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Strong short-range interactions in one-dimensional proton conductor

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The behaviour of one-dimensional proton conductor is investigated on the basis of orientational-tunnelling model. The previously proposed technique which permits the proton interactions to be taken into account in the zero-order Hamiltonian, and is based on Green's function's expansion in terms of irreducible Green's function parts, is generalized. The Larkin equation for the one-particle proton Green's function is solved, while irreducible Larkin part is calculated within the framework of the first order approximation. The proton energy spectrum and chemical potential behaviour are investigated, and the results are compared with the ones previously obtained in the Hubbard-1 type approximation.

Key words: *proton transfer, hydrogen bond, strong correlations, fermion models*

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1. Introduction

The systems with proton conductivity (superionic conductors with hydrogen bonds, quasi-one-dimensional proton conductors and others) have lately become the objects of great interest in experimental and theoretical investigations. The conductivity in these systems arises due to the proton transport, thus the problem of studying its microscopic mechanisms is very important. However, the behaviour of these systems is also affected by other factors, including the interactions of protons with phonons, proton-proton interactions, etc.

There were many attempts to describe the proton conductors using the fermion lattice models. One of the first utilizations of the lattice model for the description of such systems [1,2] made it possible to obtain the superionic phase transition in $Rb_3H(SeO_4)_2$ when considering the proton potential on hydrogen bond in simple one-minimum approximation. More complete and correct approach, which took into account the system symmetry changes and was in better agreement with the experiment, was made in [3] for a similar crystal $(NH_4)_3H(SeO_4)_2$.

Some attention was also paid to theoretical aspects of proton-phonon interactions [4–6], while the effect of the short-range proton-proton interactions is still not sufficiently studied. However, these interactions are strong and can considerably affect the system's behaviour. Several steps in this direction were made in [7] when calculating thermodynamic functions, but the method which would permit to take into account the short-range proton interactions as well as the proton transfer has not been developed. In this paper we will try to generalize the previously proposed approach [8–10], which permits the proton interactions to be taken into account exactly.

Our investigations are based on the orientational-tunnelling model for the one-dimensional proton conductor [11]. This model takes into account the two-stage proton transfer (according to Grotthuss mechanisms) as well as the short-range proton interactions and treats the protons as fermions.

It is worth pointing out that the protons should be rather described by the Pauli statistics than by the Fermi one. However, theoretical investigations of proton conductivity systems have shown a good agreement with experimental results when treating the protons as fermions.

The orientational-tunnelling model can be simplified to the well-known spinless fermion model, which apart from the nearest neighbours interactions takes into account the transfer of fermions as well. This model has been studied a lot, for example in [12–14] using the method of high density expansions. However, those results cannot be used for the case of strong fermion interactions.

In this paper we extend the technique previously proposed by us, which is based on generalized Wick's theorem. We use Green's function method to calculate the proton energy spectrum. The series for the one-particle proton Green's function is built in terms of the irreducible parts according to Larkin. We calculate the irreducible part, which is needed to solve the Larkin equation for Green's function, in the approximation which permits to take into account the simplest proton scattering. To do this, one needs to obtain the two-particle irreducible Green's function parts, which are calculated within the framework of cluster approach. By solving the Larkin equation we obtain the desired one-particle proton Green's function. The proton spectrum and chemical potential behaviour with the change of the proton concentration is investigated. The results are compared with the ones obtained in Hubbard-1 type approximation in [8–10].

2. The model

The investigations of the energy spectrum and thermodynamics of the proton subsystem of the one-dimensional proton conductor are based on the orientational-tunnelling model. For the first time this model was used in [11] (see also [15]) to describe the molecular complexes with hydrogen bonds. Later it was used to describe proton transport and to calculate the conductivity coefficients in superionic crystals of $Me_3H(XO_4)_3$ (Me = Cs, Rb, NH_4; X = S, Se) group [16,17]. This model introduces two types of proton transport according to Grotthuss mechanisms: tunnelling on the

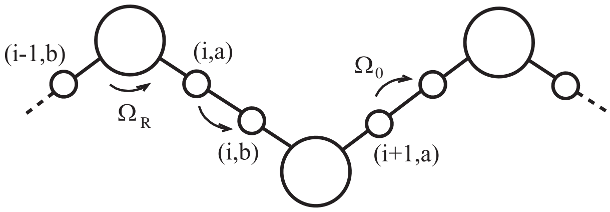


Figure 1. Proton conductor model. The large circles correspond to the ionic groups, the small ones correspond to the possible proton positions.

bond (Ω_0) and reorientational transfer (Ω_R). It also takes into account the strong short-range interactions, produced by the differences between the energies of proton configurations near the ionic groups, as well as the energies of D- and L-defects.

We consider the one-dimensional proton conductor, which consists of the ionic groups, connected by hydrogen bonds (figure 1). Two equilibrium positions (i,a) and (i,b) on each bond are taken into account. The Hamiltonian of the system in the second quantization form is as follows:

$$\hat{H} = \hat{H}_c + \hat{H}_t + \hat{H}_d - \mu\hat{N}, \tag{1}$$

where

$$\begin{aligned}
\hat{H}_c &= \sum_i [\varepsilon(1-n_{ib})n_{i+1,a} + \varepsilon n_{ib}(1-n_{i+1,a}) + w n_{ib}n_{i+1,a} \\
&\quad + w'(1-n_{ib})(1-n_{i+1,a})], \\
\hat{H}_t &= \sum_i \left[\Omega_0(c^+_{ia}c_{ib} + c^+_{ib}c_{ia}) + \Omega_R(c^+_{ib}c_{i+1,a} + c^+_{i+1,a}c_{ib})\right], \\
\hat{H}_d &= \sum_i [U n_{ia}n_{ib} + V(1-n_{ia})(1-n_{ib})], \\
\hat{N} &= \sum_i (n_{ia} + n_{ib}).
\end{aligned} \tag{2}$$

Here, $n_{i\alpha}(\alpha = a,b)$ is the occupation number in position α; U and V are the energies of formation of D- (two protons on the bond) and L- (broken bond) defects respectively; w, ε, w' – configuration energies with one, two or none protons near the ionic group (figure 2).

The model (1) is one of the fermionic lattice models. Its spectrum has a band character and its structure is defined by the ratio between the effective transfer pa-

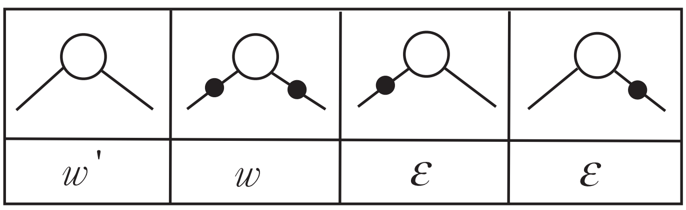


Figure 2. Proton configuration energies.

rameter Ω_{eff} (with the value of the order of $\max(\Omega_0, \Omega_{\text{R}})$) and the effective energy of short-range interaction U_{eff} (with the value of the order of $\min(U, V, w, w')$). If $\Omega_{\text{eff}} \gg U_{\text{eff}}$ the interaction between protons can be taken into account in the framework of the mean field approximation (MFA), that just causes the shift of the proton energy band (such an approach was used in [17] to calculate the dispersion curves $E(\vec{k})$ in proton bands, which describe the motion of protons in quasi-one-dimensional layers of hydrogen bonds in $(NH_4)_3H(SeO_4)_2$). In the opposite case, ($\Omega_{\text{eff}} \ll U_{\text{eff}}$) correlation leads to an additional splitting in the spectrum. These results are well-known in the Hubbard model and in similar ones [18]. Corresponding theoretical investigations cannot be carried out in the MFA, since short-range interactions have to be taken into account in the zero-order Hamiltonian.

Thus, the zero-order Hamiltonian has the following form:

$$\hat{H}_0 = \hat{H}_c + \hat{H}_d - \mu \hat{N}. \tag{3}$$

It includes the short-range proton interactions, while the expansion is made in terms of the transfer Hamiltonian $\hat{H}_t$.

3. Perturbation theory and diagram technique

We will use Green's function method to calculate the proton energy spectrum. Let us consider the proton Green's function

$$G_{i\alpha,j\beta}(\tau - \tau') = -\langle T_\tau \tilde{c}_{i\alpha}(\tau) \tilde{c}^+_{j\beta}(\tau') \rangle, \tag{4}$$

which is constructed with the creation and the annihilation operators, defined in Heisenberg representation ($0 \leqslant \tau, \tau' \leqslant \beta = 1/kT$). We use the thermodynamic perturbation theory [19] to calculate this function, considering the term H_t as a perturbation. In the interaction representation

$$\begin{aligned} G_{i\alpha,j\beta}(\tau - \tau') &= \frac{-\langle T_\tau c_{i\alpha}(\tau) c^+_{j\beta}(\tau') \sigma(\beta) \rangle_0}{\langle \sigma(\beta) \rangle_0} \equiv -\langle T_\tau c_{i\alpha}(\tau) c^+_{j\beta}(\tau') \sigma(\beta) \rangle_0^c, \\ \sigma(\beta) &= T_\tau \exp\left\{ -\int_0^\beta \hat{H}_t(\tau) \mathrm{d}\tau \right\}, \end{aligned} \tag{5}$$

where the mean values are calculated using the statistical Gibbs distribution with Hamiltonian H_0. In the middle part of the expression (5), numerator, as well as denominator, can be expanded into a series in terms of H_t, but some of the terms are cancelled. The remaining terms in the diagrammatic representation are denoted by connected diagrams. Expansion in terms of H_t leads to the following series:

