The watching operators method in the theory of Frenkel exciton.

Novel criterion of localization and its exact calculation for the non diagonal disordered 1D chain’s zero-state

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A method is proposed for manipulating with diagrammatic expansion of Green’s function of Frenkel’s exciton random walks on the perfect lattice. The method allows one to select diagrams, to supply diagrams with factors containing information about the number of sites the diagram has passed through, etc. Simple problems related to the defect lattices are considered using the proposed method. The new criterion of localization of Frenkel exciton - the number of sites covered by the wave function - is established. The number of sites covered by the zero state of 1D non-diagonally disordered chain is studied. It is shown that this problem can be solved by calculating the random walks Green’s function with modified diagrammatic expansion. By means of the developed method an exact analytical expression for the number of sites covered by the zero-state is obtained and zero-state is shown to be localized.

I. INTRODUCTION

Let us consider some lattice with sites $r_1...r_N$ and introduce matrix $W$ with elements

$$W_{rr'} = w(r - r')$$ (1)

The function $w(r)$ is supposed known. The problem of Frenkel exciton random walks along the lattice $r_1...r_N$ of twolevel atoms, can be reduced to the matrix of this kind and this problem is not the only one. In this case $w(r - r')$ represents an interaction which is able to transport an excitation from atom $r$ to atom $r'$. The study of Green’s function (GF)
which corresponds to the above matrix (1) is of particular interest [1]. We write down this function in convenient dimensionless form:

$$ G = (1 - W)^{-1} $$

(2)

If suppose the summation over the repeating indexes, the following series for GF may be written:

$$ G_{lm} = \left( \frac{1}{1 - W} \right)_{lm} = \delta_{lm} + W_{lm} + W_{lr} W_{rm} + W_{lr} W_{rp} W_{pm} + ... $$

(3)

If we denote matrix element $W_{rp}$ by an arrow directed from site $r$ to site $p$, then each product of matrix elements in (3) is being represented by diagram (trajectory), which connects sites $l$ and $m$. Then (3) can be rewritten as:

$$ G_{lm} = \left( \text{Sum of all diagrams, which connect sites } l \text{ and } m \right) $$

(4)

The similar method has been used in [2]. The above representation allows one to write down the formal expressions for Green’s functions of a certain relative problems. For example, if certain atoms $r_1...r_t$ have been removed, then the expression for Green’s function must be modified as follows:

$$ G_{lm} = \left( \text{Sum of all diagrams, which connect sites } l \text{ and } m, \text{ not passing through the sites } r_1...r_t \right) $$

(5)

If we now deal with lattice whose sites can be occupied by atoms with probability $C < 1$ and we are interested in the averaged Green’s function, then each diagram $D$ of this function should be multiplied by probability that all $n(D)$ sites $D$ has passed through, are occupied by atoms. This probability is equal to $C^{n(D)}$ and, consequently, we can write for the averaged Green’s function:

$$ \langle G_{lm} \rangle_c = \left( \text{Sum of all diagrams } D, \text{ which connect sites } l \text{ and } m, \text{ each diagram is being multiplied by } C^{n(D)}, \text{ where } n(D) - \text{ is the number of sites in the diagram} \right) $$

(6)

In the end if we are interested in $\langle G_{lm} \rangle_c, C \sim 1$, we have to calculate $\partial \langle G_{lm} \rangle_c / \partial C$, $C = 1$. Making use of (6), it is easy to obtain:
\[
\frac{\partial (G_{lm})_c}{\partial C} = \begin{pmatrix}
\text{Sum of all diagrams } D, \text{ which connect sites } l \text{ and } m, \\
\text{Each diagram is being multiplied by } n(D), \\
\text{where } n(D) - \text{ is the number of sites in } D
\end{pmatrix}
\] (7)

These examples show that Green’s functions, related to various problems, can be obtained by manipulating with one and the same series of diagrams. So, it is desirable to construct some kind of observer who, while moving along the diagram, would register the sites which diagram has visited, would count the number of sites which diagram has passed through and so on. For example, in order to obtain Green’s function (5) the above observer’s duty should be as follows: While moving along the diagram and while visiting one after another the sites of this diagram, observer should check whether site he just has visited is one of \( r_1 \ldots r_t \) which have been removed and, if it is so, observer should multiply diagram by zero.

