



ELSEVIER

Contents lists available at ScienceDirect

Opto-Electronics Review

journal homepage: <http://www.journals.elsevier.com/opto-electronics-review>

Adequate determination of micro and macro properties of optical nano-crystals

J.P. Šetrajčić

University of Novi Sad, Faculty of Sciences, Department of Physics, Trg Dositeja Obradovic'a 4, 21.000 Novi Sad, Vojvodina, Serbia

ARTICLE INFO

Article history:

Received 19 August 2016

Accepted 5 October 2016

Available online 29 September 2017

ABSTRACT

The main problem in theoretical analysis of structures with strong confinement is the fact that standard mathematical tools: differential equations and Fourier's transformations are no longer applicable. In this paper we have demonstrated that the method of Green's functions can be successfully used on low-dimension crystal samples, as a consequence of quantum size effects. We can illustrate a modified model through the prime cubic structure molecular crystal: bulk and ultrathin film. Our analysis starts with standard exciton Hamiltonian with definition of commutative Green's function and equation of motion. We have presented a detailed procedure of calculations of Green's functions, and further dispersion law, distribution of states and relative permittivity for bulk samples. After this, we have followed the same procedures for obtaining the properties of excitons in ultra-thin films. The results have been presented graphically. Besides the modified method of Green's functions we have shown that the exciton energy spectrum is discrete in film structures (with a number of energy levels equal to the number of atomic planes of the film). Compared to the bulk structures, with a continual absorption zone, in film structures exist resonant absorption peaks. With increased film thickness differences between bulk and film vanish.

© 2017 Association of Polish Electrical Engineers (SEP). Published by Elsevier B.V. All rights reserved.

1. Introduction

Interest in exciton subsystem studies appeared due to the fact that excitons are responsible for dielectric, optical (absorption, dispersion of light, luminescence), photoelectric and other properties of crystals [1–3]. Studies of excitons in crystalline subsystems culminated with laser invention.

In recent years theoretical investigations of quasi-two-dimensional exciton subsystems (nanostructures) were intensified, especially in the field of thin films, not only to obtain fundamental information regarding dielectric properties of these materials but also because of their wide practical use (nanoelectronics, optoelectronic [4–6], light energy conversion [7,8]...). What is unique for these structures is that they have changed properties compared to their bulk analogues [6,9,10].

We studied the basic physical characteristics of ultrathin dielectrics – molecular crystalline nanofilms [11,12], which could be used as surface layers for protection of electronic components or as special light filters.

This paper analyzes the influence of border-film structure on the energy spectrum of excitons (exciton dispersion law). Special attention was paid to the presence and spatial distribution of localized exciton states. Optical properties of these dielectric films were also

investigated (their dielectric permittivity was determined). Results obtained in this work were compared with the similar results for the case of ideal infinite crystals, in order to find most important differences between these two systems.

These analyzes may be conducted using methods of two-time, temperature-dependant Green's functions that are often used in quantum theory of solid state [13–15]. With adequately incorporated statistics, this method is being successfully applied in calculations of microscopic and macroscopic, as well as balanced and non-balanced properties of crystals.

A question which justifiably arises is related to the mean of calculating Green's functions, which are "borrowed" from the quantum field theory and whose definition, i.e. usage, is based on variables with continuous spectra in unlimited (both direct and impulse) space!

This work proves that the method of Green's functions may be successfully applied onto crystalline samples of such small dimensions that the quantum size effects are relevant [16]. In order to illustrate adaptation of this method, we will observe molecule crystal with a simple cubic structure: spatially unlimited (bulk) and strongly limited along one axis (ultra thin film). Our intention is to show a technique of application of Green's function onto spatially limited systems, so we excluded from calculation all really existing parameters: more complex crystalline structure, changes in boundary film parameters etc.

E-mail address: jovan.setrajcic@df.uns.ac.rs<http://dx.doi.org/10.1016/j.opelre.2017.08.003>

1230-3402/© 2017 Association of Polish Electrical Engineers (SEP). Published by Elsevier B.V. All rights reserved.

2. Excitons in bulk-structures

The discussion of dielectric properties of an ideal (with no defects, vacancies, etc) unlimited molecular crystal will start with standard exciton Hamiltonian, which has the following form in configuration space [1,15,17]:

$$H = H_0 + \sum_{\bar{n}} \Delta_{\bar{n}} P_{\bar{n}}^+ P_{\bar{n}} + \sum_{\bar{n}, \bar{m}} X_{\bar{n}\bar{m}} P_{\bar{n}}^+ P_{\bar{m}} + \sum_{\bar{n}, \bar{m}} Y_{\bar{n}\bar{m}} P_{\bar{n}} P_{\bar{m}}^+ P_{\bar{m}}, \quad (1)$$

where $P_{\bar{n}}^+$ and $P_{\bar{n}}$ represent creation and annihilation exciton operators at the node (site) \bar{n} of the crystalline lattice. Quantity $\Delta_{\bar{n}}$ represents the energy of the exciton localized at the \bar{n} node, while the quantities $X_{\bar{n}, \bar{m}}$ and $Y_{\bar{n}, \bar{m}}$ represent matrix elements of the exciton transfer from the node \bar{n} to the node \bar{m} .

Properties of the model exciton system may be analyzed using commutation Paulian Green's function [13,14,18]:

$$\Gamma_{\bar{n}\bar{m}}(t) \equiv \langle \langle P_{\bar{n}}(t) | P_{\bar{m}}^+(0) \rangle \rangle = \Theta(t) \langle [P_{\bar{n}}(t), P_{\bar{m}}^+(0)] \rangle, \quad (2)$$

which satisfies the following equation of motion:

$$i\hbar \frac{d}{dt} \Gamma_{\bar{n}\bar{m}}(t) = i\hbar \delta(t) \langle [P_{\bar{n}}(t), P_{\bar{m}}^+(0)] \rangle + \Theta(t) \langle [P_{\bar{n}}(t), H] P_{\bar{m}}^+(0) - P_{\bar{m}}^+(0) [P_{\bar{n}}(t), H] \rangle. \quad (3)$$

Using commutation relations for Pauli operators [18,19]:

$$\begin{aligned} [P_{\bar{n}}, P_{\bar{m}}^+] &= (1 - 2P_{\bar{n}}^+ P_{\bar{n}}) \delta_{\bar{n}\bar{m}}; \\ [P_{\bar{n}}, P_{\bar{m}}] &= [P_{\bar{n}}, P_{\bar{m}}^+] = 0; \end{aligned} \quad (4)$$

$$P_{\bar{n}}^2 = (P_{\bar{n}}^+)^2 = 0,$$

we obtain the equation of motion for Paulian Green's function:

$$\begin{aligned} i\hbar \frac{d}{dt} \Gamma_{\bar{n}\bar{m}}(t) &= i\hbar \delta(t) \delta_{\bar{n}\bar{m}} (1 - 2(P_{\bar{n}}^+ P_{\bar{n}})) + \\ &+ \Delta_{\bar{n}} \Gamma_{\bar{n}\bar{m}}(t) + \sum_{\bar{l}} X_{\bar{n}\bar{l}} \Gamma_{\bar{l}\bar{m}}(t) - \\ &- 2 \sum_{\bar{l}} X_{\bar{l}\bar{n}} \mathcal{T}_{\bar{n}\bar{l}\bar{m}}(t) + 2 \sum_{\bar{l}} Y_{\bar{n}\bar{l}} \mathcal{T}_{\bar{l}\bar{m}\bar{n}}(t) \end{aligned} \quad (5)$$

expressed by $\mathcal{T}_{\bar{n}\bar{l}\bar{m}}(t) = \langle \langle P_{\bar{n}}^+(t) P_{\bar{l}}(t) P_{\bar{m}}^+(0) \rangle \rangle -$ Paulian Green's function of the higher (third) order.

