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Statistics and Properties of Coupled Hole Pairs in Superconducting Ceramics

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It is shown that in site representation the hole-pair operators obey the same commutation relations (paulionic) as the Cooper pair operators in impulse representation, although the latter describe delocalized quasiparticles. In quasi-impulse representation the hole-pair operators are also delocalized but the exact commutation relations correspond to a modified parafermi statistics [1] of rank $\mathfrak{N}$ ($\mathfrak{N}$ is the number of sites in a "superlattice" formed by the centers of mass of each hole pair). From this follows that one state can be occupied by up to $\mathfrak{N}$ pairs. Even in the absence of dynamic interaction, the system of hole pairs is characterized by some immanent interaction, named after Dyson as kinematic interaction. This interaction appears because of the deviation of the quasiparticle statistics from the Bose (Fermi) statistics and its magnitude depends on the concentration of hole pairs. In spite of the non-bosonic behavior, there is no statistical prohibition on the Bose-Einstein condensation of coupled hole pairs.

At present, it is well established that the conductivity in high-T$_c$ ceramics has a hole origin with charge of carriers equal to $+2e$. In this paper, we present the results of our study of statistics and some physical properties of the hole-pair system. But before we shortly consider the properties of isolated holes in superconducting ceramics.

1. Properties of holes in cuprate oxides

Usually, holes are described as fermions. It came from atomic physics: the closed electronic shell after one electron is knocked out (the "hole" formation) has the same angular and spin momentum properties as the unclosed electronic shell with one electron. But in general case, the holes can have different values of spin S. For example, in the CuO_2 planes in high-T$_c$ ceramics where the hole conductivity is revealed, all spins are paired, the so-called Zhang-Rice singlet [2,3]. The holes in high-T$_c$ ceramics (at least in the CuO_2 planes) can be considered as spinless positive charged quasiparticles. On the CuO_2 plane, the hole is delocalized among Cu and four O coupled by covalent bonding [3], schematically we show it in Fig. 1.

In second quantization formalism in the site representation, the model Hamiltonian for one type of spinless holes is

$$H = \epsilon_0 \sum_n b_n^\dagger b_n + \sum_{nn'} M_{nn'} b_n^\dagger b_{n'} + \sum_{nn'} V_{nn'} b_n^\dagger b_{n'}^\dagger b_{n'} b_n, \quad (1)$$

where ϵ_0 is the energy for the hole creation in a lattice, $M_{nn'}$ is the so-called hopping integral and $V_{nn'}$ is the hole-hole interaction term. As we showed in [4], the hole creation, $b_n^\dagger$, and hole annihilation, b_n, operators are characterized by the paulion properties:

$$[b_n, b_{n'}^\dagger]_- = [b_n, b_{n'}]_- = [b_n^\dagger, b_{n'}^\dagger]_- = 0, \quad \text{for } n \neq n';$$
$$[b_n, b_n^\dagger]_+ = 1; \quad [b_n, b_n]_+ = [b_n^\dagger, b_n^\dagger]_+ = 0, \quad (2)$$

the operators acting on different sites obey the boson commutation relations, while the operators acting on one site obey the fermion commutation relations.

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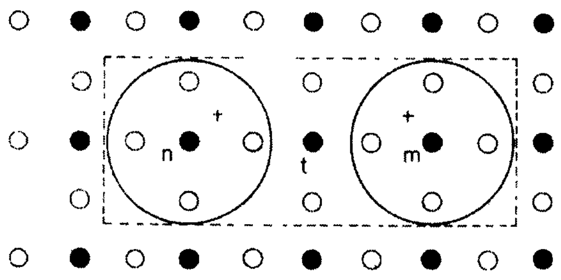

Figure 1. Example of coupled hole pair on the CuO_2 plane in high$-T_c$ superconducting ceramics, black circles are Cu, open circles are O.

Suppose that the hole-hole interaction term in (1) is attractive. In this case under some conditions, the coupled hole pairs can be formed.

