Exact results on linear response of cyclic molecular aggregates

A. V. Ilinskaia\textsuperscript{1}*, K. N. Ilinski\textsuperscript{2,3†} G. V. Kalinin\textsuperscript{1‡}
V. V. Melezhik\textsuperscript{1§} A. S. Stepanenko\textsuperscript{4,3¶}

\textsuperscript{1} Institute of Physics, Physics Department of St-Petersburg University,
St-Petersburg, 198904, Russian Federation.

\textsuperscript{2} School of Physics and Space Research, University of Birmingham,
Birmingham B15 2TT, United Kingdom.

\textsuperscript{3} Institute of Spectroscopy, Russian Academy of Sciences,
Troitsk, Moscow region, 142092, Russian Federation.

\textsuperscript{4} St-Petersburg Nuclear Physics Institute, Gatchina,
St-Petersburg, 188350, Russian Federation.

\textbf{Abstract}

Basing on the picture of Frenkel excitons in molecular crystals described by the XY-model we consider the linear response of linear cyclic aggregates at finite temperature. The exact results for characteristics of the response are obtained. In particular, we calculate time-dependent two-point correlation functions at finite temperature for the cyclic 1-D XY-model.

*E-mail: ILINSKI@PHIM.NIIF.SPB.SU
†E-mail: KNI@TH.PH.BHAM.AC.UK
‡E-mail: KALININ@PHIM.NIIF.SPB.SU
§E-mail: MELEZHIK@PHIM.NIIF.SPB.SU
¶E-mail: STEPANENKO@PHIM.NIIF.SPB.SU
1 Introduction

Last five years a number of papers were devoted to the consideration of the so-called J-aggregates, molecular linear aggregates with redshifted unusually sharp absorption bands (for the recent review see [1]). Such aggregates give the infrequent possibility to describe a nontrivial physical situation by some sort of 1-dimensional quantum Hamiltonians which could be treated exactly. To be more precise, the optical excitations of the system (excitons) after the second quantization procedure could be described by the Hamiltonian of spin chains (we will see in section 2 that this is the anisotropic XY-chain). Moreover, theoretical investigations of J-aggregates essentially use the information about the structure of the exact eigenvalues and eigenfunctions of the Hamiltonian which are well-known due to the paper by Lieb, Mattis and Schults [2] since 1961.

The purpose of this paper is to improve the results on the linear response [3] of the J-aggregates in the following aspects:

1. As we will remind in the next section, there is no freedom to restrict the consideration from the XY-model to the XX-model, because the relative anisotropy parameter is the order of unit. This fact causes a number of complications which are not only technical ones. Indeed, there is no more good quantum number like the number of particles in the chain (what is obvious from physical features of the problem) and one has to deal with a full Fock space of particles in question.

2. The same problem (i.e. the calculations in a full Fock space of the theory) appears even in the XX-model when the effects of nonzero temperature are considered and the correlation functions are some traces on a full Fock space.

Both of these problems are treated in the paper.

The next question of interest is a choice of the boundary conditions for finite linear aggregates. It is well understood that the choice of the general closed boundary conditions leads to the new nontrivial problem. Indeed, the exchange statistics for the excitons (which are statistically Paulions, i.e. fermions on site and bosons on different sites) is irrelevant for the open boundary conditions because no real permutation is allowed. The situation changes if the linear aggregate is a circle. It leads to a nontrivial loop which gives the possibility to permute particles via the 'glued' boundary. Then the effects of the exchange statistics exhibit themselves [4]. These effects are negligible in the continuous limit and were not investigated when the main interest was concentrated on the thermodynamics of the chains. A large number of the classical and recent papers concern the subjects [5, 6, 7, 8]. But the effect of the closure is relevant and important for finite systems like J-aggregates. Moreover, they allow to trace the crossover from small to macroscopic chains [1]. Namely the cyclic finite aggregates will be considered in this paper.

We have to note that the exact treatment of excitons in the aggregates on the base of the cyclic XX-model were considered in [4]. In Section 3.4 we will criticize the results of Ref. [4].

The paper is organized as follows. In the next section we give a brief description of excitons in molecular chains which are basic for understanding of the subject. While
opticians began to deal with excitons long time ago, mathematical physicists (who are mainly concentrated on exact solutions) are not so familiar with the field. The section can be considered as an introduction in the excitonic physics. It also contains the formula for the linear response function in terms of correlators of the system in the convenient for the following form. Section 3 contains a main new result of the paper. It is devoted to the exact calculation of two-point correlation functions for the cyclic XY-model in a closed form. The conclusion completes the paper with a discussion of the resulting formulae for characteristics of the linear response for the cyclic J-aggregates. Appendix A contains the evaluation of the main integrals of Section 3.

2 Linear response of excitonic system

In the present work we will calculate the optical response of a gas of molecular aggregates. We are interested in the average dipole momentum induced by an external time dependent electromagnetic field in the linear approximation with respect to the field amplitude.

The most general linear relation between the dipole momentum and the field has the form

$$p_\alpha(t) = \int_0^\infty \tilde{\sigma}_{\alpha\beta}(\tau)E_\beta(t-\tau)d\tau$$

where $p_\alpha$ is the dipole momentum per unit volume, $E_\beta$ denotes the external field, $\tilde{\sigma}_{\alpha\beta}(\tau)$ is the linear response function and $\alpha, \beta$ are tensor indices.

We suppose that the aggregates are independent, i.e. we will neglect the interaction of the aggregates. In this case the dipole momentum per unit volume is just a product of the aggregate concentration $\nu$ and the dipole momentum of a single aggregate. Hence the response $\tilde{\sigma}_{\alpha\beta}$ is also proportional to the concentration $\nu$:

$$\tilde{\sigma}_{\alpha\beta}(\tau) = \nu\sigma_{\alpha\beta}(\tau)$$

where $\sigma_{\alpha\beta}(\tau)$ is the response function of a single aggregate.

As the model for a molecular aggregate we consider the 1-D closed M-sites molecular chain (that can be regarded for example as a model for the benzene vapor under a low pressure). Let us derive the excitonic Hamiltonian of the aggregate following to the original paper \cite{10}. We start with the Hamiltonian of the molecular aggregate in the form:

$$H = \sum_{n=1}^{M} H_n + \frac{1}{2} \sum_{n,m}^\prime V_{nm} \quad (1)$$

Here $H_n$ is the Hamiltonian of a molecule on the n-th site, $V_{nm}$ is the operator the of interaction between n-th and m-th sites, $\sum^\prime$ means the absence of the term with $n = m$.

As far as the molecules are supposed to be electrically neutral, the first approximation for the interaction $V_{nm}$ is dipolar one.

Let us denote the complete set of eigenfunctions of the free molecular Hamiltonian $H_n$ by $\{\phi^f_n\}$ and the corresponding occupation number by $N_{nf}$. After the second quantisation
procedure the state of the aggregate becomes a function of occupation numbers

\[ \lfloor \ldots N_{n_f} \ldots \rfloor \]

and Hamiltonian (4) can be rewritten by the following way:

\[
H = \sum_{n,f} \epsilon_f b_{n_f}^{+} b_{n_f} + \frac{1}{2} \sum_{m,n,f,f',g,g'}^\prime \epsilon_{f'} \epsilon_g b_{m_g}^{+} b_{m_g} b_{n_f} \langle f'g' | V_{nm} | fg \rangle
\]

The creation (annihilation) operators \( b_{n_f}^{+} \) (\( b_{n_f} \)) of the \( f \)-state on the \( n \)-th site satisfies the standard commutation relations:

\[
\{b_{n_f}, b_{n_f}^{+}\} = 1
\]

\[
b_{n_f} b_{n_f} = b_{n_f}^{+} b_{n_f}^{+} = 0
\]

with the constraint (each molecule can be in a single eigenstate only),

\[
\sum_{f} b_{n_f}^{+} b_{n_f} = 1.
\]

\( \epsilon_f \) is the energy of the \( f \)-th excited state.

