# SIMPLE THEORY OF EXTREMELY OVERDOPED HTS

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We demonstrate the existence of a simple physical picture of superconductivity for extremely overdoped CuO<sub>2</sub> planes. It has all the characteristic features of HTS, such as a high superconducting transition temperature, the  $d_{x^2-y^2}$  symmetry of the order parameter, and the coexistence of a single-electron Fermi surface and a pseudogap in the normal state. The values of the pseudogap are calculated for different doping levels. Orbital paramagnetism of preformed pairs is predicted.

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#### 1. INTRODUCTION

In this work (also see earlier Letter [1]), we demonstrate that in the phase diagram of cuprate hightemperature superconductors (HTS), a small region exists where the characteristic features of HTS can be easily understood on the base of a simple theory. These characteristic features include a high superconducting transition temperature, the  $d_{x^2-y^2}$  symmetry of the order parameter (see [2]), and the coexistence of a single-electron Fermi surface and a pseudogap in the normal state [3]. The last phenomenon is usually attributed to the presence of preformed (i.e., normal-state) electron pairs (in particular, bipolarons [4–8]).

The aforementioned small region in the phase diagram is situated in the vicinity of the maximal holedoping level  $x = x_c$  compatible with superconductivity. The superconducting transition temperature  $T_c$  is zero for  $x \ge x_c$ , and hence it is low in our region near  $x = x_c$ . However,  $T_c$  increases with decreasing x for  $x < x_c$  such that it is quite high at the boundary of the region (i.e., for  $x_c - x \sim 1$ ).

Two features of our small region are important to make a simple physical picture possible. These are relatively low  $T_c$  and the clear nature of the normal state as mostly the conventional Fermi liquid.

We calculate the pseudogap. With increasing x,

the pseudogap decreases for  $x < x_c$ . As well as  $T_c$ , the pseudogap disappears at  $x = x_c$ . However, it reappears for larger doping levels  $x > x_c$ .

As a new prediction, we show the existence of an unusual orbital paramagnetism of the preformed (singlet) pairs, which can probably be experimentally separated from the Pauli spin paramagnetism of single electrons and the Landau diamagnetism of single electrons and pairs.

### 2. PAIR QUASIPARTICLES

The key point is the existence of very mobile pair quasiparticles in crystals under the tight-binding conditions, i.e., if the energy of the electron-electron interaction at a distance of the order of the atomic spacing considerably exceeds the electron tunneling amplitude to neighboring lattice cites. Quasiparticles of this type were studied earlier [9] in helium quantum crystals and more recently by Alexandrov and Kornilovitch [7] as a model of bipolarons in HTS (also see [10]).

•7	Х	•4	Х	•3
×		×		×
٠	×	•1	×	•2
×		×		×
•	×	•6	X	•5

Figure. CuO<sub>2</sub> plane: • — Cu atoms and  $\times$  — O atoms

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We consider two electrons localized at neighboring (1 and 2 in the Figure) copper atoms (to be more precise, in unit cells containing these atoms) forming a square lattice in the CuO<sub>2</sub> plane. The electron tunneling from 2 to 4 or 6 does not change the energy of the system in view of the crystal lattice symmetry. The same is true for the electron tunneling from 1 to 3 or 5. Owing to this type of transitions, an electron pair can move as a whole over the entire plane, because the  $2 \rightarrow 4$  transition can be followed by the transition  $1 \rightarrow 7$  or  $1 \rightarrow 3$ , and so on. Because the transitions do not change the energy of the system, the motion is

ized Bose quasiparticle. To calculate the quasiparticle spectrum, we consider the localized states of a pair,

fully coherent. An electron pair behaves as a delocal-

$$|\mathbf{r}, \mathbf{r}', \alpha\beta\rangle = c^+_{\mathbf{r}\alpha} c^+_{\mathbf{r}'\beta} |0\rangle, \qquad (1)$$

where  $c^+_{\mathbf{r}\alpha}$  are the electron creation operators with a spin projection  $\alpha = \uparrow, \downarrow$  at a point **r** and  $|0\rangle$  is the electron vacuum.

