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Boundary Influence on Permittivity in Molecular Films

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A microscopic theory of optical properties of thin molecular films, i.e. quasi 2D systems bounded by two surfaces parallel to XY planes was formulated. Harmonic exciton states were calculated using the method of two-time, retarded, temperature dependent Green's functions. It was shown that two types of excitations can occur: bulk and surface exciton states. Analysis of the optical properties (i.e. dielectrical permittivity) of these crystalline systems for low exciton concentration shows that the permittivity strongly depends on boundary parameters and the thickness of the film. Influences of boundary conditions on optical characteristics of these nanostructures were especially analyzed.

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1. Introduction

Molecular crystals are used as materials for light energy conversion. We study the basic physical characteristics of ultrathin dielectrics–ultrathin molecular crystalline films, which could be used as surface layers for electronic component protection, or as some specific and very narrow light filters.

The aim of this paper is the analysis of the influence of finite dimensions of crystalline ultrathin films and boundary conditions onto the optical properties (i.e. absorption of external electromagnetic field — represented by the dielectric permittivity), caused by the generation of the excitons. We base our analysis on the standard exciton Hamiltonian [1, 2]:

$$H = \sum_{\mathbf{n}} \Delta_{\mathbf{n}} P_{\mathbf{n}}^+ P_{\mathbf{n}} - \sum_{\mathbf{nm}} V_{\mathbf{nm}} P_{\mathbf{n}}^+ P_{\mathbf{m}} - \sum_{\mathbf{nm}} W_{\mathbf{nm}} P_{\mathbf{n}}^+ P_{\mathbf{n}} P_{\mathbf{m}}^+ P_{\mathbf{m}}, \quad (1)$$

where $\Delta_{\mathbf{n}}$ denotes the excitation energy of an isolated molecule localized at the

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site $\mathbf{n} \equiv (n_x, n_y, n_z)$ while V_{nm} and W_{nm} represent the matrix elements of dipole–dipole interaction. As orbitals overlap only for neighbor molecules, nearest-neighbor approximation is used.

For low exciton concentrations, in harmonic (Bose) approximation [3], we get

$$H = \sum_{\mathbf{n}} \Delta_{\mathbf{n}} B_{\mathbf{n}}^{\dagger} B_{\mathbf{n}} - \sum_{\mathbf{n}, \boldsymbol{\lambda}} V_{\boldsymbol{\lambda}} B_{\mathbf{n}}^{\dagger} B_{\mathbf{n}+\boldsymbol{\lambda}}. \quad (2)$$

The fact that the film of finite dimension only along z -directions (orthogonal to the film boundary surfaces) is expressed in terms of the conditions: $n_z = 0, 1, 2, \dots, N_z$, $N_z \propto 10$, $n_{\alpha} \in [-N_{\alpha}/2, +N_{\alpha}/2]$, $N_{\alpha} \propto 10^8$, $\alpha = (x, y)$. Exciton energies must be redefined because of the presence of film boundaries. The parameters ε_{0/N_z} define the change of the exciton energy at the surface layers of the film, and ν_{0/N_z} define the change of the transfer energy within the surface layers and the layers nearest to them (along z direction):

$$\begin{aligned} \Delta_{\mathbf{n}} &\equiv \Delta (1 + \varepsilon_0 \delta_{n_z,0} + \varepsilon_{N_z} \delta_{n_z,N_z}), \\ V_{\mathbf{n}, \mathbf{n}+\boldsymbol{\lambda}_z} &\equiv V_z (1 + \nu_0 \delta_{n_z,0} + \nu_{N_z} \delta_{n_z, N_z-1}), \\ V_{\mathbf{n}, \mathbf{n}-\boldsymbol{\lambda}_z} &\equiv V_z (1 + \nu_0 \delta_{n_z,1} + \nu_{N_z} \delta_{n_z, N_z}). \end{aligned} \quad (3)$$