2. Statistics of coupled hole pairs

The operators of creation and annihilation of the hole pair are defined as usual:

$$\begin{aligned} a_t^\dagger &= a_n^\dagger a_m^\dagger, \\ a_t &= a_m a_n, \end{aligned} \qquad (3)$$

where t denotes the localization point of the center of mass of the coupled hole pair, see Fig. 1. In high-T_c ceramics, the hole-pair localization region is not large: the correlation length in the CuO_2 planes is of the order of $(10-12)$Å.

It is easy to verify that the hole-pair operators $a_t^\dagger$ and a_t obey the same paulion commutation relations (2) as the hole operators. Let us note that the Cooper pair operators also obey the paulion commutation relations, see [5] (the commutator for $k = k'$, Eq. (2.21b) in [5], is equivalent to the fermion anticommutation relation). However, there is an essential difference: the Cooper pair operators are defined in the impulse space and so they are completely delocalized, on the other hand, the hole-pair operators $a_t^\dagger$ and a_t are defined in the site representation and are localized in some regions of the lattice. As we show below, in the quasi-impulse representation, the statistics of hole pairs radically changes.

Let us assume that the hole pairs have the same size and the region of the hole pair localization can be repeated in crystal so that the points t form a "superlattice" with $\mathfrak{N}$ sites. The model Hamiltonian for hole pairs can be presented as

$$H = \sum_t \epsilon_p a_t^\dagger a_t + \sum_{tt'} M_{tt'} a_t^\dagger a_{t'}, \qquad (4)$$

where $\epsilon_p = 2\epsilon_0 + V_0$ is the energy of the coupled hole pair, V_0 is the attractive potential between holes which we assume to be the same for all pairs, as in the BCS approach. $M_{tt'}$ is the hopping integral for a hole pair moving as a whole entity. The Hamiltonian (4) can be transformed by some unitary transformation:

$$A_{\mathbf{q}} = \frac{1}{\sqrt{\mathfrak{N}}} \sum_{t=1}^{\mathfrak{N}} u_{\mathbf{q}t} a_t, \quad A_{\mathbf{q}}^\dagger = \frac{1}{\sqrt{\mathfrak{N}}} \sum_{t=1}^{\mathfrak{N}} u_{\mathbf{q}t}^* a_t^\dagger \qquad (5)$$

to the diagonalized form in the quasi-impulse space,

$$H = \sum_{\mathbf{q}} \epsilon_{\mathbf{q}} A_{\mathbf{q}}^\dagger A_{\mathbf{q}}. \qquad (6)$$

For simple lattices with one site per cell, the unitary transformation (5) is completely determined by the translation symmetry of the lattice and the coefficients $u_{\mathbf{q}n} = \exp(-i\mathbf{q}r_n)$. The self-energy of the diagonalized Hamiltonian (6) is equal to

$$\epsilon_{\mathbf{q}} = \epsilon_p + \sum_{t'(\neq t)} M_{tt'} \exp[i\mathbf{q}\cdot(\mathbf{r}_t - \mathbf{r}_{t'})]. \qquad (7)$$

Since the operators (3) obey neither the boson nor the fermion commutation relations, the unitary transformation in general case is not canonical; this means that it does not preserve the commutation properties of the operators transformed. In particular, the operators (5) do not describe the paulion quasiparticles. As we showed in [4] for holes in quasi-impulse space, such operators obey the modified parafermi statistics with trilinear commutation relations. This statistics has been introduced by Kaplan in 1976 [1]. It was proved that the Frenkel excitons and magnons obey the modified parafermi statistics which differs from the Green parafermi statistics [6] in one essential point: the trilinear commutation relations do not contain the Kronecker symbols and their right-hand side is determined by the quasi-momentum conservation law. This leads to important physical consequences, below we will discuss some of them. The results [1] for the Frenkel excitons and magnons were extended later to polaritons [7], defectons in quantum crystals [8], and to the Wannier-Mott excitons [9].

