12th Scientific-Research Symposium with International Participation
„METALLIC AND NONMETALLIC MATERIALS“ B&H, 19th-20th April 2018

SEPARABILITY OF DISCRETE OPTICAL PROPERTIES OF MOLECULAR CRYSTALLINE NANOSTRUCTURES

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Keywords: exciton, ultra-thin film, permittivity, optical properties

ABSTRACT
This paper presents a model of molecular ultrathin (nano) crystalline film and feature research methodology of exciton system as well as analysis of dielectric properties of these spatially very restricted structures with perturbed fundamental parameters on surfaces. Using the two-time Green's functions, adapted for research of symmetry breaking crystalline structures, and graphical-numerical software, the dynamic permittivity along the direction vertical to the boundary surface of the film was calculated. It was shown that the appearance and the presence of localized states in the surfaces and in the boundary layers of the film depend on the thickness of the film and the changing values of parameters in the border areas of the film. These localized states define schedule and determine the number of (discrete and selective) resonant absorption lines in the near infrared area of the external electromagnetic radiation, which occur in the ultrathin structure instead of continuous absorption area in the bulk structure of the same chemical and crystallographic structure. It is important fact in (nano)optical engineering as well as in nanomedicine, i.e. nanopharmacy – for construction of nanomarkers, nanocarriers and nanodelivers of medical drugs.

1. INTRODUCTION
Nanostructures represent new and promising materials in wide range of possible usage. Based on our research in ultrathin crystal structures performed so far, superlattices, Q-wires and Q-dots, we will consider the materials that can act as carriers for medical drugs and tagged substances. In that processes, apparently, interaction between nanostructure and the lightis crucial, so we need to know the optical properties of nanostructured material in order to find out what conditions are necessary to trigger required request (for example request for medical drug release). The goal of multidisciplinary researches with biocompatible molecular nanomaterials is to find the parameters and the possibilities to construct border surfaces that will, in interaction with biological environment, create such properties of nanolayers that are convenient and react with particular optical response when wrapped around medical drug

material, biochips and biomarkers. These layers should demonstrate controlled disintegration of structure, better differencing dielectric properties, discrete selective luminescence and appropriate bioporosity as all these are the requirements of contemporary nanomedicine [1].
We assume that some observed material (for example medical drug) is wrapped around with layered structure, consisted of up to ten crystalline planes. These nanostructures are known as ultra-thin films (UTF's). Interaction of boundary planes (upper plane interact with surrounding environment and lower plane interact with substrate – in our example medical drug material) determine optical properties of the whole nanostructure. In our previous research [2] we determine dielectric permittivity and consequently optical properties (absorption, refraction and transparency indices) per each layer of the UTF's. However, for optical properties of the whole UTF's, we need to calculate multiple processes of refraction, absorption and reflection on every plane and determine overall optical properties.

2. OPTICAL PROPERTIES OF WHOLE UTF's

2.1. Refraction in/at/of UTF's

On the beginning we started to calculate refraction index of the sample with 2 parallel layers (Figure 1), and then with 3 layers – previous + one, and consequently with generalizing multiple refraction processes we obtain and define refraction index of the whole film with N layers, i.e. with N+1 planes.

$$\frac{N}{n_{\mathrm{f}}(\omega)} = \sum_{n_z=0}^{N} \frac{1}{n_{n_z}(\omega)} \quad \Rightarrow \quad n_{\mathrm{f}}(\omega) = N\left(\sum_{n_z=0}^{N} n_{n_z}^{-1}(\omega)\right)^{-1}. \tag{1}$$

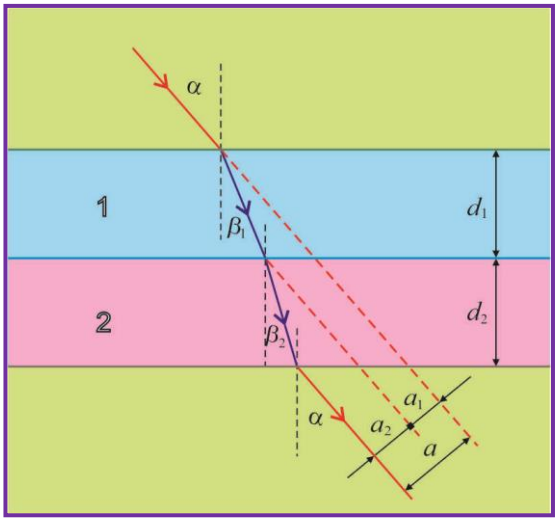

Figure 1. Refraction processes

2.2. Absorption, Reflection and Transparency in/at/of UTF's

Then we observe processes of incoming of polychromatic incoming radiation (from the IR region) with unitary intensity, when radiation goes from "upper" (n_z = 0) to "lower" (n_z = N) boundary plane with neglecting internal (inner-film) conversion (Figure 2). That is possible when we neglect all processes of multiple reflection, refraction and absorption in/on internal planes of the film [3, 4, 5]. Considering the fact that refraction indices are most important (only) on incident boundary planes (which is visible from the graphics on Fig. 2 enclosed), their contribution could be neglected, especially if we are interested in absorbed and transparent part of irradiation.

