NON-LINEAR OPTICAL EFFECTS AND ABSORPTION OF LIGHT

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ABSTRACT: The role of non-linear excitonic effects in absorption phenomena was analysed. It was shown that non-linear effects essentially define the dielectric properties of molecular crystals, such as refraction index as well as absorption coefficient.

The existing analysis of the absorption phenomena in crystals are namely founded on the idea that the basic mechanism which characterizes these phenomena is the exciton-phonon interaction (see 1,2).There is no doubt that exciton-phonon interaction plays an important, sometimes dominant role during the light absorption in condensed medium, but in our opinion, the role of other mechanisms must not be neglected especially exciton-exciton interaction.

The reason of the underestimation of the non-linear optical effects in the theoretical treatment of the absorption phenomena lays in the uncorrect application of the Green's function method. In the usual approach, higher exciton GF are decoupled in such a way that only those operators acting in the same moment of time are contracted. This introduces only minor corrections of exciton energies and infinite lifetimes of elementary excitations. In the limits of this approach and based on these results, one can easily conclude that non-linear optical effects can not play an important role in the absorption phenomena.

The correct application of the GF method, in which the higher GF are decoupled so that the operators acting in different moments are contracted too, changes at once the above described picture, leads to finite quasi-particle lifetimes and indicates that exciton-exciton interaction cannot be neglected in absorption phenomena.

The aim of this paper is to investigate the role of the non-linear optical effects in the light absorption phenomena.

Using the known procedure (see 1) which connects the dielectric permeability tensor with the exciton GF, we get the following connection:

$$\Delta^{-1}_{\alpha\beta}(\vec{K},\omega) = \frac{c^2}{\omega^2}\left\{\delta_{\alpha\beta} - i\frac{\mathcal{C}_0 \Lambda_\alpha \Lambda_\beta}{4\pi}\left[\Gamma(\vec{K},\omega) + \tilde{\Gamma}(\vec{K},\omega) + \Lambda(\vec{K},\omega) + \tilde{\Lambda}(\vec{K},\omega)\right]\right\} \tag{1.1}$$

where $\Delta_{\alpha\beta}(\vec{K},\omega) = K^2\delta_{\alpha\beta} - K_\alpha K_\beta - \frac{\omega^2}{c^2}\varepsilon_{\alpha\beta}(\vec{K},\omega)$

In the above relations the following simbols are used: $\varepsilon_{\alpha\beta}(\vec{K},\omega)$ is the dielectric permeability tensor, C is the speed of light, Λ is the vector amplitude of the electric field, $\mathcal{C}_0 = \frac{V}{\mathcal{N}}$ where V is the crystal volume and $\mathcal{N}$ is the number of cells in the crystal. $\Gamma, \tilde{\Gamma}, \Lambda, \tilde{\Lambda}$ are the retarded and advanced exciton GF.

We shall calculate the exciton GF given in formula (1.1) for the exciton Hamiltonian of the following form:

$$\hat{H} = \Delta\sum_{\vec{n}} P^+_{\vec{n}} P_{\vec{n}} + \sum_{\vec{n}\vec{m}} X_{\vec{n}\vec{m}} P^+_{\vec{n}} P_{\vec{m}} + \frac{1}{2}\sum_{\vec{n}\vec{m}} Y_{\vec{n}\vec{m}}\left(P^+_{\vec{n}} P^+_{\vec{m}} + P_{\vec{m}} P_{\vec{n}}\right) + \sum_{\vec{n}\vec{m}} Z_{\vec{n}\vec{m}} P^+_{\vec{n}} P_{\vec{n}} P^+_{\vec{m}} P_{\vec{m}} \tag{1.2}$$

Here Δ is the isolated molecule excitation energy, while X, Y and Z are matrix ellements of dipol-dipol interaction. The order of magnitude of $\Delta \sim 5eV$ while X, Y and Z are 10-100 times smaller. We shall suppose that X, Y and Z are real and even. Other details on this Hamiltonian can be found in the Ref.4.