To obtain Green’s functions (7) and (6), observer should count sites which he has passed through and should multiply the diagram by total number of sites \( n(D) \) in the diagram or by \( C^{n(D)} \) respectively. In section 2 we show that in certain cases it is possible to build up the mathematical realisation of described observer by replacing matrix elements \( W_{rp} \) in Green’s function (4) by specially constructed watching operators.

However, the random walks problems described in section 2 which can be solved up to the very end (at least at present) by above method is rather simple and are of some interest only as a demonstration of absence of errors in the mathematical scheme of the method.

In section 3 we consider much more nontrivial problem related to the character (localized-delocalized) of Frenkel’s exciton zero-state in 1D disordered chain. We establish a novel criterion of localization - the inverse number of sites covered by the wave function - and show that the problem of calculation of this value may be formulated in terms of diagrams and exactly solved by means of specially built watching operators.

II. WATCHING OPERATORS
A.

Let us consider the Green’s function $G_{0r}$ which is defined on certain periodical simple lattice. Let us now perform the Fourier transformation with respect to its second index $g_k \equiv \sum_r G_{0r} \exp(ikr)$.

\[
g_k = \frac{1}{1 - f_k}, \text{ where } f_k \equiv \sum_r w(r) \exp(ikr)
\]

in terms of diagrams:

\[
g_k = \begin{cases} 
\text{Sum of all diagrams which are starting from the site 0.} \\
\text{Each diagram is being multiplied by } \exp(ikr_f), \text{ where } r_f - \\
\text{is a coordinate of the last site in the diagram}
\end{cases}
\]

Let us consider formula (5) and denote by $L$ the set of sites occupied by atoms and by $T$ the set of sites $r_1...r_t$.

In order to convert function (9) to the Green’s function of this unperfect (defect) system we replace matrix elements $W_{rp}$ in (9) (which are denoted by diagram’s arrows) by the operators $\hat{W}_{rp}$ which act upon arbitrary function $J_q$ ($q$ is an auxiliary variable) in accordance with the rule:

\[
\hat{W}_{rp}J_q \equiv \frac{W_{rp}}{N} \sum_{q'} K(q - q')e^{iq'(p-r)}J_{q'}, \text{ where } K(q) \equiv \sum_{R \in L} \exp(irqR)
\]

Summation over $q$ is carried out over the first Brillouin zone. Now Green’s function (9) becomes the operator $g_k \rightarrow \hat{g}_k$. Let’s apply this operator to unit.

Let’s consider a certain diagram and apply the operator which corresponds to the first arrow to unit- $\hat{W}_{0r}1$. It is easy to see that if $r \in L$, then the result will be $W_{0r} \exp(iqr)$.

Otherwise we obtain zero. Consequently, if the first arrow of the diagram came to the empty site, the diagram is being multiplied by zero. By induction we come to the conclusion that it is a general result - if certain arrow of the diagram reaches the empty site $\rho$ (i.e. $\rho$ is one of the $r_1...r_t$) the operator corresponding to this arrow gives zero.

We see that operators (10) give the mathematical realisation of the observer described in the end of the previous section. That’s why we will call them the watching operators.
Consequently, if we denote the Green’s function corresponding to the lattice with defects by \( d_q \), the following formula may be written:

\[
\hat{g}_k 1 = \begin{pmatrix}
\text{Sum of all diagrams which are started from site 0, which are not passed through } r_1...r_t. \\
\text{Each diagram is multiplied by } \exp(i(k+q)r_f), \text{ where } r_f \\
\text{- the coordinate of the last site of the diagram}
\end{pmatrix} = d_{k+q} \tag{11}
\]

By replacing \( W_{0r} = w(r) \) in the explicit expression (8) for \( g_k \) (9) by the watching operators (10) and by setting \( k = 0 \), we obtain the equation for \( d_q \):

\[
1 = (1 - \hat{f}_0)d_q, \text{ where } \hat{f}_0 \equiv \sum_r \hat{W}_{0r} \tag{12}
\]

