Method for Calculating One-Exciton Absorption Spectrum or Space-Restricted Lattices

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The problem of the one-exciton absorption spectrum is considered for the lattice of two-level interacting atoms whose initial energy splitting depends on the coordinate. It is shown that for some types of interatomic interaction, this problem can be reduced to a differential equation of Schrödinger type, which, in some cases, can be solved in closed form. By way of example, problems on the one dimensional chain having an initial splitting jump and on the spherical cluster are solved. In both cases analytical solutions are obtained, which considerably reduce the time required for calculations of one-dimensional systems and permit the calculation of three-dimensional spherical clusters, whereas the numerical calculation becomes impossible for the clusters with a radius larger than ten lattice constants. The spectra calculated for small systems completely coincide with the spectra obtained by means of numerical diagonalization. The proposed method may appear to be convenient for solving problems related to Frenkel excitons in systems having no translation symmetry (disordered systems).

1. Introduction

The recent advent of technology of manufacturing small-sized crystalline structures has stimulated spectroscopic studies of such objects. These objects include, for example, quantum wells, quantum wires, J-aggregates and nanocrystals. Physical properties of such objects (absorption spectra, the specific heat, etc.) are significantly determined by their restricted sizes. From the point of view of optical spectroscopy, such systems can be treated, in some cases, as fragments of crystal lattice, and their absorption spectra can be interpreted using the concept of excitons. In this case it is useful to have simple computational technique
for estimating the scale of effects related to the restricted size of these systems. This paper deals with one such method.

In the second section, the mathematical scheme of the method is presented, and the differential equation is obtained for the exciton Green's function required for calculation of the absorption spectrum. In the third section, the one dimensional exponential model of an exciton is formulated, in which the interatomic interaction exponentially varies in space, and the equation obtained in the second section has a simpler form and can be exactly solved in some cases. As an example, expressions are obtained for the absorption spectra of a finite chain and a chain in which the distribution of the initial splitting energy has the form of meander. In the forth section, the suggested method is generalized to the case of three-dimensional restricted systems. In this case, the equation for Green's function simplified, if the interatomic interaction is described by the Yukawa potential. In this section, the expression derived for the absorption spectrum of a spherical cluster. The spectra obtained in Sections 3 and 4 exhibit a well developed structure and strongly differ from the monochromatic spectrum of an infinite crystal. Almost all spectra were tested by means of a direct computer diagonalization, and, in all cases, complete agreement was achieved. The computer calculation of the spectra of one-dimensional chains with lengths exceeding 100 lattice constants $a$ takes much more time than the calculation according the above expressions. Numerical computer-aided analysis of the spectral structure of a three-dimensional cluster requires several hours for the clusters radius $10a$. At the same time, as shown in Section 4, the spectrum of a cluster with radius of $30a$ exhibits the well-developed structure related to the restricted size of the cluster. The expressions obtained in the Section 4 can be used for estimating effects caused by the restricted size of aspherical clusters.

Note that all the expressions obtained in this paper are essentially based on the exponential (one-dimensional problems) and Yukawa (three-dimensional problem) types of interatomic interaction. This, however, does not appreciably restrict the field of application of the above method for the following reason. The exciton spectrum is often described in effective mass approximation, which adequately reflects the dispersion law only for long-wavelength
excitons. The presence of two parameters in exponential (Yukawa) potential allows one to simulate not only the effective mass of an exciton but also the exciton bandgap.