Further we shall assume that the lowest excited molecular state plays the main role in the absorption and radiation processes and therefore the index \( f \) runs only over two values 0 (ground state) and \( f \) (the first excited state). This allows us to present the Hamiltonian in the form:

\[
H = H^1 + H^2 + H^3 + H^4
\]

where the first term describes the energy of nonexcited molecules,

\[
H^1 = M \epsilon_0 + \frac{1}{2} \sum_{n,m}^\prime \langle 00 | V_{nm} | 00 \rangle,
\]

the second term is the energy of excitation of a single molecule in the aggregate:

\[
H^2 = \sum_{\bar{n}} (\Delta \epsilon_f + D_f) \hat{N}_{n_f}
\]

\[
\Delta \epsilon_f = \epsilon_f - \epsilon_0
\]

\[
D_f = \sum_{m}^\prime \{ \langle 0f | V_{nm} | 0f \rangle - \langle 00 | V_{nm} | 00 \rangle \}
\]

and the rest terms have the form:

\[
H^3 = \sum_{n,m}^\prime M_{nm} b_{n_0}^{+} b_{m_f}^{+} b_{m_f} b_{n_0}
\]

\[
H^4 = \frac{1}{2} \sum_{n,m}^\prime M_{nm} \{ b_{n_0}^{+} b_{m_0}^{+} b_{m_f} b_{n_f} + b_{n_f}^{+} b_{m_f}^{+} b_{m_0} b_{n_0} \}.
\]
We have neglected here the term

$$\frac{1}{2} \sum_{n,m}' \left( \langle 00 | V_{nm} | 00 \rangle - \langle 0f | V_{nm} | 0f \rangle + \langle ff | V_{nm} | ff \rangle \right) b_{nf}^+ b_{nf}^+ b_{mf} b_{mf}$$

which arises due to the multipolar interaction and is small comparing with $H^3$ and $H^4$. The matrix elements

$$M_{nm}^f = \langle 0f | V_{nm} | f0 \rangle,$$

$$\langle 00 | V_{nm} | ff \rangle \simeq M_{nm}^f,$$  \hspace{1cm} (5)

$$\langle ff | V_{nm} | 00 \rangle \simeq M_{nm}^f,$$  \hspace{1cm} (6)

characterize the excitation ‘hopping’ from the site $n$ to $m$. Introducing new (excitonic) operators

$$P_n = b_{nf}^+ b_{nf}, \quad P_n^+ = b_{nf}^+ b_{n0}$$

which play the role of the creation ($P_n^+$) and annihilation ($P_n$) operators of the exciton on the $n$-th site, one can write the Hamiltonian in the finite form:

$$H^2 = \sum_n (\Delta \epsilon_f + \mathcal{D}_f) P_n^+ P_n$$

$$H^3 = \sum_{n,m}' M_{nm}^f P_n^+ P_m$$

$$H^4 = \frac{1}{2} \sum_{n,m}' M_{nm}^f \left( P_m^+ P_n^+ + P_m P_n \right).$$  \hspace{1cm} (7)

The operators $P_n$ form the Paulionic algebra, i.e. they satisfy the following commutation relations. They anticommute like fermionic operators on the same site:

$$P_n P_n^+ + P_n^+ P_n = 1 \quad (P_n^+)^2 = P_n^2 = 0$$  \hspace{1cm} (8)

and commute on the different sites like bosonic ones:

$$P_n P_m^+ - P_m^+ P_n = 0 \quad P_n^+ P_m^+ - P_m P_n^+ = 0.$$  \hspace{1cm} (9)

In the second quantization representation the operator of dipole momentum $p_n$ looks like

$$p_n = p_{nf}^0 \left( b_{nf}^+ b_{n0} + b_{n0}^+ b_{nf} \right)$$

or, in excitonic operators

$$p_n = p_{nf}^0 \left( P_n^+ + P_n \right),$$

where $p_{nf}^0$ is the dipole momentum of the 0-$f$ transition. In these terms the matrix elements $M_{nm}^f$ can be rewritten as:

$$M_{nm}^f = \frac{|p_{nf}^0|^2 |n - m|^2 - 3 (p_{nf}^0, (n - m))^2}{|n - m|^5}.$$
For the 1-D chain one can use the nearest neighbor approximation, so in the following we shall carry out summation in (7) over $m = n \pm 1$ only:

$$
\sum_{n,m}' \rightarrow \sum_{n,m=n\pm1}
$$

This is strongly different from the 3-D situation when one cannot neglect distant molecules, the number of which increases as third degree of the distance, and therefore the term $\sum_{|n-m|>1} \ldots$ therefore has the same order as the nearest neighbors contribution.

One should note that the coefficient $M_{nm}^f$ of the term $P_m^+ P_n^*$ is the same as that of the term $P_m^+ P_n^*$ (see (4, 5)) up to the effects of the intermolecular electron exchange which we will not take into account. This means, that the problem of the optical response is naturally resulted in XY-model rather than XX-model which was frequently treated earlier [1, 9].

Now we will recall the formula for the linear response function. Let the aggregate be exposed in an external time dependent magnetic field. The energy of the aggregate field interaction is equal to that of the dipole momentum on the molecules in the electromagnetic field:

$$
H_t = \sum_n p_n^0 f_n \left( P_n^+ + P_n^* \right)
$$

(for every site the axis is chosen to be along with the molecular dipole moment direction).

In linear on the external field amplitude approximation the most general relation between the statistical average of dipole momentum $\tilde{P}_n = \langle p_n^0 (P_n^+ + P_n) \rangle$ and the electromagnetic field can be written as

$$
\tilde{P}_n(t) = \sum_m \int_0^\infty d\tau \sigma_{nm}(\tau) E_m(t - \tau),
$$

where

$$
\sigma_{nm}(t) = -\frac{(p_n^0)^2}{i\hbar} \text{Tr} \left( (P_m^+ + P_m)(P_n^+ + P_n)(t) | \rho \right)
$$

is the linear response function, $\rho = e^{-\beta H} / \text{Tr} e^{-\beta H}$ is the statistical operator, $\beta$ is the inverse temperature.

Making use the identity

$$
\text{Tr} \left( e^{iHt} (P_m^+ + P_m) e^{-iHt} (P_n^+ + P_n) | \rho \right) = \text{Tr} \left( (P_m^+ + P_m) e^{-iHt} (P_n^+ + P_n) e^{iHt} | \rho \right)
$$

one can write down expression (10) in the form

$$
\sigma_{nm}(t) = \frac{(p_n^0)^2}{i\hbar} \left( \pi_{nm}(t) - \pi_{nm}(-t) \right)
$$

where

$$
\pi_{nm}(t) = \text{Tr} \left( (P_n^+ + P_n)(t) (P_m^+ + P_m) | \rho \right)
$$
Expanding the last expression we get the final formula for the linear response function via the correlators of dipole momentum operators:

\[
\sigma_{nm}(t) = \frac{\rho f}{\hbar} \left[ \langle P_n^+(t) P_m^+ \rangle + \langle P_n^+(t) P_m \rangle + \langle P_n(t) P_m^+ \rangle + \langle P_n(t) P_m \rangle - \langle P_m^+(t) P_n^+ \rangle - \langle P_m^+(t) P_n \rangle - \langle P_m(t) P_n^+ \rangle - \langle P_m(t) P_n \rangle \right]
\]

We can still simplify Eqn.(12). Indeed, due to the relation:

\[
\text{Tr} \left( e^{\beta \mathbf{H}} P_m e^{-\beta \mathbf{H}} P_n e^{-\beta \mathbf{H}} \right) = \overline{\text{Tr} \left( e^{-\beta \mathbf{H}} P_n^+ e^{\beta \mathbf{H}} P_m e^{-\beta \mathbf{H}} \right)}
\]

we have

\[
\langle P_m(t) P_n \rangle = \langle P_m^+(t) P_n^+ \rangle = \langle P_m^+(t) P_n^+ \rangle
\]

Besides, the correlator \( \langle P_n^+(t) P_m \rangle \) is equal to \( \langle P_m(\tau) P_n^+ \rangle \) because of:

\[
\text{Tr} \left( e^{-(\beta-i\tau) \mathbf{H}} P_n^+ e^{-\beta \mathbf{H}} P_m \right) = \text{Tr} \left( e^{-i\beta \mathbf{H}} P_n^+ e^{-(\beta-i\tau) \mathbf{H}} P_m \right)
\]

Finally, using the time and the chain translation invariance we derive the following expression for the response function \( \sigma_{nm}(t) \):

\[
\sigma_{nm}(t) = \frac{2(\rho f)^2}{\hbar} \left( \text{Im} \left( \langle P_n^+(t) P_m^+ \rangle + \langle P_n^+(t) P_m^+ \rangle \right) + \text{Im} \left( \langle P_n(t) P_m^+ \rangle + \langle P_n(t) P_m^+ \rangle \right) \right).
\]

So, we have got the expression for the linear response function \( \sigma_{nm}(t) \). Let us emphasize that there are two different kinds of correlators in \( \langle P_n^+(t) P_m^+ \rangle \) and \( \langle P_n(t) P_m^+ \rangle \). In the next section these correlators will be found for the general case of the cyclic XY-model.

### 3 Correlators of XY-model

In this section we will consider the calculation of correlators which are needed for the evaluation of the linear response following formula \( \langle P_n(t) P_m \rangle \).

The results of this section are valid for an arbitrary XY-Hamiltonian disregard to specific relations between its coefficients, so we can write again Hamiltonian \( \mathbf{H} \) in the general notations:

\[
\mathbf{H} = \sum_{n=1}^{M} \epsilon_n P_n^+ P_n + \hbar \sum_{n=1}^{M} \sum_{m=n \pm 1} P_m^+ P_n + \frac{1}{2} \gamma \sum_{n=1}^{M} \sum_{m=n \pm 1} \left( P_m^+ P_n^+ + P_m P_n \right)
\]

where the cyclic boundary conditions are imposed and \( P_n^+ \), \( P_n \) are paulionic creation and annihilation operators obeying the commutation relations. For excitons the parameters are \( \epsilon \equiv \Delta \epsilon_f + D_f \), \( \hbar = \gamma \equiv M_{nm} \).
summand $H^1$, because statistical characteristics are independent on a constant shift in the energy operator.