For lattices, diagonalized by an exponential unitary transformation, the operators (5) obey the following trilinear commutation relations:

$$[[A^{\dagger}_{\mathbf{q}}, A_{\mathbf{q}'}]_-, A_{\mathbf{q}''}]_- = -2\mathfrak{N}^{-1}A_{\bar{\mathbf{q}}}, \quad \bar{\mathbf{q}} = \mathbf{q}' + \mathbf{q}'' - \mathbf{q} \tag{8}$$

$$[[A^{\dagger}_{\mathbf{q}}, A_{\mathbf{q}'}]_-, A^{\dagger}_{\mathbf{q}''}]_- = 2\mathfrak{N}^{-1}A^{\dagger}_{\bar{\mathbf{q}}}, \quad \bar{\mathbf{q}} = \mathbf{q} - \mathbf{q}' + \mathbf{q}'' \tag{9}$$

which correspond to the modified parafermi statistics of rank $\mathfrak{N}$. This means that one state can be occupied by up to $\mathfrak{N}$ hole pairs:

$$(A^{+}_{\mathbf{q}})^{N}|0\rangle \neq 0, \quad N \leq \mathfrak{N} \tag{10}$$

$$(A^{+}_{\mathbf{q}})^{\mathfrak{N}+1}|0\rangle = 0. \tag{11}$$

The state with N noninteracting pairs, each with the same $\mathbf{q}$, is defined by the usual expression

$$|N_{\mathbf{q}}\rangle = C_N (A^{\dagger}_{\mathbf{q}})^N |0\rangle, \tag{12}$$

where the normalization factor C_N can be found by the induction method using the operator equation obtained from the commutation relation (9)

$$A_{\mathbf{q}}A^{\dagger}_{\mathbf{q}'}A^{\dagger}_{\mathbf{q}''} = A^{\dagger}_{\mathbf{q}'}A_{\mathbf{q}}A^{\dagger}_{\mathbf{q}''} + A^{\dagger}_{\mathbf{q}''}A_{\mathbf{q}}A^{\dagger}_{\mathbf{q}'} - A^{\dagger}_{\mathbf{q}''}A^{\dagger}_{\mathbf{q}'}A_{\mathbf{q}} - \frac{2}{\mathfrak{N}}A^{\dagger}_{\bar{\mathbf{q}}}, \quad \bar{\mathbf{q}} = \mathbf{q}' + \mathbf{q}'' - \mathbf{q}. \tag{13}$$

The expression for C_N differs from that for a Bose system and is given by:

$$C_N = [N!(1 - \frac{1}{\mathfrak{N}})(1 - \frac{2}{\mathfrak{N}}) \cdots (1 - \frac{N-1}{\mathfrak{N}})]^{-\frac{1}{2}}. \tag{14}$$

Now, it is easy to find

$$A^{\dagger}_{\mathbf{q}}|N_{\mathbf{q}}\rangle = \sqrt{(N_{\mathbf{q}}+1)(1 - N_{\mathbf{q}}/\mathfrak{N})}\,|N_{\mathbf{q}}+1\rangle \tag{15}$$

$$A_{\mathbf{q}}|N_{\mathbf{q}}\rangle = \sqrt{N_{\mathbf{q}}(1 - (N_{\mathbf{q}}-1)/\mathfrak{N})}\,|N_{\mathbf{q}}-1\rangle. \tag{16}$$

As $\mathfrak{N} \longrightarrow \infty$, relations (15) and (16) turn into the well known relations for bosons. From Eqs. (15) and (16) it follows that

$$A^{\dagger}_{\mathbf{q}}A_{\mathbf{q}}|N_{\mathbf{q}}\rangle = N_{\mathbf{q}}(1 - (N_{\mathbf{q}}-1)/\mathfrak{N}). \tag{17}$$

