

# Changes in Optical Properties of Molecular Nanostructures

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This paper represents an overview about exciton systems in the molecular nanostructures (ultra thin films and superlattices) and their implications on optical properties, primarily on absorption coefficient, which is given in the form of dielectric permittivity. With utilization of Green's function method, we have calculated dispersion law, spectral weight of exciton states and dielectric permittivity for every type of nanostructures. All obtained results are compared with optical properties in bulk crystals. Dielectric permittivity in all types of nanostructures shows very narrow and discrete dependence of external electromagnetic field frequency, which is a consequence of the expressed quantum effects, very thin thickness in these structures (or at least one dimension confinement) and boundary conditions.

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## 1. Excitons in nanostructures

In this theoretical research of optical properties of nanostructure materials we have to start from the assumption that excitons are generated in materials as response on the external electromagnetic field [1]. Although excitons are not the only (quasi) particles that can be found in the nanostructures when external electromagnetic field is turned on, this statement is satisfactorily correct if we use the molecular crystals [2]. Following this fact, we would restrict our research on dielectric (non-conductive) molecular crystalline materials, where standard excitons Hamiltonian include Pauli-operators with unsuitable statistic and therefore we would have to cross onto Bose statistics [1-3]. In further calculus we would use Green's function method [4] and corresponding equation of motion in approximation of nearest neighbor, but including dimensional restrictions related to configuration and internal organization of nanostructure, in particular we would observe ultra thin films and superlattices. The next step is transition from direct space to  $k$ -space, i.e. performing the time and space Fourier transformations [3, 5]. The advantage of this transition is direct and elegant calculation of energy dispersion law. To obtain the dielectric permittivity (which is related with optical properties of the materials through the absorption coefficient), we would have to calculate Green's functions

exactly [5], with implicit spectral weights, i.e. probability of exciton creation with particular energy and position in nanostructures.

## 2. Dispersion law

We have calculated energy dispersion law for two class nanostructures: ultra thin films and superlattices. The ultra thin film consist of up to 20 parallel layers of atomic (or molecular) crystalline planes, with significant influence of boundaries, which are represented through two kind of exciton perturbations — one is localized on the site of the atom (or molecule), and the second is energy transfer between boundary plane and the first internal neighbor plane. We will indicate with  $\Delta$  exciton energy on the site of the atom, and with  $\varepsilon_{0/N}$  perturbation on that energy, in the first/last plane. Similarly, we will indicate with  $X$  energy transfer between neighbor planes, and with  $x_{0/N}$  perturbation on that energy, between the boundary planes and their first neighbor planes. Using above explained Green's function procedure, where we must perform full time and partial space Fourier-transformation<sup>†</sup>, we have obtained system of  $N$  algebraic difference equations for  $N$  unknown Green's

<sup>†</sup> Partial space Fourier's transform is performed while we assume that film is finite along  $z$ -axis, and practically infinite along other two dimensions.

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function, where  $N$  denote number of atomic planes in ultra thin films. To calculate energy dispersion law for excitons in ultra thin films, it is sufficient to resolve determinant of the system, because poles of the Green's function define exciton energies, which leads to equalizing determinant of the system with zero [3, 5, 6]. In Fig. 1 the non-dimensional form of the exciton energy law for 5-layered film is shown, depending on perturbation parameters  $(\varepsilon_{0/N}, x_{0/N})$ . The crucial result is discreteness of the energies, which is direct consequence of the ultra low dimensionality. With dashed lines are presented boundaries for continuous energy zone in bulk crystals. One can see that sufficient  $\varepsilon$ -perturbation bring one energy level out of the bulk zone and  $x$ -perturbation could bring two energy levels.<sup>‡</sup>

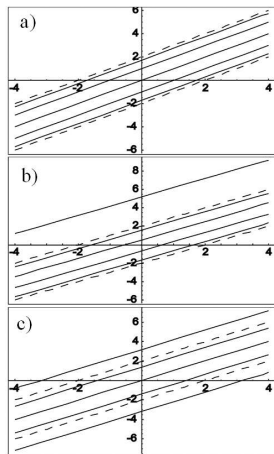


Fig. 1. Exciton dispersion law in 5-layered film: (a) non-perturbed; (b) 10%  $\varepsilon$ -perturbation; (c) 200%  $x$ -perturbation.