It is convenient to start with the consideration of the partition function of the system. After that the correlators $\langle P_1(t) P_{L+1}^+(0) \rangle$ and $\langle P_1^+(t) P_{L+1}^+(0) \rangle$ will be evaluated.

### 3.1 Partition function

As usually, we make use the Jordan–Wigner transformation

$$P_m = (-1)^{\sum_{k=1}^{m-1} c^+_k c_k} c_m, \quad P_m^+ = c_m^+ (-1)^{\sum_{k=1}^{m-1} c^+_k c_k}$$

to rewrite operator (14) in the fermionic Hamiltonian:

$$H = \epsilon \sum_{n=1}^{M} c^+_n c_n + \hbar \sum_{n=1}^{M} \left( c^+_n c_{n+1} + c^+_n c_n \right) + \gamma \sum_{n=1}^{M} \left( c^+_n c_{n+1} + c_{n+1} c_n \right) \quad (15)$$

with the following boundary conditions for the fermionic creation and annihilation operators:

$$c_{M+1} = e^{-i\pi \hat{N}} c_1 \quad c^+_{M+1} = c^+_1 e^{i\pi \hat{N}} \quad \hat{N} = \sum_{n=1}^{M} c^+_n c_n \quad (16)$$

Let us denote the orthogonal projection operators on states containing even and odd number of particles by $P_+$ and $P_-$ respectively:

$$P_\pm = \frac{1}{2} \left( 1 \pm (-1)^{\hat{N}} \right) \quad (17)$$

and consider the operators $H_\pm$ of form (15) with the boundary conditions

$$c_{M+1} = \mp c_1 \quad c^+_{M+1} = \pm c^+_1 .$$

In the momentum representation

$$c_m = \frac{e^{\pi/4}}{\sqrt{M}} \sum_{p \in A_\pm} e^{ipm} c_p, \quad A_\pm = \left\{ p \in (-\pi, \pi] : e^{ipM} = \mp 1 \right\}$$

the operators $H_\pm$ take the quasidiagonal form

$$H_\pm = \sum_{p \in A_\pm} \left\{ \varepsilon_p c^+_p c_p + \gamma \sin p (c^+_p c^+_p + c^-_p c_p) \right\} , \quad \varepsilon_p = \epsilon + 2\hbar \cos(p)$$

Then the partition function $Z$ with the chemical potential $\mu$ is represented as:

$$Z = \Tr \{ \exp(-\beta (H_+ - \mu \hat{N})) P_+ \} + \{ \Tr \exp(-\beta (H_- - \mu \hat{N})) P_- \}$$

that can be rewritten in the form:
\[ Z = \frac{1}{2} \left( \text{Tr} e^{-\beta (H_{\downarrow} - \mu \hat{N})} + \text{Tr} e^{-\beta (H_{\uparrow} - \mu \hat{N})} + \text{Tr}(-1) \hat{N} e^{-\beta (H_{\downarrow} - \mu \hat{N})} - \text{Tr}(-1) \hat{N} e^{-\beta (H_{\uparrow} - \mu \hat{N})} \right) \]  

(18)

Such form is convenient for the calculation of the partition function. Indeed, each term of Eqn.(18) is a partition function of a quadratic Hamiltonian which is quasidiagonal in the momentum representation. Moreover, the moments \( k \) and \(-k\) are only connected. So evaluating traces in each block and taking the product over all momenta we have the following result for the partition function [4]:

\[ Z = \frac{1}{2} (Z_f^+ + Z_f^- + 1/Z_b^+ - 1/Z_b^-) . \]  

(19)

Here \( Z_f^\pm \) (\( Z_b^\pm \)) are the fermionic (bosonic) partition functions

\[
Z_f^\pm = e^{-\beta \epsilon M/2} \prod_{k_\pm} e^{\beta E(k_\pm)/2} \left( 1 + e^{-\beta E(k_\pm)} \right)
\]

and

\[
Z_b^\pm = e^{\beta \epsilon M/2} \prod_{k_\pm} e^{-\beta E(k_\pm)/2} \left( 1 - e^{-\beta E(k_\pm)} \right)^{-1}
\]

for systems with the energy spectra

\[
E(k_\pm) = \left( \epsilon_{k_\pm} - \mu \right) \sqrt{1 + \frac{4\gamma^2 \sin^2(k_\pm)}{\epsilon_{k_\pm}^2 - \mu^2}}
\]

and the antiperiodic (periodic) boundary conditions:

\[
k_+ = \frac{2\pi}{M} (m + 1/2) , \quad k_- = \frac{2\pi}{M} m , \quad m = 0, \ldots, M - 1 .
\]

Using formula (19) one can calculate all equilibrium thermodynamical quantities. The partition function will be used further for calculations of the correlators. There we will put \( \mu = 0 \).

### 3.2 Correlator \( \langle P_1(t) P_{L+1}^+(0) \rangle \)

In this subsection we concentrate our attention on the correlator \( \langle P_1(t) P_{L+1}^+(0) \rangle \). It will be calculated by the coherent states method adopted for the case of the cyclic XY-model in Ref.[11] (the final result of the paper contains a mistake corrected in Ref.[4]).

By the definition, the correlator we are interested in is

\[
\langle P_1(t) P_{L+1}^+(0) \rangle = \frac{1}{Z} \text{Tr} \left( e^{-(\beta - it)H} c_1 e^{-iH} c_{L+1}^+ (-1)^{\sum_{n=1}^L c_n^+ c_n} \right) \]

(20)

As in the previous section it allows us to rewrite correlator (20) in the following form:
\[ \langle P_1(t) \, P_{L+1}^+(0) \rangle = \frac{1}{2Z} \{ K_f^+ + K_b^+ + K_f^- - K_b^- \} \] (21)

where we have introduced the notations:

\[
K_f^\pm = \text{Tr} \left( e^{-(\beta - it)H_z} c_1 e^{-iH_x t} c_{L+1}^\pm (1) \sum_{n=1}^L c_k^c c_n \right)
\]

\[
K_b^\pm = \text{Tr} \left( e^{-(\beta - it)H_z} c_1 e^{-iH_x t} c_{L+1}^\pm (1) \sum_{n=L+1}^M c_k^c c_n \right)
\]

Let us calculate accurately the first term \( K_f^+ \). We will consider the basis of coherent states

\[
|\xi_{p\pm}\rangle = e^{\sum_{p\pm} c_{p\pm}^\dagger \xi_{p\pm} |0\rangle}
\]

with the following well-known properties:

\[
\text{Tr} A = \int \prod_{p\pm} d\xi_{p\pm} \, d\bar{\xi}_{p\pm} \, e^{\bar{\xi}_{p\pm} \langle \xi_{p\pm} | A | \xi_{p\pm} \rangle}
\]

\[
id = \int \prod_{p\pm} d\xi_{p\pm} \, d\bar{\xi}_{p\pm} \, e^{-\bar{\xi}_{p\pm} | \langle \xi_{p\pm} | + | \bar{\xi}_{p\pm} \rangle}.
\]

The variables \( \xi \) are Grassmann numbers and are taken to be commuting with operators. In the Bargmann-Fock representation correlator \( K_f^+ \) is expressed as follows

\[
K_f^+ = \int \prod_{p\pm} d\xi_{p\pm} \, d\bar{\xi}_{p\pm} \int \prod_{p\pm} d\xi_{p\pm} \, d\bar{\xi}_{p\pm} \int \prod_{p\pm} d\bar{\xi}_{p\pm} \, d\xi_{p\pm} \times
\]

\[
\times \exp \sum_{p\pm} \left( \bar{\xi}_{p\pm}^1 \xi_{p\pm}^0 - \bar{\xi}_{p\pm}^0 \xi_{p\pm}^1 - \bar{\xi}_{p\pm}^2 \xi_{p\pm}^2 \right) \langle \xi_{p\pm}^0 | e^{-(\beta - it)H^+} c_1 \xi_{p\pm}^1 \rangle \times
\]

\[
\times \langle \xi_{p\pm}^1 | e^{-itH^-} \xi_{p\pm}^2 \rangle \langle \xi_{p\pm}^2 | c_{L+1}^\dagger (1) \sum_{k=1}^L c_{k}^c c_k | \xi_{p\pm}^0 \rangle \] (22)