The effective tunneling Hamiltonian  $H_{eff}$  is defined by the matrix elements of the operator

$$H = t \sum_{\mathbf{rr}'\alpha} c^+_{\mathbf{r}'\alpha} c_{\mathbf{r}\alpha}, \qquad (2)$$

which correspond to the transitions of one of the electrons to copper atoms that are next-to-nearest neighbors of the initial atom, such that the energy of the system of two electrons remains unchanged. Here, t is the tunneling amplitude, which is known to be positive (see [2, p. 1004]).

Let  $\mathbf{a}_n$  (n = x, y) be the square-lattice periods directed from point 1 to point 2 and from point 1 to point 4, respectively. We have

$$H_{eff} |\mathbf{r}, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle = t(|\mathbf{r} + \mathbf{a}_x + \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + |\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + |\mathbf{r}, \mathbf{r} - \mathbf{a}_y, \alpha\beta\rangle + |\mathbf{r}, \mathbf{r} - \mathbf{a}_y, \alpha\beta\rangle = t(-|\mathbf{r} + \mathbf{a}_x, \mathbf{r} + \mathbf{a}_x + \mathbf{a}_y, \beta\alpha\rangle + |\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + |\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x, \alpha\beta\rangle) + (|\mathbf{r} + \mathbf{a}_x - \mathbf{a}_y$$

where we used the antisymmetry of quantities (1) with respect to the arguments  $(\mathbf{r}, \alpha)$  and  $(\mathbf{r}', \beta)$ . Analogously,

$$H_{eff} |\mathbf{r}, \mathbf{r} + \mathbf{a}_y, \alpha \beta \rangle = t(-|\mathbf{r} + \mathbf{a}_y, \mathbf{r} + \mathbf{a}_x + \mathbf{a}_y, \beta \alpha \rangle + |\mathbf{r} - \mathbf{a}_x + \mathbf{a}_y, \mathbf{r} + \mathbf{a}_y, \alpha \beta \rangle + |\mathbf{r} - \mathbf{a}_x, \mathbf{r}, \alpha \beta \rangle - |\mathbf{r} - \mathbf{a}_x, \mathbf{r}, \beta \alpha \rangle).$$
(4)

The complete set of localized states of an electron pair is determined by the state vectors

$$|\mathbf{r}, n, \alpha\beta\rangle \equiv |\mathbf{r}, \mathbf{r} + \mathbf{a}_n, \alpha\beta\rangle,$$
 (5)

where  $\mathbf{r}$  labels unit cells of the square lattice.

The problem obviously splits into two independent problems for singlet and triplet pairs that are characterized by quantities (5), which are respectively antisymmetric and symmetric in the spin indices  $\alpha$ ,  $\beta$ . Assuming that the required stationary states of a pair are superpositions of localized states,

$$\sum_{\mathbf{r},n} \psi_{\alpha\beta}^{(n)} e^{i\mathbf{k}\mathbf{r}} \left| \mathbf{r}, n, \alpha\beta \right\rangle \tag{6}$$

with coefficients  $\psi_{\alpha\beta}^{(n)}$  independent of **r** (this corresponds to a definite quasimomentum **k**), we obtain

$$(E(\mathbf{k}) - \epsilon_0)\psi^{(x)} = t\psi^{(y)}(1 \pm e^{-i\kappa_x})(1 \pm e^{i\kappa_y}), (E(\mathbf{k}) - \epsilon_0)\psi^{(y)} = t\psi^{(x)}(1 \pm e^{i\kappa_x})(1 \pm e^{-i\kappa_y}),$$
 (7)

where the upper or lower sign corresponds to a singlet or triplet state, respectively. The conditions for the existence of a nontrivial solution  $\psi^{(x)}$ ,  $\psi^{(y)}$  of system (7) determine the energy  $E(\mathbf{k})$  of a pair quasiparticle. Here,  $\epsilon_0$  is the energy of the initial localized state;  $\kappa_x = \mathbf{k} \cdot \mathbf{a}_x$  and  $\kappa_y = \mathbf{k} \cdot \mathbf{a}_y$ . Everywhere in formulas (7), we omit identical spin indices  $\alpha\beta$ .

The minimal energy  $\epsilon_m = \min E(\mathbf{k}) = \epsilon_0 - 4t$  of a singlet pair is attained at  $\kappa_x = \kappa_y = 0$ . The same minimal energy of a triplet pair is attained at the nonzero quasimomentum  $\kappa_x = \kappa_y = \pi$ . This degeneracy is removed by taking the electron exchange in the initial localized pair into account. It is well known that this exchange is of an antiferromagnetic nature, and hence singlet pairs have the minimal energy.