2. Exciton energies and spectral weights

Excitons energies in molecular ultrathin films will be determined by Green's functions method [4–6]. We study single-exciton, two-time dependent commutator Green's function $G_{\mathbf{n}, \mathbf{m}}(t) = \langle \langle B_{\mathbf{n}}(t) | B_{\mathbf{m}}^{\dagger}(0) \rangle \rangle$ and corresponding equation of motion. Performing the time and partial spatial XY Fourier-transformation in the nearest neighbor approximation we obtain the system of $N_z + 1$ non-homogeneous algebraic-difference equations

$$\begin{aligned} G_{n_z, m_z} \left[\rho - \frac{\Delta}{V_z} (\varepsilon_0 \delta_{n_z,0} + \varepsilon_{N_z} \delta_{n_z, N_z}) \right] + G_{n_z+1, m_z} (\nu_0 \delta_{n_z,0} + \nu_{N_z} \delta_{n_z, N_z-1}) \\ + G_{n_z-1, m_z} (1 + \nu_0 \delta_{n_z,1} + \nu_{N_z} \delta_{n_z, N_z}) = \frac{i\hbar}{2\pi V_z} \delta_{n_z, m_z}, \end{aligned} \quad (4)$$

where

$$\rho = \frac{\hbar\omega - \Delta}{V_z} + 2(\cos a_x k_x + \cos a_y k_y). \quad (5)$$

The determination of Green's function poles, which define the spectrum of possible exciton energies, turns into the calculation of the roots of the determinant of the system of equations

$$\begin{aligned} \mathcal{D}_{N_z+1}(\rho) = \left(\rho - \frac{\Delta}{V_z} \varepsilon_0 \right) \times \left(\rho - \frac{\Delta}{V_z} \varepsilon_{N_z} \right) C_{N_z-1} - \left[\left(\rho - \frac{\Delta}{V_z} \varepsilon_0 \right) (1 + \nu_{N_z})^2 \right. \\ \left. + \left(\rho - \frac{\Delta}{V_z} \varepsilon_{N_z} \right) (1 + \nu_0)^2 \right] C_{N_z-2} + (1 + \nu_0)^2 (1 + \nu_{N_z})^2 C_{N_z-3} \equiv 0, \end{aligned} \quad (6)$$

where C_N are the characteristic N order Chebyshev's polynomials

$$(C_{N-1} = \rho C_N - C_{N+1}). \quad (7)$$

In the general case, Eq. (6) is not analytically solvable so numerical methods must be applied, although there are some analytically solvable cases of Eq. (6) for some specific boundary conditions (Dirichlet, Newman) [7]. For given numerical values of the parameters N_z , ε_{0/N_z} and ν_{0/N_z} one can obtain the numerical values for ρ_ν from Eq. (6). Substituting them into (5), the exciton dispersion law becomes

$$\mathcal{E}_{xy}(\nu) = \mathcal{F}_{xy} + \mathcal{G}_\nu, \quad (8)$$

where

$$\begin{aligned} \mathcal{E}_{xy}(\nu) &\equiv \frac{\hbar\omega}{V_z}, \quad \mathcal{F}_{xy} = \frac{\Delta}{V_z} - 2(\cos a_x k_x + \cos a_y k_y); \\ \mathcal{G}_z(k_x, k_y; \nu) &\equiv \rho(k_x, k_y; \nu). \end{aligned} \quad (9)$$

The most important conclusion is that the energy spectra of excitons is discrete with the finite number of energy levels ($N_z + 1$), compared with bulk crystal where exciton energies take continual values within band zone.

Without influence of perturbation parameters or by their suitable choice, one obtains that the whole spectrum lies within the energy band of the bulk crystal. For other values of surface parameters, there arise localized exciton states at the surface film layers and exciton energies could take values outside of bulk energy band.

To calculate the space distribution of excitons we will write the system of equations for Green's functions in matrix form

$$\hat{\mathcal{D}}_{N_z+1} \tilde{\mathcal{G}}_{N_z+1} = \tilde{\mathcal{K}}_{N_z+1}, \quad (10)$$

where $\hat{\mathcal{D}}_{N_z+1}$ is system matrix, while $\tilde{\mathcal{G}}_{N_z+1}$ and $\tilde{\mathcal{K}}_{N_z+1}$ are vectors

$$\begin{aligned} \tilde{\mathcal{G}}_{N_z+1} &= (G_{0,m_z}, G_{1,m_z}, \dots, G_{n_z,m_z}, \dots, G_{N_z,m_z}); \\ \tilde{\mathcal{K}}_{N_z+1} &= \frac{i\hbar}{2\pi V_z} (\delta_{0,m_z}, \delta_{1,m_z}, \dots, \delta_{n_z,m_z}, \dots, \delta_{N_z,m_z}). \end{aligned}$$