We have calculated the exciton dispersion law in superlattices in the same way as in ultra thin films, using Green's function method [4, 5], but in this type of nanostructure exist brake of translational symmetry along one axe, while superlattice represents infinitely repeated and mutually bounded two (or more) kind of ultra thin films, every with their own number of atomic (or molecular) layers, who built up one cell of superlattice, called supercell. For example, for two-film supercell the motive is  $(n_a, n_b)$ . Brake of translational symmetry imply on partial space Fourier's transform, relating to the final system of equations of motion to be order of  $(n_a + n_b) \times (n_a + n_b)$ . To simplify the problem we will solve the simple superlattice problem [3, 8], i.e. we will assume that the energies on the site in the both films are equal ( $\Delta_a = \Delta_b = \Delta$ ) and the energy transfer between layers is equal in both films ( $X_a = X_b = X_s$ ). In this case the influence on the dispersion law of superlattices has not only number

of layers in films  $(n_a, n_b)$ , but also transfer of the energy between two different films ( $X$ ). We have simplified calculations on these two parameters: size (or film thickness) ratio in the supercell  $(n_a, n_b)$ , and energy transfer ratio ( $x$ ) by introducing ratio between energy transfer on the boundary of neighbor films ( $X$ ) and energy transfer inside each film ( $X_s$ ), i.e.  $x = X/X_s$ . In Fig. 2 the non-dimensional energy dispersion law for some characteristic parameters in dependence of  $z$ -component of the non-dimensional wave vector  $k_z$  for the first Brillouin's zone is presented.

One can see that energies in superlattices take quasi-continuous values, forming in such a way allowed and forbidden zones, depending on the wave vector  $k_z$  values throughout the first Brillouin's zone. But, for the  $x = 1$ , superlattices lose their specific properties regarding broken symmetry and converge to the continuous energy zone of the bulk. Also, increasing parameter  $x$  expands entire energy zone, while decreasing parameter  $x$  shrinks zone.

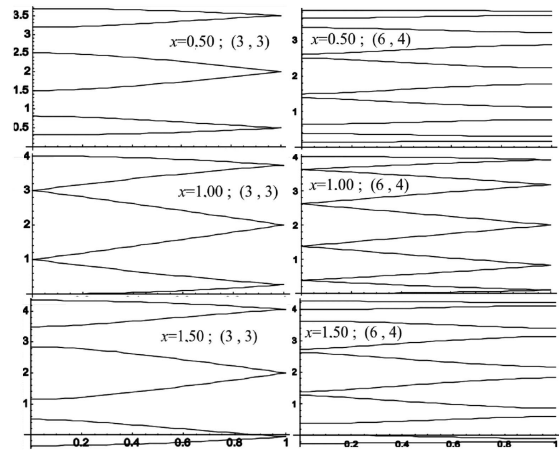


Fig. 2. Exciton dispersion law in superlattice for various  $x$  parameters and supercell disposition.

### 3. Spectral weight

To obtain spectral weights, i.e. probability of finding excitons in ultra thin films or superlattices, we must calculate Green's functions from the system of equations. This could be done if we solve system in a matrix form. Green's functions are roots of the matrix equations, and they are in general case multiplex. After performing factorization, in the numerator arise spectral weights of excitons in certain type of nanostructures. In the ultra thin films, distribution of excitons per atomic layers with particular energy is highly dependable on perturbation parameters  $(\varepsilon_{0/N}, x_{0/N})$ , but in the superlattices spectral weights depend on number and disposition of the film layers inside supercell, and form energy transfer ratio factor ( $x$ ). In Figs. 3 and 4 the spectral weights distributions in ultra thin film and superlattice are shown, respectively.