On the "upper" boundary plane (n_z = 0) comes radiation beam with unitary intensity, and here reflects part r_0, absorbs κ_0 and transfer τ_0, where it is $\tau_0 = 1 - r_0 - \kappa_0$. Then, on first internal plane (n_z = 1) comes τ_0, reflects $r_1\tau_0 \approx 0$, absorbs $\kappa_1\,\tau_0$ and transfer τ_1, where is: $\tau_1 = \tau_0 - \kappa_1\,\tau_0 = (1 - \kappa_1)\,\tau_0$. Then on the next plane (n_z = 2) comes τ_1, reflects $r_2\tau_1 \approx 0$, absorbs $\kappa_2\,\tau_1$ and transfer τ_2, where is: $\tau_2 = \tau_1 - \kappa_2\,\tau_1 = (1 - \kappa_2)\,\tau_1$. On the lower surface of the film ($n_z = N$) comes τ_{N-1}, reflects $r_N\tau_{N-1} \approx 0$, absorbs $\kappa_N\,\tau_{N-1}$ and transfer $\tau_N \equiv \tau_{\mathrm{f}}$, where is:

$$\tau_{\mathrm{f}}(\omega)=\tau_0\prod_{n_z=0}^{N}\left(1-\kappa_{n_z}\right), \tag{2}$$

and in the whole film absorb:

$$\kappa_{\mathrm{f}}(\omega)=\kappa_0(\omega)+\sum_{n_z=1}^{N}\kappa_{n_z}\tau_{n_z-1};$$
$$\tau_{n_z}=\left(1-\kappa_{n_z}\right)\tau_{n_z-1};\quad n_z=1,2,3,\ldots,N. \tag{3}$$

Thereby must energy conservation law be valid, i.e. $r_0+\kappa_{\mathrm{f}}+\tau_{\mathrm{f}}\equiv 1$.

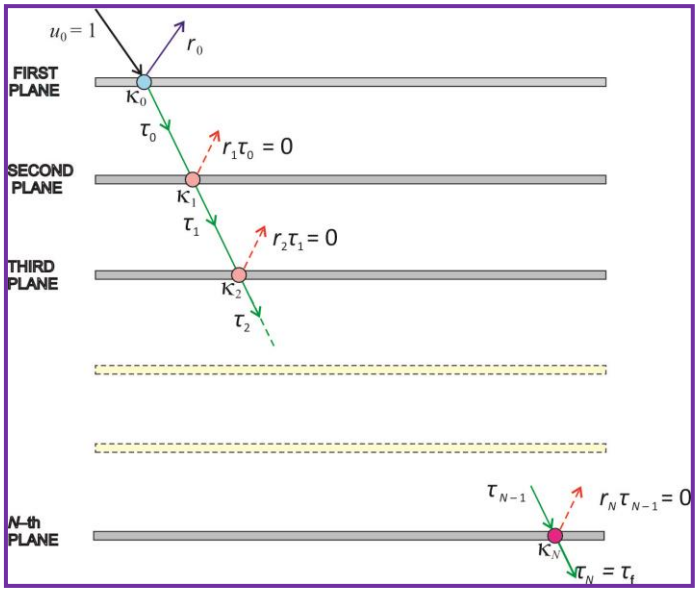

Figure 2. Absorption, reflection and transparency processes

Mechanism for dielectric permittivity is based on excitons, quasiparticles created by incident irradiation. We calculated exciton dispersion law and consequently dielectric permittivity which describe optical response of material. Here is used method of Green's function for dispersion law calculation [6], and formula of Dzyaloshinski and Pitaevski [7] in determining dynamic permittivity as a macroscopic characteristic of the crystalline film. Overall permittivity is defined as module of complex value: $\varepsilon=\varepsilon'+\mathrm{i}\,\varepsilon''$, from where is: $|\varepsilon| = (\varepsilon'^2+\varepsilon''^2)^{1/2}$, and in respect with [7]: $\varepsilon^{1/2} = n + \mathrm{i}\kappa$, from there follows:

$$\varepsilon_{\mathrm{f}}(\omega)\equiv\left|\varepsilon_{\mathrm{f}}(\omega)\right|=n_{\mathrm{f}}^2(\omega)+\kappa_{\mathrm{f}}^2(\omega). \tag{4}$$