$$\begin{aligned} G_{i\alpha,j\beta}(\tau - \tau') &= -\langle T_\tau c_{i\alpha}(\tau) c^+_{j\beta}(\tau') \rangle_0 \\ &\quad + \sum_{k\gamma,l\delta} t_{k\gamma,l\delta} \langle T_\tau c_{i\alpha}(\tau) c^+_{j\beta}(\tau') \int_0^\beta \mathrm{d}\tau_1 c^+_{k\gamma}(\tau_1) c_{l\delta}(\tau_1) \rangle_0^c \end{aligned}$$

$$
-\frac{1}{2}\sum_{\substack{k\gamma,l\delta\\ m\mu,n\nu}} t_{k\gamma,l\delta}t_{m\nu,n\mu}\langle T_\tau c_{i\alpha}(\tau)c^+_{j\beta}(\tau')\int\limits_0^\beta \mathrm{d}\tau_1 c^+_{\nu\gamma}(\tau_1)c_{l\delta}(\tau_1)
$$

$$
\times\int\limits_0^\beta \mathrm{d}\tau_2 c^+_{m\nu}(\tau_2)c_{n\mu}(\tau_2)\rangle_0^c + \ldots, \tag{6}
$$

where we introduced the matrix of the proton transfer the elements of which are

$$
t_{ia,ib} = \Omega_0, \qquad t_{ib,i+1a} = \Omega_R \tag{7}
$$

and the others are equal to zero.

Since the Hamiltonian $\hat{H}_0$ includes the terms, which describe the interaction between protons, Wick's theorem in its usual form cannot be used to calculate the mean values of the products of Fermi operators. To avoid additional expansions in terms of interaction constants, we use the method similar to that introduced in [20] and later developed in [21,22] for Hubbard model, employing the irreducible many-particle parts. Let us define the one-particle Green's function as

$$
-\langle T_\tau c_{i\alpha}(\tau)c^+_{j\beta}(\tau')\rangle_0 = g^0_{i\alpha,j\beta}(\tau-\tau') \equiv \delta_{ij}\delta_{\alpha\beta}g^0_\alpha(\tau-\tau') \tag{8}
$$

or in shorthand notation

$$
-\langle T c_1 c_2^+\rangle_0 = g^0_{12}\,.
$$

Two and three-particle Green's functions are presented in the following form:

$$
\begin{aligned}
&-\langle T_\tau c_1 c_2^+ c_3 c_4^+\rangle_0^c = -g^0_{12}g^0_{34} + g^0_{14}g^0_{32} + \Gamma^{(2)}_{12,34}\,,\\
&-\langle T_\tau c_1 c_2^+ c_3 c_4^+ c_5 c_6^+\rangle_0^c = g^0_{12}g^0_{34}g^0_{56} - g^0_{12}g^0_{36}g^0_{54} - g^0_{14}g^0_{32}g^0_{56} - g^0_{14}g^0_{52}g^0_{36} + g^0_{16}g^0_{32}g^0_{54}\\
&\qquad - g^0_{16}g^0_{34}g^0_{52} + g^0_{12}\Gamma^{(2)}_{34,56} - g^0_{14}\Gamma^{(2)}_{32,56} + g^0_{16}\Gamma^{(2)}_{32,54} + \Gamma^{(3)}_{12,34,56}\,,
\end{aligned} \tag{9}
$$

where

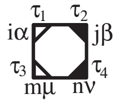
$$
\begin{aligned}
&\Gamma^{(2)}_{i\alpha,j\beta;m\mu,n\nu}(\tau_1,\tau_2,\tau_3,\tau_4) = -\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{m\mu}(\tau_3)c^+_{n\nu}(\tau_4)\rangle_0^{\mathrm{ir}}\,,\\
&\Gamma^{(3)}_{i\alpha,j\beta;m\mu,n\nu;k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4,\tau_5,\tau_6) =\\
&\qquad = -\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{m\mu}(\tau_3)c^+_{n\nu}(\tau_4)c_{k\gamma}(\tau_5)c^+_{l\delta}(\tau_6)\rangle_0^{\mathrm{ir}}.
\end{aligned} \tag{10}
$$

are irreducible Green's function parts. Many-particle Green's function can be written in a similar manner.

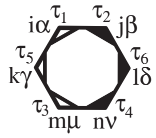
Expressions (9,10) are a generalization of Wick's theorem for the case, when Hamiltonian H_0 includes the terms, which describe the interaction. In this case, in addition to the sum of usual terms having the form of products of one-particle Green's function, which appear due to the all possible pairings, the expression for Green's function also includes the irreducible parts (10).

We will use the diagram technique to operate with perturbation theory expansions. To do so we introduce the following notations

$g^0_{i\alpha,j\beta}(\tau-\tau') =$ 

, $\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau_1,\tau_2,\tau_3,\tau_4) =$ 

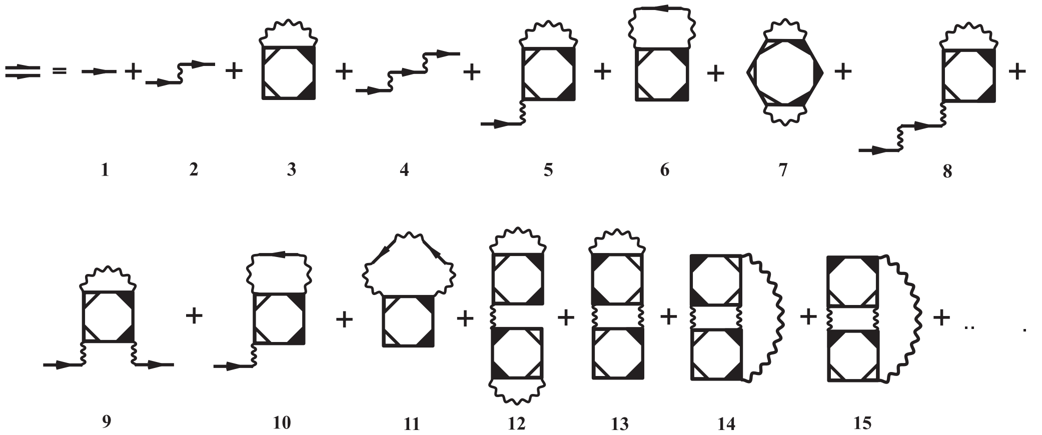
,

$\Gamma^{(3)}_{i\alpha,j\beta,m\mu,n\nu,k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4,\tau_5,\tau_6) =$ 

, $G_{i\alpha,j\beta}(\tau-\tau') =$ 

.

which makes it possible to present a series for the one-particle Green function in the following form:



. (11)

This diagram representation is the schematic one. We leave out the site and time indices and show only the topologically nonequivalent diagrams, which give the non-zero contribution to Green's function. Furthermore, the coefficients at the diagrams in (11) are omitted and have to be calculated via the combinatoric method.

The wavy lines in the diagrams represent the proton transfer. These lines are joined to Green's function vertices or to the vertices of irreducible parts $\Gamma^{(n)}$ ($2n$-vertex polygons). The proton transfer always connects the incoming vertex of Green's function or polygon (this vertex corresponds to the fermionic annihilation operator $c_{i\alpha}$) with the outgoing vertex (it corresponds to the creation operator $c^+_{i\alpha}$). Time arguments of the vertices, connected with transfer, are equal and have to be integrated, whereas the corresponding site indices are subject to summation. Expression (11) contains the terms up to the second order of perturbation theory (in terms of transfer) as well as the several terms of the third order.

The obtained series for function G can be formally presented as the infinite sum

$$G = \Sigma + \Sigma t \Sigma + \Sigma t \Sigma t \Sigma + \ldots \qquad (12)$$

which corresponds to the Larkin equation

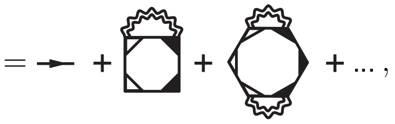
$$G = \Sigma + \Sigma t G, \qquad (13)$$

where Σ is the full irreducible part according to Larkin.

Contributions to Σ can be presented as the expansion in terms of irreducible Green's function parts $\Gamma^{(n)}$

$$\Sigma_{i\alpha,j\beta}(\tau-\tau') = g^0_{i\alpha,j\beta}(\tau-\tau') - \int\limits_0^\beta \mathrm{d}\tau_1 \sum_{m\mu,n\nu} \tilde{t}_{m\mu,n\nu}\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau,\tau',\tau_1,\tau_1)$$

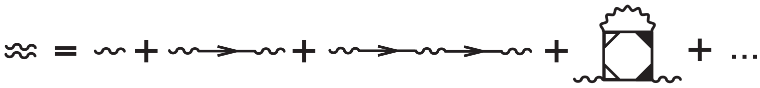
$$+ \int\limits_0^\beta \mathrm{d}\tau_1 \int\limits_0^\beta \mathrm{d}\tau_2 \sum_{\substack{m\mu,n\nu\\k\gamma,l\delta}} \tilde{t}_{m\mu,n\nu}\tilde{t}_{k\gamma,l\delta}\Gamma^{(3)}_{i\alpha,j\beta,m\mu,n\nu,k\gamma,l\delta}(\tau,\tau',\tau_1,\tau_1,\tau_2,\tau_2) + \ldots$$



1 2 3 (14)

where we introduced the generalized transfer

$$\tilde{t} = t + tg^0t + tg^0tg^0t + \ldots \quad ,$$



(15)

The simplest approximation for Σ ($\Sigma = g^0$, the diagram 14.1) which is similar to the well-known Hubbard-1 approximation for the strongly correlated electron systems [23], was used by us in [8–10]. In the present work the irreducible Larkin part will be calculated in the first order approximation with respect to transfer, which besides 14.1 takes into account the diagram 14.2 (but enclosed with the simple, not generalized transfer). Such an approximation permits the simplest proton scattering processes to be included in our consideration.