<sup>‡</sup> Those states are well known as Tamm's or localized states [7, 8].

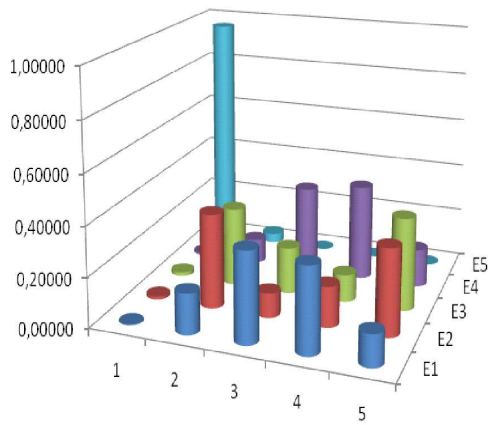


Fig. 3. Spectral weight distribution for 5-layered 10%  $\varepsilon$ -perturbed film.

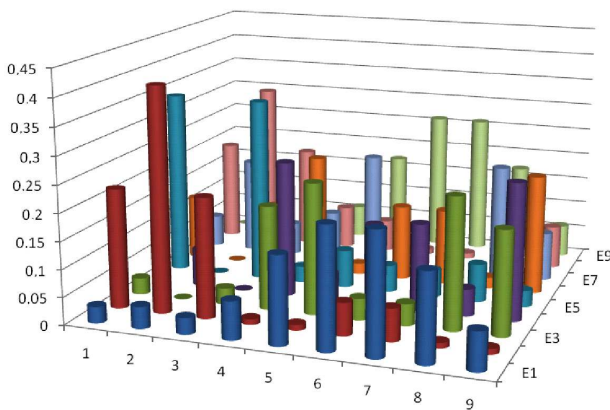


Fig. 4. Spectral weight distribution for superlattice with motive (3, 6) and energy transfer ratio  $x = 0.5$ .

#### 4. Dielectric permittivity

Optical properties of nanostructures are represented by absorption coefficient, quantity which is implicit included in the general form of the refraction index. On the other hand, refraction index is related with dielectric permittivity with  $n(\omega) = \sqrt{\varepsilon_\nu(\omega)}$ , and if we calculate dielectric permittivity we can actually find out optical characteristics of nanostructures. Dielectric permittivity is possible to calculate if we know Green's functions with the Dzyaloshinski–Pitaevski's formula [3, 9]. Depending on the type of the nanostructure, boundary conditions and perturbation parameters, dielectric response of the nanostructure on the external electromagnetic field is in general demonstrating narrow and selective absorption characteristics, showing in that way quantum effects on the macroscopic level, what is exclusively implicated by the reduced size in one direction (ultra thin films), or broken symmetry (superlattices). In Figs. 5 and 6 the dependences of dielectric permittivity from the reduced external electromagnetic field in ultra thin film and su-

perlattice are presented, respectively.

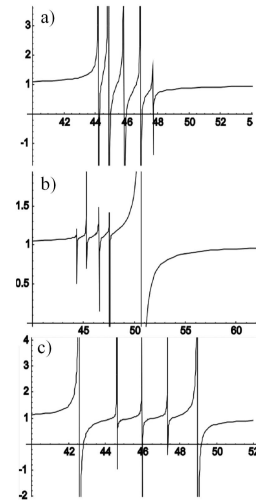


Fig. 5. Dielectric permittivity in 5-layered film: (a) non-perturbed; (b) 10%  $\varepsilon$ -perturbation; (c) 200%  $x$ -perturbation.