2. Equation for the exciton Green’s function

Consider a regular lattice of two-level atoms. We assume that the initial (neglecting the interatomic interaction) splitting of atomic levels is a given function $\varepsilon(r)$ of the atomic coordinate $r$. Consider also the interatomic interaction, which can cause the energy transfer between atoms, the dependence of this interaction on the interatomic distance being determined by the function $w(r)$ We will study only one particle excited states of this system and the absorption spectrum related to the transitions to these states from the ground state, i.e. the one-exciton absorption spectrum. If the transition dipole moment is the same for all atoms in the lattice, this spectrum can be found by diagonalization of the matrix $H_{rr'} = \delta_{rr'}\varepsilon(r) + w(r - r')$, the positions of spectral lines being determined by eigenvalues, and their intensites—by the squares of sums of components of corresponding column eigenvectors (it is in this way that squares of moduli of corresponding matrix elements upon transitions from ground state are calculated). Below, however, we will use the following method of calculation of the above spectrum. We will construct Green’s function $g_{rr'} = (E - H)^{-1}_{rr'}$ for matrix $H$ and define the function $G(r, E)$ as follows

$$G(r, E) = \sum_l g_{rl}$$

Then, the absorption spectrum $A(E)$, correct to insignificant factors, has the form

$$A(E) = -\text{Im} \sum_r G(r, E + i\delta) \quad (1)$$

each line in the spectrum being discribed by Lorentzian with the half-width $\delta$. By considering $w(r - r')$ in the matrix $H$ as a perturbation, we write Dyson equation for Green’s function
\[ g_{rr'} = (E - \varepsilon(r))^{-1} \delta_{rr'} + \sum_l (E - \varepsilon(r))^{-1} w(r - l) g_{lr'} \]

Summation over \( r' \) yields the equation for the function \( G \) in which we will pass from summation over \( l \) to the integration:

\[ G(r)(E - \varepsilon(r)) = 1 + \rho \int w(r - r') G(r') dr' \tag{2} \]

Here \( \rho \) is the lattice density. The passage from summation to integration in (2) is the only approximation we use, and it should be noted that such passage is acceptable. The sum over \( l \) in the Dyson equation is close to the integral in (2), provided the function \( w(r - r') G(r') \) changes only slightly when \( r' \) changes by a lattice constant \( a \). For this to happen, first, it is required that \( R > a \). Second, \( G(r) \) also should not strongly change on a scale \( \sim a \), which should be checked after calculations according to the procedure suggested below. Note that in the region of absorption spectrum, the function \( G \) oscillates at the spacial frequency of the resonant exciton. Because the main contribution to the absorption spectrum (1) is made by long-wavelength excitons, the passage from summation to integration in (2) is justified. It should be emphasized that the function \( G \) in (1) describes the absorption spectrum rather than the density of states whose calculation would require the consideration of short-wavelength excitons.

Let us now define the function \( \Psi(r) \equiv G(r)(E - \varepsilon(r)) \) It follows from (2) that

\[ \Psi(r) = \rho \int w(r - r') \left[ \lambda^2 + \frac{\Psi(r')}{E - \varepsilon(r')} \right] dr' \tag{3} \]

where

\[ \lambda^{-2} \equiv \rho \int w(r) dr \]

Integral equation (3) can be reduced to the differential equation in the following way. One can construct the differential operator \( L(\partial/\partial r) \) for wide class of functions \( w(r) \), so that \( w(r) \) will be the source function (Green’s function) for this operator, i.e.,
\[ L(\partial/\partial r)w(r) = \delta(r) \]  

(4)

To do this, equation (4) should be written in the Fourier representation

\[ w(r) = \frac{1}{2\pi} \int e^{ikr}\tilde{w}(k)dk, \]

\[ L(jk)\tilde{w}(k) = 1 \]

(5)

The function \( L \) is determined from the latter equation. Consider now the inhomogeneous equation

\[ L(\partial/\partial r)\Psi = \Phi(r) \]

(6)

The particular solution of this equation can be obtained with the help of the source function \( w(r) \):

\[ \Psi(r) = \int w(r - r')\Phi(r')dr' \]

(7)

If

\[ \Phi = \rho \left[ \lambda^2 + \frac{\Psi(r)}{E - \varepsilon(r)} \right], \]

then expression (7) coincides with (3). Therefore, the required solution \( \Psi(r) \) of integral equation (3) satisfies the differential equation

\[ L(\partial/\partial r)\Psi(r) = \rho \left[ \lambda^2 + \frac{\Psi(r)}{E - \varepsilon(r)} \right] \]