In addition to the one-particle proton Green's function (4) we can also consider the two-particle one

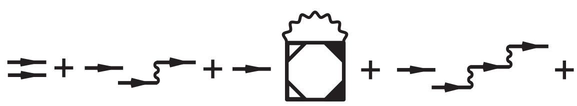
$$G_{i\alpha,j\beta,k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4) = -\langle T_\tau \tilde{c}_{i\alpha}(\tau_1)\tilde{c}^+_{j\beta}(\tau_2)\tilde{c}_{k\gamma}(\tau_3)\tilde{c}^+_{l\delta}(\tau_4)\rangle, \tag{16}$$

which can be expanded into a series, similar to (6)

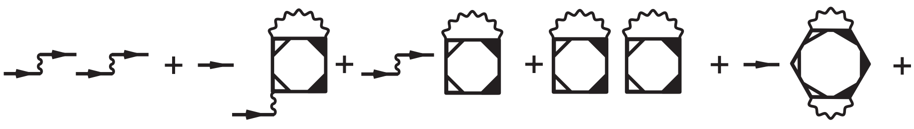
$$G_{i\alpha,j\beta,k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4) = -\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{k\gamma}(\tau_3)c^+_{l\delta}(\tau_4)\rangle_0$$

$$+ \sum_{m\mu,n\nu} t_{m\mu,n\nu}\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{k\gamma}(\tau_3)c^+_{l\delta}(\tau_4) \int\limits_0^\beta \mathrm{d}\tau \langle c^+_{m\mu}(\tau)c_{n\nu}(\tau)\rangle^c_0 - \ldots. \tag{17}$$

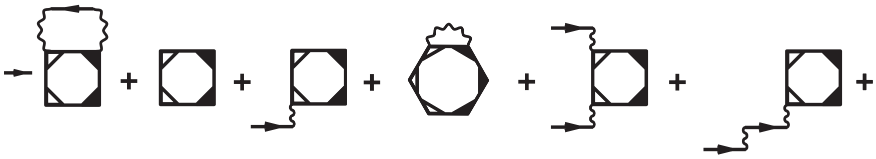
Using generalized Wick's theorem (9,10) and the diagram technique, proposed above, this series can be presented in the following form:

$G_{i\alpha,j\beta,k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4) =$ 

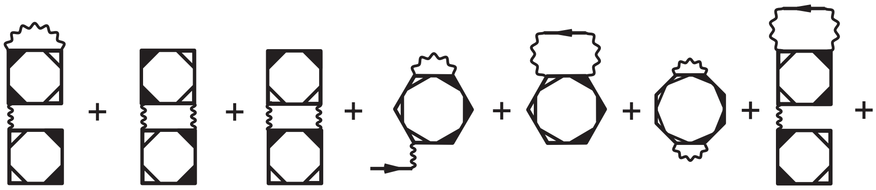
1 2 3 4



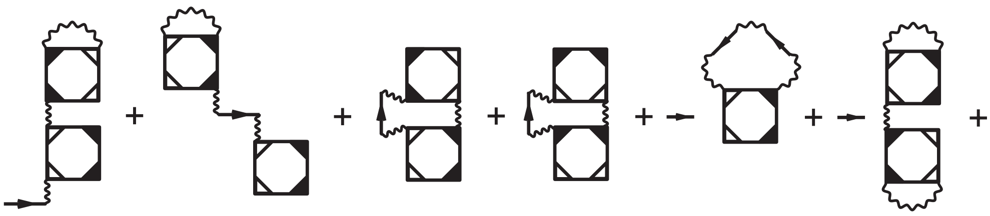
5 6 7 8 9



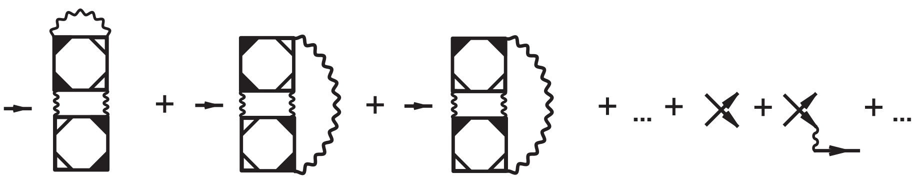
10 11 12 13 14 15



16 17 18 19 20 21 22



23 24 25 26 27 28

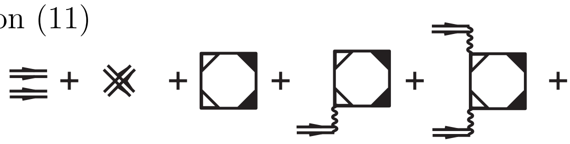


(18)

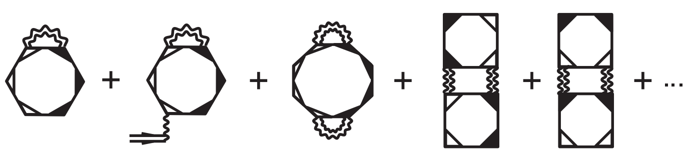
29 30 31 32 33

Similarly to (11) this series includes only the topologically nonequivalent diagrams. The diagrams of the first and the second order as well as the several ones of the third order are shown.

The series (18) can be rewritten using the lines of generalized transfer (15) and the full one-particle Green's function (11)

$G_{i\alpha,j\beta,k\gamma,l\delta}(\tau_1,\tau_2,\tau_3,\tau_4) =$ 

1 2 3 4 5



(19)

6 7 8 9 10

It is worth pointing out that the diagrams (19.9, 19.10) are the representatives of the diagram class, which is taken into account in the Generalized Random Phase Approximation (GRPA), first proposed in [24] for $(t-J)$ model. Later this approximation was used in the Hubbard and pseudospin-electron model investigations. For instance, in [25] the authors have shown that GRPA results are in good agreement with the results of dynamical mean-field approximation (which is exact in the limit of infinite dimension) in the case of strong one-site electron interactions. This makes it possible to use GRPA when taking into account the strong (in our case proton) interactions to calculate Green's function (16). This will be the aim of our future investigation.

Analyzing the diagram series (11) and (18), one can see that the common structural elements of all the diagrams are zero-order Green's function and irreducible parts $\Gamma^{(n)}$. The zero-order Green's function was calculated by us in [8,9]. Thus, we will focus on the evaluation of the most simple irreducible part – $\Gamma^{(2)}$ (four-vertex polygon), which will enable us to obtain the first-order contribution to the irreducible Larkin part.

4. Evaluation of four-vertex irreducible part

Thus, taking into account (14), we need to calculate all possible matrix elements $\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau,\tau',\tau_1,\tau_1)$ at different values of $m\mu, n\nu$ and at fixed $i\alpha, j\beta$.

According to (9)

$$\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau_1,\tau_2,\tau_3,\tau_4) = -\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{m\mu}(\tau_3)c^+_{n\nu}(\tau_4)\rangle_0 + g^0_{i\alpha,j\beta}(\tau_1-\tau_2)g^0_{m\mu,n\nu}(\tau_3-\tau_4) - g^0_{i\alpha,n\nu}(\tau_1-\tau_4)g^0_{j\beta,m\mu}(\tau_3-\tau_2). \quad (20)$$

Thus, we have to calculate the function

$$G^0_{i\alpha,j\beta,m\mu,n\nu}(\tau_1,\tau_2,\tau_3,\tau_4) = -\langle T_\tau c_{i\alpha}(\tau_1)c^+_{j\beta}(\tau_2)c_{m\mu}(\tau_3)c^+_{n\nu}(\tau_4)\rangle_0\,. \quad (21)$$

This mean value is not equal to zero only if all site indices are equal or when $i\alpha = j\beta, m\mu = n\nu$ or $i\alpha = n\nu, j\beta = m\mu$. At first we will consider the case when all site indices are equal, i.e. $i = j = m = n$; $\alpha = \beta = \mu = \nu = a$ or $\alpha = \beta = \mu = \nu = b$.

In this case we need to consider the auxiliary problem for the cluster, which consists of a single site in the nearest surroundings (figure 3) and calculate the function (21). The corresponding mean value of this kind is calculated on the basis of the zero-order Hamiltonian (without transfer), but this Hamiltonian also includes an interaction with the site neighborhood.

Let us consider the cluster i, a (figure 3a) as an example. Its neighborhood consists of the sites $i-1, b$ and i, b, so Hamiltonian of this cluster has the following form:

$$\widetilde{H}_{ia} = \varepsilon(1-n_{i-1,b})n_{ia} + \varepsilon n_{i-1,b}(1-n_{ia}) + wn_{i-1,b}n_{ia} + w'(1-n_{i-1,b})(1-n_{ia}) + Un_{ia}n_{ib} + V(1-n_{ia})(1-n_{ib}) - \mu n_{ia}\,. \quad (22)$$

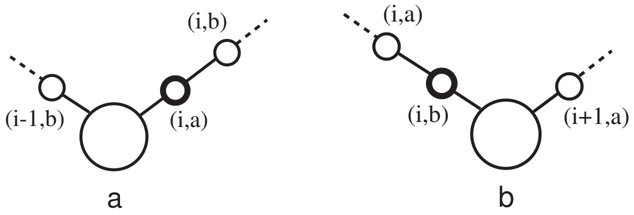


Figure 3. The simplest (one-site) cluster which consists of the given site (in figure (a) – (i,a), in (b) – (i,b)) and its neighbourhood.