The simple calculations shows that \( d_q \) may be introduced in the form:

\[
d_q = \frac{1 - \sum_{R \in T} X_R \exp(iqR)}{1 - f_q} \tag{13}
\]

where parameters \( X_R \) may be obtained from the equations:

\[
\sum_{R' \in T} G_{R-R'} X_{R'} = G_R, \quad R \in T, \tag{14}
\]

where

\[
G_R \equiv \frac{1}{N} \sum_q e^{-iqR} / (1 - f_q) \tag{15}
\]

- is the Green’s function of the periodical lattice. If the amount of removed atoms is not too large, the solution of (14) may be presented in a compact form. For example, if the only one atom have been removed from the site \( R \), then the solution of (14) is: \( X_R = G_R / G_0 \).

The further analysis of (14) is possible either if the empty sites forms the periodical structure. It should be pointed out that while obtaining (14) we have supposed that the site \( 0 \in L \). If it is not so, then \( d_q = 0 \). Formulas (13) and (14) gives it (in this case \( X_0 = 1, X_{R \neq 0} = 0 \)), but an exact solution of (12) is non-zero and represents the sum of diagrams which start from the zero site and never return back to this site more.

At last let us note that the initial site 0 is not especial one and the Green’s functions having another first index may be calculated by the same way.
B.

In this subsection we will introduce another type of watching operators which give possibility to multiply the diagrams by factors, containing the information about the sites which diagram has visited.

Let’s introduce the watching operators dependent on a parameter $\alpha$ which operate as follows:

$$\hat{W}_{rp}J_q \equiv W_{rp}(1 + \frac{\alpha - 1}{N} \sum_q e^{iq(p-r)}J_q)$$ (16)

Let’s apply the operator corresponding to certain diagram $D$ containing in $\hat{g}_k$ to some function $\Phi_q \equiv \sum_R \phi_R \exp(-iqR)$ (summation over all lattice).

Operator corresponding to the first arrow of the diagram operate as follows: $\hat{W}_{0r}\Phi_q = W_{0r}\exp(iqr)\Phi'_q$, where $\Phi'_q = \sum_R \phi'_R \exp(-iqR)$, and $\phi'_R = \phi_R$ if $R \neq r$ and $\phi'_r = \alpha \phi_r$.

Moving further along the diagram and applying step by step the watching operators corresponding to the arrows of the diagram , one can see that the diagram $D$ will be multiplied by $\exp(iqr)\Phi'_q(D) = \exp(iqr_f(D)) \sum_R \tilde{\phi}_R(D) \exp(-iqR)$, and if $R \neq 0$, $\tilde{\phi}_R(D) = \phi_R \alpha^r$ (The number of visits of the site R by the diagram D). $r_f(D)$ - is the last site of the diagram $D$.

The site 0 ( which the diagram started from) is being taken into account in a special way: $\tilde{\phi}_0(D) = \phi_0 \alpha^{(\text{number of diagram’s D visits of site 0})}$. Consequently, $\tilde{\Phi}_q(D)$ carry the information about sites, which the diagram $D$ has visited and about corresponding number of visits. For this reason we call this function carrier. The arbitrary function $\Phi_q$, which we have acted on upon by operator, may be called the carrier in the initial state. So, we see, that after applying $\hat{g}_k$ (containing the watching operators (16)) to the carrier in initial state $\Phi_q$, each diagram is being multiplied by her own carrier. Let’s now obtain the function (7) by means of the watching operators (16). It is clear now, that if we take the carrier in initial state in the form: $\Phi_q = \sum_{R \neq 0} \exp(-iqR) + \alpha = N\delta_{q0} + \alpha - 1$ and apply $\hat{g}_k$ (containing the watching operators (16)), the following formula is justified:
\( \hat{g}_k \Phi_q = \left( \begin{array}{c} \text{Sum of all diagrams which are started from site 0.} \\ \text{Each diagram is being multiplied by carrier: } \sum_R e^{-q R} \alpha^{V(D,R)}, \\ \text{Where } V(D,R) - \text{the number of diagram's } D \text{ visits of site } R. \\ \text{Each diagram is being multiplied by } e^{(k+q)r_f}, \\ \text{where } r_f - \text{is the coordinate of the last site of the diagram.} \end{array} \right) \equiv \gamma_q \)  