Following the general theory of double-time temperature dependant GF[5] from (1.2) one obtains the equations of motion for Γ and Λ:

$$i\hbar\frac{d}{dt}\Gamma_{\vec{f}\vec{g}}(t) - \Delta\Gamma_{\vec{f}\vec{g}}(t) - \sum_{\vec{m}}\left[X_{\vec{f}\vec{m}}\Gamma_{\vec{m}\vec{g}}(t) + Y_{\vec{f}\vec{m}}\Lambda_{\vec{m}\vec{g}}(t)\right] = i\hbar\delta(t)\delta_{\vec{f}\vec{g}}\left[1 - 2\langle P^+_{\vec{f}}(0) P_{\vec{f}}(0)\rangle\right] -$$

$$- 2\sum_{\vec{m}}\left[X_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{f}}(t) P_{\vec{f}}(t) P_{\vec{m}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle + Y_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{m}}(t) P^+_{\vec{f}}(t) P_{\vec{f}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle - Z_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{m}}(t) P_{\vec{m}}(t) P^+_{\vec{f}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle\right]$$

$$i\hbar\frac{d}{dt}\Lambda_{\vec{f}\vec{g}}(t) + \Delta\Lambda_{\vec{f}\vec{g}}(t) + \sum_{\vec{m}}\left[X_{\vec{f}\vec{m}}\Lambda_{\vec{m}\vec{g}}(t) + Y_{\vec{f}\vec{m}}\Gamma_{\vec{m}\vec{g}}(t)\right] = 2\sum_{\vec{m}}\left[X_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{m}}(t) P^+_{\vec{f}}(t) P_{\vec{f}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle + \right.$$

$$\left. + Y_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{f}}(t) P_{\vec{f}}(t) P_{\vec{m}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle - Z_{\vec{f}\vec{m}}\langle\langle P^+_{\vec{f}}(t) P^+_{\vec{m}}(t) P_{\vec{m}}(t) \mid P^+_{\vec{g}}(0)\rangle\rangle\right] \tag{1.3}$$

The essential element of further analysis is the treatment of higher (Paulion) GF appering on the right hand side of the system (1.3). The direct decoupling of higher Paulionic GF, as

in [5] would give only minor corrections to the energy and infinite lifetimes, so the influence of non-linear effects on the absorption phenomena would be neglected [2]. In order to obtain finite lifetimes one should set the system of equations of motion for higher Paulionic GF, which would extremlly complicate the calculations. It is much simpler to express higher Paulionic GF in terms of Boson GF and decouple them strictly according to the Wick's theorem. First, we must express Pauli-operators in terms of Bose-operators B^+ and B, using the exact boson representation for Pauli-operators [6] in the approximate form:

$$P = B - B^+BB \quad ; \quad P^+ = B^+ - B^+B^+B \tag{1.4}$$

After the substitution of (1.4), higher Paulionic GF are decoupled after the following scheme:

$$\ll P_a^+ P_b P_c | P_d^+ \gg = N_{ba} G_{cd} + N_{ca} G_{bd} + \tilde{M}_{cb} T_{ad} - 2(G_{bd} G_{cd} \tilde{G}_{ad} + G_{bd} T_{ad} \tilde{T}_{cd} + G_{cd} T_{ad} \tilde{T}_{bd})$$

$$\ll P_a^+ P_b^+ P_c | P_d^+ \gg = M_{ba} G_{cd} + N_{ca} T_{bd} + N_{cb} T_{ad} - 2(T_{ad} T_{bd} \tilde{T}_{cd} + T_{bd} G_{cd} \tilde{G}_{ad} + T_{ad} G_{cd} \tilde{G}_{bd})$$

$$G_{ab} \equiv \ll B_a(t) | B_b^+(0) \gg ; \quad \tilde{G}_{ab} \equiv \ll B_a^+(t) | B_b(0) \gg ; \quad T_{ab} \equiv \ll B_a^+(t) | B_b^+(0) \gg$$

$$\tilde{T}_{ab} \equiv \ll B_a(t) | B_b(0) \gg ; \quad N_{ab} \equiv \langle B_b^+(t) B_a(t) \rangle ; \quad M_{ab} \equiv \langle B_b^+(t) B_a^+(t) \rangle$$

$$\tilde{M}_{ab} \equiv \langle B_b(t) B_a(t) \rangle ; \quad N_{aa} \equiv N ; \quad M_{aa} \equiv M ; \quad \tilde{M}_{aa} \equiv \tilde{M} \tag{1.5}$$

One should mention that in (1.5) all terms proportional to the square of exciton concentration are neglected. As (1.4) is only approximate, all terms containg products of more than three GF are also dropped.

