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Different regions of exciton localized states in ultrathin dielectric films

Jovan P. Šetrajčić[a,*], Stevo K. Jaćimovski[b]

[a] University of Novi Sad, Faculty of Sciences, Department of Physics, Vojvodina, Serbia
[b] Academy of Criminalistic and Police Studies, Zemun, Belgrade, Serbia

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ABSTRACT

This paper presents the results of research conducted in the field of confinement effects in ultrathin dielectric films. Method of choice is the method of Green's functions which proved to be a very powerful tool for theoretical research in solid state physics. Among many other properties of materials, such as optical, conductive, etc. with this method it is possible to obtain critical values of boundary parameters corresponding to all transitions from bulk to localized exciton states. This research is valid for four layered crystalline film, since that type of ultrathin structure was the object of research. Conditions for occurrence of one, two, three, or even four localized states have been found and analyzed and regions with equal number of localized states have been defined. This corresponds to the process of reconstruction of the energy spectra of excitons in quasi 2D nanostructures with respect to those in corresponding bulk-structures.

1. Introduction

If we are interested in what happens when external electromagnetic field is applied on material sample we can use the concept of excitons. It is very important to theory of optical engineering [1,2]. If the system boundaries are present (sample of the nano-dimensional) then we have a set of interesting phenomena comparing such as occurrence of localized states. Using of the Green's functions method [3–6], perturbation of values of boundary parameters which correspond to transitions from continuous zone of bulk exciton states to different regions of localized exciton states can be determined and analyzed here.

As noted in our review papers [7,8], the application of nanostructures requires knowledge of their fundamental physical (mechanical, electromagnetic, optical, etc.) characteristics [9–11]. Theoretical research of low-dimensional crystalline systems (nanostructures) have been intensified recently in order to obtain fundamental information relating to extremely different physical and chemical properties of material, and also due to their wide practical application in nanotechnology [12–14].

A special feature of these "tiny" structures is that presence of surfaces and boundary layers causes highly altered fundamental properties of these materials and occurrence of nonspecific phenomena (as a consequence of quantum size and confinement effects [15–17]) in comparison to the properties of corresponding "large", i.e. bulk samples. Reduction of sizes in nanostructures leads to the so-called confinement of elementary excitation due to which their branches are quantized (dimensional quantization) and a substantive modification of their energy spectrum, group velocity and polarization occur. Due to the reflections from the inner surface of the structure, elementary excitations hybridize or localize and cease to be transparent, and their energy is reduced compared to the case in the bulk structure.

Nevertheless, the uncharted part of low-dimensional samples properties is the one due to presence of physically different structure boundaries and changed fundamental energy parameters of elementary excitation systems at those surface layers. Changing values of these parameters that correspond to levels of intermolecular interactions in boundary regions has the important role in creating differences in physical properties of nanoscopic structures in comparison to corresponding bulk structures [18–20].

The absorption of photons in dielectric solid can lead to located excitations – Frenkel's excitons, which are responsible for organic crystals optical characteristics. Interest in the study of exciton subsystem appeared because excitons are responsible for dielectric, optic (absorption, dispersion and luminescence), photoelectric and other properties of crystals [21–24]. Ultrathin organic (dielectric) films are of potential importance for future electronic compounds and optic devices and they are in the focus of current intensive studies [24–26].

During the past decade, we have studied the basic physical characteristics of different ultrathin crystalline films [7,8,27–31], and one can see that essential properties of these systems arise with perturbation conditions which appear at and within their surface layers. Based on the formed models of ultrathin films and superlattices, as well as monitored microscopic and macroscopic features of such crystalline systems, we showed an extremely large influence of the

* Corresponding author.

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decrease of spatial dimensions and boundary conditions to the change of physically relevant (dielectrics, i.e. optics) characteristics of crystal substances [32–35]. This was investigated in molecular crystalline nano-films, which are typical examples of optically active materials.

Our research of optical properties of nanoscopic samples [35–38] have shown that the appearance of drastic differences of fundamental physical properties, for example. certain number and selective arrangement of resonant absorption lines at molecular ultrathin films, instead of continual absorption zone with the bulk-samples of the same chemical and crystallographic structure, can be associated with the number and discreet exciton spectra, especially with the emergence of those non-bulk (i.e. out of bulk), or localized states. What has never been explored is how the sizes of boundary exciton parameters in the film affect the occurrence of an adequate number of absorption lines, or under what conditions will mono-absorption occur, or be absorbed by only two or three frequency lines from the entire absorption zone of adequate bulk-samples.

It is very important problem in theory of optical engineering and optical transitions [1,2,7,39–42], and exactly that is the topic of research that we show in this paper.

2. Exciton model

The starting point is the exciton Hamiltonian in harmonic (Bose) approximation and nearest-neighbors approximation (because orbital wave functions overlap only for neighboring molecules) [23–25], which we take in the following form:

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B_{\vec{n}}^{+} B_{\vec{n}} + \sum_{\vec{n},\vec{m}} X_{\vec{n}\vec{m}} B_{\vec{n}}^{+} B_{\vec{m}}, \tag{1}$$

where $B_{\vec{n}}^{+}$ and $B_{\vec{n}}$ are creation and annihilation operators of exciton at the site $\vec{n}$ of a crystal lattice, $\Delta_{\vec{n}}$ is energy of isolated exciton in that site, when $X_{\vec{n}\vec{m}}$ is matrix element of dipole-dipole interaction represent of excitons transfer from site $\vec{n}$ to neighboring site $\vec{m} = \vec{n} + \vec{e}$, removed for $\vec{e}$.