The equation for \( \gamma_q \): \( \Phi_q = (1 - \hat{f}_k)\gamma_q \) (being built by using the watching operators (16)) may be easily solved in terms of Green’s functions (8) and (15):

\[
\gamma_q = N g_k \delta_{q0} + \frac{(\alpha - 1)g_{q+k}g_k}{1 - (\alpha - 1)(G_0 - 1)} 
\]  

The comparison of the diagrammatic formulas (7) and (17) shows, that the Fourier transformation of (7) with respect to the second index (similar to that in (8)) may be represented in the form:

\[
\frac{\partial (g_k)_c}{\partial C}(C = 1) = N g_k - \gamma_0(\alpha = 0) = \frac{g_k^2}{G_0} 
\]  

An other types of the watching operators are also possible \[4\]. In the next section we apply the developed method for solving the problem which considerably differs from those, which we have considered in this section.

### III. THE EXPLORATION OF FRENKEL EXCITON ZERO-STATE BY MEANS OF THE WATCHING OPERATORS METHOD

#### A. The criterion of localisation

Let us consider the random process on the 1D chain of sites \( i = 1, 2, 3...n \), which is defined by the following recurrent relation:

\[
\varphi_i = \eta_i \varphi_{i-1}, \varphi_0 = 1 
\]  

Where \( \eta_i \equiv U_i/U'_i \), and \( U_i, U'_i \) - are independent, similarly distributed, positive random variables, which can have the values \( a > 0 \) and \( b > 0 \) with probabilities \( C \) and \( 1 - C \).
respectively \((a > b)\). \(\varphi_i\) represents the square module of the Frenkel’s exciton zero-state in the 1D non-diagonal disordered chain \(3\), when the Hamiltonian matrix elements can have values \(\sqrt{a}\) and \(\sqrt{b}\) with probabilities \(C\) and \(1 - C\) respectively. Let us characterize the zero-state by the number of sites \(N^*\), covered by the corresponding wave function and calculate this number as follows. If \(\varphi_i = 0\) on certain site \(i\), then this site is not covered and is being not taken into account while calculating \(N^*\). Vice versa, if \(\varphi_i\) reaches its maximum \(\varphi_{max}\) on the site \(i\), then this site is covered completely and its contribution while calculating \(N^*\) is equal to unit. In the general case, the contribution of the arbitrary site \(i\) is equal to \(\varphi_i/\varphi_{max}\) and we obtain the following formula:

\[
N^* = \frac{1}{\varphi_{max}} \sum_i \varphi_i
\]

\((21)\)

\(1/N^*\) may be treated as a criteria of localisation - it is finite when zero-state is localized and is going down to zero as the inverse chain length \(n^{-1}\), if zero-state is delocalized.

If \(\lim_{n \to \infty} N^* < \infty\), then for the averaged quantities the following formula may be written:

\[
\lim_{n \to \infty} \langle N^* \rangle = \langle\langle N^* \rangle\rangle
\]

\((22)\)

Where \(\langle\rangle\) denotes the averaging over the realisations of the random process and \(\langle\langle\rangle\rangle\) denotes the averaging over all chains lengths \(n\). In the next subsection we will describe the method for exact calculation of \(\langle\langle N^* \rangle\rangle\) by means of methods developed in section 2.

B. The diagrammatic representation of the random process \(\varphi_i\). The method for calculating \(\langle\langle N^* \rangle\rangle\)

Let us introduce the diagrammatic representation of random process \(\varphi_i\) as follows. The four possible values are acceptable for \(\varphi_i\). Each value may be represented by horizontal and vertical arrows as follows:

\[\text{Diagrammatic representation of } \varphi_i\]

\(^1\text{In the considered random process always } \varphi_i \neq 0, \text{ but it is not important for this reasoning}\]
η_i = \begin{cases} 
\frac{a}{a} \uparrow &= C^2 t \\
\frac{b}{b} \downarrow &= (1 - C)^2 t \\
\frac{a}{b} \rightarrow &= (1 - C)C t \\
\frac{b}{a} \leftarrow &= (1 - C)C t 
\end{cases} \tag{23}

The length of each arrow is supposed to be equal to unit. Then the arbitrary realisation of random process \( \varphi_i \), related to the chain consisting of \( n \) sites, is being represented by a trajectory - diagram - on the two dimensional square lattice. These diagrams has \( n \) arrows. Without loss of generality we can suppose that each diagram is being started from the zero site of this lattice.