Thus, solitary Bose quasiparticles can exist in the  $CuO_2$  plane; these particles are characterized by a doubled electric charge and by zero momentum and spin in the ground state. It can be readily seen from Eqs. (7)that the effective mass of quasiparticles is  $m = \hbar^2/ta^2$ , where  $a = |\mathbf{a}_x| = |\mathbf{a}_y|$ . In addition, quasiparticles have a specific quantum number n = x, y, which determines the orientation of a two-electron «dumb-bell». Substituting  $E(\mathbf{k}) = \epsilon_m$  and  $\mathbf{k} = 0$  in Eqs. (7), we obtain  $\psi^{(x)} = -\psi^{(y)}$  in the ground state. Because the orientations n = x and n = y are transformed into each other under lattice rotation through the angle  $\pi/2$  and under reflection in the diagonal plane passing through points 1 and 3 in the figure, the ground-state wave function  $\psi \equiv \psi^{(x)} = -\psi^{(y)}$  of quasiparticles transforms in accordance with the nontrivial 1D representation (usually denoted by  $d_{x^2-y^2}$ ) of the symmetry group of the  $CuO_2$  plane (see [2]).

### 3. SUPERCONDUCTIVITY

We further assume that all the other two-electron, three-electron, etc., configurations localized at distances of the order of the atomic spacing are energetically disadvantageous compared to the pair configuration considered above. In addition, we assume that electrons are repulsed at large distances such that the electron-electron interaction energy is of the order of the one-electron tunneling amplitude. Under these conditions, only single-electron Fermi particles and the pair Bose particles considered above play significant role.

Finally, we assume that the minimal energy  $\epsilon_m$  of pair quasiparticles is such that  $\epsilon_m/2$  is within the single-electron energy band. We note the following. Under the tight-binding conditions, there are two different situations in which  $\epsilon_m/2$  can be within the single-electron energy band. First, if single electrons and electrons in pairs correspond to the same energy band, the singleelectron tunneling amplitude must be of the order of the electron-electron interaction energy in the pairs, while the one-electron tunneling amplitude t in pairs, introduced in Sec. 2, must be much smaller than the interaction. The last condition, which is the condition of the applicability of the procedure used in Sec. 2, can be a result of the large polaron effect in pairs. Second, if single electrons and electrons in pairs correspond to different bands, both one-electron amplitudes can be of the same order. The analysis carried out by Alexandrov and Kornilovitch in [7] shows that the conditions formulated above are likely to be realistic.

We now trace the change of the state of the system at T = 0 as the number of electrons increases (the hole-doping level decreases). Until  $\epsilon_m/2 > \epsilon_F$ , only single-electron quasiparticles are present and the system behaves as an ordinary Fermi liquid. The condition  $\epsilon_m/2 = \epsilon_F$  determines the minimal hole-doping level compatible with the state of a normal Fermi liquid. Let  $n_c$  denote the corresponding electron density n. Upon a further decrease in the hole-doping level, all additional  $n - n_c$  electrons pass into a Bose–Einstein (BE) condensate of pair quasiparticles (we everywhere consider the case of small  $n - n_c$  values, for which the concentration of pairs is low and their interaction can be disregarded). The system becomes a superconductor. The superconducting order parameter is given by the boson ground-state wave function  $\psi \equiv \psi^{(x)}$  normalized by the condition  $|\psi|^2 = (n - n_c)/2$ ; the wave function transforms in accordance with the  $d_{x^2-y^2}$  representation of the symmetry group of the  $CuO_2$  plane.

It is important to note the following. In the system

ground state (i.e., for complete filling of all fermion states with the energies smaller than  $\epsilon_F$ ), the uncertainty in the energy of a boson quasiparticle with low excitation energy  $\epsilon = k^2/2m$ , arising due to its collisions with single-electron Landau quasiparticles, is proportional to  $\epsilon^2$ . As in the conventional theory of Fermi liquid, this is, first, because of a low density of fermions in an order- $\epsilon$  neighborhood of  $\epsilon_F$ , with which the given boson can collide due to energy conservation. Second, the statistical weight of the final states to which fermionic transitions are possible is small. The probability of the boson decay into two fermions per unit time is also small: as suggested at the beginning of this section, the boson must overcome a significant energy barrier. Thus, the proposed picture of superconductivity in the vicinity of the maximal doping level remains valid even in the region of appreciable densities of fermions, where the interaction between bosons and fermions is significant. The critical electron density  $n_c$  is determined from the condition that the electron chemical potential is equal to half the minimal boson energy. In the general case, this energy is a functional of the distribution function for single-electron Landau quasiparticles.