Thus, the operator $A^{\dagger}_{\mathbf{q}}A_{\mathbf{q}}$ is not a particle number operator in a state $\mathbf{q}$, as in the case of boson, fermion or paulion operators. It can be proved that for the modified parafermi statistics, the operator of particle number in a state $\mathbf{q}$ does not exist, see [1] or [4]. This is the consequence of the absence of the Kronecker symbols in the commutation relations (8) and (9). What can be defined is the operator of the total number of hole pairs, $\hat{N}$. For the commutator, the following relation is valid [1,4]:

$$[A_{\mathbf{q}}, A^{\dagger}_{\mathbf{q}}]_- = 1 - \frac{2\hat{N}}{\mathfrak{N}}. \tag{18}$$

Only for small concentrations, $\langle \hat{N} \rangle / \mathfrak{N} << 1$, the hole pairs satisfy the Bose statistics.

3. Some properties of the hole-pair system

As we showed above, the operator $A^{\dagger}_{\mathbf{q}}A_{\mathbf{q}}$ is not the hole-pair number operator, so, the diagonalized Hamiltonian (6) does not describe the hole-pair ideal gas, the latter does not exist. Even in the absence of dynamical interactions, some immanent interaction in the hole-pair system is always present. The origin of this interaction, which called after Dyson [10] the kinematic interaction, is in the deviation of the hole-pair statistics from the Bose (Fermi) statistics.

Let us estimate the magnitude of the kinematics interaction in the state (12) with N noninteracting hole pairs, each pair with energy $\epsilon_{\mathbf{q}}$ (7). Using the equation (13) for shifting the operator $A_{\mathbf{q}}$ to the right, after straightforward although cumbersome calculations, we obtain [1,4]

$$E(N_{\mathbf{q}}) = \left\langle N_{\mathbf{q}} \left| \sum_{\mathbf{q}'} \epsilon_{\mathbf{q}'} A_{\mathbf{q}'}^{\dagger} A_{\mathbf{q}'} \right| N_{\mathbf{q}} \right\rangle = N\,[\epsilon_{\mathbf{q}} + \frac{N-1}{\mathfrak{N}}(\bar{\epsilon} - \epsilon_{\mathbf{q}})], \qquad (19)$$

where $\bar{\epsilon} = \frac{1}{\mathfrak{N}-1} \sum_{\mathbf{q}' \neq \mathbf{q}} \epsilon_{\mathbf{q}'}$ is the mean energy of the hole-pair band. The second term in the last line of Eq. (19) is the kinematic interaction. It is proportional to the concentration of hole pairs and its magnitude is larger the larger is the difference between the $\epsilon_{\mathbf{q}}$ and the mean energy of the hole pair band. According to Eq. (19), there is an immanent coupling among all states of the hole pair band. Therefore, we cannot define the independent quasi-particles in some particular state. As we mentioned above, the ideal gas of the hole pairs does not exist fundamentally. It can exist only in the low concentration limit in which the kinematic energy becomes small and we get the case of the Bose statistics, cf. Eq. (18).

In real cuprate ceramics, the maximum T_c is achieved for a hole concentration in CuO_2 planes equal to $0.2 - 0.25$ per CuO_2 unit [11,12]. The same order of magnitude has to be for the hole-pair concentration because the latter is counted not per CuO_2 units, but per the number of sites $\mathfrak{N}$ in the superlattice (Fig. 1). Thus, the deviations from the Bose statistics for the hole-pair system are not negligible and have to be taken into account.

As we showed above, the hole pairs obey the modified parafermi statistics of rank $\mathfrak{N}$, so, one state can be occupied by up to $\mathfrak{N}$ hole pairs. The number of hole pairs N cannot exceed the number of sites $\mathfrak{N}$ in the superlattice. This means that, in spite of the non-bosonic behavior of the hole-pair system, there is no statistical prohibition of the Bose-Einstein condensation. On the other hand, the hole-pair system is always non-ideal (because of the kinematic interaction). For a rigorous study of the Bose-Einstein condensation phenomenon, we have to include also a dynamic interaction and consider an interplay between kinematic and dynamic interactions to study the stability of the Bose condensate, as was done for the molecular exciton system in Ref. [13].

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