We will consider each multiplier in details and start with the third one. Making use the identity (\( N \) is the normal ordering symbol)

\[ e^{\alpha c^+ c} = N \exp \left( (e^\alpha - 1) c^+ c \right) \]

one can rewrite the operator \( (1) \sum_{k=1}^L c_k^c c_k \) in the normal ordered form:

\[ (-1) \sum_{k=1}^L c_k^c c_k = N \exp \left\{ -2 \sum_{p\pm, p\pm'} c_{p\pm}^+ c_{p\pm'}^V f_{p\pm, p\pm'}^f \right\} \]

with the matrix \( V_f^f \):

\[ V_{pp'}^f = \frac{1}{M} \sin \frac{1}{2} (p' - p) L \] (23)
Then, substituting the momentum representation for the operator $c_{L+1}^+$

$$c_{L+1}^+ = \frac{e^{-i\pi/4}}{\sqrt{M}} \sum_{p_+} e^{-ip_+(L+1)} c_{p_+}^+$$

we come to the expression for the third multiplier in (22):

$$\langle \bar{\xi}_{p_+}^2 | c_{L+1}^+(-1) \sum_{k=1}^L c_k^+ c_k | \xi^0_{p_+} \rangle = \frac{e^{-i\pi/4}}{\sqrt{M}} \sum_{p'_+} e^{-ip'_+(L+1)} \bar{\xi}_{p'_+}^2 \exp \left\{ - \sum_{p_+p'_+} \bar{\xi}_{p_+}^2 W^f_{p_+p'_+} \xi^0_{p'_+} \right\}$$

where

$$W^f_{p_+p'_+} = -2V^f_{p_+p'_+} + \delta_{p_+p'_+}.$$  

Let us now consider the first multiplier in the integral (22). Using (24) one can rewrite it as follows:

$$\langle \xi^0_{p_+} | e^{-(\beta-\alpha)H} c_1 | \xi^1_{p_+} \rangle = \frac{e^{i\pi/4}}{\sqrt{M}} \sum_{p''_+} e^{i\alpha p''} c_1^+ \langle \xi^0_{p_+} | e^{-(\beta-\alpha)H} | - \xi^1_{p_+} \rangle$$

To calculate the matrix element we have to present the operator $e^{-(\beta-\alpha)H}$ in the normal ordered form. First of all we will extract terms in $H$ with the momentum $p = \pi$ (if it is presented at all). All other terms can be grouped in pairs with opposite momenta, $\{p_+, -p_+\}$. Then the exponent can be put down:

$$e^{-(\beta-\alpha)H} = e^{-(\beta-\alpha)H^\pi} \prod_{\{p_+, -p_+\} \neq \pi} e^{-(\beta-\alpha)H^{p_+}}$$

where the first multiplier is only presented if $M$ is odd and

$$H^\pi_p = \varepsilon_p \left( c_p^+ c_p + c_{-p}^+ c_{-p} \right) + 2\gamma \sin(p \left( c_{-p} c_p + c_p^+ c_{-p}^+ \right)$$

One can derive the following expression for the normal ordered exponent of the last operator:

$$e^{-(\beta-\alpha)H^{p_+}} = e^{-(\beta-\alpha)\varepsilon_{p_+}} \varepsilon_{p_+} K_{p_+}(\beta - it) N \exp \left\{ \frac{1}{K_{p_+}(\beta - it)} - 1 \right\} (c_{p_+}^+ c_{p_+} + c_{-p_+}^+ c_{-p_+} +$$

$$+ \sigma_{p_+}(\beta - it) (c_{p_+}^+ c_{-p_+} + c_{-p_+}^+ c_{p_+}) \right\}$$

where

$$K_{p}(\beta) = \cos^2 \frac{\theta_p}{2} e^{\beta E_p} + \sin^2 \frac{\theta_p}{2} e^{-\beta E_p}$$

$$\sigma_p(\beta) = \frac{1}{K_p(\beta)} \sin \theta_p \sinh \beta E_p$$
and \( \theta_p \) is so-called Bogoliubov’s angle:
\[
\sin \theta_p = -\frac{2\gamma \sin p}{E_p}, \quad \cos \theta_p = \frac{\varepsilon_p}{E_p}, \quad E_p = \varepsilon_p\sqrt{\frac{4\gamma^2 \sin^2 p}{\varepsilon_p^2} + 1}.
\]

Now one can get the expression for the matrix element in (26):
\[
\langle \xi^0_{p+} | e^{-(\beta - it)H} | -\xi^1_{p+} \rangle = \prod_{\{p_+, -p_+\} \neq \pi} e^{-(\beta - it)\varepsilon_{p+}} K_{p+} (\beta - it) \times
\]
\[
\exp \left\{ -\frac{1}{K_{p+} (\beta - it)} \left( \xi^0_{p+} \xi^1_{p+} + \xi^1_{-p+} \xi^0_{-p+} \right) - \sigma_{p+} (\beta - it) \left( \xi^0_{p+} \xi^0_{-p+} + \xi^1_{-p+} \xi^1_{p+} \right) \right\} \exp \left( -e^{-(\beta - it)\varepsilon_{p+}} \xi^0_{p+} \xi^1_{-p+} \right)
\]

This expression allows us to consider the product over all momenta \( p_+ \) (instead of the product over the pairs \( \{p_+, -p_+\} \)). Then the terms with the momentum \( k = \pi \) can be taken into account in the product over all \( p_+ \) and the term (26) can be presented as
\[
\langle \tilde{\xi}^0_{p+} | e^{-(\beta - it)H} c_1 | \xi^1_{p+} \rangle = \frac{e^{i\pi/4}}{\sqrt{M}} \sum_{p_+} e^{ip_+} \xi^1_{p+} \left( \prod_{p_+} e^{-(\beta - it)\varepsilon_{p+}} K_{p+} (\beta - it) \right)^{\frac{1}{4}} \times
\]
\[
\exp \left\{ -\frac{1}{K_{p+} (\beta - it)} \tilde{\xi}^0_{p+} \xi^1_{p+} - \sigma_{p+} (\beta - it) \left( \tilde{\xi}^0_{p+} \tilde{\xi}^0_{-p+} + \xi^1_{-p+} \xi^1_{p+} \right) \right\}
\]

(28)

In close analogue with this term we can derive an expression for the second matrix element in (23). It is given by
\[
\langle \tilde{\xi}^1_{p+} | e^{i\hat{H}c_1} | \xi^2_{p+} \rangle = \left( \prod_{p_-} e^{-it\varepsilon_{p-}} K_{p-} (it) \right)^{\frac{1}{4}} \times
\]
\[
\exp \left\{ \frac{1}{K_{p-} (it)} \tilde{\xi}^1_{p-} \xi^2_{p-} - \frac{\sigma_{p-} (it)}{2} \left( \tilde{\xi}^1_{p-} \tilde{\xi}^1_{-p-} + \xi^2_{-p-} \xi^1_{p-} \right) \right\}
\]

(29)

where the variables \( \xi_{p_-} \) are connected with the variables \( \xi_{p_+} \) by the unitary transformation:
\[
\xi_{p_-} = \sum_{p_+} U_{p_-p_+} \xi_{p_+}, \quad \tilde{\xi}_{p_-} = \sum_{p_+} \tilde{\xi}_{p_+} U^+_{p_+p_-}, \quad U_{p_-p_+} = \frac{1}{M} \sum_{k=1}^M e^{ik(p_+ - p_-)}.
\]

Substituting (23), (28) and (29) in the integral (22) one can get the final integral expression:
\[ K_{f(b)}^+ = \left( \prod_{p_+} e^{-(\beta - it)\xi_{p_+} K_{p_+}} (\beta - it) \prod_{p_-} e^{-it\xi_{p_-} K_{p_-}} (it) \right) \frac{1}{M} \sum_{p_+ p'_+} e^{i\sigma_{p_+} - ip_+(L+1)} \times \]
\[ \times \int d\xi^0 d\bar{\xi}_0 \, d\xi^1 d\bar{\xi}_1 \, d\xi^2 d\bar{\xi}_2 \, \exp \left\{ \xi^0 \xi^0 - \bar{\xi}_0 \xi^1 + \bar{\xi}_2 \xi^2 \right\} \xi_{p'_+}^1 \bar{\xi}_{p_+}^2 \times \]
\[ \times \exp \left\{ -\xi^0 D^{(1)} \xi^1 + \xi^0 B^{(1)} \xi^0 - \xi^1 B^{(1)} \xi^1 + \xi^1 U D^{(2)} U \xi^2 + \bar{\xi}^1 U^+ B^{(2)} U \xi^2 - \xi^2 W_{f(b)}^+ (\xi^0) \right\} \]

where we use the matrix notations:

\[ D^{(1)} = \text{diag}(\frac{1}{K_{p,(\beta - it)}}, \frac{1}{K_{p,(it)}}), \quad B^{(1)}_{pp'} = -\delta_{p_- p'_+} \frac{\sigma_p (\beta - it)}{2} \]
\[ D^{(2)} = \text{diag}(\frac{1}{K_{p,(it)}}, \frac{1}{K_{p,(\beta - it)}}), \quad B^{(2)}_{pp'} = -\delta_{p_- p'_+} \frac{\sigma_p (it)}{2} \]

indices “+” and “−” at matrices point the momentum space (\(A_+\) or \(A_-\)) in which these indices are considered.