Using the properties of inverse matrix, one can get Green's functions in the following form:

$$G_{n_z;m_z} = \frac{i\hbar}{2\pi V_z} \frac{D_{n_z;m_z}}{\mathcal{D}_{N_z+1}}, \quad (11)$$

where $D_{n_z;m_z}$ are cofactors of \mathcal{D}_{N_z+1} determinant. Factorizing the expression (11) we can write [4-10]:

$$G_{n_z;m_z} = \frac{i\hbar}{2\pi V_z} \sum_{\nu=1}^{N_z+1} \frac{g_{n_z;m_z}(\rho_\nu)}{\rho - \rho_\nu}, \quad (12)$$

where spectral weights are

$$g_{n_z;n_z} = \frac{D_{n_z;n_z}(\rho_\nu)}{\frac{d}{d\rho} \mathcal{D}_{N_z+1}(\rho)|_{\rho=\rho_\nu}}. \quad (13)$$

3. Relative permittivity

The expression for the relative permittivity of the system has the following form [11]:

$$\varepsilon_r^{-1}(\omega) = 1 - 2\pi i S [G(+\omega) + G(-\omega)], \quad (14)$$

where $S = \tau_0 E_0^2 / 8\pi \hbar$ (τ is the elementary cell volume and E_0 is the electrical field per elementary cell). We can rewrite this expression using the factorized Green functions

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - \frac{\hbar S}{V_z} \sum_{\nu=1}^{N_z+1} \left[\frac{g_{n_z}(\rho_\nu)}{\rho(+\omega) - \rho_\nu} + \frac{g_{n_z}(\rho_\nu)}{\rho(-\omega) - \rho_\nu} \right]. \quad (15)$$

Relative permittivity is directly related with optical properties (i.e. absorption) of materials, it is a measure of “dielectric response” of material on external electromagnetic field. The most important parameters on optical behavior of ultrathin films are film thickness (number of layers) and boundary conditions which are represented with perturbation parameters ε_{0/N_z} and ν_{0/N_z} . In the past theoretical research of these exciton systems in ultrathin film structures [12] each of these perturbation parameters was investigated in particular, but in this paper we will present results of parallel influence of both perturbations, but only on one side

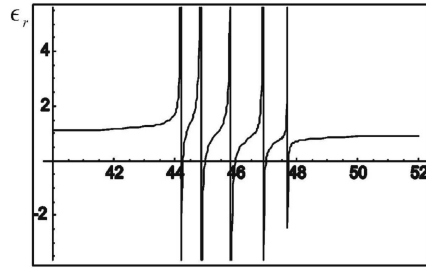


Fig. 1

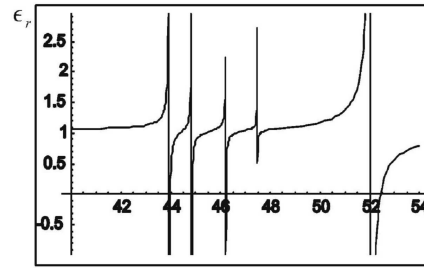


Fig. 2

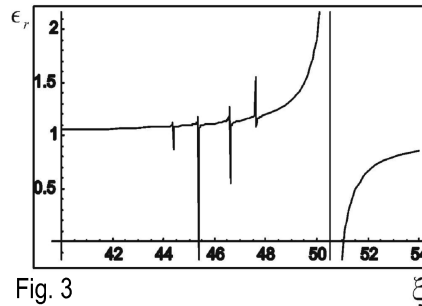


Fig. 3

Fig. 1. Dielectric permittivity ε_{n_z} dependence of non-dimensional electromagnetic field $\xi = \hbar\omega/|V \in [40, 25]$ on last layer of 5-layered film with $\varepsilon_{N_z} = 0$, $\nu_{N_z} = 0$, i.e. without perturbation.

Fig. 2. Dielectric permittivity on last layer with perturbation $\varepsilon_{N_z} = 0.1$, $\nu_{N_z} = 2$.

