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Adaption and application of the Green function method to research on molecular ultrathin film optical properties

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Abstract

Interest in the study of the exciton subsystem in crystalline structures (in this case nanostructures, i.e. thin films) occurred because dielectric, optical, photoelectric and other properties of materials can be explained by means of it. The basic question to be solved concerning theoretical research into the spatially strongly bounded structures is the inability to apply the standard mathematical tools: differential equations and Fourier analysis. In this paper, it is shown how the Green function method can also be efficiently applied to crystalline samples so constrained that quantum size effects play a significant role on them. For the purpose of exemplification of this method's application, we shall consider a molecular crystal of simple cubic structure: spatially unbounded (bulk) and strongly bounded alongside one direction (ultrathin film).

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(Some figures in this article are in colour only in the electronic version.)

1. Excitons in bulk structures

The starting point in our theoretical analysis of the exciton subsystem in bulk crystalline structures will be the standard exciton Hamiltonian [1, 2]

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

along with definition expression of the commutator Paulian Green function [3–5]:

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

with equation of motion

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

where $P_{\vec{n}}^+$ and $P_{\vec{n}}$ are the creation and annihilation operators of excitons on site \vec{n} of the crystalline lattice, $\Delta_{\vec{n}}$ is the corresponding exciton energy, while $X_{\vec{n},\vec{m}}$ and $Y_{\vec{n},\vec{m}}$ are the matrix elements of exciton transfer between sites \vec{n} and \vec{m} . Using commutator identities for Pauli operators [5, 6],

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

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

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

where $\mathcal{T}_{\vec{n}\vec{l}\vec{m}}(t) = \langle \langle P_{\vec{n}}^+(t) P_{\vec{l}}(t) P_{\vec{m}}(t) | P_{\vec{m}}^+(0) \rangle \rangle$ is the Paulian Green function of third order.

The main difficulty of the exciton theory lies in the fact that Pauli operators are neither bosonic nor fermionic operators, but a hybrid between the two, with kinematics (4) that which is fermionic for one node and bosonic for different nodes. For exact analysis of exciton systems, which include interexciton exchange interactions, it is not sufficient to replace Pauli operators with bosonic operators, but the following replacement in Hamiltonian (1) must be made [6]:

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

Our key target, however, is to adapt Green's functions method to a spatially bounded structure so that the influence of spatial restraint on the change of its macroscopic physical properties can be seen. For this reason, Paulian Green function from equation (2) will be substituted with the corresponding bosonic Green's function on the basis of approximations resulting from (6):

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

In this way, we obtain

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

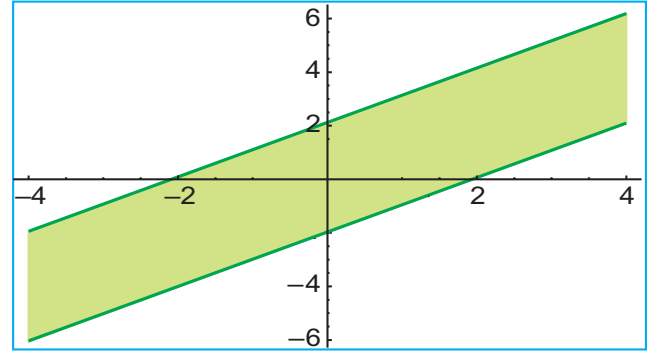


Figure 1. Exciton dispersion law in a monomolecular bulk crystal.

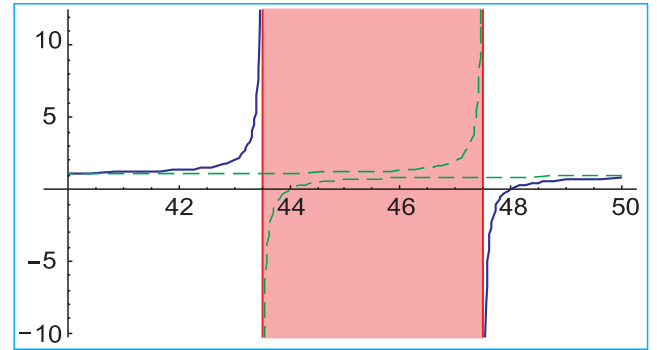


Figure 2. Permittivity of a monomolecular bulk crystal.

Carrying out the equation of motion (3), the expression for Green functions is obtained in form

$$\begin{aligned} G_{\vec{k}}^-(\omega) &= \frac{i\hbar}{2\pi} \\ &\times \frac{1}{\hbar\omega - \Delta - 2[X_x \cos a_x k_x + X_y \cos a_y k_y + X_z \cos a_z k_z]} \\ &\equiv \frac{i\hbar}{2\pi} \frac{1}{\hbar\omega - E_{\vec{k}}}, \end{aligned} \quad (9)$$

from which the exciton dispersion law is derived in non-dimensional form:

$$\begin{aligned} \mathcal{E}_{\vec{k}} &\equiv \frac{E_{\vec{k}} - \Delta}{|X|} \\ &= \mathcal{F}_{xy} + \mathcal{G}_z, \quad \begin{cases} \mathcal{F}_{xy} = -2(\cos ak_x + \cos ak_y), \\ \mathcal{G}_z = -2 \cos ak_z. \end{cases} \end{aligned} \quad (10)$$

This law is shown in terms of \mathcal{F}_{xy} in figure 1, from which the continual energy zone is observed.