One can see that \(K_{f}^+\) can be written in the same form as \(K_{f}^+\). There is the only difference in the third matrix element in (30). It leads to replacing of the matrix \(W^b_+\) by the matrix \(W^b_+\). The matrix \(W^b_+\) can be easy calculated and results in

\[ W^b_{p_+ p'_+} = \delta_{p_+ p'_+} - \frac{2}{M} \exp \left\{ \frac{1}{2} i(p'_+ - p_+)(M + L + 1) \right\} \frac{\sin \frac{1}{2}(p'_+ - p_+)(M - L)}{\sin \frac{1}{2}(p'_+ - p_+)} = -W^f_{p_+ p'_+} \]

That is why we have the general expression for \(K_{f}^+\) and \(K_{f}^+\) in (30).

To obtain \(K_{f(b)}^-\) one should replace the matrix \(U\) by the matrix \(U^+, \text{“+” by “−” (and visa-versa) in Eqn. (31)\). It can be easy understood from the calculating procedure. Thus \(K_{f(b)}^-\) is presented by:

\[ K_{f(b)}^- = \left( \prod_{p_-} e^{-(\beta - it)\xi_{p_-} K_{p_-}} (\beta - it) \prod_{p_+} e^{-it\xi_{p_+} K_{p_+}} (it) \right) \frac{1}{M} \sum_{p_- p'_-} e^{i\sigma_{p_-} - ip_- (L+1)} \times \]
\[ \times \int d\xi^0 d\bar{\xi}_0 \, d\xi^1 d\bar{\xi}_1 \, d\xi^2 d\bar{\xi}_2 \, \exp \left\{ \xi^0 \xi^0 - \bar{\xi}_0 \xi^1 + \bar{\xi}_2 \xi^2 \right\} \xi_{p'_-}^1 \bar{\xi}_{p_-}^2 \times \]
\[ \times \exp \left\{ -\xi^0 D^{(1)} \xi^1 + \xi^0 B^{(1)} \xi^0 - \xi^1 B^{(1)} \xi^1 + \xi^1 U D^{(2)} U \xi^2 + \bar{\xi}^1 U^+ B^{(2)} U \xi^2 - \xi^2 W_{f(b)}^- (\xi^0) \right\} \]

So we have obtained all terms in (31). Now we should calculate the integrals in expressions (31, 32). To do it we introduce four generating functions \(I_{f(b)}^+ (\bar{\eta}, \eta)\) and \(I_{f(b)}^- (\bar{\eta}, \eta)\) as follows:
\[ I^+_{f(b)}(\bar{\eta}, \eta) = \int d\xi^0 d\xi^0 d\xi^1 d\xi^2 d\xi^2 \exp \left( \xi^0 \xi^0 - \xi^1 \xi^1 - \xi^2 \xi^2 \right) \times \]
\[
\times \exp \left\{ -\xi^0 D^{(1)} \xi^1 + \xi^0 B^{(1)} \xi^0 - \xi^1 B^{(1)} \xi^1 + \xi^1 U D^{(2)} U \xi^2 + \right. 
\[
\left. + \xi^1 U B^{(2)} U \xi^1 - \xi^2 U B^{(2)} U \xi^2 - \xi^2 W^{(b)} \xi^0 + \bar{\eta} \xi^1 + \bar{\eta} \xi^2 \right\} . \]
\]
\[
I^-_{f(b)}(\bar{\eta}, \eta) = \int d\xi^0 d\xi^0 d\xi^1 d\xi^2 d\xi^2 \exp \left( \xi^0 \xi^0 - \xi^1 \xi^1 - \xi^2 \xi^2 \right) \times \]
\[
\times \exp \left\{ -\xi^0 D^{(1)} \xi^1 + \xi^0 B^{(1)} \xi^0 - \xi^1 B^{(1)} \xi^1 + \xi^1 U D^{(2)} U \xi^2 + \right. 
\[
\left. + \xi^1 U B^{(2)} U \xi^1 - \xi^2 U B^{(2)} U \xi^2 - \xi^2 W^{(b)} \xi^0 + \bar{\eta} \xi^1 + \bar{\eta} \xi^2 \right\} . \]
\]

The detailed calculation of these integrals and corresponding derivatives is placed in Appendix A. Here we only put down the final results for \( K^{\pm}_{f(b)} \):

\[
K^{\pm}_{f(b)} = (-1)^{M(M-1)/2} \text{Pf}(G^{f(b)}_{\pm}) \sqrt{\det R_{\pm}^{-1}} \times \]
\[
\times \left( \prod_{p_{\pm}} e^{-(\beta - it) \varepsilon_{p_{\pm}} K_{p_{\pm}} (\beta - it)} \prod_{p_{\pm}} e^{-it \xi_{p_{\pm}} K_{p_{\pm}} (it)} \right)^{1/2} \times \]
\[
\times \frac{1}{M} \sum_{p_{\pm} p'_{\pm}} e^{ip'_{\pm} - ip_{\pm} (L+1)} \left( Q^{f(b)}_{\pm} + T^{f(b)}_{\pm} \left( Q^{f(b)}_{\pm} \right)^{-1} S_{\pm} \right)_{p'_{\pm} p_{\pm}}^{-1} \]
\[
\text{(33)} \]

with the following notations:

\[
Q^{f(b)}_{+} = W^{f(b)}_{+} D^{(1)}_{+} + U D^{(2)}_{+} R_{-} U \]
\[
T^{f(b)}_{+} = 2 \left\{ W^{f(b)}_{+} B^{(1)}_{+} \left( W^{f(b)}_{+} \right)^{t} + U B^{(2)}_{+} R_{-} U \right\} \]
\[
S_{+} = -2 \left\{ B^{(1)}_{+} + U B^{(2)}_{+} R_{-} U \right\} \]
\[
Q^{f(b)}_{-} = W^{f(b)}_{-} D^{(1)}_{-} + U D^{(2)}_{+} R_{+} U \]
\[
T^{f(b)}_{-} = 2 \left\{ W^{f(b)}_{-} B^{(1)}_{-} \left( W^{f(b)}_{-} \right)^{t} + U B^{(2)}_{-} R_{+} U \right\} \]
\[
S_{-} = -2 \left\{ B^{(1)}_{-} + U B^{(2)}_{-} R_{+} U \right\} \]
\[
\text{(34)(35)} \]

and the matrix \( G^{f(b)}_{\pm} \) has the form

\[
G^{f(b)}_{\pm} = \begin{pmatrix} S_{\pm} & \left( Q^{f(b)}_{\pm} \right)^{t} \\ -Q^{f(b)}_{\pm} & T^{f(b)}_{\pm} \end{pmatrix} , \]
\[
\text{(36)} \]
where the matrix $R$ is defined as

$$R = \left\{ (D^{(2)})^2 - 4 (B^{(2)})^2 \right\}^{-1} = \text{diag} \left\{ \frac{K^2_{p}(it)}{1 + \tilde{K}^2_{p}(it)} \sigma^2_{p}(it) \right\}. \tag{37}$$

### 3.3 Correlator $\langle P^+_1(t) P^+_{L+1}(0) \rangle$

Let us now consider another correlator

$$\langle P^+_1(t) P^+_{L+1}(0) \rangle \equiv \frac{1}{Z} \text{Tr} \left( e^{-\beta - it} H c^+_1 e^{-i t} H c^+_i c^+_{L+1} (-1)^{\sum_{k=1}^{L} c^+_k c^+_k} \right)$$

In close analogue with $\langle P_1(t) P^+_{L+1}(0) \rangle$ one can rewrite the correlator as:

$$\langle P^+_1(t) P^+_{L+1}(0) \rangle = \frac{1}{2Z} \left( \tilde{K}^+_f + \tilde{K}^+_b + \tilde{K}^-_f - \tilde{K}^-_b \right) \tag{38}$$

where

$$\tilde{K}^+_f = \text{Tr} \left( e^{-\beta - it} H c^+_1 e^{-i t} H c^+_i c^+_{L+1} (-1)^{\sum_{k=1}^{L} c^+_k c^+_k} \right)$$

$$\tilde{K}^+_b = \text{Tr} \left( e^{-\beta - it} H c^+_1 e^{-i t} H c^+_i c^+_{L+1} (-1)^{\sum_{k=L+1}^{M} c^+_k c^+_k} \right)$$

The calculating procedure is the same as in the previous subsection. But there are several differences on which we will concentrate here.

First of all, let us consider expression (22). There is the only difference here for $\tilde{K}^+_f$ in two first matrix elements in (22). For $\tilde{K}^+_f$ they are:

$$\langle \tilde{\xi}^0_{p+} | e^{-(\beta - it) H} | \tilde{\xi}^1_{p+} \rangle \langle \tilde{\xi}^1_{p+} e^{-i t H} | \tilde{\xi}^2_{p+} \rangle$$

to provide the normal ordering. We have estimated all matrix element for $\tilde{K}^+_f$ in the previous section in details. From these calculations one can see that for $\tilde{K}^+_f$ we should change the matrix $D$ by the matrix $-D$ in (30), change the sign in one of the exponents in front of the integral and put the multiplier $e^{-ix/2} = -i$ due to the properties of Fourier transformation.