Further calculation is standard, but rather complicated, and will not be given here. We use the approximations of the nearest neighbor interaction and the small wave vectors, neglecting all the terms of the order $\left(\frac{\gamma}{\Delta}\right)^2$ and the spatial dispersion.

The final result is the following:

$$\Gamma(\omega) = \frac{i}{2\pi} \left[\left(\frac{1}{\mu} + \frac{C_1}{\mu^2} - \frac{C_2}{\mu^2 \eta} \right) - i \left(\frac{D_1}{\mu^2} + \frac{D_2}{\mu \eta} \right) \right]$$

$$\Lambda(\omega) = -\frac{i}{2\pi} 6\Omega_\gamma \left[\left(\frac{1+C_3}{\mu \eta} + \frac{C_1}{\mu^2 \eta} \right) - i \left(\frac{D_3}{\mu \eta} + \frac{D_4}{\eta} \right) \right] \tag{1.6}$$

$$\mu = \omega - \Omega_\Delta \; ; \quad \eta = \omega + \Omega_\Delta \; ; \quad \Omega_\Delta = \hbar^{-1} \Delta ; \quad \tilde{\Gamma}(\omega) = \Gamma(-\omega) ; \quad \tilde{\Lambda}(\omega) = \Lambda(-\omega)$$

where: $C_1 = \frac{6\Omega_y^2}{\Omega_\Delta}$; $C_2 = \frac{36\Omega_x\Omega_y^2}{\Omega_\Delta}\left(1-\frac{\Omega_z}{\Omega_x}\right)$; $C_3 = \frac{\Omega_x}{\Omega_\Delta}\left(1-\frac{\Omega_z}{\Omega_x}\right)$

$$D_1 = \frac{Q^4}{32\pi^3}\left[3\frac{\Omega_y^2}{\Omega_x^2} + \left(3-\tfrac{1}{2}Q^2\right)\left(1-\frac{\Omega_z}{\Omega_x}\right) - \frac{3\Omega_y^2}{\Omega_x\Omega_\Delta}\left(6-\tfrac{1}{2}Q^2\right)\right] ; \quad D_2 = \frac{Q^4}{32\pi^3}\frac{3\Omega_y^2}{\Omega_x}\left(\tfrac{1}{2}Q^2-6\right)$$

$$D_3 = \frac{Q^4}{32\pi^3}\left\{\tfrac{1}{2}Q^2\left[\frac{\Omega_x}{\Omega_x^2} - \frac{6\Omega_x}{\Omega_\Delta}\left(1-\frac{\Omega_z}{\Omega_x}\right) + \frac{6\Omega_y^2}{\Omega_x\Omega_\Delta}\right] + 3\left[\frac{\Omega_y^2}{\Omega_x^2} - 1 + \frac{6\Omega_x}{\Omega_\Delta}\left(1-\frac{\Omega_z}{\Omega_x}\right) - \frac{6\Omega_y^2}{\Omega_x\Omega_\Delta}\right]\right\}$$

$$D_4 = \frac{Q^4}{32\pi^3}\left\{\frac{1}{\Omega_x} - \frac{3}{\Omega_\Delta} - \frac{6\Omega_z}{\Omega_x\Omega_\Delta} - \frac{1}{4}Q^2\left[\frac{1}{6\Omega_x} - \frac{1}{\Omega_\Delta}\left(1-\frac{\Omega_z}{\Omega_x}\right)\right]\right\} ; \quad Q = (6\pi^2)^{1/3} ; \quad \Omega_\alpha = \hbar^{-1}R_\alpha$$

$$\alpha \in (X, Y, Z) \qquad (1.7)$$

Here X, Y and Z are the matrix elements of the dipol-dipol interaction between the nearest neighbours.