The basic problem with exciton theory is the fact that Pauli-operators P^+ and P are not Bose or Fermi operators, but a certain hybrid of both with a kinematics described by Eq. (4), that is Fermian for one mode and Bosonian for different modes. For a precise analysis of exciton systems, which encompass effects of inter-exciton interaction, simple replacing of Pauli-operators with Bose-operators is not enough. Therefore, in Hamiltonian (1), Pauli-operators are replaced by their exact Bosonian represents [20]:

$$\begin{aligned} P &= \left[\sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} (B^+)^{\nu} B^{\nu} \right]^{\frac{1}{2}} B; \\ P^+ &= B^+ \left[\sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} (B^+)^{\nu} B^{\nu} \right]^{\frac{1}{2}}; \\ P^+ P &= \sum_{\nu=0}^{\infty} \frac{(-2)^\nu}{(1+\nu)!} (B^+)^{\nu+1} B^{\nu+1}. \end{aligned} \quad (6)$$

Our goal is to adapt Green's function method to spatially quantum (discrete, not continuous) structures and to see the influence of spatial limits and disturbances of inner translational symmetry on changes of their macroscopic physical properties. Paulian Green's functions from Eq. (7) will be, therefore expressed using

appropriate Bosonian Green's functions on the basis of approximate equations following from (6):

$$\begin{aligned} P &\approx B - B^+ B B; \\ P^+ &\approx B^+ - B^+ B^+ B; \\ P^+ P &\approx B^+ B - B^+ B^+ B B. \end{aligned} \quad (7)$$

By this we obtain:

$$\begin{aligned} \Gamma_{\bar{n}\bar{m}}(t) &= \langle \langle P_{\bar{n}}(t) | P_{\bar{m}}^+(0) \rangle \rangle = \langle \langle B_{\bar{n}}(t) | B_{\bar{m}}^+(0) \rangle \rangle - \\ &- \langle \langle B_{\bar{n}}(t) | B_{\bar{m}}^+(0) B_{\bar{m}}^+(0) B_{\bar{m}}(0) \rangle \rangle - \langle \langle B_{\bar{n}}^+(t) B_{\bar{n}}(t) B_{\bar{m}}^+(0) \rangle \rangle + \\ &+ \langle \langle B_{\bar{n}}^+(t) B_{\bar{n}}(t) B_{\bar{m}}^+(0) B_{\bar{m}}^+(0) B_{\bar{m}}(0) \rangle \rangle. \end{aligned} \quad (8)$$

Further, by decoupling higher Green's functions using known Bose-commutation relations:

$$[B_k^-, B_l^+] = \delta_{kl}; [B_k^-, B_l] = [B_k^+, B_l^+] = 0 \quad (9)$$

and by introducing retarded (Bosonian) Green's function:

$$\langle \langle B_{\bar{n}}(t) | B_{\bar{m}}^+(0) \rangle \rangle = G_{\bar{n}\bar{m}}(t), \quad (10)$$

terms in Eq. (8) become:

$$\begin{aligned} \langle \langle B_{\bar{n}}(t) | B_{\bar{m}}^+(0) B_{\bar{m}}^+(0) B_{\bar{m}}(0) \rangle \rangle &= \Theta(t) \langle [B_{\bar{n}}, B_{\bar{m}}^+ B_{\bar{m}}^+ B_{\bar{m}}] \rangle = \\ &= \Theta(t) \langle (\delta_{\bar{n}\bar{m}} + B_{\bar{m}}^+ B_{\bar{n}}) B_{\bar{m}}^+ B_{\bar{m}} \rangle - \langle B_{\bar{m}}^+ B_{\bar{m}}^+ B_{\bar{m}} B_{\bar{n}} \rangle = \\ &= 2G_{\bar{n}\bar{m}}(t) \mathcal{N}_0; \\ \langle \langle B_{\bar{n}}^+(t) B_{\bar{n}}(t) B_{\bar{m}}^+(0) \rangle \rangle &= 2G_{\bar{n}\bar{m}}(t) \mathcal{N}_0; \\ \langle \langle B_{\bar{n}}^+(t) B_{\bar{n}}(t) B_{\bar{m}}^+(0) B_{\bar{m}}^+(0) B_{\bar{m}}(0) \rangle \rangle &= 2R_{\bar{n}\bar{m}}(t) G_{\bar{n}\bar{m}}^2(t), \end{aligned} \quad (11)$$

where \mathcal{N}_0 is the concentration of excitons, and $R_{\bar{n}\bar{m}}(t)$ is the advanced Green's function:

$$\begin{aligned} \mathcal{N}_0 = \langle B^+ B \rangle &= \frac{1}{N} \sum_{\bar{k}} (e^{\hbar\omega_0(\bar{k})/\theta} - 1)^{-1}; \\ R_{\bar{n}\bar{m}}(t) &= \langle \langle B_{\bar{n}}^+(t) | B_{\bar{m}}(0) \rangle \rangle. \end{aligned} \quad (12)$$

When Eqs. (10) and (11) are substituted into Eq. (8) we obtain final equation for Paulian Green's function expressed using Bosonian Green's functions:

$$\begin{aligned} \Gamma_{\bar{n}\bar{m}}(t) &= (1 - 4\mathcal{N}_0) G_{\bar{n}\bar{m}}(t) + \\ &+ 2R_{\bar{n}\bar{m}}(t) G_{\bar{n}\bar{m}}^2(t) + O(\mathcal{N}^2). \end{aligned} \quad (13)$$