In calculating the superconducting transition temperature, the fermion distribution function may be considered as corresponding to T = 0, because the temperature corrections (proportional to  $T^2$ ) to the thermodynamic functions of the Fermi liquid are considerably smaller than the corrections included below.

The density of uncondensed bosons at a finite temperature  $T < T_c$  is

$$N' = \int \frac{2\pi k \, dk}{(2\pi\hbar)^2} \, \frac{1}{e^{\epsilon/T} - 1} = \frac{mT}{2\pi\hbar^2} \lg \frac{T}{\tau}.$$
 (8)

The integral in Eq. (8) diverges at small  $\epsilon$  and is therefore cut off at  $\epsilon \sim \tau$ , where  $\tau$  is a small tunneling amplitude of electrons in the direction perpendicular to the CuO<sub>2</sub> plane.

The excess number  $n - n_c$  of electrons in the system is equal to the doubled sum of N' and the number  $N_0$  of bosons in the condensate. This leads to the dependence of the superconducting transition temperature on the doping level for small values of  $n - n_c$ :

$$n - n_c = \frac{mT_c}{\pi\hbar^2} \lg \frac{T_c}{\tau}.$$
 (9)

The number of pairs in the condensate

$$N_0 = \frac{n - n_c}{2} \left( 1 - \frac{T}{T_c} \frac{\lg T/\tau}{\lg T_c/\tau} \right)$$
(10)

determines the modulus of the order parameter  $|\psi|^2 = N_0$  at finite temperatures. The superconducting transition temperature defined by Eq. (9) is quite high. To within the logarithmic term, this temperature is of the order of the one-electron tunneling amplitude t at the boundary of the applicability region (i.e., for  $n - n_c \sim a^{-2}$ ). The possibility that the superconducting transition temperature may have such an order of magnitude was pointed out in the aforementioned paper by Alexandrov and Kornilovitch [7].

The interaction of fermions with the BE condensate (effective electron–electron interaction), which is described by the order parameter  $\psi$ , creates an effective potential  $\Delta_{\mathbf{k}}$  acting on fermions as in conventional superconductors:

$$H_{int} = \sum_{\mathbf{k}} (\Delta_{\mathbf{k}} c^+_{\mathbf{k}\uparrow} c^+_{-\mathbf{k}\downarrow} + \text{H.c.}).$$
(11)

In view of the symmetry of  $\psi$ , we have

$$\Delta_{\mathbf{k}} = V(\hat{k}_x^2 - \hat{k}_y^2)\psi, \qquad (12)$$

where  $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$  and V is invariant under the symmetry group.

Owing to this interaction, fermions in the superconducting state considered acquire features typical of an ordinary superconductor with the  $d_{x^2-y^2}$  symmetry.

### 4. NORMAL STATE THERMODYNAMICS. THE PSEUDOGAP

The total number of pairs for  $T < T_c$  is independent of the temperature and is equal to  $(n-n_c)/2$ . The electron chemical potential for  $T < T_c$  is also temperature-independent and equal to  $\mu = \mu(n_c) = \epsilon_m(n_c)/2$ , where  $\epsilon_m = \epsilon_m(n)$  is the pair minimal energy, which depends on the fermion density, as shown above.