Now, we have to consider all possible ways of the neighborhood occupation.

a) $n_{i-1,b} = 0, n_{i,b} = 0$.

Hamiltonian (22) reduces to

$$\widetilde{H}_{ia} = \varepsilon n_{ia} + w'(1 - n_{ia}) + V(1 - n_{ia}) - \mu n_{ia}\,. \tag{23}$$

Using Wick's theorem and definition (8) we obtain

$$\begin{aligned} G^0_{ia,ia,ia,ia}(\tau_1, \tau_2, \tau_3, \tau_4) \;&=\; g^0_{ia,ia}(\tau_1 - \tau_2) g^0_{ia,ia}(\tau_3 - \tau_4) \\ &+ g^0_{ia,ia}(\tau_1 - \tau_4) g^0_{ia,ia}(\tau_3 - \tau_2). \end{aligned} \tag{24}$$

Let us perform the Fourier transformation to the frequency representation

$$\begin{aligned} & g_{i\alpha,j\beta}(\tau) = \frac{1}{\beta} \sum_{\omega_n} g_{i\alpha,j\beta}(\omega_n) \mathrm{e}^{\mathrm{i}\omega_n \tau}, \\ & G^0_{i\alpha,j\beta,m\mu,n\nu}(\tau_1, \tau_2, \tau_3, \tau_4) = \\ & = \frac{1}{\beta^4} \sum_{\substack{\omega_{n_1},\omega_{n_2} \\ \omega_{n_3},\omega_{n_4}}} G^0_{i\alpha,j\beta,m\mu,n\nu}(\omega_{n_1}, \omega_{n_2}, \omega_{n_3}, \omega_{n_4}) \mathrm{e}^{\mathrm{i}\omega_{n_1}\tau_1} \mathrm{e}^{-\mathrm{i}\omega_{n_2}\tau_2} \mathrm{e}^{\mathrm{i}\omega_{n_3}\tau_3} \mathrm{e}^{-\mathrm{i}\omega_{n_4}\tau_4} \end{aligned} \tag{25}$$

and write (24) in the following form:

$$\begin{aligned} G^0_{ia,ia,ia,ia}(\omega_{n_1}, \omega_{n_2}, \omega_{n_3}, \omega_{n_4}) = \beta^2 [\delta(\omega_{n_2} - \omega_{n_1}) \delta(\omega_{n_4} - \omega_{n_3}) \\ + \delta(\omega_{n_2} - \omega_{n_3}) \delta(\omega_{n_4} - \omega_{n_1})] g^0_{ia,ia}(\omega_{n_1}) g^0_{ia,ia}(\omega_{n_3}). \end{aligned} \tag{26}$$

The function $g^0_{ia,ia}$ can be calculated, for example, using the method of equations of motion

$$g^0_{ia,ia}(\omega_n) = \frac{1}{\mathrm{i}\omega_n + \mu + w' - \varepsilon + V}. \tag{27}$$

b) $n_{i-1,b} = 1, n_{i,b} = 0$.

Hamiltonian (22) in this case will be as follows:

$$\widetilde{H}_{ia} = \varepsilon(1 - n_{ia}) + w n_{ia} + V(1 - n_{ia}) - \mu n_{ia}\,. \tag{28}$$

It differs from (23) and this leads to the change of the poles of the function $g^0_{ia,ia}$:

$$g^0_{ia,ia}(\omega_n) = \frac{1}{\mathrm{i}\omega_n + \mu + w' - \varepsilon + V}. \tag{29}$$

Expression (26) is valid in this case as well.

Similarly we can consider the other possible occupations of the neighbouring sites: (c) $n_{i-1,b} = 0, n_{i,b} = 1$ and (d) $n_{i-1,b} = 1, n_{i,b} = 1$.

Each of the cases mentioned above will give the contribution to the final Green's function with the corresponding statistical weight C_α. Finally,

$$\begin{aligned} G^0_{ia,ia,ia,ia}(\omega_{n_1}, \omega_{n_2}, \omega_{n_3}, \omega_{n_4}) = \beta^2[\delta(\omega_{n_2} - \omega_{n_1})\delta(\omega_{n_4} - \omega_{n_3}) \\ + \delta(\omega_{n_2} - \omega_{n_3})\delta(\omega_{n_4} - \omega_{n_1})] \sum_{\alpha=1}^{4} \frac{C_\alpha}{(\mathrm{i}\omega_{n_1} - E_\alpha)(\mathrm{i}\omega_{n_3} - E_\alpha)}, \end{aligned} \tag{30}$$

where C_α are the following correlation functions:

$$\begin{aligned} C_1 &= \langle(1 - n_{i-1,b})(1 - n_{i,b})\rangle, \qquad C_2 = \langle(1 - n_{i-1,b})n_{i,b}\rangle, \\ C_3 &= \langle n_{i-1,b}(1 - n_{i,b})\rangle, \qquad C_4 = \langle n_{i-1,b}n_{i,b}\rangle \end{aligned} \tag{31}$$

and E_α are the energies which are the poles of one-particle Green's function at different occupations of neighbouring sites

$$\begin{aligned} E_1 &= -w' + \varepsilon - V - \mu, \qquad E_2 = -w' + \varepsilon + U - \mu, \\ E_3 &= w - \varepsilon - V - \mu, \qquad E_4 = w - \varepsilon + U - \mu. \end{aligned} \tag{32}$$

The evaluation of $\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau_1, \tau_2, \tau_3, \tau_4)$ in the cases when site indices are pairwise by two is based on the procedure, similar to the one described above, which involves the calculation of two-particle Green's function localized on a two-site cluster. Two sites of the corresponding cluster can be both the nearest neighbours and the ones separated with some number of sites. The details of calculation of the four-vertex irreducible part on the two-site cluster of the nearest neighbours are shown in appendix A. Final expression for the four-vertex irreducible part in this case will be as follows:

$$\begin{aligned} &\Gamma^{(2)}_{ib;ib;i+1,a;i+1,a}(\omega_{n_1}, \omega_{n_2}, \omega_{n_3}, \omega_{n_4}) = -\beta\delta(\omega_{n_1} - \omega_{n_2} + \omega_{n_3} - \omega_{n_4})J \\ &\times \Bigg[\frac{\left(1-\frac{n}{2}\right)^4}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_1)(\mathrm{i}\omega_{n_4}-E_1)} \left(1 + \frac{J}{\mathrm{i}\omega_{n_1} + \mathrm{i}\omega_{n_3} - E_1 - E_3}\right) \\ &+ \frac{\frac{n}{2}\left(1-\frac{n}{2}\right)^3}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_2)(\mathrm{i}\omega_{n_4}-E_2)} \left(1 + \frac{J}{\mathrm{i}\omega_{n_1} + \mathrm{i}\omega_{n_3} - E_2 - E_3}\right) \\ &+ \frac{\frac{n}{2}\left(1-\frac{n}{2}\right)^3}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_3)(\mathrm{i}\omega_{n_4}-E_3)} \left(1 + \frac{J}{\mathrm{i}\omega_{n_1} - \mathrm{i}\omega_{n_4}}\right) \\ &+ \frac{\frac{n^2}{4}\left(1-\frac{n}{2}\right)^2}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_4)(\mathrm{i}\omega_{n_4}-E_4)} \left(1 + \frac{J}{\mathrm{i}\omega_{n_1} - \mathrm{i}\omega_{n_4} - E_3 + E_4}\right) + \ldots \Bigg]. \end{aligned} \tag{33}$$

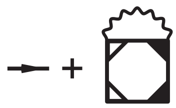
This expression consists of 16 terms (only the first four of them are shown for brevity). Each term includes its own energy poles and statistical weight but has the structure similar to that of the shown ones. The correlation functions which appeared during the calculation of $\Gamma^{(2)}_{ib;ib;i+1,a;i+1,a}$ are taken in mean filed approximation in (33) (for details see appendix A).

5. Green's function and energy spectrum

In the first order approximation the irreducible Larkin part of Green's function is equal to

$$\Sigma_{i\alpha,j\beta}(\tau-\tau') \;=\; g^{0}_{i\alpha,j\beta}(\tau-\tau') - \int\limits_0^\beta \mathrm{d}\tau_1 \sum_{m\mu,n\nu} t_{m\mu,n\nu}\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau,\tau',\tau_1,\tau_1)$$

$$=$$



, (34)

including the first order correction for Σ, which takes into account the simplest contribution of the proton scattering.