For Paulian Green's functions of higher order ($\mathcal{T}_{\bar{a}\bar{a}\bar{b}\bar{c}}$) at the left side of Green's function we simply replace Pauli operators by Bose-operators, and on the right side approximation (7) takes place. In this way it follows:

$$\begin{aligned} \mathcal{T}_{\bar{a}\bar{a}\bar{b}\bar{c}} &= \langle \langle P_{\bar{a}}^+(t) P_{\bar{a}}(t) P_{\bar{b}}(t) | P_{\bar{c}}^+(0) \rangle \rangle = \\ &= \langle \langle B_{\bar{a}}^+(t) B_{\bar{a}}(t) B_{\bar{b}}(t) | B_{\bar{c}}^+(0) \rangle \rangle - \\ &- \langle \langle B_{\bar{a}}^+(t) B_{\bar{a}}(t) B_{\bar{b}}(t) | B_{\bar{c}}^+(0) B_{\bar{c}}^+(0) B_{\bar{c}}(0) \rangle \rangle = \\ &= \mathcal{N}_0 G_{\bar{b}\bar{c}}(t) + \mathcal{N}_{\bar{b}\bar{a}} G_{\bar{a}\bar{c}}(t) - \\ &- 2R_{\bar{a}\bar{c}}(t) G_{\bar{b}\bar{c}}(t) G_{\bar{a}\bar{c}}(t) + O(\mathcal{N}_0^2). \end{aligned} \quad (14)$$

Equations for $\Gamma_{\bar{n}\bar{m}}$, $\mathcal{T}_{\bar{n}\bar{m}}^+$ and $\mathcal{T}_{\bar{l}\bar{m}}$, which are expressed using Bosonian Green's functions, are substituted in an equation of movement for Paulian Green's function (5):

$$\begin{aligned}
 & i\hbar \frac{d}{dt} [(1 - 4\mathcal{N}_0)G_{\bar{n}\bar{m}}(t) + 2R_{\bar{n}\bar{m}}(t)G_{\bar{n}\bar{m}}^2(t)] = \\
 & = i\hbar\delta(t)\delta_{\bar{n}\bar{m}}(1 - 2(P_{\bar{n}}^+ P_{\bar{n}})) + \\
 & + \Delta_{\bar{n}}[(1 - 4\mathcal{N}_0)G_{\bar{n}\bar{m}}(t) + 2R_{\bar{n}\bar{m}}(t)G_{\bar{n}\bar{m}}^2(t)] + \\
 & + \sum_{\bar{l}} X_{\bar{n}\bar{l}} [(1 - 4\mathcal{N}_0)G_{\bar{l}\bar{m}}(t) + 2R_{\bar{l}\bar{m}}(t)G_{\bar{l}\bar{m}}^2(t)] - \\
 & - 2 \sum_{\bar{l}} X_{\bar{n}\bar{l}} [\mathcal{N}_0 G_{\bar{l}\bar{m}}(t) + \mathcal{N}_{\bar{l}\bar{n}} G_{\bar{n}\bar{m}}(t) - 2R_{\bar{n}\bar{m}}(t)G_{\bar{l}\bar{m}}(t)G_{\bar{n}\bar{m}}(t)] + \\
 & + 2 \sum_{\bar{l}} Y_{\bar{n}\bar{l}} [\mathcal{N}_0 G_{\bar{n}\bar{m}}(t) + \mathcal{N}_{\bar{n}\bar{l}} G_{\bar{l}\bar{m}}(t) - 2R_{\bar{l}\bar{m}}(t)G_{\bar{n}\bar{m}}(t)G_{\bar{l}\bar{m}}(t)].
 \end{aligned} \quad (15)$$

Since concentration of Frenkel's excitons in molecular crystals is very low ($\mathcal{N} < 1\%$), the equation above may be solved in the lowest approximation (this approximation is appropriate for neglecting anharmonic and nonlinear effects, i.e. non-calculating higher orders terms of exciton–exciton, as well as exciton–phonon interactions, in agreement to estimates in Refs. [1–3,13–15]):

$$\begin{aligned}
 \langle P_{\bar{n}}^+ P_{\bar{n}} \rangle & \approx \langle B_{\bar{n}}^+ B_{\bar{n}} \rangle = \mathcal{N}_0 \approx 0; \\
 \mathcal{N}_{\bar{a}\bar{b}} & \approx 0; G \cdot G \approx 0; G \cdot R \approx 0.
 \end{aligned} \quad (16)$$

“Decoupled” Eq. (15) then obtains the following form:

$$i\hbar \frac{d}{dt} G_{\bar{n}\bar{m}}(t) = i\hbar\delta(t)\delta_{\bar{n}\bar{m}} + \Delta_{\bar{n}} G_{\bar{n}\bar{m}}(t) + \sum_{\bar{l}} X_{\bar{n}\bar{l}} G_{\bar{l}\bar{m}}(t). \quad (17)$$

It is important to notice that this equation has to be obtained in the same form starting from effective Bosonian exciton Hamiltonian in a harmonic approximation:

$$H_{ex} = \sum_{\bar{n}} \Delta_{\bar{n}} B_{\bar{n}}^+ B_{\bar{n}} + \sum_{\bar{n}, \bar{m}} X_{\bar{n}\bar{m}} B_{\bar{n}}^+ B_{\bar{m}},$$

and estimating Bosonian Green's function (10):

$$G_{\bar{n}\bar{m}}(t) = \langle \langle B_{\bar{n}}(t) | B_{\bar{m}}^+(0) \rangle \rangle = \Theta(t) \langle [B_{\bar{n}}(t), B_{\bar{m}}^+(0)] \rangle,$$

with its equation motion:

$$\begin{aligned}
 & i\hbar \frac{d}{dt} G_{\bar{n}\bar{m}}(t) = i\hbar\delta(t) \langle [B_{\bar{n}}(t), B_{\bar{m}}^+(0)] \rangle + \\
 & + \Theta(t) \langle [B_{\bar{n}}(t), H_{ex}] B_{\bar{m}}^+(0) - B_{\bar{m}}^+(0) [B_{\bar{n}}(t), H_{ex}] \rangle.
 \end{aligned} \quad (18)$$

This (by time) differential Eq. (16) is solved using temporal Fourier's transformation:

$$f_{\bar{a}\bar{b}}(t) = \int_{-\infty+\infty} d\omega f_{\bar{a}\bar{b}}(\omega) e^{-i\omega t}; \delta(t) = \frac{1}{2\pi} \int_{-\infty+\infty} d\omega e^{-i\omega t}, \quad (19)$$

and, thus we obtain:

$$\hbar\omega G_{\bar{n}\bar{m}}(\omega) = \frac{i\hbar}{2\pi} \delta_{\bar{n}\bar{m}} + \Delta_{\bar{n}} G_{\bar{n}\bar{m}}(\omega) + \sum_{\bar{l}} X_{\bar{n}\bar{l}} G_{\bar{l}\bar{m}}(\omega). \quad (20)$$

By using nearest neighbours approximation ($\bar{l} \rightarrow \bar{n} \pm \bar{\lambda}_i$): $\bar{n} \pm \bar{\lambda}_1 = n_x \pm 1, n_y, n_z$; $\bar{n} \pm \bar{\lambda}_2 = n_x, n_y \pm 1, n_z$; $\bar{n} \pm \bar{\lambda}_3 = n_x, n_y, n_z \pm 1$ and taking into account that we are observing an ideal cubic structure, where exciton energy is the same at every node, and the energy transfer between neighbours is also the same: $\Delta_{\bar{a}} \equiv$

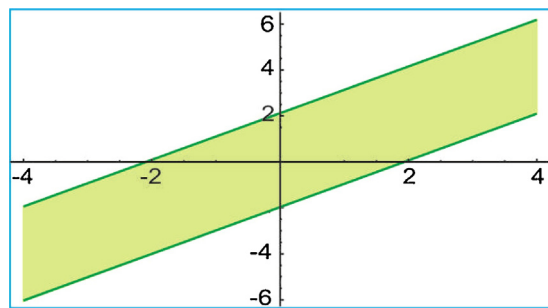


Fig. 1. Exciton dispersion law of bulk crystal.