For all mentioned above we have prepared and developed procedure in *Wolfram Mathematica* software, with help of *CorelDraw*, where we carried out numerical processing and converted corresponding graphs. Characteristic graphs on Fig. 3 and Fig. 4 show some results of our research of representative cases for perturbed films for weaker (Fig. 3) and heavier (Fig. 4) perturbation. In all columns of these graphs are shown dynamical optical index spectra in relative frequency range $f\in$ (43.5, 47.5) from IR spectra for the whole film! Values $d_{0/N}$ and $x_{0/N}$ are perturbation parameters which describe intensity of boundary perturbations for exciton energy localized on site and perturbation on transfer of exciton energy between particular site and first neighbors. Labels "0" and "*N*" refer to boundary planes in UTF's (the first and the last plane).

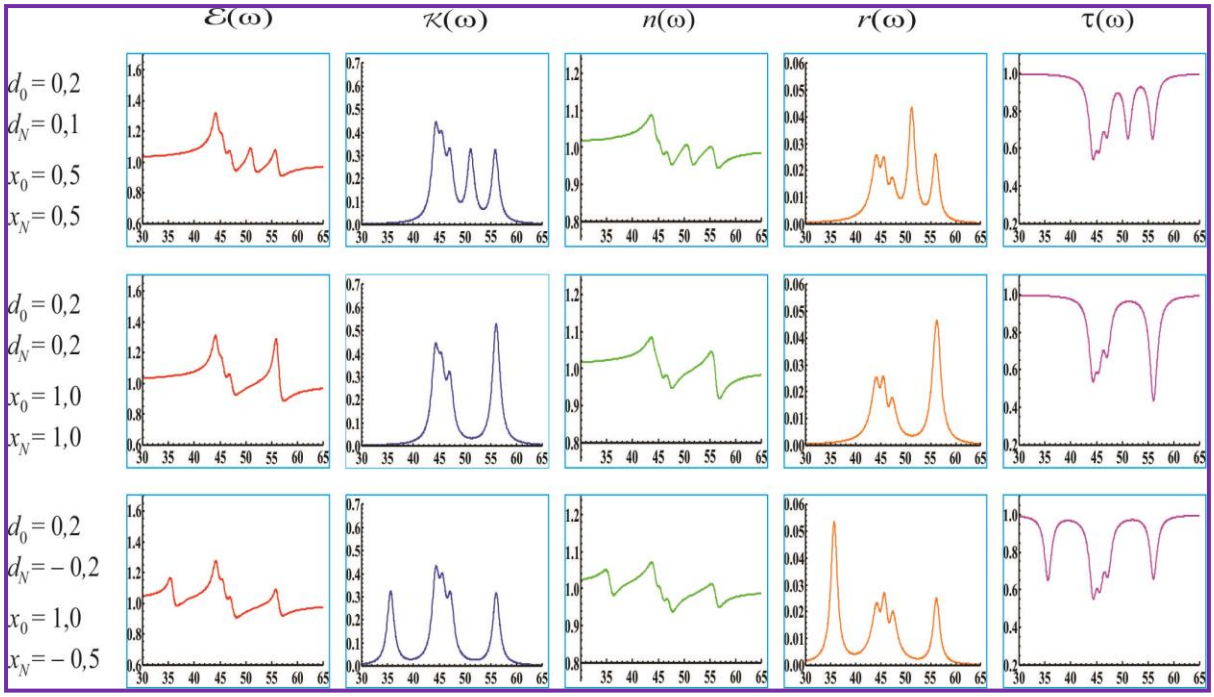

Figure 3: Absorption, reflection and transparency processes

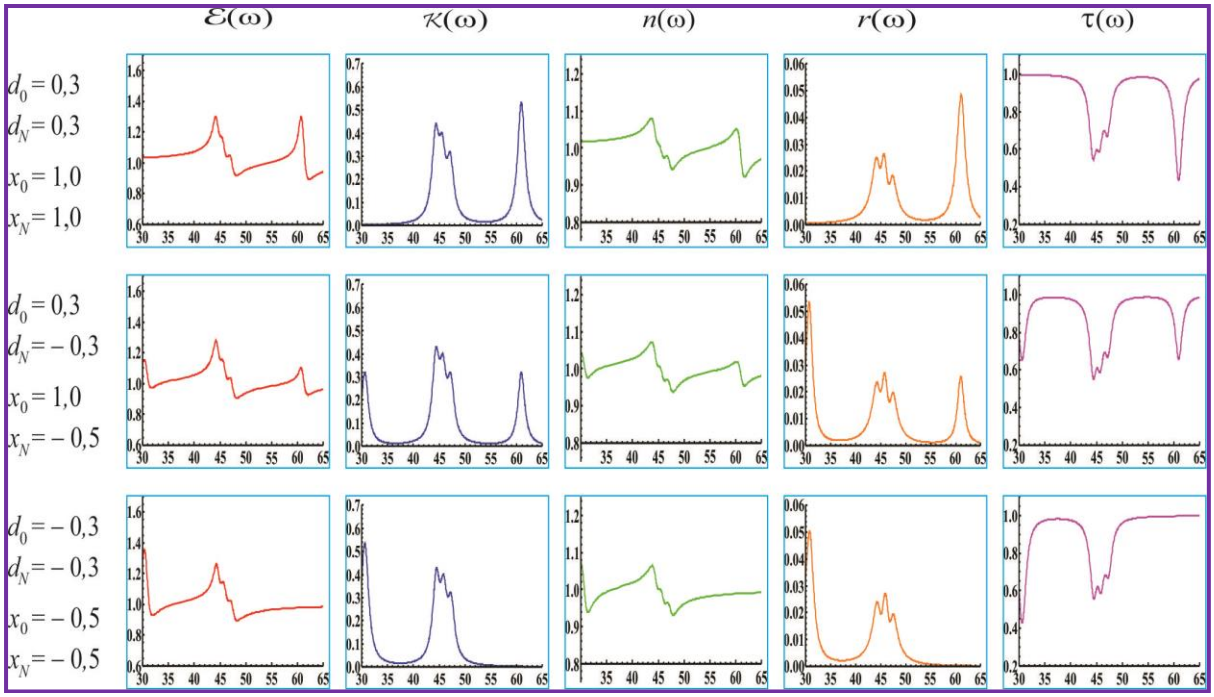

Figure 4: Absorption, reflection and transparency processes

Significant differences in dielectric response (macroscopic, but dimensionally quantum properties) of excitons between bulk and symmetrical film-structures represent results of this research. This is exclusive consequence from the limited dimensionality of the film along z – axe and existence of perturbation parameters on boundary surfaces and boundary layers. Dielectric (permittivity) and optical properties (absorption, refraction, reflection and transparency) of the film show property of selectivity, i.e. appearance of discrete resonant absorption peaks on exactly determined energies, where their number and

disposition strongly depend on number of the layers of the film, and perturbation parameters. These properties give to the film advantage when compared with bulk (where dielectric response is continual for determined energy zone), therefore in this case films could be used as some kind of electromagnetic filter from external electromagnetic radiation. Number of absorption peaks is lower, i.e. dominant frequencies exist which will be actually absorbed. In region where absorption index increase – refraction index decrease, and on region where absorption index change are refraction index singularities.