So one can infer the expression for $\tilde{K}^+_{f(b)}$:

$$\tilde{K}^+_{f(b)} = \left( \prod_{p+} e^{-(\beta - it)\xi_{p+} K^+_{p+} (\beta - it) \prod_{p-} e^{-i t \xi_{p-} K^-_{p-} (it)} \right)^{1/2} \left( \frac{-i}{M} \right) \sum_{p+, p'_+} e^{-ip'_+ - ip_+ (L+1)} \times$$

$$\times \int d\xi^0 d\xi^0' d\xi^1 d\xi^1' d\xi^2 d\xi^2' \exp \left\{ \tilde{\xi}^0 \xi^0 - \tilde{\xi}^1 \xi^1 - \tilde{\xi}^2 \xi^2 \right\} \tilde{\xi}^1 \tilde{\xi}^2 \times$$

$$\times \exp \left\{ \xi^0 D^{(1)}_+ \xi^1 + \xi^0 B^{(1)}_+ \xi^0 - \xi^1 B^{(1)}_+ \xi^1 - \tilde{\xi}^1 U + D^{(2)}_+ U \xi^2 + \tilde{\xi}^1 U + B^{(2)}_+ \tilde{\xi}^1 - \xi^2 U + B^{(2)}_+ U \xi^2 - \tilde{\xi}^2 W^{(b)}_+ \xi^0 \right\}. \tag{39}$$
where all notations have been introduced in the previous subsection. Using the same arguments as above for $K_{f(b)}^-$ we can derive the analogous expression for $\tilde{K}_{f(b)}^-$

$$\tilde{K}_{f(b)}^- = \left( \prod_{p_-} e^{-(\beta - it)\varepsilon_{p_-}} K_{p_-}(\beta - it) \prod_{p_+} e^{-it\varepsilon_{p_+}} K_{p_+}(it) \right)^{\frac{i}{2}} \frac{(-i)}{M} \sum_{p_- p_+} e^{-ip'_- - ip_-(L+1)} \times$$

$$\times \int d\xi^0 d\xi^1 d\xi^1 d\xi^2 d\xi^2 \exp \left\{ \xi^0 \xi^0 - \xi^1 \xi^1 - \xi^2 \xi^2 \right\} \tilde{f}_p \tilde{f}_{p'} \times$$

$$\times \exp \left\{ \xi^0 D^{(1)}_+ \xi^1 + \xi^0 B^{(1)}_+ \xi^0 - \xi^1 B^{(1)}_+ \xi^1 - \xi^2 U D^{(2)}_+ U \xi^2 + \xi^1 U B^{(2)}_+ U^t \xi^1 - \xi^2 U B^{(2)}_+ U \xi^2 - \xi^2 W^{(b)}_+ \xi^0 + \xi^1 \eta_1 + \xi^2 \eta_2 \right\}$$

The next step is to calculate the integrals in (39,40). We will consider just one of them and write another one by analogue. Let us introduce the generating function for the integral in $\tilde{K}_{f(b)}^+$:

$$J_{f(b)}^+(\eta_1, \eta_2) = \int d\xi^0 d\xi^1 d\xi^2 d\xi^2 \exp \left\{ \xi^0 \xi^0 - \xi^1 \xi^1 - \xi^2 \xi^2 \right\} \times$$

$$\times \exp \left\{ \xi^0 D^{(1)}_+ \xi^1 + \xi^0 B^{(1)}_+ \xi^0 - \xi^1 B^{(1)}_+ \xi^1 - \xi^2 U D^{(2)}_+ U \xi^2 + \xi^1 U B^{(2)}_+ U^t \xi^1 - \xi^2 U B^{(2)}_+ U \xi^2 - \xi^2 W^{(b)}_+ \xi^0 + \xi^1 \eta_1 + \xi^2 \eta_2 \right\}$$

Integrating in the same way as in the previous section and neglecting terms with $\eta_1$, $\eta_1$ and $\eta_2$, $\eta_2$ one can obtain

$$J_{f(b)}^+(\eta_1, \eta_2) = (-1)^{M(M+1)/2} \text{Pf}(G_{f(b)}^+) \sqrt{\det R^{-1}} \exp \left\{ \eta_1 F_{f(b)}^+ \eta_2 \right\}$$

Here matrices $Q$, $S$ and $T$ are the same as in (34) and matrices $G_{f(b)}^+$ and $F_{f(b)}^+$ are determined by

$$\tilde{G}_{f(b)}^+ = \left( \begin{array}{cc} S^+ \quad - (Q_{f(b)}^+)^t \\ Q_{f(b)}^+ T_{f(b)}^+ \end{array} \right)$$

$$F_{f(b)}^+ = \left( 2B^+(1) + D^+(1) (W^+(b))^t (Q_{f(b)}^+)^{-t} S^+ \right) \left( Q_{f(b)}^+ + T_{f(b)}^+ (Q_{f(b)}^+)^{-t} S^+ \right)^{-1}$$

Using this generating function we can write expressions for all $\tilde{K}$ in (38) applying the same calculations as in the previous section. The result is given by the following formula:

$$\tilde{K}_{f(b)}^+ = (-1)^{M(M+1)/2} \left( \prod_{p_-} e^{-(\beta - it)\varepsilon_{p_-}} K_{p_-}(\beta - it) \prod_{p_+} e^{-it\varepsilon_{p_+}} K_{p_+}(it) \right)^{\frac{i}{2}} \times$$

$$\times \text{Pf}(G_{f(b)}^+) \sqrt{\det R^{-1}} \frac{(-i)}{M} \sum_{p_- p_+} e^{-ip'_- - ip_-(L+1)} (F_{f(b)}^+)_{p_- p_+}$$

(41)
Here and matrices $Q_-, S_-$ and $T_-$ are the same as in (35). So formula (41) gives us all the necessary terms to calculate correlator (38).

4 Correlation functions for $\gamma = 0$ (XX-model)

Up to day there are three original works devoted to the calculation of the correlators for the XX-models at finite temperature. The first of them is the paper by Colomo, Izergin, Korepin and Tognetti [7] where the correlator for the XX-model was calculated in the thermodynamic limit. The correlators for finite cyclic chains were calculated by Suzuura, Tokihiro and Ohta in [9] and by Ilinski, Kalinin and Kapitonov [4] for the qXX-model (which produces the XX-model for the particular value of the deformation parameter $q = -1$). Thus, there are three crucial points for the verification of the results obtained in this paper. Besides this, it is possible to compare our result with that of calculated by for small chains. It means to represent the Hamiltonian and the creation-annihilation operators as matrices $2^M \times 2^M$ for the $M$-site chain and then to evaluate the trace of the matrix $e^{-(\beta - it)H}P_1e^{-itH}P_{L+1}^+$. The result of the comparison will be reviewed in this section.

Let us start with the finite XX-chain correlator. One can extract it from the formulae (33–37) putting $\gamma = 0$. Then $\theta_p = 0$ for all $p$ and $E_p = \epsilon_p$.

$$\langle P_1(t) P_{L+1}^+(0) \rangle = \frac{1}{2Z} (K^f_+ + K^f_- + K^b_+ - K^b_-)$$ (42)

$$K^f_{\pm} = (-1)^{M(M-1)/2} \prod_{p \in A_{\pm}} e^{-it\epsilon_p} \text{Pf} \left( \begin{array}{cc} 0 & (F^f_{\pm})^t \\ -F^f_{\pm} & 0 \end{array} \right) \text{Tr}(F^f_{\pm}^{-1}G) = e^{-it\epsilon M} \det F^f_{\pm} \text{Tr}(F^f_{\pm} G)$$ (43)

where

$$F^f_{\pm} = \left[ W^f_{\pm} D^{(1)}_{\pm} + U^\pm D^{(2)}_{\pm} R - U \right] \big|_{\gamma = 0}$$

$$G_{p,p'} = \frac{1}{M} e^{-ip(L+1)+ip'}$$ (44)

If we rewrite this formula in the coordinate representation we will get the formula for the correlator in the qXX-model obtained in [4] for the case $q = -1$.

$$K^f_{\pm} = \frac{e^{-it\epsilon M}}{2Z} \det \tilde{F}^f_{\pm} (\tilde{F}^f_{\pm})^{-1}_{1,L+1}$$ (45)
\[
(F^f_{\pm})_{m,m'} = \frac{1}{M} \sum_{r \in A_{\pm}} e^{it\epsilon_r + i(r - m')\epsilon_p} + \frac{1}{M} \sum_{p \in A_{\pm}} e^{ip(m - m') + (it - \beta)\epsilon_p} \left(1 - 2 \times \begin{cases} 1 \text{ if } m \leq L \\ 0 \text{ if } m > L \end{cases} \right)
\]
\[
(F^b_{\pm})_{m,m'} = \frac{1}{M} \sum_{r \in A_{\pm}} e^{it\epsilon_r + i(r - m')\epsilon_p} - \frac{1}{M} \sum_{p \in A_{\pm}} e^{ip(m - m') + (it - \beta)\epsilon_p} \left(1 - 2 \times \begin{cases} 1 \text{ if } m \leq L \\ 0 \text{ if } m > L \end{cases} \right)
\]

One should note that our result is different from that announced in [9]. First of all in our opinion there is a misprint in signs of two last terms in Eqn.(15) of Ref.[9]. Moreover, the numerical calculations for \( t = 0 \) and particular values of parameters \( \{\epsilon = 1, h = 5\}, \{\epsilon = 1, h = 2\} \) reveal the difference between the results of [9] and the calculation by the definition for both choices of the sign.