For  $T > T_c$ , the fermion distribution function, as above, corresponds to T = 0, but with the temperature-dependent chemical potential. The pair energy spectrum is  $E = \epsilon_m(\mu) + \epsilon$ , where  $\epsilon = k^2/2m$ . The pair density above  $T_c$  is given by

$$N = \int_{0}^{\infty} \frac{2\pi k \, dk}{(2\pi\hbar)^2} \, \frac{1}{e^{(\epsilon+\zeta)/T} - 1} = \frac{mT}{2\pi\hbar^2} \lg \frac{1}{1 - e^{-\zeta/T}}.$$
 (13)

The parameter  $\zeta$  ( $\zeta \gg \tau$ ) is defined by

$$\zeta = \frac{\partial \epsilon_m}{\partial \mu} \delta \mu - 2\delta \mu, \tag{14}$$

where  $\delta \mu = \mu - \mu(n_c)$ . With changing the temperature, the total electron number conservation gives

$$n - n_c = 2N + \frac{\partial n}{\partial \mu} \delta \mu. \tag{15}$$

From the last equation, we find  $\zeta = \zeta(T)$  and then all the other quantities.

For  $n > n_c$  and not too high temperature  $T \ll$  $\ll T_c \log(T_c/\tau)$ , the pair density is determined by

$$\frac{N(T) - N(T_c)}{N(T_c)} = \frac{\partial n/\partial \mu}{2(2 - \partial \epsilon_m/\partial \mu)} T e^{-\Delta_p/T}, \quad (16)$$

where  $N(T_c) = (n - n_c)/2$  and

$$\Delta_p = T_c \lg \frac{T_c}{\tau} = \frac{\pi \hbar^2}{m} (n - n_c) \tag{17}$$

is the pseudogap for  $n > n_c$ . As well as  $T_c$ , it is zero at the critical value of the doping level  $n = n_c$ . For higher doping level  $n < n_c$  ( $T_c = 0$ ), we have

$$N(T) = \frac{mT}{2\pi\hbar^2} e^{-\Delta'_p/T},$$
(18)

where

$$\Delta'_{p} = \left(2\frac{\partial\mu}{\partial n} - \frac{\partial\epsilon_{m}}{\partial n}\right)(n_{c} - n)$$
(19)

is the pseudogap for  $n < n_c$ . Equation (18) holds in the low-temperature region  $T \ll \Delta'_p$ . For  $n < n_c$ , the pseudogap  $\Delta'_p$  is the gap in the energy spectrum of the pair quasiparticles. For high temperatures  $T \gg \Delta_p, \Delta'_p$ (but  $T \ll t$ ), the pair density is a linear function of temperature,

$$N(T) = \frac{z\partial n/\partial\mu}{2(2 - \partial\epsilon_m/\partial\mu)}T$$
(20)

where z is the solution of the equation  $\lambda z = e^{-z}$  with

$$\lambda = \frac{\pi\hbar^2}{m} \frac{\partial n/\partial\mu}{2 - \partial\epsilon_m/\partial\mu}.$$
 (21)

The entropy of pairs is determined by the equation

$$S(T) = \frac{m}{2\pi\hbar^2} \int_0^\infty d\epsilon \{ (1+f) \lg(1+f) - f \lg f \}, \quad (22)$$

where  $f = \{e^{(\epsilon+\zeta)/T} - 1\}^{-1}$ . For  $n > n_c$  in the low-temperature region  $T \ll \Delta_p$ , we have

$$\frac{S(T)}{T} - \left(\frac{S}{T}\right)_{T=T_c} = -\frac{m}{2\pi\hbar^2} \frac{\Delta_p}{T} e^{-\Delta_p/T}, \qquad (23)$$

where

$$\left(\frac{S}{T}\right)_{T=T_c} = \frac{\pi m}{12\hbar^2}.$$
(24)

The function S(T) is almost linear in T, with exponentially small deviations. For  $n < n_c$ , the pair entropy is exponentially small at low temperatures  $T \ll \Delta'_p$ :

$$S(T) = \frac{mT}{2\pi\hbar^2} e^{-\Delta'_p/T}.$$
(25)

At high temperatures  $T \gg \Delta_p, \Delta'_p$ , the entropy is

$$S(T) = \frac{m\sigma}{2\pi\hbar^2}T.$$
 (26)

The temperature-independent factor  $\sigma$  is determined by

$$\sigma = \int_{z}^{\infty} \frac{x \, dx}{e^x - 1} - \lambda z^2. \tag{27}$$

The entropy is again a linear function of temperature.