Δ ; $X_{\bar{a}, \bar{a} \pm \bar{\lambda}_i} \equiv X_i \in \{x, y, z\}$, equation above is taking the following form:

$$\begin{aligned}
 & \hbar\omega G_{n_x n_y n_z, m_x m_y m_z}(\omega) \equiv \hbar\omega G_{n_x n_y n_z, \bar{m}}(\omega) = \\
 & = \frac{i\hbar}{2\pi} \delta_{n_x n_y n_z, \bar{m}} + \Delta G_{n_x n_y n_z, \bar{m}}(\omega) + \\
 & + X_x [G_{n_x+1, n_y n_z, \bar{m}}(\omega) + G_{n_x-1, n_y n_z, \bar{m}}(\omega)] + \\
 & + X_y [G_{n_x n_y+1, n_z, \bar{m}}(\omega) + G_{n_x n_y-1, n_z, \bar{m}}(\omega)] + \\
 & + X_z [G_{n_x n_y n_z+1, \bar{m}}(\omega) + G_{n_x n_y n_z-1, \bar{m}}(\omega)].
 \end{aligned} \quad (21)$$

Since the crystal is unlimited, when solving this linear differential equation we may use the full spatial Fourier's transformation:

$$f_{\bar{a}\bar{b}}(\omega) = \frac{1}{N} \sum_{\bar{k}} f_{\bar{k}}(\omega) e^{i\bar{k}(\bar{a}-\bar{b})}; \delta_{\bar{a}\bar{b}} = \frac{1}{N} \sum_{\bar{k}} e^{i\bar{k}(\bar{a}-\bar{b})}. \quad (22)$$

By using these transformations and by composing the equation above, we obtain:

$$\begin{aligned}
 & \hbar\omega G_{\bar{k}}(\omega) = \frac{i\hbar}{2\pi} + \Delta G_{\bar{k}}(\omega) + \\
 & + 2 (X_x \cos a_x k_x + X_y \cos a_y k_y + X_z \cos a_z k_z) G_{\bar{k}}(\omega),
 \end{aligned} \quad (23)$$

and from there we may express Green's function:

$$\begin{aligned}
 & G_{\bar{k}}(\omega) = \frac{i\hbar}{2\pi} [\hbar\omega - \Delta - 2 (X_x \cos a_x k_x + X_y \cos a_y k_y + X_z \cos a_z k_z)]^{-1} \\
 & \equiv \frac{i\hbar}{2\pi} \frac{1}{\hbar\omega - E_{\bar{k}}}.
 \end{aligned} \quad (24)$$

We obtain the energy spectrum in a bulk monomolecular crystal [13,14] by calculating real part of the pole of this Green's function:

$$E_{\bar{k}} = \Delta + 2 (X_x \cos a_x k_x + X_y \cos a_y k_y + X_z \cos a_z k_z). \quad (25)$$

In order to perform comparison with dispersion law of excitons in the film, this expression will be written in a simpler ($X_x = X_y = X_z \equiv -|X|$, $a_x = a_y = a_z \equiv a$) and non-dimensional form:

$$\varepsilon_{\bar{k}} \equiv \frac{E_{\bar{k}} - \Delta}{|X|} = \mathcal{F}_{xy} + \mathcal{G}_z, \quad (26)$$

where

$$\mathcal{F}_{xy} = -2 (\cos a k_x + \cos a k_y); \mathcal{G}_z = -2 \cos a k_z.$$

This dispersion law is shown in Fig. 1, as a function of two-dimensional value \mathcal{F}_{xy} :

$$\varepsilon_{\bar{k}} = \varepsilon_z (\mathcal{F}_{xy}),$$

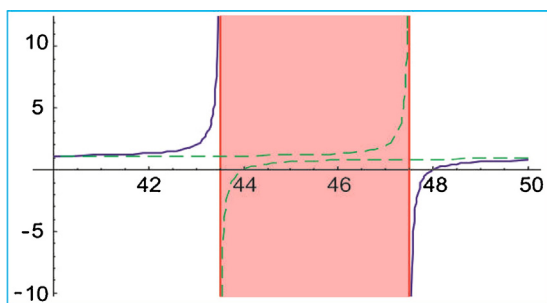


Fig. 2. Relative permittivity of bulk crystal.

It is clear that for $ak_i \in [0, +\pi]$, $i = x, y, z$ (the first Brillouin zone), these values are within the intervals:

$$\left. \begin{array}{l} \mathcal{L}_{xy} \in [-4, +4]; \\ \mathcal{G}_z \in [-2, +2], \end{array} \right\} \Rightarrow \varepsilon_{\vec{k}} \in [-6, +6].$$

The presence of permitted (continuous) energy levels is visible.

Since molecular crystals are dielectric, it is essential to determine relative permittivity of these structures. The dynamic permittivity is defined by systems response to external perturbation [1,15,20], by equation:

$$\varepsilon^{-1}(\omega) = 1 - \frac{\pi S |X|}{i\hbar} [\Gamma(\omega) + \Gamma(-\omega)], \quad (27)$$

where S is a frequency property of a given crystal and external variable electromagnetic field. As it was mentioned before, in this (zero) approximation Paulian Green's functions (Γ) are transforming into Bosonian ones (G), therefore:

$$\varepsilon^{-1}(\omega) = 1 - \frac{\pi S |X|}{i\hbar} [G(\omega) + G(-\omega)]. \quad (28)$$

Substituting (24) with (25) in (28) and by denoting $\frac{\hbar\omega}{|X|} \equiv |f|$ and $\frac{\Delta}{|X|} \equiv |p|$, we obtain the expression for dynamic permittivity in a bulk sample of monomolecular crystal (molecular crystal with simple cell):

$$\varepsilon_{\vec{k}}(\omega) = \left[1 + S |X| \frac{E_{\vec{k}}}{(\hbar\omega)^2 - E_{\vec{k}}^2} \right]^{-1} \equiv \left[1 + S \frac{\varepsilon_{\vec{k}} + |p|}{|f|^2 - (\varepsilon_{\vec{k}} + |p|)^2} \right]^{-1}. \quad (29)$$

Dependence of relative dynamic permittivity, Eq. (29), on reduced frequency (non-dimensional factor $\hbar\omega/\Delta$) of the external electromagnetic field is shown in Fig. 2.