(8)

In a number of cases, it is easier to solve the equation (8) than (3). If the function \( \Psi \) is known, the absorption spectrum is determined by an expression that is similar to (1):

\[ A(E) = -\text{Im} \int_S \frac{\Psi(r)}{E + j\delta - \varepsilon(r)}dr \]

(9)

where \( S \) is lattice area.
3. One-dimensional chain with exponential interatomic interaction

Consider a one-dimensional chain with interatomic interaction of the form \( w(r) = V \exp(-|r|/R) \). One can obtain from (5) the following expression for the operator \( L(d/dr) \)

\[
L(d/dr) = \frac{R}{2V} \left( R^{-2} - \frac{d^2}{dr^2} \right)
\]

and equation (8) is transformed to the equation

\[
\Psi'' + \beta^2 \Psi = -R^{-2}, \tag{10}
\]

\[
\beta^2 = R^{-2} \left( \frac{W}{E - \varepsilon(r)} - 1 \right)
\]

\[
W = 2\rho VR,
\]

Which is similar to the inhomogeneous Schrödinger equation with the 'potential' \( \beta^2(r) \). For this reason, the function \( \Psi \) has a continuous first derivative. Let us find \( \Psi \) for a finite chain whose ends have coordinates \( \pm l \). In this case, \( \varepsilon(r) \) has the form

\[
\varepsilon(r) = \begin{cases}
\infty & r \leq -l \\
\infty & r \geq l \\
0 & -l < r < l
\end{cases}
\]

i.e., the region outside the chain is as if filled by infinitely detuned atoms to which the excitation cannot arrive. Of course, this is only the 'variable' component of the splitting. The 'constant' component results in a shift of the spectrum as a whole, and we will not take it into account below. In each region, the solution of (10) can be obtained quite easily. Taking into account the symmetry of the chain, the solution can be written in the form

\[
\Psi(r) = \begin{cases}
C_1 \cos(\beta r) - 1/(\beta R)^2 & -l < r < l \\
C_2 \exp(-r/R) + 1 & r > l \\
C_2 \exp(r/R) + 1 & r < -l
\end{cases}
\]

where
\[
\beta^2 = R^{-2} \left( \frac{W}{E} - 1 \right)
\]

If \( E \) is not too close to zero (see below), then \( \beta \) is the wave number of an exciton with energy \( E \). In regions outside the chain, we retained only decreasing exponentials, because the function \( G \) vanishes there. This can be done passing to the limit \( \varepsilon \to \infty \) for \( r < -l \) and \( r > l \), if the function \( \Psi \) is limited. Constants \( C_1 \) and \( C_2 \) are determined by the continuity condition for the function \( \Psi \) and its derivative at the chains ends. By dropping simple calculations, we present the final result for the function \( G \) inside the chain:

\[
G(r) = \frac{1}{E - W} \left( 1 + \frac{W}{E} \frac{\cos(\beta r)}{\beta l \sin(\beta l) - \cos(\beta l)} \right) \tag{11}
\]

Let us indicate the region of energies \( E \) where the absorption spectrum calculated from (1) and (11) can be used. The passage from summation to integration in Dyson equation (2) will be justified, if the spacial half-period of \( G \) (equal to \( \pi/\beta \)) is grater than the lattice constant \( a \). This results in the condition

\[
E > E_C \equiv \frac{W}{1 + (\pi R/a)^2} \tag{12}
\]

Figure 1 (There are no figures in this version, see figures in Optics and Spectroscopy, Vol.82, No. 2, 1997, pp 242-246) shows the absorption spectrum calculated from (11) and (1) for the chain parameters \( l = 50, R = 2, V = 1 \), and \( \delta = 0.1 \), the energy \( E \) being plotted in units of \( V \). The vertical bar along the abscissa axis shows the energy \( E_C \). One can see that in the "forbidden" region, the spectrum is in fact absent, and this region is of no interest. The spectrum of this chain was also obtained by numerical diagonalization and proved to be completely coincident with the spectrum in Fig.1.

