

ANTIFERROMAGNETIC CORRELATIONS IN A POLAR MODEL FOR OXIDE SUPERCONDUCTORS

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A planar tight-binding system of $\text{Cu}(3d^9)$ and $\text{O}(2p^6)$ electrons is considered in the framework of a polar model for metals. A second-quantized Hamiltonian is derived as a series expansion in powers of a small overlapping parameter, $\epsilon S \ll 1$, for $d(x^2 - y^2)$ and p_x -, p_y -orbitals. A generalized two-sublattice Hubbard model is obtained and treated perturbatively to the fourth order in ϵS . Various perturbative contributions are considered as effective spin Hamiltonians. Some comments on recent suggestions for the superconducting electron pairing due to antiferromagnetic $\text{Cu}(3d) - \text{O}(2p)$ exchange are given.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Антиферромагнитные корреляции в полярной модели оксидных сверхпроводников

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В рамках полярной модели металла изучается двумерная система с сильной связью для электронов $\text{Cu}(3d^9)$ и $\text{O}(2p^6)$. Вторичноквантованный электронный гамильтониан представлен в виде ряда по степеням малого параметра перекрытия, $\epsilon S \ll 1$, для $d(x^2 - y^2)$ и p_x -, p_y -орбиталей. Получена обобщенная двумерная модель Хаббарда, которая исследуется в рамках операторной формы теории возмущений с точностью до четвертого порядка по ϵS . Установлено соответствие между различными вкладками теории возмущений и спиновыми гамильтонианами. Обсуждаются предложенные недавно механизмы сверхпроводящего спаривания электронов за счет антиферромагнитного $\text{Cu}(3d) - \text{O}(2p)$ обмена.

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The existence of well-separated CuO_2 layers is a common and prominent structure peculiarity of new high- T_c superconductors. Now there is no doubt that it is just these layers that are the source of superconducting behaviour. We believe that the key electronic and magnetic

properties of oxide superconductors can be understood in terms of a two-dimensional tight-binding model which includes only copper d-orbitals of $(x^2 - y^2)$ type overlapping oxygen p_x , p_y -orbitals on a square network of Cu - O bonds. The objective of this paper is to derive an effective electron Hamiltonian for that planar system and to make its preliminary analysis. To carry it out, we follow the approach suggested by Bogolubov long ago^{1,2/} in developing the so-called polar model of metals^{3/}. This approach allows us, first, to represent the second-quantized Hamiltonian as an expansion in powers of a small overlapping parameter, $\epsilon S \ll 1$, of the Cu - O bond and, second, to employ a perturbation scheme in the operator form taking into account a strong degeneracy of the electron system examined. The general expressions derived will serve as a starting point for further studies of electronic and magnetic properties of layered superconducting compounds.

Consider a planar system with Cu ions at the square lattice points $\vec{r} = n\vec{a} + m\vec{b}$ and with two O ions per unit cell at the positions $\vec{g} = \vec{r} + \vec{\tau}$, ($\vec{\tau} = \vec{a}/2, \vec{b}/2$). Let \mathcal{H}_0 be the one-particle electron Hamiltonian of the system. Then starting from the ionic Cu^{2+} (d^9) state at an \vec{r} -site and solving the Schrödinger equation $\mathcal{H}_0 |\Psi^{(\lambda)}(\vec{r})\rangle = \epsilon^{(\lambda)} |\Psi_{\vec{r}}^{(\lambda)}(\vec{r})\rangle$ for d-electrons one finds that $\lambda = (x^2 - y^2)$ is the d-orbital with the highest atomic energy $\epsilon^{(x^2 - y^2)} \equiv E_d$ and thus half-filled (see, e.g.^{4/}). Further one adopts the fact that the wave function $\Psi_{\vec{r}}^{(\lambda)}(\vec{r})$ of the $\lambda = (x^2 - y^2)$ type is overlapped through the (pd σ)-bond with four nearest oxygen orbitals: two of them $\Phi_{\vec{r} \pm \vec{a}/2}^{(x)}(\vec{r})$ are of the p_x -type and two $\Phi_{\vec{r} \pm \vec{b}/2}^{(y)}(\vec{r})$ are of the p_y -type. These orbitals are of equal energy $\langle \Phi_{\vec{g}}^{(\alpha)} | \mathcal{H}_0 | \Phi_{\vec{g}}^{(\alpha)} \rangle = E_p$ and each of Cu - O bonds are characterized by the same overlap integral $\langle \Psi_{\vec{r}}^{(\lambda)}(\vec{r}) | \Phi_{\vec{r} \pm \vec{\tau}}^{(\alpha)}(\vec{r}) \rangle \equiv \epsilon S = \epsilon S^* \ll 1$. A chemical bond considered is largely ionic and its covalency degree is measured by the matrix element $\langle \Psi_{\vec{r}}^{(\lambda)}(\vec{r}) | \mathcal{H}_0 | \Phi_{\vec{r} \pm \vec{\tau}}^{(\alpha)}(\vec{r}) \rangle \equiv \epsilon SV - \epsilon S(E_d + E_p)/2$. All other atomic orbitals are assumed to exhibit much smaller overlaps for symmetry reasons and disregarded.