The presence of a single absorption zone is visible within certain boundary frequencies. This energy zone was calculated for a two-dimension center of Brillouin's zone ($k_x = k_y = 0$; $k_z \in [0, \pi]$). For all other energies this crystal is transparent and has no spatial non-homogeneity.

3. Excitons in thin film-structures

Opposite to ideal unlimited structures, real crystals have no translation invariance property. The presence of certain boundary conditions is one of reasons for symmetry breaking [4–7]. Lets observe the ideal ultrathin film with simple cubic structure, made in the substrate, i.e. by doping process. Here, by the term "ideal", we wanted to denote that there exist no breaking of inner crystal structure (no defects, ingredients, etc), and not as in no spatial limits. The film dimensions are such that it is unlimited in XY planes, and in z -axis has final thickness (L). This means that this film has

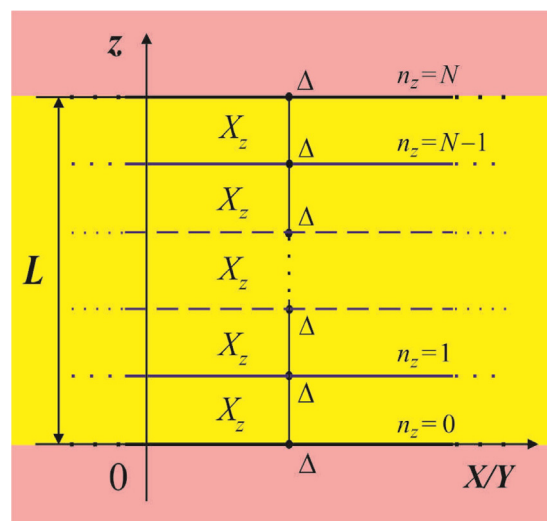


Fig. 3. Cross-section of a crystalline film-model.

two unlimited boundary planes parallel to XY planes, for $z = 0$ and $z = L \equiv n_z$.

3.1. The model

The film-structure with a primitive crystalline lattice (one molecule per elementary cell): monomolecular crystalline film, with specified parameters is shown in Fig. 3.

Since boundary planes of the film are taken as being normal to z -axis, the index of parallel XY planes n_z has values $n_z = 0, 1, 2, \dots, N$ where $N \in [2, 8]$ is for ultra thin films. Indices n_x and n_y , determining position of a molecule in every XY plane may have arbitrary whole-number values (practically from $-\infty$ to $+\infty$).

For calculating exciton energies in this film, we start from Eq. (21) on which, due to spatial limitations of the film at z -direction, we may apply partial spatial Fourier transformation:

$$\begin{aligned} \delta_{\vec{n}\vec{m}} &= \frac{1}{N_x N_y} \sum_{k_x k_y} e^{ik_x a_x (n_x - m_x)} e^{ik_y a_y (n_y - m_y)} \delta_{n_z m_z} \\ f_{\vec{n}\vec{m}}(\omega) &= \frac{1}{N_x N_y} \sum_{k_x k_y} e^{ik_x a_x (n_x - m_x)} e^{ik_y a_y (n_y - m_y)} \times \\ &\times f_{n_z m_z}(k_x, k_y, \omega) \end{aligned} \quad (30)$$

(only along x and y directions). For expression shortening, it is convenient to introduce markings $G_{n_z m_z}(k_x, k_y, \omega) \equiv G_{n_z m_z}$. For $X_x = X_y = X_z \equiv -|X|$, $a_x = a_y = a_z \equiv a$ and $\mathcal{K} = \frac{i\hbar}{2\pi|X|} \delta_{n_z, m_z}$, we obtain:

$$G_{n_z-1, m_z} + \rho G_{n_z m_z} + G_{n_z+1, m_z} = \mathcal{K} \delta_{n_z, m_z}, \quad (31)$$

where denotation is introduced:

$$\begin{aligned} \rho &= \frac{\hbar\omega - \Delta}{|X|} + 2(\cos a k_x + \cos a k_y) \equiv \\ &\equiv \frac{E_{\vec{k}} - \Delta}{|X|} - \mathcal{F}_{xy} \equiv \varepsilon_{\vec{k}} - \mathcal{F}_{xy} \end{aligned} \quad (32)$$

(the quantity \mathcal{F}_{xy} is defined in Eq. (26), while, $\varepsilon_{\vec{k}}$ i.e. $E_{\vec{k}}$ which express a possible energy of excitons in films, will be calculated latter).

Eq. (31) is in fact a system of $N+1$ nonhomogeneous algebraic differential equations with (starting boundary) conditions: $G_{n_z, m_z} = 0$, for $n_z < 0$ and $n_z > N+1$:

$$\begin{aligned}
 \rho G_0 + G_1 &= \mathcal{K}_0 \\
 G_0 + \rho G_1 + G_2 &= \mathcal{K}_1 \\
 G_1 + \rho G_2 + G_3 &= \mathcal{K}_2 \\
 &\dots\dots\dots \\
 G_{n_z-2} + \rho G_{n_z-1} + G_{n_z} &= \mathcal{K}_{n_z-1} \\
 G_{n_z-1} + \rho G_{n_z} + G_{n_z+1} &= \mathcal{K}_{n_z} \\
 G_{n_z} + \rho G_{n_z+1} + G_{n_z+2} &= \mathcal{K}_{n_z+1} \\
 &\dots\dots\dots \\
 G_{N-3} + \rho G_{N-2} + G_{N-1} &= \mathcal{K}_{N-2} \\
 G_{N-2} + \rho G_{N-1} + G_N &= \mathcal{K}_{N-1} \\
 G_{N-1} + \rho G_N &= \mathcal{K}_N
 \end{aligned} \tag{33}$$

where is describe: $G_{n_z} \equiv G_{n_z m_z}$ and $\mathcal{K} \delta_{n_z, m_z} \equiv \mathcal{K}_{n_z}$, because m_z is the blinding index.