Let us also consider here the somewhat less trivial case of a chain in which \( \varepsilon(r) \) has the form of a meander:

\[
\varepsilon(r) = \begin{cases} 
\infty & r < -h \text{ or } r > h \\
\varepsilon & l < r < h \text{ or } -l > r > -h \\
0 & -l < r < l
\end{cases}
\]
We assume for the simplicity of calculations, that this chain is closed to a ring, i.e., the point $h$ coincides with $-h$. The solution of (10) is obtained in similar manner, the only difference being that it is necessary to require the values of the function $\Psi$ and its derivative to be the same in the points $h$ and $-h$. The result for integrated Green’s function, whose imaginary part determines the absorption spectrum, is

$$\frac{1}{2} \int_{-h}^{h} Gdr = \frac{l}{E - W} + \frac{h - l}{E - W - \varepsilon} + \frac{\beta_1^2 - \beta_2^2}{\beta_1 \beta_2} \frac{(W - E)^{-1} - (W + \varepsilon - E)^{-1}}{\beta_2 \operatorname{ctg}(\beta_1 l) + \beta_1 \operatorname{ctg}(\beta_2 (h - l))}$$

where

$$\beta_i = R^{-2} \left( \frac{W}{E - \varepsilon_i} - 1 \right)$$

$$\varepsilon_{1,2} = 0, \varepsilon$$

In this case, condition (12) should be supplemented by the requirement

$$\varepsilon - E_C > E > \varepsilon + E_C$$

because for energies lying within the $E_C$ vicinity of $\varepsilon$, the function $G$ has a spatial period smaller than $a$ on the chain fragments with initial splitting $\varepsilon$. Note, however, that in this case, the contribution from the above fragments will be small compared to that from the rest of the chain, where the function $G$ oscillates not so rapidly. For this reason, the absorption spectrum can be realistic even when condition (4) is violated.

The spectrum of the chain with a jump of the initial splitting is presented in Fig. 2. The parameters are: $h = 30, l = 10, R = 2, V = 1, \delta = 0.1, \text{ and } \varepsilon = 2.5$; the energy is plotted in units of $V$. The spectrum in Fig. 2a is obtained by numerical diagonalisation, and that in Fig 2b is calculated from (13). The regions of forbidden energies are indicated by a vertical bar $E_C$ and horizontal bar [condition (14)]. For the chains of length $\sim 100a$, calculation by means of the above equations takes much less time than numerical diagonalization. In the next section the problem of three-dimensional spherical cluster will be solved. The numerical calculation of such a cluster with radius $> 20a$ represents a vast computer problem, while clusters with radii $\sim 150a$ still exhibit the distinct structure, related to their finite size.
4. Spherical cluster with interatomic interaction of Yukawa type

The approach presented in section 2 can be generalized to the case of an arbitrary dimensionality. In this section we consider a three-dimensional lattice with an interaction of \( w(r) = V \exp(-r/R)/r \) (the Yukawa potential). It is well known [and can be easily verified from (5)] that

\[
\left( \Delta - R^{-2} \right) \left( \frac{1}{4\pi} \frac{\exp(-|r|/R)}{|r|} \right) = \delta(r)
\]

After calculating the integral \( \lambda^{-2} \) in (3) in the spherical coordinate system, we find that in this case, equation (8) again has the form of the inhomogeneous Shredinger equation

\[
\Delta \Psi + R^{-2} \left( \frac{W}{E - \varepsilon(r)} - 1 \right) \Psi = -R^{-2}
\]

where

\[
W \equiv 4\pi \rho V R^2
\]

and, hence, function \( \Psi \) is continuous with its first derivative.