The definition of Green's function, which in theoretical analysis has been provided by starting method [3,4,25,43–45], is as follows:

$$G_{\vec{n}\vec{m}}(t) = \langle\langle B_{\vec{n}}(t) | B_{\vec{m}}^{+}(0) \rangle\rangle, \tag{2}$$

and this relation satisfies the following equation of motion:

$$i\hbar \frac{d}{dt} G_{\vec{n}\vec{m}}(t) = i\hbar\delta(t)\delta_{\vec{n}\vec{m}} + \Delta_{\vec{n}} G_{\vec{n}\vec{m}}(t) + \sum_{\vec{l}} X_{\vec{n}\vec{l}} G_{\vec{l}\vec{m}}(t). \tag{3}$$

It should be noted that the correct description of exciton model in the solid state is performed by using Pauli's Hamiltonian [21–25]:

$$H = H_0 + \sum_{\vec{n}} \Delta_{\vec{n}} P_{\vec{n}}^{+} P_{\vec{n}} + \sum_{\vec{n},\vec{m}} X_{\vec{n}\vec{m}} P_{\vec{n}}^{+} P_{\vec{m}} + \sum_{\vec{n},\vec{m}} Y_{\vec{n}\vec{m}} P_{\vec{n}}^{+} P_{\vec{n}} P_{\vec{m}}^{+} P_{\vec{m}}$$

and by using two-time dependent Pauli's Green's function [25]:

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

with corresponding equation of motions. However, as we have shown in the work [25], in the approximation of small exciton concentration, completely identical results are obtained by using boson representation of excitons - expressions (1)–(3).

In this way, we obtain a form of Green's function by full time and space Fourier transform [25] and later, from the pole of the same, we obtain the required exciton dispersion law which has the following, non-dimensional, form:

$$E_{\vec{k}} \equiv \frac{\hbar\omega - \Delta}{|X|} = R_{xy} + S_z ;$$
$$R_{xy} \equiv 2(\cos ak_x + \cos ak_y) ; \quad S_z \equiv 2\cos ak_z \tag{4}$$

The possible energy of excitons $E_{\vec{k}}$ as a function of two-dimensional quantity R_{xy} is illustrated on the Fig. 1. The second quantity S_z is parameter function. It is clear that for $ak_i \in [0, \pi]$, $i = x, y, z$ (the first Brillouin zone), and these values are within the intervals:

$$R_{xy} \in [-4, +4]; \quad S_z \in [-2, +2] \quad \Rightarrow \quad E_{\vec{k}} \in [-6, +6].$$

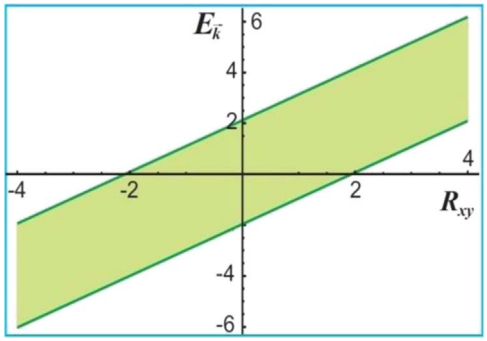

Fig. 1. Dispersion law of excitons in bulk-structure (as in [5]).

As it is evident, all possible exciton states are continuously distributed in a limited/bounded zone – these are well known bulk states of excitons.

3. Excitons in ultrathin film-structures

The same approach can be used for investigation of nano-sized samples. Contrary to bulk samples, ultrathin films do not have property of the translational invariance and therefore the absence of translational invariance is the main reason for fascinating different properties of nanosized samples.

Because the most of well-controlled ultrathin crystalline films are made by molecular doping or deposition of/on massive specimens [32–37], nanofilm is formed in/on the bulk structure (Fig. 2). In this case, boundary parameters of a film cannot be independent or different from each other. This is why we have a model of a general – unsymmetrical crystalline nanofilm whose parameters are changing in following boundaries:

$$\Delta_{\vec{n}} \equiv \Delta(1 + d_0\delta_{n_z,0} + d_N\delta_{n_z,N});$$
$$X_{\vec{n},\vec{n}+\vec{\lambda}} \equiv X(1 + x_0\delta_{n_z,0} + x_N\delta_{n_z,N-1});$$
$$X_{\vec{n},\vec{n}-\vec{\lambda}} \equiv X(1 + x_0\delta_{n_z,1} + x_N\delta_{n_z,N}). \tag{5}$$

where parameter $d_{0/N} \in [-0{,}2; +0{,}2]$ defines perturbation of the exciton energy at the site of boundary areas, and parameter $x_{0/N} \in [-0{,}99; +2{,}0]$ represents perturbation of exciton transfer energy within boundary layers, along the z-axis: n_z=0, 1, 2, ... N.

Having in mind the Hamiltonian expression (1), the equation of motion (3) for Green's functions and boundary conditions (5), we can

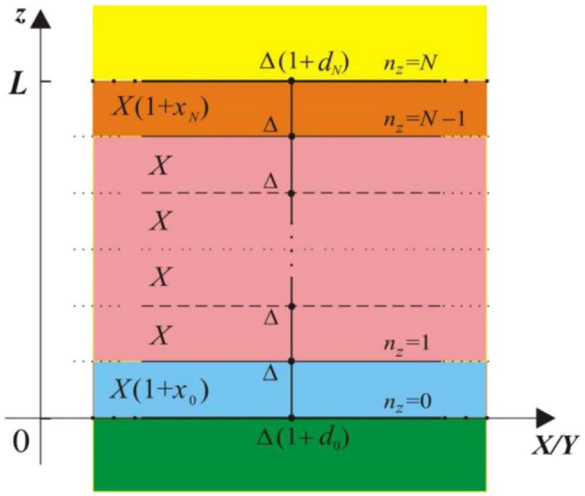

Fig. 2. Cross section of asymmetrical ultrathin film model.