The relative dynamic permittivity of the bulk molecular crystal is [1, 2, 7]

$$\varepsilon_{\vec{k}}^-(\omega) = \left[1 + S \frac{\mathcal{E}_{\vec{k}} + |p|}{|f|^2 - (\mathcal{E}_{\vec{k}} + |p|)^2} \right]^{-1}, \quad (11)$$

where $|f| = \hbar\omega/|X|$ and $|p| = \Delta/|X|$, while S is the frequency characteristic of crystal observed and of the outer electromagnetic field. Figure 2 shows the relative permittivity of the monomolecular bulk crystal in terms of reduced exciton frequency of the outer electromagnetic field $\hbar\omega/\Delta$.

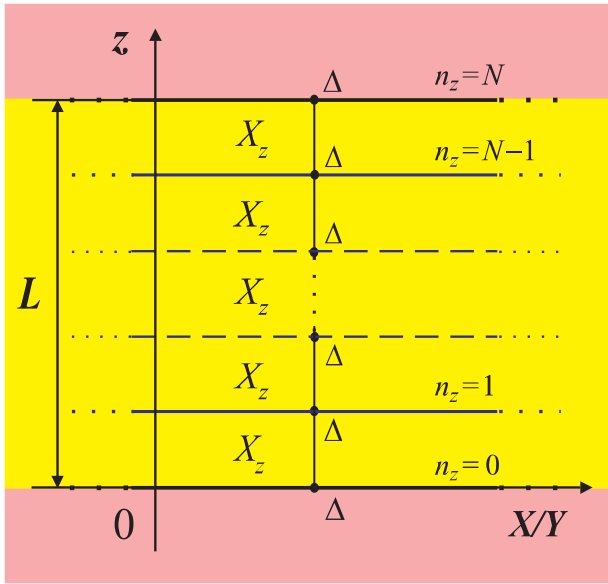


Figure 3. Cross-section of the monomolecular crystalline film in the $X(Y)Z$ plane.

The existence of an absorption zone within specified cut-off frequencies is visible. For all other energies this crystal is transparent.

2. Excitons in thin crystalline films

Crystalline films are confined crystalline structures in which translational symmetry is broken along the direction perpendicular to the film (z -direction, figure 3) [8–11].

In this paper we observe an ideal ultrathin film of simple cubic crystalline structure (one molecule per elementary cell) made on the substrate with the use of some appropriate technological process (deposition, sputtering, etc). Index n_z takes values $n_z = 0, 1, 2, \dots, N$, where N is the number of layers along the z -direction ($N \in [2, 8]$). Energy spectra and states will be determined similarly as in the case of unbounded crystalline structures, by using the Green's function method. By using the partial spatial Fourier transformation (because the translational symmetry has been disturbed only along the z -direction), we obtain the system of $N + 1$ non-homogeneous algebraic-difference equations:

$$G_{n_z-1, m_z} + \varrho G_{n_z, m_z} + G_{n_z+1, m_z} = \mathcal{K} \delta_{n_z, m_z}, \quad (12)$$

where

$$\begin{aligned} \varrho &= \frac{\hbar\omega - \Delta}{|X|} + 2(\cos ak_x + \cos ak_y) \\ &\equiv \frac{E_{\vec{k}} - \Delta}{|X|} - \mathcal{F}_{xy} \\ &\equiv \mathcal{E}_{\vec{k}} - \mathcal{F}_{xy}. \end{aligned} \quad (13)$$

In order to find the spectra of the allowed exciton energies amounts, it is necessary to determine the zeros of the determinant of system (12). By carrying out this task, the exciton dispersion law in thin films is obtained in

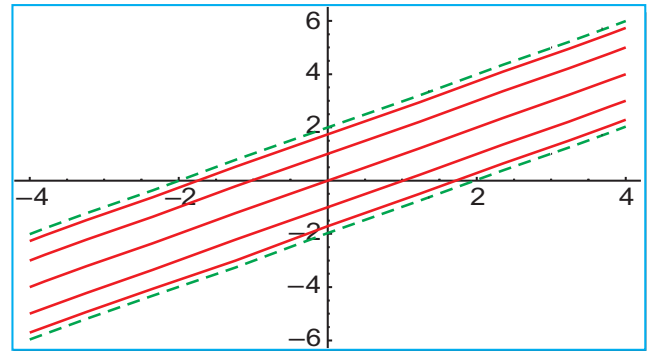


Figure 4. Exciton dispersion law for a monomolecular thin film consisting of five layers.