Fig. 3. Dielectric permittivity on last layer with $\varepsilon_{N_z} = 0.1$, $\nu_{N_z} = -0.6$.

TABLE
Probabilities of finding excitons
with particular energy $g_{n_z;n_z}$.

	Fig. 1	Fig. 2	Fig. 3
E_1	0.08333	0.09076	0.00052
E_2	0.25000	0.05030	0.00184
E_3	0.33333	0.03553	0.00294
E_4	0.25000	0.01338	0.00182
E_5	0.08333	0.81002	0.99287

of the film (non-symmetrical case). This means that one side of the film will be perturbed in pairs (regardless $\varepsilon_0; \nu_0$ or $\varepsilon_{N_z}; \nu_{N_z}$), but the other side of the film will be without perturbation (substrate of the film is of the same material, but there is no interaction between film and substrate).

We have analyzed relative permittivity for 5-layer ultrathin film and these calculations are presented in Figs. 1–3 and in Table with calculated probabilities, i.e. spectral weights $g_{n_z;n_z}$ showing what probability arising exciton will have in particular layer of the film, with particular energy. Limited with space, we can present only few extreme cases, which can show how perturbation influence looks like.

Among handful results, we have to mark out only most significant ones.

4. Conclusions

There are essential differences in optical properties in film structures in comparison with bulk:

1. Dielectric permittivity (absorption of external electromagnetic field) caused by generation of excitons in the crystalline film is a discrete one with the finite number of piques equal to the number of atomic planes in the film along z -direction. In bulk, absorption will be continual band zone.
2. Dielectric permittivity dependence is a function of layer n_z . For some layers number of resonant piques will be less than number of atomic planes, while on those layers some energies are forbidden, i.e. $g_{n_z;n_z} = 0$. This is true only without perturbation influence. With various combinations of perturbation parameters, all piques will be present, but some with negligible probabilities.
3. In general, perturbation ε_{0/N_z} shifts one pique toward higher energies, while positive change ν_{0/N_z} broaden absorption zone. The most significant combination of perturbation parameters is in the case of “monochromatic absorber”, with positive ε_{0/N_z} , and negative ν_{0/N_z} .

References

- [1] V.M. Agranovich, V.L. Ginzburg, *Crystaloptics with Space Dispersion and Theory of Excitons*, Nauka, Moscow 1979, p. 43.
- [2] D.Lj. Mirjanić, U.F. Kozmidis-Luburić, M.M. Marinković, B.S. Tošić, *Can. J. Phys.* **60**, 1838 (1982).
- [3] V.M. Agranovich, B.S. Toshich, *Zh. Eksp. Teor. Fiz.* **53**, 149 (1967).
- [4] G. Mahan, *Many Particle Physics*, Plenum Press, New York 1990, p. 518.
- [5] V. Sajfert, J.P. Šetrajić, D. Popov, B.S. Tošić, *Physica A* **353**, 217 (2005).
- [6] J.P. Šetrajić, S.M. Vučenović, D.Lj. Mirjanić, V.D. Sajfert, S.K. Jaćimovski, *Mater. Sci. Forum* **494**, 49 (2005).
- [7] S. Lazarev, Ž.M. Škrbić, J.P. Šetrajić, D.Lj. Mirjanić, Lj. Ristovski, *J. Phys. Chem. Solids* **58**, 793 (1997).
- [8] J.P. Šetrajić, S.M. Stojković, D.D. Šijačić, I.D. Vragović, *J. Res. Phys.* **27/2**, 155 (1998).
- [9] B.S. Tošić, M. Pantić, S.B. Lazarev, *J. Phys. Chem. Solids* **58**, 1995 (1997).
- [10] I.D. Vragović, R. Scholz, J.P. Šetrajić, *Mater. Sci. Forum* **518**, 41 (2006).
- [11] I.E. Dzialoshinski, L.P. Pitaevski, *Zh. Eksp. Teor. Fiz.* **36**, 1977 (1959).
- [12] S.M. Vucenovic, D. Ilic, J.P. Setrajcic, V. Sajfert, D. Mirjanic, *Mater. Res. Soc. Symp. Proc.* **1017E**, PA 1017-DD08-50 (2007).