Eqs.(42,45) coincide with the correlator calculated by the definition for the number of sites \( M = 3 \). In this case it is possible to compare the analytical expressions for the correlators (the calculation was performed using the system of symbolical calculations REDUCE).

Let us now consider the thermodynamic limit \( (M \to \infty) \) for the XX-model \( (\gamma = 0) \). At first we will treat the partition function. The “bosonic” contributions \( Z^b_{\pm} \) are equal and, hence, disappear. By the same reason the “fermionic” terms are equal and cancel the factor 2 in the formula (19). This is due to the absence of the difference of momentum spectrum \( A_{+} \) and \( A_{-} \) (in the thermodynamic limit the boundary conditions are irrelevant). So the partition function of the XX-model in the thermodynamic limit is equal to the partition function of free fermions on the infinite chain.

In the same way the correlator for the XX-model in the thermodynamic limit is obtained from Eqn.(12) putting \( K^f_{\pm} = K^f_{-} \equiv K, K^b_{\pm} = K^b_{-} \). So in the thermodynamic limit we have

\[
\langle P_0(t) P^+_L(0) \rangle = \frac{K}{Z} \quad (48)
\]

where

\[
Z = \prod_p (1 + e^{-\beta \epsilon_p}) \quad (49)
\]

is the fermionic partition function and

\[
K = e^{-it\epsilon M} \det(F) \frac{1}{M} \sum_{p,p'} e^{ipL} F^p_{p'}^{-1},
\]

\[
F = R(it - \beta) + R(it) - 2VR(it - \beta),
\]

\[
R(\tau) = \text{diag} \{ e^{\tau \epsilon_p} \}
\]

and the matrix \( V \) is given by Eqn.(23).

It is easy to show that the matrix \( F \) can be represented in the following form:

\[
F = \theta^{-1/2} [1 - 2\theta^{1/2} V \theta^{1/2}] \theta^{-1/2} R(it - \beta)
\]

where \( \theta \) is the following diagonal matrix

\[
\theta = \text{diag} \left\{ \frac{1}{1 + e^{\beta \epsilon_p}} \right\}.
\]
And finally we obtain
\[
\det(F) = Ze^{it\varepsilon M} \det[1 - 2\theta^{1/2} V \theta^{1/2}],
\]
hence
\[
\langle P_0(t) P^+_L(0) \rangle = \det[1 - 2\theta^{1/2} V \theta^{1/2}] \times \frac{1}{M} \sum_{p,p'} \delta^{pL} R_{p'p'}(\beta - it) \theta^{1/2}_{p'p'}[1 - 2\theta^{1/2} V \theta^{1/2}]^{-1} \theta^{1/2}_{pp}.
\]

Let us consider the following unitary transformation of \(V\):
\[
V = U^{-1} v U
\]
where
\[
U = \text{diag}\{e^{ip(L+1)/2}\}, \quad v_{pp'} = \frac{\sin p' - p L}{\sin \frac{p'}{2}}.
\]

Then the correlator takes the form
\[
\langle P_0(t) P^+_L(0) \rangle = \det[1 - 2\theta^{1/2} v \theta^{1/2}] \frac{1}{M} \sum_{p,p'} e^{i(p+p')L/2 + i(p-p')/2} R_{p'p'}(\beta - it) \times \theta^{1/2}_{p'p'}[1 - 2\theta^{1/2} v \theta^{1/2}]^{-1} \theta^{1/2}_{pp} \times \theta^{1/2}_{p'p'}[1 - 2\theta^{1/2} v \theta^{1/2}]^{-1} \theta^{1/2}_{pp} \times e^{i(p+p')L/2}\frac{1}{2}[e^{i(p-p')/2 + (\beta - it)\varepsilon_p} + e^{i(p'-p)/2 + (\beta - it)\varepsilon_p}]
\]

And finally we obtain the following expression for the correlator
\[
\langle P_0(t) P^+_L(0) \rangle = \det[1 - 2\theta^{1/2} v \theta^{1/2}] \text{Tr} \left\{ \theta^{1/2} r(\beta - it) \theta^{1/2} [1 - 2\theta^{1/2} v \theta^{1/2}]^{-1} \right\} = \frac{\partial}{\partial z} \det[1 - 2\theta^{1/2} v \theta^{1/2} + z\theta^{1/2} r(\beta - it) \theta^{1/2}] \bigg|_{z=0}
\]
where \(v\) is defined in \((51)\) and
\[
r_{pp'}(\tau) = e^{i(p+p')L/2}\frac{1}{2}[e^{i(p-p')/2 + \tau\varepsilon_p} + e^{i(p'-p)/2 + \tau\varepsilon_p}].
\]

In the same way expression for correlator \(\langle P^+_0(t) P_L(0) \rangle\) is obtained
\[
\langle P^+_0(t) P_L(0) \rangle = \det[1 - 2\theta^{1/2} v \theta^{1/2}] \text{Tr} \left\{ \theta^{1/2} r(it) \theta^{1/2} [1 - 2\theta^{1/2} v \theta^{1/2}]^{-1} \right\} = \frac{\partial}{\partial z} \det[1 - 2\theta^{1/2} v \theta^{1/2} + z\theta^{1/2} r(it) \theta^{1/2}] \bigg|_{z=0}
\]
The form of expression (54) is similar to that in Ref. [7]. Let us substitute \( t = 0 \) in Eqn.(54):

\[
\langle P_0^+ P_L \rangle = \det[1 - 2\theta^{1/2}v\theta^{1/2}] \Tr \left\{ \theta^{1/2}r\theta^{1/2}[1 - 2\theta^{1/2}v\theta^{1/2}]^{-1} \right\} = \frac{\partial}{\partial z} \det[1 - 2\theta^{1/2}v\theta^{1/2} + z\theta^{1/2}r\theta^{1/2}] \bigg|_{z=0}
\]

(55)

where

\[
r_{pp'} \equiv r_{pp'}(0) = e^{i(p+p')L/2} \cos \frac{(p - p')}{2}
\]

(56)

Now we can see that expression (55) is different from Eqn.(39) of Ref.[7] in two aspects. At first, the matrix \( r \) contains the additional factor \( \cos \frac{(p - p')}{2} \). Secondary, in the matrix \( v \) we should replace \( L \) by \( L - 1 \). We will show that these two expressions for the correlator \( \langle P_0^+ P_L \rangle \) are the same. Indeed, we can write down from the definition

\[
\langle P_0^+ P_L \rangle = \frac{1}{Z} \Tr \left[ e^{-\beta H} P_0^+ P_L \right] = \frac{1}{Z} \int d\xi_0 d\bar{\xi}_0 d\xi_1 d\bar{\xi}_1 \exp[\bar{\xi}_0\xi_0 - \bar{\xi}_1\xi_1] \times \langle \bar{\xi}_0 | e^{-\beta H} | \xi_1 \rangle N c_0^+ \exp\left\{ -2 \sum_{k=1}^{L-1} c_k^+ c_k \right\} c_L | \xi_0 \rangle .
\]

(57)

Using the method described in Section 3 we obtain the following result

\[
\langle P_0^+ P_L \rangle = \det[1 - 2\theta^{1/2}\bar{v}\theta^{1/2}] \Tr \left\{ \theta^{1/2}\bar{r}\theta^{1/2}[1 - 2\theta^{1/2}\bar{v}\theta^{1/2}]^{-1} \right\} = \frac{\partial}{\partial z} \det[1 - 2\theta^{1/2}\bar{v}\theta^{1/2} + z\theta^{1/2}\bar{r}\theta^{1/2}] \bigg|_{z=0}
\]

(58)

where

\[
\bar{r}_{pp'} = e^{i(p+p')L/2} \quad \bar{v}_{pp'} = \frac{\sin \frac{1}{2}(p' - p)(L - 1)}{\sin \frac{1}{2}(p' - p)}
\]

As \( c_0^+ c_L = c_0^+ \exp[i\pi c_0^+ c_0] c_L \) we can rewrite (57) in the following form

\[
\langle P_0^+ P_L \rangle = \frac{1}{Z} \int d\xi_0 d\bar{\xi}_0 d\xi_1 d\bar{\xi}_1 \exp[\bar{\xi}_0\xi_0 - \bar{\xi}_1\xi_1] \times \langle \bar{\xi}_0 | e^{-\beta H} | \xi_1 \rangle N c_0^+ \exp\left\{ -2 \sum_{k=0}^{L-1} c_k^+ c_k \right\} c_L | \xi_0 \rangle .
\]

(59)

Repeating the above calculation we can come to expression (55). It follows from the previous consideration that expressions (55) and (58) are in fact the same.