## 5. ORBITAL PARAMAGNETISM OF PAIRS

In this section, we show that the orbital motion of electrons inside the pairs cause a peculiar paramagnetism. Let a pair be at rest as a whole. For singlet pairs at  $\mathbf{k} = 0$ , the Hamiltonian in Eqs. (3) and (4) can be written as the 2 × 2 matrix

$$H = 4t \begin{pmatrix} 0 & 1\\ 1 & 0 \end{pmatrix} \equiv 4t\sigma_1, \tag{28}$$

acting on a state vector

$$\psi = \psi^{(x)} \begin{pmatrix} 1\\ 0 \end{pmatrix} + \psi^{(y)} \begin{pmatrix} 0\\ 1 \end{pmatrix}, \qquad (29)$$

where  $\psi^{(n)}$ , n = x, y, are quantum amplitudes of two orientations of the two-electron dumb-bell and  $\sigma_1$  is a Pauli matrix.

In the x-state, coordinates of two electrons (with respect to the center of gravity of the pair) are  $x_1 = -a/2$ ,  $y_1 = 0$  and  $x_2 = a/2$ ,  $y_2 = 0$ , respectively. In the y-state, we have  $x_1 = 0$ ,  $y_1 = -a/2$  and  $x_2 = 0$ ,  $y_2 = a/2$ . From this, we find the coordinate operators for both electrons:

$$x_{1} = -x_{2} = -\frac{a}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix},$$
  

$$y_{1} = -y_{2} = -\frac{a}{2} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$
(30)

The velocity operators are determined by the commutators

$$\dot{\mathbf{r}}_{1,2} = \frac{i}{\hbar} \left[ H, \mathbf{r}_{1,2} \right].$$
 (31)

Simple calculation gives

$$\dot{x}_1 = -\dot{x}_2 = -\dot{y}_1 = \dot{y}_2 = -\frac{2at}{\hbar} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \equiv = -\frac{2at}{\hbar} \sigma_2. \quad (32)$$

The operator of the pair magnetic moment, which is directed along the z axis, is

$$\mu \equiv \mu_z = \frac{e}{2c} \sum_{1,2} (x\dot{y} - y\dot{x}) = -\frac{eta^2}{\hbar c} \sigma_2, \qquad (33)$$

where e is the electron charge and c is the velocity of light.

In the presence of an external magnetic field  $B \equiv B_z$ , the Hamiltonian of the pair is

$$H = 4t\sigma_1 - \mu B. \tag{34}$$

The energy eigenvalues are

$$E = \epsilon_0 \mp 4t \left[ 1 + \left( \frac{ea^2}{4\hbar c} B \right)^2 \right]^{1/2}.$$
 (35)

In weak fields, the minimal energy is

$$E_{min} = \epsilon_0 - 4t - t \frac{e^2 a^4}{8\hbar^2 c^2} B^2.$$
 (36)

The average magnetic moment of the pair is

$$\langle \mu \rangle = -\frac{\partial E_{min}}{\partial B} = \alpha B,$$
 (37)

where

$$\alpha = \frac{e^2 a^4}{4\hbar^2 c^2} t = \frac{e^2 a^2}{4mc^2} \tag{38}$$

is the pair paramagnetic polarizability.

We note that pairs with  $\mathbf{k} = 0$  in the upper energy band (the lower sign in (35)) are diamagnetic.

The pair contribution to the paramagnetic susceptibility of a 3D sample is

$$\chi = \frac{e^2 a^2}{4mc^2} N^{(3)},\tag{39}$$

where  $N^{(3)} = N(T)/L$  is the 3D density of pairs and N(T) is the 2D density determined by formulas (16), (18), and (20). Here, L is the distance between neighboring CuO<sub>2</sub> planes.

Generally, we have three competing contributions to the magnetic susceptibility: the orbital paramagnetism of pairs considered above, the Pauli spin susceptibility of single electrons (pairs are singlet), and the Landau diamagnetism of single electrons and pairs. Spin susceptibility is isotropic. Orbital paramagnetism and Landau diamagnetism are both strongly anisotropic (the magnetic moment is directed along the z axis independently of the direction of the magnetic field) because of a 2D character of single electrons and pairs. However, Landau diamagnetism, especially in the 2Dcase, is very sensitive to inhomogeneities. For example, it is easily suppressed by localization of charge carriers. Orbital paramagnetism is finite at zero velocity of a pair as a whole. Therefore, it has to be much more stable against inhomogeneities. We hope that orbital paramagnetism can be experimentally separated from the other two contributions to susceptibility.

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