3.2. Dispersion law

In order to find exciton energies, we need poles of Green's functions, which are obtained when a determinant of a system (33) is equalized with zero, i.e.

$$D_{N+1}(\rho) = \begin{vmatrix} \rho & 1 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ 1 & \rho & 1 & 0 & \dots & 0 & 0 & 0 & 0 \\ 0 & 1 & \rho & 1 & \dots & 0 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & \ddots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & 1 & \rho & 1 & 0 \\ 0 & 0 & 0 & 0 & \dots & 0 & 1 & \rho & 1 \\ 0 & 0 & 0 & 0 & \dots & 0 & 0 & 1 & \rho \end{vmatrix}_{N+1} \equiv 0, \tag{34}$$

and this determinant is actually a note for Chebyshev's polynomials of second kind (and $(N+1)$ -th order) [21,22]:

$$D_{N+1}(\rho) \equiv C_{N+1}(\rho) = \rho C_N(\rho) - C_{N-1}(\rho). \tag{35}$$

The condition $D_{N+1}(\rho) = 0$ is reduced to $C_{N+1}(\rho) = 0$ and is satisfied by $N+1$ solutions in form:

$$\rho_v = -2 \cos \frac{v\pi}{N+2}; v = 1, 2, \dots, N+1. \tag{36}$$

Using this and replacing Eq. (32) we find:

$$E_{k_x k_y}(v) = \Delta - 2|X| \left(\cos a k_x + \cos a k_y + \cos \frac{\pi v}{N+2} \right). \tag{37}$$

In order to compare with dispersion law of excitons in a bulk we will write this expression in more simple, non-dimensional form ($\rho_v = -2 \cos a_z k_z(\mu)$):

$$E_{k_x k_y}(v) = \mathcal{F}_{xy} + \mathcal{G}_z(v); \mathcal{G}_z(v) \equiv \frac{1}{2} [1 - \cos a_z k_z(v)]. \tag{38}$$

Previous expression represents the dispersion law of excitons of ideal monomolecular film and has the same form as the Eq. (26) obtained for corresponding ideal unlimited structures, with difference that in Eq. (26) k_z is practically continuous variable (interval $[0, \pi/a]$) as k_x and k_y , while here is discrete and is given by expression:

$$k_z(v) = \frac{\pi}{a} \frac{v}{N+2}; v = 1, 2, \dots, N+1. \tag{39}$$

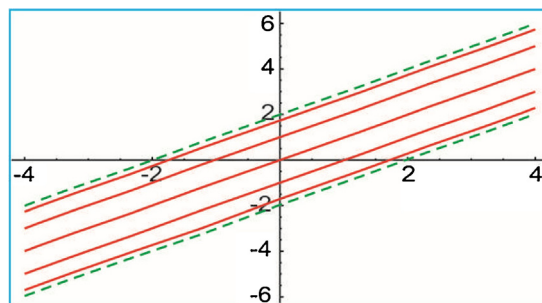


Fig. 4. Exciton energies of a molecular film.

Graphical representation of dispersion law is given on Fig. 4, showing possible exciton energies in ideal five-layer monomolecular film (full lines) together with bulk boundaries (dotted lines). Same as for corresponding bulk crystalline structures, we will use ordinate for values of reduced non-dimensional energies ϵ_v , depending on two-dimensional function \mathcal{F}_{xy} , for which is used graph abscissa.

These analyzes have shown significant differences regarding dispersion law for excitons in spatially strongly limited systems (nanofilm-structures) as strictly result of border presence of these structures, in which energy spectra is highly discrete and have two gaps. Sizes of gaps depend on film thickness and decrease rapidly with its increase.

3.3. Spectral weights

In order to find certain Green's function we will start from the system of Eq. (31), which is now suitable to represent in the operator form:

$$\hat{D}_{N+1} \hat{G}_{N+1} = \hat{K}_{N+1} \Rightarrow \hat{G}_{N+1} = \hat{D}_{N+1}^{-1} \hat{K}_{N+1}, \tag{40}$$

where: \hat{D}_{N+1} is a matrix corresponding to the determinant of system D_{N+1} , \hat{G}_{N+1} and \hat{K}_{N+1} are vectors of Green's functions and Kronecker's delta symbols:

$$\hat{G}_{N+1} = \begin{pmatrix} G_{0, m_z} \\ G_{1, m_z} \\ \vdots \\ G_{n_z, m_z} \\ \vdots \\ G_{N, m_z} \end{pmatrix}; \hat{K}_{N+1} = -\frac{i\hbar}{2\pi|X|} \begin{pmatrix} \delta_{0, m_z} \\ \delta_{1, m_z} \\ \vdots \\ \delta_{n_z, m_z} \\ \vdots \\ \delta_{N, m_z} \end{pmatrix}. \tag{41}$$

Since the inverse matrix \hat{D}_{N+1}^{-1} may be expressed through adjunct matrix, whose elements D_{ik} are cofactors of elements d_{ik} from the direct matrix, we may write:

$$\begin{aligned}
 G_{n_z, m_z} &= \frac{1}{D_{N+1}} \sum_q D_{n_z, q} K_{q, m_z} = \\
 &= -\frac{1}{D_{N+1}} \frac{i\hbar}{2\pi|X|} \sum_q D_{n_z, q} \delta_{q, m_z} = \\
 &= -\frac{i\hbar}{2\pi|X|} \frac{D_{n_z, m_z}}{D_{N+1}}.
 \end{aligned} \tag{42}$$

Cofactor D_{n_z, m_z} calculation is based on knowing the system determinant D_{N+1} .

Since for the equilibrium processes within system are important only diagonal Green's functions $G_{n_z; n_z} \equiv G_{n_z}$, calculating cofactors

Table 1
Exciton probabilities in the ideal four-layered film.

Reduced relative ENERGY	ULTRATHIN FILM atomic plane				
	upper boundary	first inner	central inner	last inner	lower boundary
-1.73205	0.08333	0.25000	0.33333	0.25000	0.08333
-1.00000	0.25000	0.25000	0.00000	0.25000	0.25000
0.00000	0.33333	0.00000	0.33333	0.00000	0.33333
1.00000	0.25000	0.25000	0.00000	0.25000	0.25000
1.73205	0.08333	0.25000	0.33333	0.25000	0.08333

$D_{n_z, m_z} \equiv D_{n_z}$ is significantly simplified. It turns out that they are equal to the product of two auxiliary determinants:

$$D_{n_z} = C_{n_z} C_{N-n_z}, \quad (43)$$

where C_{n_z-1} and C_{N-n_z} are corresponding Chebyshev's polynomials of second kind. Therefore, Green's function of the ideal film is:

$$G_{n_z} = \frac{i\hbar}{2\pi|X|} \frac{C_{n_z} C_{N-n_z}}{C_{N+1}}. \quad (44)$$

These Green's functions are multipolar, since denominator consists of a polynomial C_{N+1} of $N+1$ -th order. Therefore, factorization on simple poles must be performed [21]:

$$G_{n_z} = -\frac{i\hbar}{2\pi|X|} \sum_{v=1}^{N+1} \frac{g_{n_z; n_z}(\rho_v)}{\rho - \rho_v}. \quad (45)$$

Spectral weights $g_{n_z; n_z}(\rho_v) \equiv g_{n_z}^v$ then may be expressed using:

$$g_{n_z}^v = \frac{C_{n_z}(\rho_v) C_{N-n_z}(\rho_v)}{\frac{d}{d\rho} C_{N+1}(\rho)|_{\rho=\rho(v)}}. \quad (46)$$

Using the rule for derivative of determinant we obtain:

$$\begin{aligned} \left[\frac{d}{d\rho} C_{N+1}(\rho) \right]_{\rho=\rho_v} &= \sum_{i=1}^{N+1} C_{i-1}(\rho_v) C_{N+1-i}(\rho_v) = \\ &= \sum_{i=1}^{N+1} \frac{ini\xi_v \sin(N+2-i)\xi_v}{in^2\xi_v} = \\ &= \frac{in^2(n_z+1)\xi_v}{\sum_{i=1}^{N+1} in^2i\xi_v}; \xi_v = \frac{\pi v}{N+2}, \end{aligned} \quad (47)$$

and spectral weights became:

$$g_{n_z}^v = \frac{2}{N+2} in^2 \left[(n_z+1) \frac{\pi v}{N+2} \right]. \quad (48)$$

The spectral weights of Green's functions are squares of the modules of the wave function of excitons [1–3, 13–15] and enable determination of spatial distribution, i.e. probability to find excitons with certain energies per layers of crystalline film. This is in fact the spatial distribution of probability to find certain energy state of excitons.