Let us now solve the problem on a spherical cluster with radius \( \sigma \), i.e., the function \( \varepsilon(r) \) will be taken in the form

\[
\varepsilon(r) = \begin{cases} 
0 & |r| < \sigma \\
\infty & |r| > \sigma 
\end{cases}
\]

By representing the Laplace operator in (15) in spherical coordinates, for function \( \Psi \) (it has only the radial dependence), we obtain the equation

\[
\left( \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \beta^2 \right) \Psi = -\frac{1}{R^2}
\]

where

\[
\beta^2 = \left( \frac{W}{E - \varepsilon(r)} - 1 \right) R^{-2}
\]
In our case, 

\[ \beta^2 = \begin{cases} 
-\frac{R}{r} & r > \sigma \\
(W/E - 1)\frac{R}{r} & r < \sigma 
\end{cases} \]

The general solution of equation (16) for both regions has the form

\[ \Psi = -\left(\frac{1}{R\beta}\right)^2 + a \frac{\sin \beta r}{r} + b \frac{\cos \beta r}{r} \]

Taking into account the boundedness of \( \Psi \) in the region \( r > \sigma \), we obtain that in this region, 

\[ \Psi = 1 + a_1\frac{\exp(-r/R)}{r} \quad (17) \]

Function should be also bounded at \( r = 0 \). Taking this into account, we obtain that in the region \( r < \sigma \),

\[ \Psi = E G_\infty + a_2 \frac{\sin \beta r}{r} \quad (18) \]

where

\[ G_\infty \equiv (E - W)^{-1} \]

Function \( E G_\infty \) is the solution of (15) in the case of an infinite homogeneous lattice. For this reason, \( \text{Im} G_\infty(E + j\delta) \) determines the absorption spectrum of such a lattice. Constants \( a_1 \) and \( a_2 \) are determined from continuity conditions for the function \( \Psi \) and its first derivative for \( r = \sigma \) The absorption spectrum is determined from (9)

\[ A(E) = -\text{Im} \int_0^\sigma \frac{\Psi(r, E + j\delta)}{E + j\delta} r^2 dr \]

which yields the result

\[ A(E) = -\text{Im} \left\{ \left( \frac{\sigma^3}{3} - \frac{W(R + \sigma)(\sin \sigma - \sigma \cos \sigma)}{\alpha^2(E + j\delta)(R \cos \sigma + \sin \sigma)} \right) G_\infty(E + j\delta) \right\} \]

where

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Expression (19) contains two contributions: the bulk contribution (the first term in parentheses) and the surface contribution (the second term). The first term gives the spectral line that corresponds to an infinite lattice, while the second one is related to the structure caused by the finite size of the cluster.

Figure 3 shows the absorption spectrum of a spherical cluster calculated from (19) for the parameters $V = 1, R = 1, \sigma = 5$, and $\delta = 0.15$; the energy is plotted in units of $V$. The vertical bar shows the energy $E_C$. The spectrum obtained by numerical diagonalization coincides completely with the spectrum in Fig. 3. However, it should be noted that the Yukawa potential has a singularity at $r = 0$. For this reason, the question arises upon numerical calculations as to what form the diagonal elements of the $H_{rr'}$ matrix should take (see Section 2). Although these matrix elements do not affect the shape of the absorption spectrum, they may cause its shift. In the numerical verification of the spectrum in Fig. 3, we assumed that $H_{rr'} = 0$, because in the calculation of integrals with Yukawa potential, the contribution from the region $r \sim 0$ is insignificant due to the smallness of the volume $r^2dr$, and, in fact, the “effective potential” $w(r)r^2$ is used everywhere, which vanishes for $r = 0$. Computer calculations performed with other values of parameters are also in complete agreement with (19).

Figure 4 shows the spectrum of spherical cluster for $V = 1, R = 2, \sigma = 30$, and $\delta = 0.6$. Comparison with numerical diagonalization was not performed, because, in this case, computer calculations are time consuming. Figure 4 shows that despite large radius of the cluster, its spectrum differs from that of infinite lattice (the singlet at $E = W$) and exhibits a structure. Clusters with a radius of $150a$ also show a noticeable structure (on the scale of the bandgap $W$).

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