After applying the Fourier-transformation to the momentum and frequency representation we have to calculate all possible sums and integrals to obtain the expression for irreducible Larkin part. Due to the fact that the transfer line in (34) connects the sites, which are the nearest neighbours, only the contributions with $\Gamma^{(2)}_{ib;ib;i+1,a;i+1,a}$ and $\Gamma^{(2)}_{ia;ia;ib;ib}$ should be left among the others. Thus, we can present the irreducible Larkin part in the form of a matrix

$$\Sigma_{\alpha\beta}(k,\omega_n) = \begin{pmatrix} \Sigma_{aa}\Sigma_{ab} \\ \Sigma_{ba}\Sigma_{bb} \end{pmatrix}, \tag{35}$$

which elements are given by the following expressions

$$\begin{aligned}
&\Sigma_{ab} = t_{ab}(k)F(\omega_n), \qquad \Sigma_{ba} = t_{ba}(k)F(\omega_n), \qquad \Sigma_{aa} = \Sigma_{bb} = g^0_{aa}(\omega_n),\\
&t_{ab}(k) = \Omega_0 + \Omega_{\mathrm{R}}\mathrm{e}^{\mathrm{i}k(\delta+\Delta)}, \qquad t_{ba}(k) = \Omega_0 + \Omega_{\mathrm{R}}\mathrm{e}^{-\mathrm{i}k(\delta+\Delta)},\\
&F(\omega_n) = \frac{1}{\beta}\sum_{\omega_{n_1}}\Gamma^{(2)}_{ia,ib,ib,ia}(\omega_n,\omega'_n,\omega_{n_1},\omega_{n_1}) = -\delta(\omega_n-\omega'_n)J\\
&\times\left[\frac{\left(1-\frac{n}{2}\right)^4}{(\mathrm{i}\omega_n-E_1)^2}\left\{n'_+(E_1) - \frac{J}{\mathrm{i}\omega_n-E_3}\left(\frac{n_+(E_1)-n_-(E_1+E_3)}{\mathrm{i}\omega_n-E_3} - n'_+(E_1)\right)\right\}\right.\\
&\left.+\frac{\frac{n}{2}\left(1-\frac{n}{2}\right)^3}{(\mathrm{i}\omega_n-E_1)^2}\left\{n'_+(E_2) - \frac{J}{\mathrm{i}\omega_n-E_3}\left(\frac{n_+(E_2)-n_-(E_2+E_3)}{\mathrm{i}\omega_n-E_3} - n'_+(E_2)\right)\right\} + \ldots\right].
\end{aligned} \tag{36}$$

$F(\omega_n)$ consists of 16 terms which arise from the respective ones of (33). Here, $n_+(E_\alpha)$ and $n_-(E_\alpha)$ are Fermi and Bose distributions with the energy E_α, respectively, and

$n'_+(E_\alpha)$ is the first derivative of Fermi distribution. These functions arise as a result of the following summations in the expression for Σ

$$
\begin{aligned}
&\frac{1}{\beta}\sum_{\omega_{n'}}\frac{1}{\mathrm{i}\omega_{n'}-E_m}=\frac{1}{\mathrm{e}^{\beta E_m}+1}=n_+(E_m),\\
&\frac{1}{\beta}\sum_{\omega_{n'}+\omega_{n''}}\frac{1}{\mathrm{i}\omega_{n'}+\mathrm{i}\omega_{n''}-E_m}=\frac{1}{\mathrm{e}^{\beta E_m}-1}=n_-(E_m),\\
&\frac{1}{\beta}\sum_{\omega_{n'}}\frac{1}{(\mathrm{i}\omega_{n'}-E_m)^2}=\frac{1}{\beta}\sum_{\omega_{n'}}\frac{\partial}{\partial E_m}\Big(\frac{1}{\mathrm{i}\omega_{n'}-E_m}\Big)=\\
&\qquad=\frac{\partial}{\partial E_m}\Big(\frac{1}{\beta}\sum_{\omega_{n'}}\frac{1}{\mathrm{i}\omega_{n'}-E_m}\Big)=n'_+(E_m).
\end{aligned}
\tag{37}
$$

Here, it is taken into account, that the frequencies $\omega_{n'}, \omega_{n''}$ are the Fermi-frequencies and their sum is the Bose-frequency.

From the Larkin equation for Green's function

$$
G_{\alpha\beta}=\Sigma_{\alpha\beta}+\sum_{\gamma\delta}\Sigma_{\alpha\gamma}t_{\gamma\delta}G_{\delta\beta}
\tag{38}
$$

we obtain

$$
G_{aa}=\frac{g^0_{aa}}{(1+F|t_{ab}|^2)^2-(g^0_{aa})^2|t_{ab}|^2}.
\tag{39}
$$

In general, the poles of this function cannot be found analytically. Therefore, we use an independent subband approximation. We assume that each energy level E_α gives an independent contribution to G_{aa}. It is valid when the distance between these levels is larger than the effective value of the transfer parameter responsible for the width of the bands. The distance between the levels is determined by proton correlation energies which, in our problem, are considerably larger than the transfer parameters $t_{ab}=\Omega_0,\Omega_\mathrm{R}$. In this approximation, Green's function will have the following form:

$$
\begin{aligned}
G_{aa} \;=\; \frac{1}{4}\sum_{\alpha=1}^{4}\Bigg\{&\frac{C_\alpha+\frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{i}\omega_n-E_\alpha-\frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2+C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}}}\\
&+\frac{C_\alpha+\frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{i}\omega_n-E_\alpha+\frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2+C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}}}\\
&+\frac{C_\alpha-\frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{i}\omega_n-E_\alpha-\frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2-C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}}}\\
&+\frac{C_\alpha-\frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{i}\omega_n-E_\alpha+\frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2-C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}}}\Bigg\}.
\end{aligned}
\tag{40}
$$

The A_α coefficients can be presented as follows:

$$A_\alpha = JC_\alpha \sum_{\beta=1}^{4} C_\beta n'_+(E_\beta), \tag{41}$$

but only in the case when correlation functions (31) and (A.16) are calculated in the mean field approximation (A.18). The first correction to the irreducible Larkin part contains A_α. Thus, taking $A_\alpha = 0$ in (40) we obtain G_{aa} in Hubbard-1 type approximation, i.e. the same approximation that was used in [9,10].

Using the spectral theorem in (40) we can obtain the equation, which links up the chemical potential with the average proton concentration

$$\begin{aligned} n \;=\; \sum_k \frac{1}{2N} \sum_{\alpha=1}^{4} \Bigg\{ & \frac{C_\alpha + \frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{e}^{\beta(E_\alpha + \frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2+C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}})}+1} \\ & + \frac{C_\alpha + \frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{e}^{\beta(E_\alpha - \frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2+C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}})}+1} \\ & + \frac{C_\alpha - \frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{e}^{\beta(E_\alpha + \frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2-C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}})}+1} \\ & + \frac{C_\alpha - \frac{C_\alpha^2+2A_\alpha^2}{\sqrt{C_\alpha^2+4A_\alpha^2}}}{\mathrm{e}^{\beta(E_\alpha - \frac{|t_{ab}|}{\sqrt{2}}\sqrt{C_\alpha^2+2A_\alpha^2-C_\alpha\sqrt{C_\alpha^2+4A_\alpha^2}})}+1} \Bigg\}. \end{aligned} \tag{42}$$

By solving this equation, one can get the dependence of the chemical potential on the average proton concentration. Such a dependance obtained numerically is given in figure 4 (together with the dependence of the proton band edges on the proton concentration). The following parameter values were used in calculations: $U = 3280$ cm^{-1}, $V = 3130$ cm^{-1} [28], $w - \varepsilon = 10000$ cm^{-1}, $J = w + w' - 2\varepsilon = 9400$ cm^{-1} [29], $\Omega_0 = 40\ldots250$ cm^{-1}, $\Omega_\mathrm{R} = 50\ldots2500$ cm^{-1} [30].

As one can see in figure 4 and from (40), the energy spectrum of the proton subsystem consists of 16 bands, which are separated into four groups. Every group is connected with the corresponding energy level E_α. As was mentioned above taking $A_\alpha = 0$, we restrict ourselves to the Hubbard-1 type approximation. In this case the proton energy spectrum consists of 8 bands. As it was shown in [8–10], at low temperatures there exist the regions of proton concentration, where the chemical potential decreases with the increase of concentration ($\partial\mu/\partial n < 0$). It points out to the possible separation of the system on the areas with different average concentration of protons. This effect was considered as a possible explanation of the so-called precursor effect, observed in some superionic conductors, particularly in $CsDSO_4$ [31–33].

By taking into account the first-order contribution to the irreducible Larkin part ($A_\alpha \neq 0$) one gets a more complicated spectrum, but the areas of instability

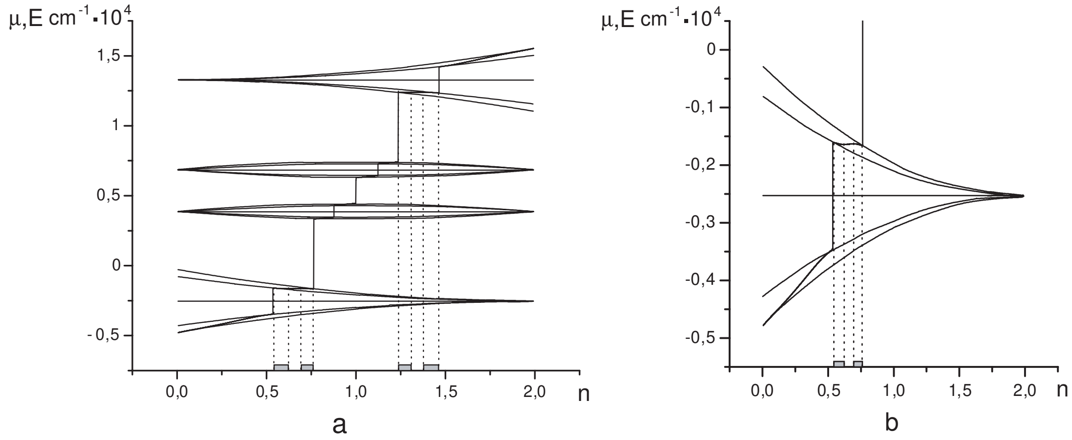


Figure 4. Dependence of the proton bands' edges and the chemical potential on the proton concentration. $T = 10$ K, $\Omega_0 = 250$ cm^{-1}, $\Omega_{\mathrm{R}} = 2000$ cm^{-1}. Dotted lines limit the areas, where $\partial\mu/\partial n < 0$; (a) is the whole spectrum, (b) is the lowest group of the bands.