In the ultra thin films, dielectric permittivity indicates discrete absorption, with number of resonant peaks equal to the number of atomic planes inside the film. One can see that the  $\varepsilon$ -perturbation results in movement absorption zone toward higher energies and emphasizing only one of the all resonant piques, while the  $x$ -perturbation spreads entire absorption zone.

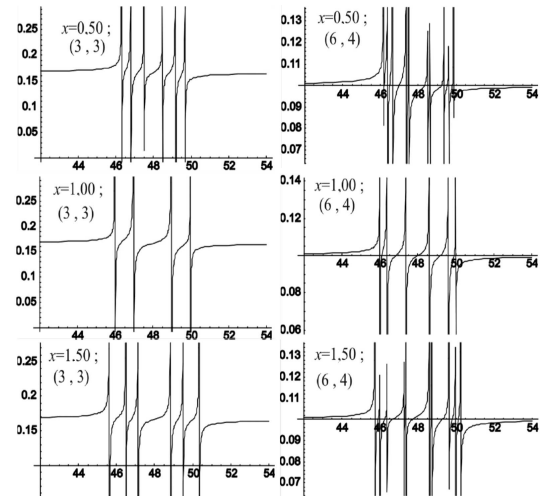


Fig. 6. Dielectric permittivity in superlattice for various parameters  $x$  and supercell disposition.

Dielectric permittivity in superlattices remains of the same shape as in ultra thin films, with discrete and resonant peaks, but disposition of the resonant peaks inside absorption zone strongly depends on the setup of the supercell and energy transfer ratio ( $x$ ). Generally, the increase of the parameter  $x$  broadens entire absorption

zone, but some of the resonant piques can be degenerated or nearly overlapped. This is more rendered in the superlattices with films in supercell with the rule  $n_b = n_a \pm 1$ . Degeneration of the absorption resonant peaks take place regularly for  $x = 1$ , where superlattice converge to thin films in the meaning of the optical properties. For the superlattice with the same number of atomic planes in both films ( $n_a = n_b$ ), but for  $x \neq 1$ , degeneration can not take place regardless of the value of  $x$ -parameter.

This result may be explained by experimental facts regarding resonating optical peaks in similar molecular layered nanostructures. In papers [10–12] this was evidenced in perylene chemical compounds and explained by resonating effects at specific unoccupied levels. These effects are manifested by narrow optic absorption in close infrared band. Good agreement in resonating absorption may be attributed and explained by presence of boundary conditions and quantum size effects. Differences in profile of absorption lines appear because in our work we observed only electron line spectra, disregarding oscillatory and rotational contributions.

## 5. Conclusions

In this paper we have theoretically studied behavior of the ultra thin films and superlattices in external electromagnetic field and calculated dispersion law, spectral weight and dielectric permittivity. The most important results and conclusions are:

1. Energy levels are discrete in ultra thin films, and quasi-continuous in superlattices. Position of energy levels strongly depends on boundary parameters which are characterized by perturbation parameters in ultra thin films or setup of supercell and energy transfer ratio parameter  $x$  in superlattices.
2. Localized or Tamm's states arise with sufficient perturbation parameters in ultra thin films, or energy transfer ratio parameter  $x$  in superlattices.
3. Spectral weights indicate probability of exciton creation in particular plane, with particular energy. The general rule is the greater is perturbation (or boundary condition influence), the greater is probability of creation of exciton in particular plane, where boundary influences take place. In addition, states with values of spectral weights equal to zero (forbidden states) exist inside the nanostructures.
4. Optical properties of nanostructures demonstrate very narrow or discrete absorption characteristics,

where dielectric permittivity dependence on external electromagnetic field indicate existence of discrete resonant peaks, with number is in general equal to the number of atomic layers in nanostructure. Exception from this rule is internal planes in ultra thin film, where forbidden states exist, or for the degenerate or overlapped states in superlattices. Bandwidth of the absorption zone is adjustable and dependable on perturbation parameters in ultra thin films, or energy transfer ratio parameter  $x$  in superlattices.

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