vec{k})\, e^{i\vec{k}(\vec{a}-\vec{b})} \qquad (6)$$

and introducing the matrices: $\hat{A} = \| A_{\alpha\beta} \|$, $\hat{A}_d = \| A_{\alpha\alpha}\delta_{\alpha\beta} \|$, $\hat{E} = E\cdot\hat{1}$ and $\hat{1} = \|\delta_{\alpha\beta}\|$, the system of equations (2) can be written in the matrix form as follows:

$$[\hat{E} - \hat{Z}(\vec{k})]\, \hat{\Gamma}(\vec{k},E) = \frac{i}{2\pi}(\hat{1} - 2\hat{N}_d) -$$

$$- 2N^{-1}\sum_{\vec{q}} \{ \hat{N}_d(\vec{q}) \hat{X}(\vec{k}) \hat{G}(\vec{k},E) + [\hat{X}(\vec{q})\hat{N}(\vec{q})]_d \hat{G}(\vec{k},E) -$$

$$- [S_p(\hat{Y}(0)\hat{N}_d(\vec{q}))]_d \hat{G}(\vec{k},E) - [\hat{Y}(\vec{k}-\vec{q}) \otimes \hat{N}(\vec{q})] \hat{G}(\vec{k},E)\} +$$

$$+ 4N^{-2}\sum_{\vec{q}_1,\vec{q}_2} \int_{-\infty}^{+\infty} dE_1\, dE_2 \{[\hat{G}(\vec{q}_1,E_1) \otimes \tilde{\hat{D}}(\vec{q}_2,E_2)] \otimes [\hat{X}(\vec{q}_3)\hat{G}(\vec{q}_3,\tilde{E}_3)] -$$

$$- [(\hat{Y}(\vec{k}-\vec{q}_1) \otimes \tilde{\hat{D}}(\vec{q}_2,E_2)) \hat{G}(\vec{q}_3,\tilde{E}_3)] \otimes \hat{G}(\vec{q}_1,E_1)\},$$

$$\hat{\Gamma}(\vec{k},E) = \hat{G}(\vec{k},E)[\hat{1} - 2\hat{N}_d - 2\hat{G}^{-1}(\vec{k},E)\hat{N}_d\hat{G}(\vec{k},E) +$$

$$+ \frac{2}{N^2}\sum_{\vec{q}_1,\vec{q}_2}\int_{-\infty}^{+\infty} dE_1 dE_2\, \hat{G}(\vec{q}_1,E_1)\otimes\hat{\tilde{D}}(\vec{q}_2,E_2)\otimes\hat{G}(\vec{q}_3,\tilde{E}_3)\,, \tag{7}$$

where: $\vec{q}_3 = \vec{k} - \vec{q}_1 + \vec{q}_2$, $\tilde{E}_3 = E - E_1 - E_2$, $\hat{A}\hat{B} = \| \sum_{\gamma} A_{\alpha\gamma}B_{\gamma\beta} \|$,

$\hat{A}\otimes\hat{B} = \| A_{\alpha\beta}B_{\alpha\beta} \|$, $[\hat{A}\hat{B}]_d = \| \delta_{\alpha\beta}\sum_{\gamma} A_{\alpha\gamma}B_{\gamma\alpha} \|$, $[S_r(\hat{A}\hat{B})]_d = \| \delta_{\alpha\beta}\sum_{\gamma\gamma'} A_{\alpha\gamma}B_{\delta\delta'} \|$,

and $\sim$ denotes the transposition of the matrix.

As the first step the equation (7) will be solved in the zero order approximation, consisting in the substitution $\hat{\Gamma} \approx \hat{G}$ and omitting all terms proportional to $\hat{N}$ and $\hat{G}\hat{D}\hat{G}$. As the result we obtain:

$$\hat{G}^{(0)}(\vec{k},E) = [\hat{E} - \hat{U}_z^{-1}\hat{Z}(\vec{k})\hat{U}_z]^{-1}\frac{i}{2\bar{u}}\,, \quad \hat{G}^{(0)}(\vec{k},E) = \hat{U}_z^{-1}\hat{G}(\vec{k},E)\hat{U}_z\,,$$

$$\hat{N}^{(0)}(\vec{k}) = 2\int_{-\infty}^{+\infty} dE\, \frac{\mathrm{Re}\,\hat{G}^{(0)}(\vec{k},E)}{e^{E/\tau} - 1} = \left\| \frac{\delta_{\alpha\beta}}{e^{\frac{\Omega_{\alpha\alpha}}{\tau}} - 1} \right\|, \quad \hat{U}_z^{-1}\hat{Z}(\vec{k})\hat{U}_z = \| \Omega_{\alpha\alpha}(\vec{k})\delta_{\alpha\beta} \| \tag{8}$$

$$\tau = k_B T$$

The zero order matrices $G^{(0)}$ and $N^{(0)}$ are diagonal.