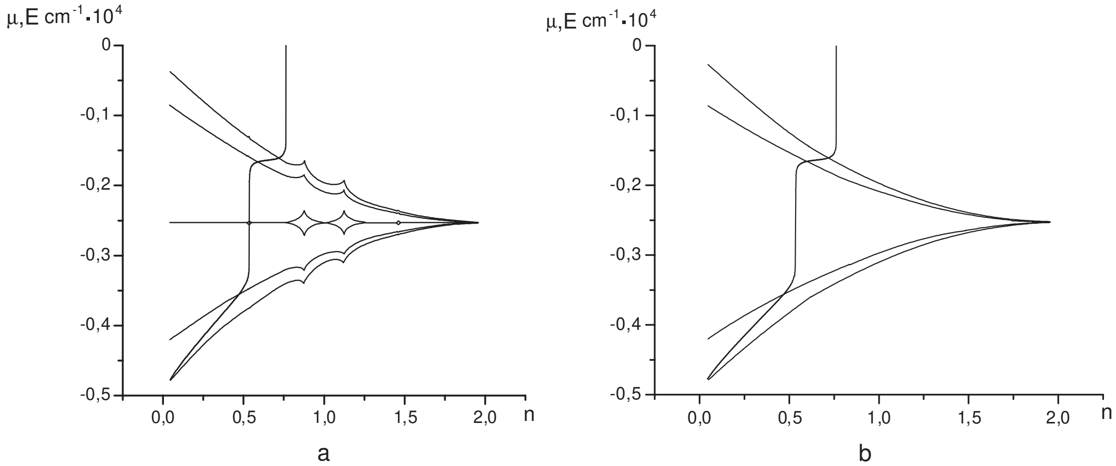


Figure 5. The lowest group of proton bands at $T = 100$ K, $\Omega_0 = 250$ cm^{-1}, $\Omega_{\mathrm{R}} = 2000$ cm^{-1}; (a) – $A_\alpha \neq 0$, (b) – $A_\alpha = 0$.

($\partial\mu/\partial n < 0$) still exist. Furthermore, their number increases (figure 4). At the given values of the energy constants and of the temperature, the negative slope of the chemical potential exists at $n \approx 0.54\ldots 0.62$, $n \approx 0.69\ldots 0.76$, $n \approx 1.24\ldots 1.31$ and $n \approx 1.38\ldots 1.46$. With the increase of temperature these intervals reduce and disappear. The important point to note here is the fact that these areas exist only at $\Omega_0/\Omega_{\mathrm{R}} \gg 1$ or $\Omega_{\mathrm{R}}/\Omega_0 \gg 1$, and the larger is the difference between the transfer parameter values, the wider are the intervals of $\partial\mu/\partial n < 0$. We also have to note that the contribution of A_α is small at low temperatures and it affects the spectrum only at considerably high temperatures (figure 5).

Thus, the first-order approximation for the irreducible Larkin part confirms the fact of the existence of the proton concentration regions, with the separation instability ($\partial\mu/\partial n < 0$), obtained in the Hubbard-1 type approximation in [8–10]. However, for a more complete analysis one needs to perform more accurate calculations of the correlation functions.

6. Conclusions

The present paper extends and generalizes the method based on generalized Wick's theorem and expansions in terms of irreducible Green's function parts which permits to take into account the short range proton interactions in an exact way. The corresponding diagram technique is proposed which enables us to sum Green's function series. The cluster technique of the calculation of zero-order Green's functions is extended to the case of the two-particle irreducible Green's function parts, which made it possible to obtain the irreducible Larkin part in the first order four-vertex approximation. The proton energy spectrum in the corresponding approximation is calculated. The investigations of chemical potential behaviour have confirmed the fact of the existence of the regions with $\partial\mu/\partial n < 0$, previously obtained in [8–10]. In this case the proton subsystem is unstable with respect to the phase separation.

7. Acknowledgement

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A. Evaluation of four-vertex irreducible part on a two-site cluster

Here we will consider the evaluation of four-vertex irreducible part $\Gamma^{(2)}_{i\alpha,j\beta,m\mu,n\nu}(\tau,\tau',\tau_1,\tau_1)$ in the case when the site indices are pairwise equal and correspond to the nearest neighbouring sites, separated by ionic group ($i = j = m+1 = n+1$, $\alpha = \beta = b$, $\mu = \nu = a$) or placed on the same bond ($i = j = m = n$, $\alpha = \beta = a$, $\mu = \nu = b$). Despite the fact that the general idea of calculations remains the same as described in section 4, this case is more complicated since the short range proton interactions act inside the cluster.

We will take the cluster shown in figure 6a as an example. Calculations for the cluster 6b can be done in the same manner and will give the same result.

The neighbourhood of the chosen cluster consists of two sites (i,a and $i+1,b$). An important problem is that we cannot use usual Wick's theorem for Fermi operators to calculate Green's function (21), because the cluster Hamiltonian (which is used for averaging) includes interaction. Therefore, we will pass from the Fermi creation and annihilation operators to the Hubbard ones. The quantum state basis of the given cluster consists of four states $|n_{ib}, n_{i+1,a}\rangle$:

$$|1\rangle = |0,0\rangle, \quad |2\rangle = |1,0\rangle, \quad |3\rangle = |0,1\rangle, \quad |4\rangle = |1,1\rangle. \tag{A.1}$$

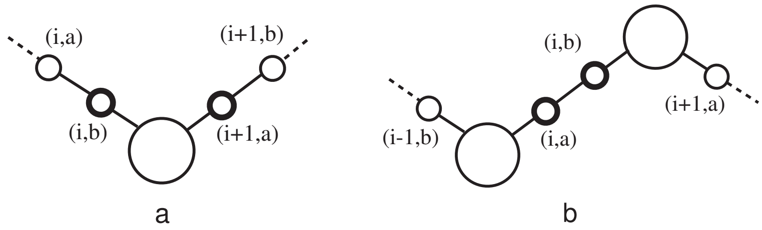

Figure 6. The cluster which consists of two neighbouring sites on different bonds (a), or on the same bond (b).

The Hubbard operators defined on this basis, are connected with the Fermi operators by the following relations

$$\begin{aligned} c_{i,b} &= X^{12} + X^{34}, \qquad c^{+}_{i,b} = X^{21} + X^{43}, \\ c_{i+1,a} &= X^{13} - X^{24}, \qquad c^{+}_{i+1,a} = X^{31} - X^{42}. \end{aligned} \tag{A.2}$$

Now, we have to consider all possible cases of occupation of the cluster neighbourhood.

a) $n_{i,a} = 1, n_{i+1,b} = 1.$

The Hamiltonian will be as follows:

$$\begin{aligned} \widetilde{H}_{ib;i+1,a} &= \varepsilon(1 - n_{ib})n_{i+1,a} + \varepsilon n_{ib}(1 - n_{i+1,a}) + w n_{ib} n_{i+1,a} \\ &\quad + w'(1 - n_{ib})(1 - n_{i+1,a}) + U(n_{ib} + n_{i+1,a}) - \mu(n_{ib} + n_{i+1,a}) \end{aligned} \tag{A.3}$$

or, in the X-operator representation

$$\widetilde{H}_{ib;i+1,a} = \sum_{j=1}^{4} \varepsilon_j X^{jj}, \tag{A.4}$$

where

$$\varepsilon_1 = w', \quad \varepsilon_2 = \varepsilon + U - \mu, \quad \varepsilon_3 = \varepsilon + U - \mu, \quad \varepsilon_4 = w + 2U - 2\mu. \tag{A.5}$$

Substituting (A.2) into (21) one can write Green's function as a sum of the mean values of the T-products of Hubbard operators

$$\begin{aligned} G^{0}_{ib;ib;i+1,a;i+1,a}(\tau_1, \tau_2, \tau_3, \tau_4) &= -\langle T_\tau X^{12}(\tau_1) X^{21}(\tau_2) X^{13}(\tau_3) X^{31}(\tau_4)\rangle_0 \\ &- \langle T_\tau X^{12}(\tau_1) X^{21}(\tau_2) X^{24}(\tau_3) X^{42}(\tau_4)\rangle_0 + \langle T_\tau X^{12}(\tau_1) X^{43}(\tau_2) X^{24}(\tau_3) X^{31}(\tau_4)\rangle_0 \\ &+ \langle T_\tau X^{34}(\tau_1) X^{21}(\tau_2) X^{13}(\tau_3) X^{42}(\tau_4)\rangle_0 - \langle T_\tau X^{34}(\tau_1) X^{43}(\tau_2) X^{13}(\tau_3) X^{31}(\tau_4)\rangle_0 \\ &- \langle T_\tau X^{34}(\tau_1) X^{43}(\tau_2) X^{24}(\tau_3) X^{42}(\tau_4)\rangle_0 \,, \end{aligned} \tag{A.6}$$

where we leave only the terms, which give non-zero contributions.

For every term in (A.6) we use Wick's theorem for Hubbard operators [26]. We use the priority rule: $X^{12} > X^{34} > X^{24} > X^{23} > X^{14}$ at the pairing of operators.