non-dimensional form:

$$\begin{aligned} \mathcal{E}_{k_x k_y}(v) &= \mathcal{F}_{xy} + \mathcal{G}_z(v), \\ \mathcal{G}_z(v) &\equiv \frac{2 + \varrho_v}{4} = \frac{1}{2} [1 - \cos a_z k_z(v)], \end{aligned} \quad (14)$$

where

$$k_z(v) = \frac{\pi}{a} \frac{v}{N+2}, \quad v = 1, 2, \dots, N+1. \quad (15)$$

The derived expression is similar to that of unbounded (bulk) structures. The main difference is that the z -component of the wave vector k_z is strictly discrete here. Graphic presentation of the exciton dispersion law for a monomolecular thin film consisting of five layers is shown in figure 4. Broken lines represent the boundaries of the corresponding bulk structure.

It can be seen that the energy spectra of excitons in thin films are predominantly discrete inside the bulk boundaries.

2.1. Permittivity of the thin film

In order to determine dynamical permittivity of the thin film, it is possible to make use of the same expression that has been used for bulk structures [7], considering that permittivity of a thin film depends on the number of layers n_z :

$$\varepsilon_{n_z}(\omega) = \left[1 + S \sum_{v=1}^{N+1} g_{n_z}^v \frac{\varrho_v - |p| + \mathcal{F}_{xy}}{|f|^2 - (\varrho_v - |p| + \mathcal{F}_{xy})^2} \right]^{-1}, \quad (16)$$

where

$$g_{n_z}^v = \frac{2}{N+2} \sin^2 \left[(n_z + 1) \frac{\pi v}{N+2} \right] \quad (17)$$

are the spectral weights for Green's functions of a thin crystalline film. Dynamical permittivity in terms of frequency of the external radiation (i.e. reduced relative energy) for a monomolecular thin film composed of four layers is shown in figure 5.

Different from bulk structures, where the continual absorption zone appears in the definite frequency band of external radiation, resonant peaks with film structures exist only on some resonant frequencies.

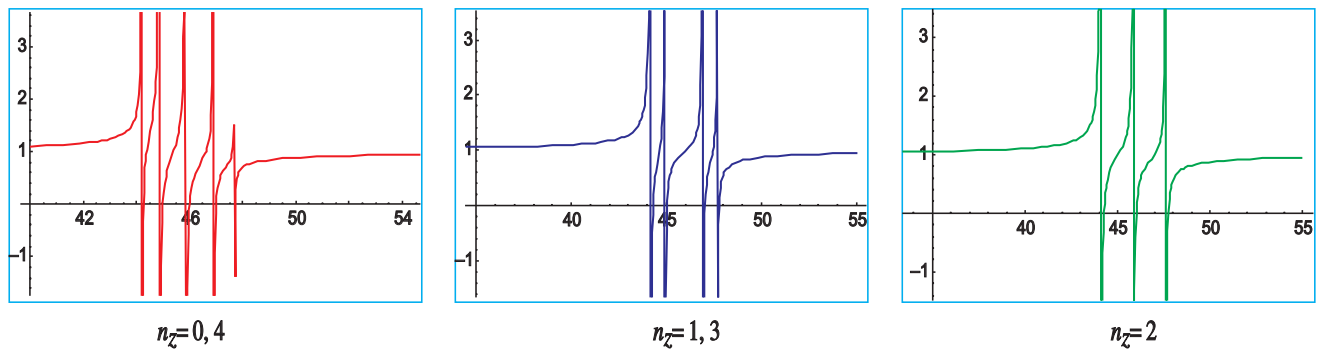


Figure 5. Dynamical permittivity of an ideal monomolecular thin film.

3. Conclusion

In this paper, it is shown that the Green function method can be efficiently applied on crystalline samples so constrained that quantum size effects play a significant role on them. The intention of the authors was to analyze the influence of boundaries on the exciton dispersion law. Our findings for thin films are compared with those for massive (bulk) structures in order to recognize the main differences between them.

In addition to the basic task to adapt the Green function method to quantum systems, it is shown in this paper that the energy spectra of excitons in thin films are predominantly discrete inside the bulk boundaries. Thereat, the number of discrete energy levels is equal to the number of atomic planes (including boundary surfaces) along the direction in which the spatial restraint exists. All these discrete levels are located inside bulk boundaries.

Examination of relative dynamical permittivity versus frequency of the thin film has shown that resonant peaks with film structures exist only on some resonant frequencies (i.e. corresponding energies). The number of these peaks depends on the location of the observed atomic plane (with respect to the boundary surfaces) and decrease towards the inside of the thin film.

As the observed film is thicker, the differences between its properties and the corresponding bulk structure become drastically smaller. All this indicates the existence, and represents the result, of the quantum size effect [12].

Acknowledgments

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