So it is not now surprising that expression (54) for correlator \( \langle P_0^+(t) P_L(0) \rangle \) is different from that in Ref.[7] because they are derived with different methods and as we have seen
above it is difficult to transform one form to another. However, due to the verification for finite $M$ and for $t = 0, M \to \infty$ we can be sure in the correctness of our formulae in $M \to \infty$ limit and $t \neq 0$. Finally, our result is obviously simpler. Indeed, expressions (52, 54) for the correlators contain the time dependence only in the matrix $r$ and trivially generalize the $t = 0$ case.

5 Conclusion

Now we can summarize the results of the previous sections. Formula (13) together with formulae (21, 33, 38, 41) for the correlation functions give the final expression for the linear response of the molecular aggregate. In our opinion, the result has the following advantages:

1. It can be used for the numerical calculations to investigate the finite size effects and the closure effects for cyclic aggregates. As we could note during computer calculations for the XX-model, to deal with our expressions is significantly easier than with the corresponding formulae of Ref.[9].

2. We can say the same about the resulting representations for the correlators in the thermodynamic limit. We cannot check our expressions directly in this case but the positive results for small finite chains assures us.

Besides, we want to add that our Fredholm determinant representation of two-point correlation functions of the XY-model also allows to write differential equations and to calculate their asymptotic by the standard way [12].

In conclusion, in the paper we considered the linear response function of a gas of cyclic aggregates in the framework of Frenkel excitons. To do this we reminded that the problem is effectively equivalent to the calculation of the correlation functions for the cyclic 1-D XY-model. We obtained the exact formulae for two-point correlation functions at finite temperature for the model and compared them with previous results. In particular, we showed that for the XX-model our result for the correlation function $\langle P_n(t)P_m^+ \rangle$ coincides with the straightforward calculation (using the definition of the correlation function) for the simplest nontrivial case ($M = 3$) and is reduced in general to the result of paper [4] for an arbitrary number of sites. We also found that the result of Ref.[9] for the correlation function is incorrect. The thermodynamical limit of our formulae was discussed.

We wish to thank V.M.Agranovich and V.S.Kapitonov for the valuable discussions. This work was supported by the Russian Fund of Fundamental Investigations, N 95-01-00548 and partially (K.I.) by the UK EPSRC under Grant number GR/J35221, Euler stipend of German Mathematical Society and grant INTAS-939, (V.M.) by President stipend, (A.S.) ICFPM Fellowship, ISF grant No A602-F.
A Appendix

In this appendix we will calculate integrals (32) using the following formula:

\[
\int d\phi \exp \left( \frac{1}{2} \phi K \phi + \phi a \right) = \text{Pf}(K) \exp \left( \frac{1}{2} a K^{-1} a \right) \tag{60}
\]

where \( \phi \) and \( a \) are Grassmann vectors and \( \text{Pf}(K) \) is a Pfaffian of matrix \( K \).

Let us consider \( I^b_{f(b)} \) and integrate over \( \xi^0, \bar{\xi}^0 \) first, using formula (60), where we will put

\[
\phi = \begin{pmatrix} \xi^0 \\ \bar{\xi}^0 \end{pmatrix}
\]

Then the result of the integration is given by:

\[
\exp \left\{ \bar{\xi}^2 W^b_{+} B_{-}^{(1)} \left( W^b_{+} \right)^t \xi^2 - \bar{\xi}^2 W^b_{+} D_{+}^{(1)} \xi^1 \right\}
\]

Now we will integrate the remaining expression over \( \xi^2, \bar{\xi}^1 \) to keep aside the terms with \( \eta, \bar{\eta} \). The result takes the form:

\[
\sqrt{\det R^{-1}} \exp \left\{ \bar{\xi}^2 U^b_{+} B_{-}^{(2)} R_{-} \bar{\xi}^2 - \xi^1 U^b_{+} B_{-}^{(2)} R_{-} \xi^1 - \xi^2 U^b_{+} (D_{-}^{(2)})^{-1} R_{-} \xi^1 \right\}
\]

where for a convenience we have introduced the diagonal matrix \( R \) (37). The third integration over \( \xi^1, \bar{\xi}^2 \) gives us the final result. We will neglect the terms in the exponent containing \( \bar{\eta}, \bar{\eta} \) or \( \eta, \eta \) because they will vanish if we calculate the integrals in \( K^b_{f(b)} \) using generating function \( I^b_{f(b)}(\bar{\eta}, \eta) \) (by taking derivatives on \( \eta \) and \( \bar{\eta} \)). So we obtain the following expression:

\[
I^b_{f(b)}(\bar{\eta}, \eta) = (-1)^{M(M-1)/4} \text{Pf}(G^b_{+}) \sqrt{\det R^{-1}} \exp \left\{ \bar{\eta} \left( Q^b_{+} + T^b_{+} \left( Q^b_{+} \right)^{-t} S_{+} \right)^{-1} \eta \right\}
\]

where

\[
G^b_{+} = \begin{pmatrix} S_{+} & \left( Q^b_{+} \right)^{t} \\ -Q^b_{+} & T^b_{+} \end{pmatrix}
\]

and for the sake of brevity we have introduced the new matrices \( Q^b_{+}, T^b_{+} \) and \( S_{+} \) which are determined by (34).

In the same manner we can present a result for the generating function \( I^b_{f(b)} \):

\[
I^b_{f(b)}(\bar{\eta}, \eta) = (-1)^{M(M-1)/4} \text{Pf}(G^b_{-}) \sqrt{\det R^{-1}} \exp \left\{ \bar{\eta} \left( Q^b_{-} + T^b_{-} \left( Q^b_{-} \right)^{-t} S_{-} \right)^{-1} \eta \right\}
\]

21
Here $G_{f(b)}^\pm$ is defined by changing all indices \( + \) at operators by indices \( - \) in $G_{\pm}^{f(b)}$ and $Q_{f(b)}^\pm, T_{f(b)}^\pm, S_\pm$ are determined in (33).

To obtain an expression for the integrals in $K_{f(b)}^\pm$ one should consider

$$\frac{\partial}{\partial \bar{\eta}_{p+}} \frac{\partial}{\partial \eta_{p+}} I_{f(b)}^\pm (\bar{\eta}, \eta)$$

and then the final result for $K_{f(b)}^\pm$ can be written as:

$$K_{f(b)}^\pm = (-1)^{M(M-1)/2} \text{Pf}(G_{\pm}^{f(b)}) \sqrt{\det R_{\mp}^{-1}} \times$$

$$\left( \prod_{p_\pm} e^{-(\beta - it)\epsilon_{p_\pm}} K_{p_\pm}(\beta - it) \prod_{p_\mp} e^{-it\epsilon_{p_\mp} K_{p_\mp}(it)} \right)^{1/2} \times$$

$$\frac{1}{M} \sum_{p_\pm, p_\pm'} e^{i p_\pm' - i p_\pm (L+1)} \left( Q_{\pm}^{f(b)} + T_{\pm}^{f(b)} (Q_{\pm}^{f(b)})^{-t} S_\pm \right)_{p_\pm}^{-1}$$
References

[1] F.S.Spano, J.Knoester, in *Advances in magnetic and optical resonance* 18, 117 (1994);
[2] E.Lieb, T.Schults, D.Mattis, *Ann.Phys.(N.Y.)* 16, 407, (1961);
[3] Exact treatment of nonlinear response is in our forthcoming paper.
[4] K.N.Ilinski, G.V.Kalinin, V.S.Kapitonov, preprint hep-th 9404038;
[5] Th.Niemeijer, *Physica* 36, 377 (1967);
[6] E.Barouch, B.McCoY *Phys.Rev A* 3, 786 (1971);
[7] F.Colomo, A.G.Izergin, V.E.Korepin, V.Tognetti, *Phys.Lett. A* 169, 243 (1992);
[8] A.R.Its,A.G.Izergin, V.E.Korepin, N.A.Slavnov, *Phys.Rev.Lett.* 70, 1704 (1993); *Algebra and Analysis* 6, N2 (1994) (in Russian);
[9] H.Suzuura, T.Tokihiro, Y.Ohta, *Phys.Rev. B* 49, N 6, 4344 (1994);
[10] V.M.Agranovich, Zh.ETF 37, 430 (1959);
[11] V.S.Kapitonov, K.N.Ilinski, *Zapiski Seminarov POMI*, v.224, 72, (1994) (in Russian);
[12] V.E.Korepin, A.G.Izergin, and N.M.Bogoliubov, *Quantum inverse scattering method, correlation functions and algebraic Bethe ansatz*, Cambridge Univ. Press, Cambridge, 1992;