Numerically calculated, values of reduced energies and corresponding spectrum functions (spatial distribution of probability) for four-layered film ($N=4$, where $k_x=k_y=0$) are shown in the table. Table 1. shows spatial distribution of exciton energies occurrence probabilities in ideal monomolecular film.

This table shows that for one certain energy, probability of exciton occurrence per all layers is equal to one, and that probability per one layer for all energies is also equal to one, i.e.

$$\sum_{n_z=0}^N g_{n_z}^v = 1; \sum_{v=1}^{N+1} g_{n_z}^v = 1. \quad (49)$$

3.4. The permittivity

While determining dynamic permittivity of a crystalline film, the equation by Dzyaloshinski and Pitaevski [20] may also be used in the same form (26) in which was used for calculating permittivity of corresponding bulk structures, with difference that in this case permittivity depends on a film layer n_z , i.e:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - \frac{\pi S|X|}{i\hbar} [G_{n_z}(\omega) + G_{n_z}(-\omega)]. \quad (50)$$

Since starting Hamiltonian was taken in harmonic approximation, ignoring (small) members of exciton-phonon interaction [1, 6, 15], permittivity tensor has the real elements only. It is led to that all elements of permittivity tensor in one crystalline plane parallel to boundary planes are mutually equivalent, i.e. they depend on plane position ($n_z \in [0, N]$).

Substituting expression for Green's functions (45) to (50), we obtain equation for the relative dynamic permittivity tensor elements in direction normal to boundary planes in form:

$$\varepsilon_{n_z}^{-1} = 1 - \frac{S}{2} \sum_{v=1}^{N+1} \sum_{s=+,-} \frac{g_{n_z}^v}{\rho_s - \rho_v}, \quad (51)$$

where: $\rho_{\pm} = \mp|f| - |\rho| - \mathcal{F}_{xy}$, and after arranging the expression we finally follow:

$$\varepsilon_{n_z}(\omega) = \left[1 + S \sum_{v=1}^{N+1} g_{n_z}^v \frac{\rho_v - |\rho| + \mathcal{F}_{xy}}{|f|^2 - (\rho_v - |\rho| + \mathcal{F}_{xy})^2} \right]^{-1}. \quad (52)$$

Figure 5(a)–(c) show a dependence of dynamical permittivity (ε) on reduced relative energy, i.e. the frequency of external electromagnetic field ($f \equiv \hbar\omega/|X|$) for four-layered monomolecular film. Dependence was calculated for plane center of the Brillouin's zone ($k_x=k_y=0$), but individually per atom planes (parallel boundary areas) of crystalline film, that is for $n_z=0$, and $n_z=1, 2, 3, 4$. Each graph shows number and position of resonating peaks. The resonating peaks on frequency dependence of dynamic permittivity are the positions – resonating frequencies where permittivity diverges to $\pm\infty$. These are also the energies (wavelengths) of electromagnetic radiation which model crystal in given place practically “swallows”, i.e. these energies are absolutely absorbed there.

A final number of resonating peaks is present, because k_z component of exciton wave vector is discrete. Only for certain values of k_z component for wave vector (with given values k_x and k_y), resonating and radiation absorption may occur. Therefore, at least three and maximum five peaks occur – number is equal to number of permitted states along axis of translation symmetry breakage, in this case along z -axis. Due to the symmetry of model, distribution of peaks in complementary planes is the same: $n_z=0$ and $n_z=4$ (two boundary planes), as well as for $n_z=1$ and $n_z=3$ (first two inner planes). Only $n_z=2$ is different, since for the odd total number of atomic planes the middle plane has no complementary plane!

This result may be explained by experimental facts regarding resonating optical peaks in similar molecular layered nanostructures. In Refs. [23–25] this was evidenced in perylene chemical

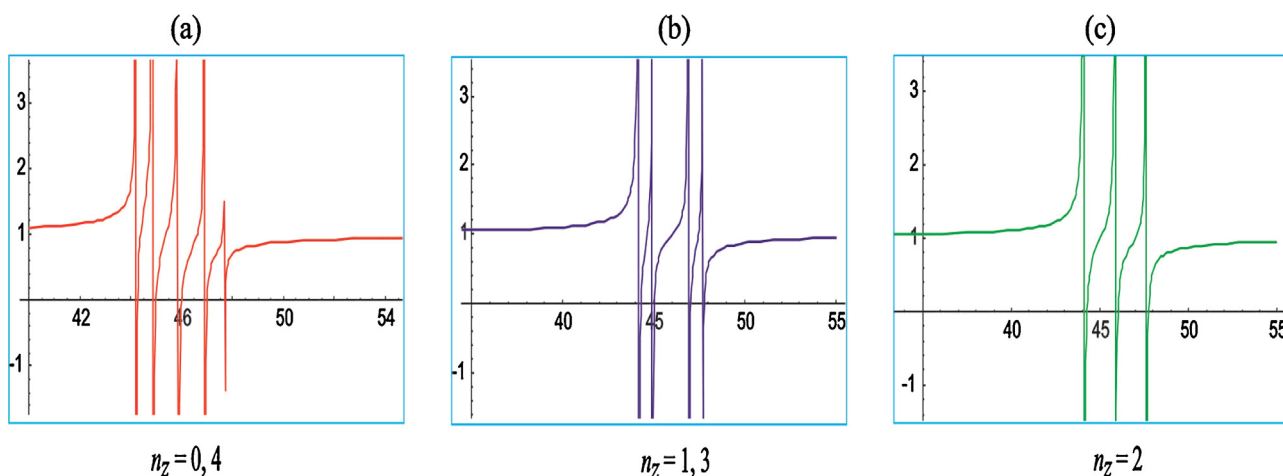


Fig. 5. Dynamic permittivity of ideal films.

compounds (PTCDA, PTCS, PTFE and PBI) and explained by resonating effects at specific unoccupied levels. These effects are manifested by narrow optic absorption in close infra red band. In comparison with our results, which are concerning deeper infra red band in electromagnetic radiation, it may be concluded that these differences are effect of differences in crystalline (chemical and physical) structure, as well as in the model (real and ideal) of samples investigated.