Iterating (7), i.e. substituting matrices $\hat{G}$, $\hat{D}$, $\hat{N}$ and $\hat{\mathcal{L}}$ by their zero order values, we obtain the following equation for the boson Green's function:

$$[\hat{E} - \hat{F}(\vec{k})]\hat{G}(\vec{k},E) = \frac{i}{2\bar{u}}(\hat{1} + 2\hat{N}^{(0)})[\hat{1} + 2\bar{u}i\hat{W}(\vec{k},E)]^{-1} +$$

$$+ O(\hat{N}\hat{G}^3)\,, \tag{9}$$

where:

$$\hat{M}(\vec{k}) = \| N^{-1}\sum_{\vec{q}}[\delta_{\alpha\beta}Y_{\alpha\alpha}(\vec{k}-\vec{q})N_{\alpha\alpha}^{(0)}(\vec{q}) + \delta_{\alpha\beta}\sum_{\gamma}Y_{\alpha\gamma}(0)N_{\gamma\gamma}^{(0)}(\vec{q}) - \delta_{\alpha\beta}X_{\alpha\alpha}(\vec{q})N_{\alpha\alpha}^{(0)}(\vec{q}) -$$

$$- X_{\alpha\beta}(\vec{k})N_{\alpha\alpha}^{(0)}(\vec{q})]\|\,, \quad N_{\alpha\alpha}^{(0)}(\vec{k}) = [e^{\frac{\Omega_{\alpha\alpha}(\vec{k})}{\tau}} - 1]^{-1}\,,$$

$$\hat{W}(\vec{k},E) = \| \frac{2}{N^2}\sum_{\vec{q}_1\vec{q}_2}\int_{-\infty}^{+\infty} dE_1 dE_2\, [2X_{\alpha\alpha}(\vec{q}_3) - 2Y_{\alpha\alpha}(\vec{k}-\vec{q}_1) - E + \Omega_{\alpha\alpha}(\vec{k})] \times$$

$$\times G^{(0)}_{\alpha\alpha}(\vec{q}_1, E_1)\, G^{(0)}_{\alpha\alpha}(\vec{q}_2, E_2)\, G^{(0)}_{\alpha\alpha}(\vec{q}_3, E_3) \| \,, \quad E_3 = E - E_1 + E_3 \tag{10}$$

With the help of the unitary matrix $\hat{U}_Q$ we diagonalize the matrix

$$\hat{Q}(\vec{k}, E) = [\hat{E} - \hat{F}(\vec{k})]^{-1} [\hat{1} - 2\hat{N}^{(0)}] [\hat{1} + 2\bar{u} i \hat{W}(\vec{k}, E)]^{-1} \tag{11}$$

In the case of the crystal with two sublattices, taking in (9) $\hat{F} \approx \hat{Z}$, $\hat{1} + 2\hat{N}^{(0)} \approx \hat{1}$ and neglecting the spatial dispersion: $X_{\alpha\beta}(\vec{k}), Y_{\alpha\beta}(\vec{k}) \to X_{\alpha\beta}, Y_{\alpha\beta}$ we obtain after diagonalization

$$\hat{G}(E) = \frac{i}{2\bar{u}} \frac{1}{(E-\Omega_{11})(E-\Omega_{22})(E-\varphi_{11})(E-\varphi_{22})} \begin{Vmatrix} p(E)+q(E) & 0 \\ 0 & p(E)-q(E) \end{Vmatrix} \tag{12}$$

where

$$\Omega_{11,22} = \frac{\Delta_1 + \Delta_2 + X_{11} + X_{22}}{2} \pm \left[\left(\frac{\Delta_1 - \Delta_2 + X_{11} - X_{22}}{2} \right)^2 + X_{12} X_{21} \right]^{1/2}, \tag{13}$$

are the energies of the normal exciton levels, and

$$\varphi_{\alpha\alpha} = \Omega_{\alpha\alpha} + \frac{2}{3} (X_{\alpha\alpha} - Y_{\alpha\alpha}), \quad \alpha = 1, 2 \tag{14}$$

are the energies of the kinematical ones.

As we see the kinematical levels are shifted with respect to the normal levels for $\frac{2}{3}(X_{\alpha\alpha} - Y_{\alpha\alpha})$ .It means that the Davydov splitting between kinematical levels is the same as between normal levels.