These results, as consequences of quantum-dimensionally and confinement effect, could be used as good basis for the theory of manipulation of boundary parameters for the purpose of obtaining targeted features of nanostructured samples in the frame of optical engineering, which is in his early stage [8–10]. The goal is production of some different electronic, rather – photonic nano-elements for new-generation computers, then more efficient converters of solar energy, nano-robot elements, and ultimately production and study of nanoparticle medical drug carriers.

3. CONCLUSION REMARKS

This paper describes theoretical investigation of specificity in microscopic and macroscopic optical properties of exciton systems in molecular ultrathin film-structures. Most important results of this analysis are as follows.

1) Opposite of bulk structures, where excitons may be found at any position with equal probability, in molecular film structures probabilities to find excitons are strongly dependent from film thickness and intensity of parameter change at border areas of the film.
    - Whether exciton will be separated at border areas of a film depends from perturbation energy of molecules in those layers. Increase of this energy proportionally increases probability of exciton localization at border areas, and these excitons have higher possible energies.
    - Localization of excitons between border and adjoining planes is determined by changes of transfer energy of excitons between borders of these layers. Increase of these parameters brings to increase of probability to find excitons in border areas of film considered.
2) In molecular film structures, resonating peaks exist at precisely determined energies. Number of these peaks depends on position of planes in film for which permittivity is calculated, but also from size of perturbation parameters.
    - By changing energy values for molecules at border areas, absorption zone widens, and dominating resonating peaks are visible only at those border areas.
    - By increasing vault energy of excitons in border layer of the film, symmetrical widening of absorption zone occurs, and also quenching certain inner resonating peaks.

Acknowledge

This work was 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 High Education, Science and Technological Development of the Vojvodina (Grant: 142-451-2469/2017-01/02) as well as by the Ministry of Science and Technological Development of the Republic of Srpska (Grant: 19/6-020/961-16/15).

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