Now let us ascribe to the \( i \)-th arrow of the diagram the probability of the corresponding value of \( \eta_i \), in the same manner it have been done in (23). The parameter \( t \), \( 0 < t < 1 \) -is an auxiliary one and in the end of the calculation \( t \to 1 \).

Consequently, the diagram completely describes the distribution of \( \eta_i \) in corresponding realisation and the diagram’s value is equal to the probability of this realisation. Let’s now explain how the \( \varphi_{\text{max}} \) and \( \sum_i \varphi_i \) can be extracted from the diagram.

Introduce the coordinate system \( XY \) with zero point coinciding with the zero of the above mentioned square lattice.

If \( r \) is the \( x \)- projection of the right extremal site (sites) of the diagram, then \( \varphi_{\text{max}} = \xi^r \), where \( \xi \equiv \frac{a}{b} > 1 \).

In order to calculate \( \sum_i \varphi_i \) for certain realisation, let us suppose that we have multiplied the corresponding diagram \( D \) by the following carrier \( \Phi_q(D) = \sum_x V(D, x) \exp(-i qx) \), where \( V(D, x) \) - the number of diagram’s visits of the sites whose \( x \)- projection (contrary to (17)) is equal to \( x \).

After the Fourier transformation the carrier becomes: \( \phi_x(D) = V(D, x) \). Then \( \sum_i \varphi_i = \sum_x \xi^x \phi_x \).

Now let’s introduce the matrix \( W(1) \) defined on the above mentioned square lattice by means of the following function \( w(r) \):
\[ w(r) = \begin{cases} 
C^2t, & \text{if } r = (0, 1) \uparrow \\
(1 - C)^2t, & \text{if } r = (0, -1) \downarrow \\
(1 - C)t, & \text{if } r = (1, 0) \rightarrow \\
(1 - C)t, & \text{if } r = (-1, 0) \leftarrow 
\end{cases} \quad (24) \]

and build up the following function in accordance with the first section:

\[ F(q, q', k, \alpha, \beta) = \begin{cases} 
\text{Sum of all diagrams which are starting from the site 0.} \\
\text{Each diagram is being multiplied by the following carrier:} \\
\left( \sum_x e^{-iqx} \alpha^V(D,x) \right) \left( \sum_x e^{-iq'x} \beta^V(D,x) \right), \\
\text{where } V(D, x) - \text{is a number of diagram’s } D \text{ visits} \\
of the sites whose } x-\text{coordinate is } x. \\
The diagram is also multiplied by \\
e^{i(k+q+q')xf}, \text{where } x_f - x-\text{coordinate of the last site of the diagram}
\end{cases} \quad (25) \]

Defining the operation \( D/Dx \) as \( Dy/Dx \equiv y(x + 1) - y(x) \), we introduce the function:

\[ U(x, x') \equiv -\frac{D}{Dx} \left( \frac{1}{N} \right)^2 \sum_{qq'} e^{i(qx + q'x')} \int_0^1 d\alpha \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} F(q, q', -q - q', \alpha, 1) \quad (26) \]

Where \( N - \) is the number of sites along the \( x- \) direction. \( N \to \infty \) in the end of the calculations. In terms of diagrams the expression for \( U(x, x') \) is as follows:

\[ U(x, x') = \begin{cases} 
\text{Sum of all diagrams which are being started from} \\
\text{the site 0. All diagrams are being multiplied by the carrier} \\
\left( \delta_{x,r} - \delta_{x,l-1} \right) V(D, x'), \\
\text{where } V(D, x') - \text{is the number of diagram’s } D \text{ visits} \\
of the sites whose } x-\text{coordinate is } x. \\
\text{Where } r(l) - x-\text{projection of the right (left) extremal site} \\
\text{(or sites) of the diagram } D.
\end{cases} \quad (27) \]

Let us explain the sense of operation \( D/Dx \) in (26). After the Fourier transformation with respect to \( q \) and integration over \( \alpha \), the dependence on \( x \) for carrier of any diagram is
being represented by a set of \emph{ordered} $\delta$-symbols: $\delta_{x,r} + \delta_{x,r-1} + \delta_{x,r-2} + \ldots \delta_{x,l}$, where $r(l)$ - is the $x$-projection of the right (left) extremal site (or sites) of the diagram.