Now, one can finally calculate dielectric constant $\varepsilon(\omega)$, refraction index $n(\omega)$ and absorption coefficient $\varkappa(\omega)$. In the isotropic approximation $\Delta_{\alpha\beta}(\vec{k},\omega) = -\frac{\omega^2}{c^2}\varepsilon(\omega)\delta_{\alpha\beta}$ and $\Delta_{\alpha\beta} = E_0^2\delta_{\alpha\beta}$ so by combining (1.1) and (1.6) we arrive to:

$$\varepsilon(x) = \beta_1(x) + i\gamma(x) ; \quad x = \frac{\omega}{\Omega_\Delta} ; \quad \beta_1(x) = \frac{(x^2-1)^2(x^4+\alpha_1 x^2+\alpha_2)}{(x^4+\alpha_1 x^2+\alpha_2)^2 + \beta_1^2(x^2-1)^2}$$

$$\gamma(x) = \frac{\beta_1(x^2-1)^3}{(x^4+\alpha_1 x^2+\alpha_2)^2+\beta_1^2(x^2-1)^2} ; \quad \alpha_1 \approx \gamma - 2 ; \quad \alpha_2 \approx 1-\gamma ; \quad \beta_1 \approx \gamma ; \quad \gamma = \frac{E_0^2\tau_0}{4\pi\hbar\Omega_\Delta} \qquad (1.8)$$

From the relation $n(\omega) + i\varkappa(\omega) = \sqrt{\varepsilon(\omega)}$ we obtain:

$$n(x) = \frac{|(x^2-1)|}{\sqrt{2}}\left\{\frac{\sqrt{p^2(x)+q^2(x)} + p(x)}{p^2(x)+q^2(x)}\right\}^{1/2}$$

$$\varkappa(x) = \frac{|(x^2-1)|}{\sqrt{2}}\left\{\frac{\sqrt{p^2(x)+q^2(x)} - p(x)}{p^2(x)+q^2(x)}\right\}^{1/2}$$

$$p(x) = x^4 + (\gamma-2)x^2 + 1 - \gamma \quad ; \quad q(x) = \gamma(x^2-1) \qquad (1.9)$$

The estimation of the coefficients α_1, α_2 and β_1 was performed under the assumption that Ω_x, Ω_y and Ω_z are of the same sign and the same order of magnitude. $n(x)$ and $\varkappa(x)$ are presented on the Fig.1 for $\gamma = 0.5$, 1 and 2.

We can summarize our results in the following way:

Exciton-exciton interaction plays an important role in the light absorption processes. Its contribution is comparable to those of exciton-phonon interaction. The essential element in the theoretical treatment of the exciton-exciton interaction is the decoupling of higher GF, which must be founded on Wick's theorem,

involving the contractions of the operators acting both in the same and diferent moments of time (see 1.5). Numerical calculation (see Fig.1) shows that the role of exciton-exciton interaction has strongest influence on weak dielectrics ($\gamma < 1$) because it gives absorption maximum in the interval $0 \leq \omega \leq \Omega_A$. Absorption is allways present due to the exciton non-conservation effects. Neglecting these effects might in certain cases (kinematical and dinamical exciton interaction approximately equal) lead to the wrong conclusion about the small absorption.

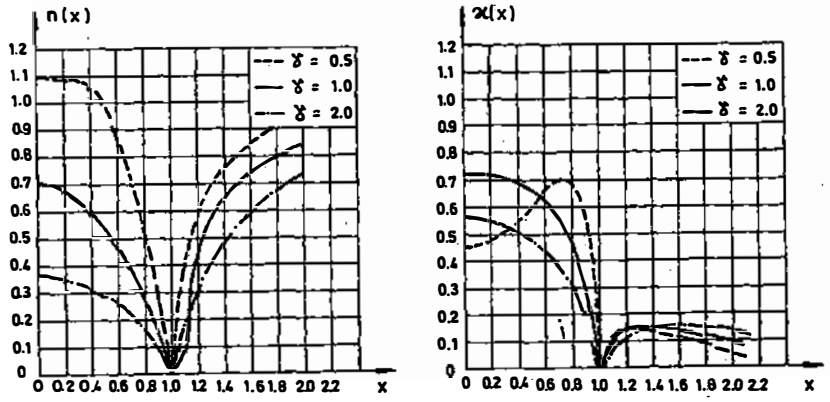

Fig.1

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