We also have to take into account that some of the X-operators are of Bose-type (X^{23}, X^{32}, X^{14} and X^{41}), while the others are of Fermi-type. After performing all possible pairings for the first term in (A.6) we obtain

$$\begin{aligned}
\langle T_\tau X^{12}(\tau_1)X^{21}(\tau_2)X^{13}(\tau_3)X^{31}(\tau_4)\rangle_0 &= \widetilde{g}^{12}(\tau_1-\tau_2)\widetilde{g}^{13}(\tau_3-\tau_4)\langle X^{11}\rangle^* \\
&+ \widetilde{g}^{12}(\tau_1-\tau_4)\widetilde{g}^{13}(\tau_3-\tau_2)\widetilde{g}^{23}(\tau_2-\tau_4)\langle X^{22}-X^{33}\rangle^* \\
&- \widetilde{g}^{12}(\tau_1-\tau_2)\widetilde{g}^{13}(\tau_3-\tau_2)\widetilde{g}^{13}(\tau_2-\tau_4)\langle X^{11}+X^{33}\rangle^* \\
&- \widetilde{g}^{12}(\tau_1-\tau_4)\widetilde{g}^{13}(\tau_3-\tau_4)\widetilde{g}^{12}(\tau_4-\tau_2)\langle X^{11}+X^{22}\rangle^*, \qquad (A.7)
\end{aligned}$$

where

$$\widetilde{g}^{pq}(\tau_1-\tau_2) = -\langle T_\tau X^{pq}(\tau_1)X^{qp}(\tau_2)\rangle, \qquad (A.8)$$

and in the frequency representation

$$\widetilde{g}^{pq}(\omega_n) = \frac{1}{\mathrm{i}\omega_n-\lambda_{pq}}, \qquad \lambda_{pq} = \varepsilon_q-\varepsilon_p\,. \qquad (A.9)$$

After applying Wick's theorem we have to deal with the mean values of Hubbard operators. Since we consider a specific configuration of the cluster's neighbourhood ($n_{i,a}=1, n_{i+1,b}=1$), these mean values have to be calculated after the insertion of the product of operators $n_{i,a}n_{i+1,b}$ into the mean value brackets. The operation of averaging with a corresponding statistical weight in (A.7) and further on is denoted as $\langle\ldots\rangle^*$.

The pairing procedure similar to (A.7) is performed in every term of (A.6).

We use the relations

$$\begin{aligned}
\widetilde{g}^{12}(\omega_{n_1})\left[\widetilde{g}^{32}(\omega_{n_1}-\omega_{n_4})-\widetilde{g}^{13}(\omega_{n_4})\right] &= \widetilde{g}^{13}(\omega_{n_4})\widetilde{g}^{32}(\omega_{n_1}-\omega_{n_4}), \\
\widetilde{g}^{13}(\omega_{n_3})\left[\widetilde{g}^{32}(\omega_{n_2}-\omega_{n_3})+\widetilde{g}^{12}(\omega_{n_2})\right] &= \widetilde{g}^{12}(\omega_{n_2})\widetilde{g}^{32}(\omega_{n_2}-\omega_{n_3}) \qquad (A.10)
\end{aligned}$$

and similar ones which allow us to symmetrize the expression, obtained after applying Wick's theorem to all the terms in (A.6). Now

$$\begin{aligned}
G^0_{ib;ib;i+1,a;i+1,a}&(\omega_{n_1},\omega_{n_2},\omega_{n_3},\omega_{n_4}) = \beta^2\delta(\omega_{n_2}-\omega_{n_1})\delta(\omega_{n_4}-\omega_{n_3}) \\
&\times\left[\widetilde{g}^{12}(\omega_{n_1})\widetilde{g}^{13}(\omega_{n_3})\langle X^{11}\rangle^* + \widetilde{g}^{12}(\omega_{n_1})\widetilde{g}^{24}(\omega_{n_3})\langle X^{22}\rangle^*\right. \\
&\left.+ \widetilde{g}^{34}(\omega_{n_1})\widetilde{g}^{13}(\omega_{n_3})\langle X^{33}\rangle^* + \widetilde{g}^{34}(\omega_{n_1})\widetilde{g}^{24}(\omega_{n_3})\langle X^{44}\rangle^*\right] \\
&- \beta\delta(\omega_{n_1}-\omega_{n_2}+\omega_{n_3}-\omega_{n_4}) \\
&\times\left[\widetilde{g}^{12}(\omega_{n_1})\widetilde{g}^{12}(\omega_{n_2})\widetilde{g}^{13}(\omega_{n_3})\widetilde{g}^{13}(\omega_{n4})J\{1+J\widetilde{g}^{14}(\omega_{n_1}+\omega_{n_3})\}\langle X^{11}\rangle^*\right. \\
&+ \widetilde{g}^{12}(\omega_{n_1})\widetilde{g}^{12}(\omega_{n_2})\widetilde{g}^{24}(\omega_{n_3})\widetilde{g}^{24}(\omega_{n4})J\{1+J\widetilde{g}^{23}(\omega_{n_1}-\omega_{n_4})\}\langle X^{22}\rangle^* \\
&+ \widetilde{g}^{34}(\omega_{n_1})\widetilde{g}^{34}(\omega_{n_2})\widetilde{g}^{13}(\omega_{n_3})\widetilde{g}^{13}(\omega_{n4})J\{1-J\widetilde{g}^{23}(\omega_{n_1}-\omega_{n_4})\}\langle X^{33}\rangle^* \\
&\left.+ \widetilde{g}^{34}(\omega_{n_1})\widetilde{g}^{34}(\omega_{n_2})\widetilde{g}^{24}(\omega_{n_3})\widetilde{g}^{24}(\omega_{n4})J\{1-J\widetilde{g}^{14}(\omega_{n_1}+\omega_{n_3})\}\langle X^{44}\rangle^*\right], \qquad (A.11)
\end{aligned}$$

where $J = w'+w-2\varepsilon$ is the effective proton correlation constant. It should be noted that the procedure used here is similar to that used in [27] for the calculation of the four-vertex irreducible part for the Hubbard model.

We can calculate the poles λ_{pq} of the functions $\widetilde{g}^{pq}(\omega_n)$ in (A.11) using (A.9) and (A.5)

$$
\begin{aligned}
&\lambda_{12} = \varepsilon_2 - \varepsilon_1 = -w' + \varepsilon + U - \mu = E_2\,,\\
&\lambda_{13} = \varepsilon_3 - \varepsilon_1 = -w' + \varepsilon + U - \mu = E_2\,,\\
&\lambda_{24} = \varepsilon_4 - \varepsilon_2 = w - \varepsilon + U - \mu = E_4\,,\\
&\lambda_{34} = \varepsilon_4 - \varepsilon_3 = w - \varepsilon + U - \mu = E_4\,,\\
&\lambda_{14} = \varepsilon_4 - \varepsilon_1 = w - w' + 2U - 2\mu = E_2 + E_4\,,\\
&\lambda_{23} = \varepsilon_3 - \varepsilon_2 = 0.
\end{aligned}
\tag{A.12}
$$

The Hubbard operators X^{pq} in (A.11) can be expressed in terms of the occupation numbers $n_{i\alpha}$ using the following expressions which follow from (A.2)

$$
\begin{aligned}
&X^{11} = (1-n_{i,b})(1-n_{i+1,a}), \quad X^{22} = n_{i,b}(1-n_{i+1,a}),\\
&X^{33} = (1-n_{i,b})n_{i+1,a}\,, \quad X^{44} = n_{i,b}n_{i+1,a}\,,
\end{aligned}
\tag{A.13}
$$

Consequently, the expression (A.11) can be rewritten in the following way:

$$
\begin{aligned}
&G^0_{ib;ib;i+1,a;i+1,a}(\omega_{n_1},\omega_{n_2},\omega_{n_3},\omega_{n_4}) = \beta^2\delta(\omega_{n_2}-\omega_{n_1})\delta(\omega_{n_4}-\omega_{n_3})\\
&\quad\times\left[\frac{\langle(1-n_{i,b})(1-n_{i+1,a})\rangle^*}{(\mathrm{i}\omega_{n_1}-E_2)(\mathrm{i}\omega_{n_3}-E_2)} + \frac{\langle n_{i,b}(1-n_{i+1,a})\rangle^*}{(\mathrm{i}\omega_{n_1}-E_2)(\mathrm{i}\omega_{n_3}-E_4)}\right.\\
&\quad\left. + \frac{\langle(1-n_{i,b})n_{i+1,a}\rangle^*}{(\mathrm{i}\omega_{n_1}-E_4)(\mathrm{i}\omega_{n_3}-E_2)} + \frac{\langle n_{i,b}n_{i+1,a}\rangle^*}{(\mathrm{i}\omega_{n_1}-E_4)(\mathrm{i}\omega_{n_3}-E_4)}\right]\\
&\quad-\beta\delta(\omega_{n_1}-\omega_{n_2}+\omega_{n_3}-\omega_{n_4})\\
&\quad\times\left[\frac{J\langle(1-n_{i,b})(1-n_{i+1,a})\rangle^*}{(\mathrm{i}\omega_{n_1}-E_2)(\mathrm{i}\omega_{n_2}-E_2)(\mathrm{i}\omega_{n_3}-E_2)(\mathrm{i}\omega_{n_4}-E_2)}\left\{1+\frac{J}{(\mathrm{i}\omega_{n_1}+\mathrm{i}\omega_{n_3}-E_2-E_4)}\right\}\right.\\
&\quad+\frac{J\langle n_{i,b}(1-n_{i+1,a})\rangle^*}{(\mathrm{i}\omega_{n_1}-E_2)(\mathrm{i}\omega_{n_2}-E_2)(\mathrm{i}\omega_{n_3}-E_4)(\mathrm{i}\omega_{n_4}-E_4)}\left\{1+\frac{J}{(\mathrm{i}\omega_{n_1}-\mathrm{i}\omega_{n_4})}\right\}\\
&\quad+\frac{J\langle(1-n_{i,b})n_{i+1,a}\rangle^*}{(\mathrm{i}\omega_{n_1}-E_4)(\mathrm{i}\omega_{n_2}-E_4)(\mathrm{i}\omega_{n_3}-E_2)(\mathrm{i}\omega_{n_4}-E_2)}\left\{1-\frac{J}{(\mathrm{i}\omega_{n_1}-\mathrm{i}\omega_{n_4})}\right\}\\
&\quad\left.+\frac{J\langle n_{i,b}n_{i+1,a}\rangle^*}{(\mathrm{i}\omega_{n_1}-E_4)(\mathrm{i}\omega_{n_2}-E_4)(\mathrm{i}\omega_{n_3}-E_4)(\mathrm{i}\omega_{n_4}-E_4)}\left\{1-\frac{J}{(\mathrm{i}\omega_{n_1}+\mathrm{i}\omega_{n_3}-E_2-E_4)}\right\}\right].
\end{aligned}
\tag{A.14}
$$