The matrix method will be applied also to high concentration analysis of the exciton system. In this case, the higher order paulion Green's function, figuring in (2) will be decoupled as follows[2]:

$$\langle\langle P^+_\alpha(\vec{a}t) P_\alpha(\vec{a}t) P_\omega(\vec{m}t) | P^+_\beta(\vec{b}0) \rangle\rangle = \mathcal{L}_{\alpha\alpha} \Gamma_{\omega\beta}(\vec{m}, \vec{b}, t),$$

$$\langle\langle P^+_\omega(\vec{m}t) P_\omega(\vec{m}t) P_\alpha(\vec{a}t) | P^+_\beta(\vec{b}0) \rangle\rangle = \mathcal{L}_{\omega\omega} \Gamma_{\alpha\beta}(\vec{a}, \vec{b}, t) \tag{15}$$

So we obtain the following matrix equation which defines the Green's functions $\Gamma_{\alpha\beta}(\vec{k},E)$:

$$[\hat{E}-\hat{J}(\vec{k})]\hat{\Gamma}(\vec{k},E)=\frac{\hat{i}}{2\bar{u}}(\hat{1}-2\hat{\mathcal{L}}_d) \tag{16}$$

where $\hat{\mathcal{L}}_d=\|\mathcal{L}_{\alpha\alpha}\delta_{\alpha\beta}\|$,

$$\hat{J}(\vec{k})=\|Z_{\alpha\beta}(\vec{k})-2\mathcal{L}_{\alpha\alpha}X_{\alpha\beta}(\vec{k})+2\delta_{\alpha\beta}\sum_{\gamma}Y_{\alpha\gamma}(0)\mathcal{L}_{\gamma\gamma}\| \tag{17}$$

Introducing the unitary matrix $\hat{U}_J$ which diagonalizes the matrix $\hat{J}(\vec{k})$ i.e. $\hat{J}(\vec{k})\hat{U}_J=\hat{U}_J\hat{I}(\vec{k})$, $\hat{I}(\vec{k})=\|I_{\alpha\alpha}(\vec{k})\delta_{\alpha\beta}\|$ we obtain

$$\hat{\Gamma}_U(\vec{k},E)=[\hat{E}-\hat{I}(\vec{k})]^{-1}\frac{i}{2\bar{u}}(\hat{1}-2\hat{\mathcal{L}}_d),\quad \hat{\Gamma}_U(\vec{k},E)=\hat{U}_J^{-1}\hat{\Gamma}(\vec{k},E)\hat{U}_J \tag{18}$$

and $\hat{\mathcal{L}}(\vec{k})=2\int_{-\infty}^{+\infty}dE(e^{\frac{E}{\tau}}-1)\,\mathrm{Re}\,\hat{\Gamma}_U(\vec{k},E)=$

$$=\|[\delta_{\alpha\beta}-2\sum_{\gamma}\mathcal{L}_{\gamma\gamma}U^{*(J)}_{\alpha\gamma}U^{(J)}_{\gamma\beta}][e^{\frac{I_{\alpha\alpha}(\vec{k})}{\tau}}-1]^{-1}\| \tag{19}$$

As we see the occupation number matrix is not diagonal, and the actual occupation numbers are obtained by their diagonalization with the help of the unitary matrix $\hat{U}_{\mathcal{L}}$ i.e.:

$$\hat{\mathcal{L}}(\vec{k})\hat{U}_{\mathcal{L}}=\hat{U}_{\mathcal{L}}\hat{\mathcal{D}}(\vec{k}),\quad \hat{\mathcal{D}}(\vec{k})=\|\mathcal{D}_{\alpha\alpha}(\vec{k})\delta_{\alpha\beta}\| \tag{20}$$

So, the exciton energies at high concentrations are given by $I_{\alpha\alpha}(\vec{k})$ and the corresponding occupation numbers by $\mathcal{D}_{\alpha\alpha}(\vec{k},T)$.

It should be notticed that the mean values $\mathcal{L}_{\alpha\beta}(\vec{k})$ for $\alpha\neq\beta$ are different from zero..It means that the processes of simultaneous extinguishment and appearance of excitons of the different kinds also contribute to the ordering parameter of the system

$$\mu(T)=1-\frac{1}{N}\sum_{\vec{k}\alpha}\mathcal{D}_{\alpha\alpha}(\vec{k},T) \tag{21}$$

and, consequently, have an influence on phase transitions[4] in the system, but their contribution cannot be obtained without numerical computing.

References

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