The absence of gaps in the series of the $\delta$-symbols is take place because an arrows, which correspond to the function $w(r)$ (24), can connect only neighbour sites (along the $x$-direction)

Consequently, after operation $D/Dx$ only right $\delta_{x,r}$ and left $\delta_{x,l-1}$ $\delta$-symbols (shifted per unit) are survive. Then the following formula for the average number of sites (22) is justified:

$$\langle\langle N^* \rangle\rangle = \lim_{t \to 1} (1 - t) \sum_{x=0}^{\infty} \sum_{x' = -\infty}^{\infty} U(x, x') \xi^{x'-x}$$  \hspace{1cm} (28)

The $1 - t$ - is the normalisation factor related to the averaging over chain lengths and is equal to inverse sum of all diagrams, i.e. $g_0^{-1}$ (formula (8), constructed by means of (24)). The explicit expression for the function (25) can be obtained by manipulating with diagrammatic expansion of the Green’s functions (8),(9), by means of the watching operators of the following form:

$$\hat{w}(r) = \begin{cases} 
(r = (0, 1)) \quad & C^2 t[1 + \frac{\alpha - 1}{N} \sum_q][1 + \frac{\beta - 1}{N} \sum_{q'}] \\
(r = (0, -1)) \quad & (1 - C)^2 t[1 + \frac{\alpha - 1}{N} \sum_q][1 + \frac{\beta - 1}{N} \sum_{q'}] \\
(r = (1, 0)) \quad & (1 - C) C t[1 + \frac{\alpha - 1}{N} \sum_q][1 + \frac{\beta - 1}{N} \sum_{q'}] e^{i(q+q')} \\
(r = (-1, 0)) \quad & (1 - C) C t[1 + \frac{\alpha - 1}{N} \sum_q][1 + \frac{\beta - 1}{N} \sum_{q'}] e^{-i(q+q')} 
\end{cases}$$  \hspace{1cm} (29)

These operators differ from (16) by that depend on two auxiliary wave vectors $q, q' (-\pi < q, q' < \pi)$, and that they watch only $x$ projections of the diagrams arrows on two dimensional lattice. By applying $\hat{g}_k$ to $(N\delta_{q0} + \alpha - 1)(N\delta_{q'0} + \beta - 1)$, we obtain the standart equation for $F(q, q', k, \alpha, \beta)$:

$$(1 - \hat{f}_k)F = (N\delta_{q0} + \alpha - 1)(N\delta_{q'0} + \beta - 1)$$  \hspace{1cm} (30)

The solution of this equation is rather clumsy. It may be reduced to the integral equation of convolution type, which can be solved by Fourier transformation. The solution can be expressed in terms of known Green’s function of the Frenkel’s exciton on one dimensional lattice with only nearest neighbour interaction.
Using (25),(26),(28) we obtain the exact expression for $N^*$:

$$\langle\langle N^* \rangle\rangle = \frac{\xi(\xi + 1)}{(\xi - 1)^2 C(1 - C)}, \quad \xi > 1 \quad (31)$$

Let us to note in the conclusion that the above problem is not the most simple problem, related to the random process (20), which can be solved by means of the watching operators method. By applying the diagrammatic representation of the random process (20) and the watching operators method one would obtain such nontrivial characteristics of (20) as distribution function for $\varphi_{\text{max}}$ and the dependence of $\langle \varphi_{\text{max}} \rangle$ as a function of chain’s length $n$.

We present the result (31) as an argument in favour of localized type of the zero state, contrary to [3], where zero state was declared to be delocalized because of its zero inverse localization length (ILL). This criterion of localization is not correct because the above model also has zero ILL, but (31) shows that zero state is always localized.

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