The cases (b) $n_{i,a}=1, n_{i+1,b}=0$, (c) $n_{i,a}=0, n_{i+1,b}=1$ and (d) $n_{i,a}=0, n_{i+1,b}=0$ are considered in the same way.

Summing the results of each case and taking into account the corresponding statistical weights one will obtain

$$
\begin{aligned}
&G^0_{ib;ib;i+1,a;i+1,a}(\omega_{n_1},\omega_{n_2},\omega_{n_3},\omega_{n_4}) =\\
&\qquad = \beta^2\delta(\omega_{n_2}-\omega_{n_1})\delta(\omega_{n_4}-\omega_{n_3})\sum_{\alpha,\beta=1}^{4}\frac{C_{\alpha\beta}}{(\mathrm{i}\omega_{n_1}-E_\alpha)(\mathrm{i}\omega_{n_3}-E_\beta)}
\end{aligned}
$$

$$
\begin{aligned}
&- \beta\delta(\omega_{n_1} - \omega_{n_2} + \omega_{n_3} - \omega_{n_4}) \\
&\times J \sum_{\alpha,\beta=1}^{4} \frac{D_{\alpha\beta}}{(\mathrm{i}\omega_{n_1} - E_\alpha)(\mathrm{i}\omega_{n_2} - E_\alpha)(\mathrm{i}\omega_{n_3} - E_\beta)(\mathrm{i}\omega_{n_4} - E_\beta)}\,, \qquad \text{(A.15)}
\end{aligned}
$$

where poles E_α are defined by expression (30) and $C_{\alpha\beta}$ are the coefficients

$$
\begin{aligned}
C_{11} &= \langle(1-n_{i,a})(1-n_{i+1,a})(1-n_{i,b})(1-n_{i+1,b})\rangle, \\
C_{12} &= \langle(1-n_{i,a})(1-n_{i+1,a})(1-n_{i,b})n_{i+1,b}\rangle, \\
C_{13} &= \langle(1-n_{i,a})(1-n_{i+1,a})n_{i,b}(1-n_{i+1,b})\rangle, \\
C_{14} &= \langle(1-n_{i,a})(1-n_{i+1,a})n_{i,b}n_{i+1,b}\rangle, \\
C_{21} &= \langle n_{i,a}(1-n_{i+1,a})(1-n_{i,b})(1-n_{i+1,b})\rangle, \\
C_{22} &= \langle n_{i,a}(1-n_{i+1,a})(1-n_{i,b})n_{i+1,b}\rangle, \\
&\ \vdots \qquad \text{(A.16)}
\end{aligned}
$$

and so on, according to the previously used notations. Coefficients $D_{\alpha\beta}$ have the following form

$$
\begin{aligned}
D_{11} &= C_{11}\left(1 + \frac{J}{\mathrm{i}\omega_{n_1} + \mathrm{i}\omega_{n_3} - E_1 - E_3}\right), \\
D_{12} &= C_{12}\left(1 + \frac{J}{\mathrm{i}\omega_{n_1} + \mathrm{i}\omega_{n_3} - E_2 - E_3}\right), \\
&\ \vdots \qquad \text{(A.17)}
\end{aligned}
$$

Now, we have to calculate the correlation functions which enter the expressions (A.16). In the one-dimensional case these functions can be calculated exactly using the transfer matrix method. In [9,10] we have performed the investigation of energy spectrum and chemical potential behaviour in the Hubbard-1 type approximation for this case when calculating correlation functions via both the transfer matrix method (TMM) and the mean field approximation (MFA). The comparison of the results has shown that the results for correlation functions obtained via MFA are in good agreement with the exact results of TMM only at small and at large proton concentrations. Nevertheless, the MFA for correlation functions gives the right structure of proton energy spectrum and chemical potential behaviour. Thus, here we use the MFA to calculate the statistical weights in order to perform the evaluation of Green's function and chemical potential, leaving the TMM for a more complete future analysis. The correlation functions, calculated in MFA have the following form:

$$
\begin{aligned}
&C_1^0 = \left(1 - \frac{n}{2}\right)^2, \qquad C_2^0 = C_3^0 = \frac{n}{2}\left(1 - \frac{n}{2}\right), \qquad C_4^0 = \frac{n^2}{4}, \\
&C_{\alpha\beta}^0 = C_\alpha^0 \cdot C_\beta^0, \qquad \alpha,\beta = 1,4. \qquad \text{(A.18)}
\end{aligned}
$$

Here n is the average proton concentration per one bond ($0 \leqslant n \leqslant 2$).

Taking into account (9), (A.15) and the following expression for the zero-order Green's function

$$g^0_{ia,ia}(\omega_n) = g^0_{ib,ib}(\omega_n) = \sum_{\alpha=1}^{4} \frac{C^0_\alpha}{\mathrm{i}\omega_n - E_\alpha}, \qquad g^0_{ia,ib} = g^0_{ib,ia} = 0, \qquad \text{(A.19)}$$

obtained in [9,10], as well as the expressions for correlation functions (A.18), we can calculate the irreducible part $\Gamma^{(2)}_{ib;ib;i+1,a;i+1,a}$

$$\begin{aligned}
&\Gamma^{(2)}_{ib;ib;i+1,a;i+1,a}(\omega_{n_1},\omega_{n_2},\omega_{n_3},\omega_{n_4}) = -\beta\delta(\omega_{n_1}-\omega_{n_2}+\omega_{n_3}-\omega_{n_4})J \\
&\times \Bigg[\frac{\left(1-\frac{n}{2}\right)^4}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_1)(\mathrm{i}\omega_{n_4}-E_1)} \left(1+\frac{J}{\mathrm{i}\omega_{n_1}+\mathrm{i}\omega_{n_3}-E_1-E_3}\right) \\
&+ \frac{\frac{n}{2}\left(1-\frac{n}{2}\right)^3}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_2)(\mathrm{i}\omega_{n_4}-E_2)} \left(1+\frac{J}{\mathrm{i}\omega_{n_1}+\mathrm{i}\omega_{n_3}-E_2-E_3}\right) \\
&+ \frac{\frac{n}{2}\left(1-\frac{n}{2}\right)^3}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_3)(\mathrm{i}\omega_{n_4}-E_3)} \left(1+\frac{J}{\mathrm{i}\omega_{n_1}-\mathrm{i}\omega_{n_4}}\right) \\
&+ \frac{\frac{n^2}{4}\left(1-\frac{n}{2}\right)^2}{(\mathrm{i}\omega_{n_1}-E_1)(\mathrm{i}\omega_{n_2}-E_1)(\mathrm{i}\omega_{n_3}-E_4)(\mathrm{i}\omega_{n_4}-E_4)} \left(1+\frac{J}{\mathrm{i}\omega_{n_1}-\mathrm{i}\omega_{n_4}-E_3+E_4}\right) + \cdots \Bigg].
\end{aligned} \qquad \text{(A.20)}$$

This expression consists of 16 terms but only a few of them are shown for brevity. Each term possesses the same structure but differs from the others in statistical weights and in energies of the poles.

A similar procedure in calculating the four-vertex irreducible part can be used when the sites in the cluster are separated by one or more intermediate sites. In this case the neighbourhood of the cluster consists of three and four sites, correspondingly.

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Короткосяжні взаємодії в одновимірному протонному провіднику

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В роботі вивчається поведінка одновимірного протонного провідника на основі орієнтаційно-тунельної моделі. Узагальнено запропоновану раніше схему, яка дозволяє точно враховувати протонні взаємодії в гамільтоніяні нульового наближення і базується на розкладах функції Гріна за незвідними частинами. Розв'язано рівняння Ларкіна для одночастинкової функції Гріна у випадку, коли незвідна частина за Ларкіним була розрахована в першому наближенні. Досліджено протонний енергетичний спектр і поведінку хемічного потенціялу, проведено порівняння результатів з раніше отриманими в наближенні типу Габбард-1.

Ключові слова: *протонний перенос, водневий зв'язок, сильні кореляції, ферміонні моделі*

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