4. Conclusions

This paper describes original the application of Paulian Green's function method onto theoretical studies of optical properties of molecular crystals. Using Boson representation, microscopic (dispersion law and exciton state distribution) and macroscopic (dynamic permittivity) properties of these crystals may be successfully described.

Strictly following the defined procedure, this paper shows that this method may be adapted and successfully applied to the study of dielectric properties in structures with disturbed spatial-translational symmetry, such as ultra thin films. Functioning of a newly developed approach is illustrated through the problem of finding energy spectra and exciton states, as well as for determining relative permittivity of ideal monomolecular film.

In presence of two parallel boundaries in the system, energy spectrum is determined and possible exciton states were found. Important differences, comparing with unlimited crystalline structures, have been observed. Energy spectrum of excitons in monomolecular films is explicitly discrete, and the number of discrete levels is equal to the number of atomic planes (including boundary areas) along the axis of the spatial limitations of ultra thin film. In bulk sample, a single zone where excitons "take" all possible energy values exists. All discrete levels are located within bulk boundaries, and the difference in zone width depends strictly (and inversely) on film thickness.

Comparing with bulk structures, where excitons may be found at any place with equal probability, in monomolecular film structures probability of finding exciton strongly depends on film thickness.

In exciton systems of monomolecular crystal bulk, where relative dynamic permittivity depends on frequency, continuous absorption zone exists in certain range of external radiation energy. In monomolecular film-structures resonating peaks exist with precisely determined energies, i.e. resonating frequencies. Number of these peaks depends on position of atomic plane (regarding bound-

ary planes of the film) for which permittivity is being calculated: it decreases with the depth of ultra thin film.

Differences between properties of the observed film and corresponding bulk structures drastically decrease as the thickness of film is higher. All this implies to the existence, and is a consequence, of the quantum size effects.

Method of Green's differential functions, adapted on described manner should be applied further to the study of behaviour and properties of more realistic quantum structures, for instance ultra thin films with perturbed boundary conditions.

Acknowledgements

Investigations which results are presented in this paper were partially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants: OI-171039 and TR-34019) and by the Provincial Secretariat for Science and Technological Development of Vojvodina (114-451-972/2016), as well as by the Ministry of Science and Technological Development of the Republic of Srpska (Grant: 19/6-020/961-16/15).

References

- [1] V.M. Agranovich, V.L. Ginzburg, *Crystal Optic with Space Dispersion and Theory of Excitons*, Nauka, Moskwa, 1979 (in Russian).
- [2] Ch. Kittel, *Quantum Theory of Solids*, Wiley & Sons, New York, 1963.
- [3] G. Mahan, *Many Particle Physics*, Plenum Press, New York, 1990.
- [4] M.G. Cottam, D.R. Tilley, *Introduction to Surface and Superlattice Excitations*, University Press, Cambridge, 1989.
- [5] S.G. Davison, M. Steslicka, *Basic Theory of Surface States*, Clarendon Press, Oxford, 1996.
- [6] V.M. Agranovich, K. Schmidt, K. Leo, Surface states in molecular chains with strong mixing of frenkel and charge-transfer excitons, *Chem. Phys. Lett.* 325 (2000) 308.
- [7] A. Langner, A. Hauschild, S. Fahrenholz, M. Sokolowski, Structural properties of tetracene films on Ag(1 1 1) investigated by SPA-LEED and TPD, *Surf. Sci.* 574 (2–3) (2005) 153.
- [8] W.J. Doherty III, A.G. Simmonds, S.B. Mendes, N.R. Armstrong, S.S. Saavedra, Molecular ordering in monolayers of an alkyl-substituted perylene-bisimide dye by attenuated total reflectance ultraviolet-visible spectroscopy, *Appl. Spectrosc.* 10 (2005) 1248.
- [9] L.L. Chang, L. Esaki, Semiconductor quantum heterostructures, *Phys. Today* 45 (10) (1992) 36.
- [10] I. Vragovich, R. Scholz, M. Schreiber, Model calculation of the optical properties of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) thin films, *Europhys. Lett.* 57 (2002) 288.
- [11] J.P. Šetrajčić, D.I. Ilić, B. Markoski, A.J. Šetrajčić, S.M. Vučenić, D. Lj. Mirjanić, B. Škipina, S. Pelemiš, Adapting and application of the green's functions method onto research of the molecular ultrathin film optical properties, in: 15th Central European Workshop on Quantum Optics, Belgrade, 2008.
- [12] I.D. Vragovich, R. Scholz, J.P. Šetrajčić, Optical properties of PTCDA bulk crystals and ultrathin films, *Mater. Sci. Forum* 518 (2006) 41.

- [13] G. Rickayzen, *Green's Functions and Condensed Matter*, Academic Press, London, 1980.
- [14] E.N. Economou, *Green's Functions in Quantum Physics*, Springer, Berlin, 1949.
- [15] A.S. Davydov, *Theory of Molecular Excitons*, Nauka, Moskwa, 1908 (in Russian).
- [16] M.C. Tringides, M. Jatochawski, E. Bauer, Quantum size effects in metallic nanostructures, *Phys. Today* 60 (4) (2007) 50.
- [17] I. Frenkel, On the transformation of light into heat in solids. I & II, *Phys. Rev.* 37 (17) (1931) 1276.
- [18] R.P. Djajić, D. Lj. Mirjanić, B. Nikin, J.P. Šetrajčič, B.S. Tošić, Stimulated absorption in ferroelectrics, *J. Phys. C* 20 (1987) 5585.
- [19] V.M. Agranovich, B.S. Toshich, Collective properties of frenkel excitons, *Zh. Eksp. Teor. Fiz.* 53 (1967) 149 (*Sov. Phys.-JETP* 26 1968 104).
- [20] I.E. Dzyaloshinskii, L.P. Pitaevskii, Van der waals forces in an inhomogeneous dielectric, *Zh. Eksp. Teor. Fiz.* 36 (1959) 1797 (*Sov. Phys. JETP* 9 1959 1282).
- [21] G. Arfken, *Mathematical Methods for Physicists*, 3rd ed., Academic Press, Orlando, 1985.
- [22] T.J. Rivlin, *Chebyshev Polynomials*, Wiley, New York, 1990.
- [23] A.B. Djurisić, T. Fritz, K. Leo, Modeling the optical constants of organic thin films: application to 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), *Opt. Commun.* 183 (2000) 123.
- [24] R. Friedlen, M.P. de Jong, S.L. Sorensen, W. Osikowicz, S. Marciniak, G. Öwall, A. Lindgren, W.R. Salaneck, Resonant auger spectroscopy on perylene, porphyrine and hexabenzocoronene thin films, in: *The 2 nd Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications*, Kanagawa, 2003.
- [25] F. Würthner, C. Bauer, V. Stepanenko, S. Yagai, A black perylene bisimide super gelator with an unexpected J-type absorption bank, *Adv. Mater.* 20 (2008) 1695.