To obtain the second-quantized Hamiltonian of the system, we follow^{1,2/} and construct the set of orthogonalized atomic functions $\tilde{\Psi}_{\vec{r}}^{(\lambda)}(\vec{r})$, $\tilde{\Phi}_{\vec{g}}^{(\alpha)}(\vec{r})$ instead of the just introduced nonorthogonalized orbitals $\Psi_{\vec{r}}^{(\lambda)}(\vec{r})$, $\Phi_{\vec{g}}^{(\alpha)}(\vec{r})$. They can be written to the second order in (ϵS) as

$$\tilde{\Psi}_{\vec{r}}^{(\lambda)}(\vec{r}) = \left(1 + \frac{3}{2} \epsilon^2 S^2\right) \Psi_{\vec{r}}^{(\lambda)}(\vec{r}) - \frac{1}{2} \epsilon S \sum_{\pm \vec{\tau}'} \Phi_{\vec{r} + \vec{\tau}'}^{(\beta)}(\vec{r}) + \quad (1)$$

$$+ \frac{3}{8} \epsilon^2 S^2 \sum_{\pm \vec{r}'} \Psi_{\vec{f}+2\vec{r}'}(\vec{r}),$$

$$\tilde{\Phi}_{\vec{f}+\vec{r}}^{(\alpha)}(\vec{r}) = \Phi_{\vec{f}+\vec{r}}^{(\alpha)}(\vec{r}) - \frac{1}{2} \epsilon S [\Psi_{\vec{f}}(\vec{r}) + \Psi_{\vec{f}+2\vec{r}}(\vec{r})] + \quad (1)$$

$$+ \frac{3}{8} \epsilon^2 S^2 \sum_{\pm \vec{r}'} [\Phi_{\vec{f}+\vec{r}}^{(\beta)}(\vec{r}) + \Phi_{\vec{f}+2\vec{r}'}^{(\beta)}(\vec{r})],$$

and possess the property $\langle \tilde{\Psi}_{\vec{f}}(\vec{r}) | \tilde{\Phi}_{\vec{f} \pm \vec{r}}^{(\alpha)}(\vec{r}) \rangle = 0$. Now let us introduce the set of Fermi-operators $a_{j\sigma}^{\pm}$ ($a_{j\sigma}$) each of which creates (destroys) an electron with a spin σ in a state $|\Psi_{\vec{f}}(\vec{r})\rangle$ if $j = \vec{f}$ and in $|\Phi_{\vec{g}}^{(\alpha)}(\vec{r})\rangle$ if $j = \vec{g}$. Then the one-particle part of the electron Hamiltonian to the second order in ϵS can be represented in the form

$$\begin{aligned} \mathcal{H}_0 = & E_d \sum_{\vec{f}, \sigma} n_{\vec{f}, \sigma} + E_p \sum_{\vec{g}, \sigma} n_{\vec{g}, \sigma} + \epsilon t_{fg} \sum_{\langle \vec{f}, \vec{g} \rangle, \sigma} (a_{\vec{f}, \sigma}^+ a_{\vec{g}, \sigma} + \text{h.c.}) + \\ & + \epsilon^2 t_{ff} \sum_{\langle \vec{f}, \vec{f}' \rangle, \sigma} a_{\vec{f}, \sigma}^+ a_{\vec{f}', \sigma} + \epsilon^2 t_{gg} \sum_{\langle \vec{g}, \vec{g}' \rangle, \sigma} a_{\vec{g}, \sigma}^+ a_{\vec{g}', \sigma}, \end{aligned} \quad (2)$$

where $\langle i, j \rangle$ refers to neighbouring sites, and the hopping integrals can be expressed in terms of the above defined quantities as $\epsilon t_{fg} = \epsilon S [V - (E_d + E_p) / 2]$, $\epsilon^2 t_{ff} = \epsilon^2 S^2 [3/4 E_d + 1/4 E_p - V]$, $\epsilon^2 t_{gg} = \epsilon^2 S^2 [3/4 E_p + 1/4 E_d - V]$. Proceeding to the interaction Hamiltonian one should consider the dependence of Coulomb matrix elements

$$V(\vec{i}j / \vec{i}'j') = \int d^3 r_1 \int d^3 r_2 \psi_{\vec{i}}^*(\vec{r}_1) \psi_{\vec{j}}^*(\vec{r}_2) e^2 / r_{12} \psi_{\vec{j}'}(\vec{r}_2) \psi_{\vec{i}'}(\vec{r}_1)$$

on mutual electron site positions $\vec{i}, j, i', j' = \vec{f}, \vec{g}$. The main contributions up to the second order in ϵS are due to

$$V(\vec{i}j / \vec{i}j) \sim 0(1),$$

$$V(\vec{i}j / \vec{i}j') \sim V(\vec{i}j / \vec{i}'j) \sim \epsilon S, \text{ if } (j, j') = \text{n.n. or } (i, i') = \text{n.n.},$$

$$V(\vec{i}j / \vec{i}j') \sim V(\vec{i}j / \vec{i}'j) \sim \epsilon^2 S^2, \text{ if } (j, j') = \text{n.n.n. or } (i, i') = \text{n.n.n.},$$

$$V(\vec{i}\vec{j}/\vec{i}'\vec{j}') \sim \epsilon^2 S^2, \quad \text{if } (\vec{j}, \vec{j}') = \text{n.n.} \quad \text{and} \quad (\vec{i}, \vec{i}') = \text{n.n.n.}$$

Here n.n. and n.n.n. mean the nearest-neighbour and the next-to-nearest-neighbour sites. As a result, the interaction Hamiltonian can be written as

$$\begin{aligned} \mathcal{H}_{\text{int}} &= \mathcal{H}_{\text{int}}^{(0)} + \mathcal{H}_{\text{int}}^{(1)} + \mathcal{H}_{\text{int}}^{(2)}, \\ \mathcal{H}_{\text{int}}^{(0)} &= \frac{1}{2} \sum_{\vec{i}, \vec{j}; \sigma, \sigma'} V(\vec{i}\vec{j}/\vec{i}\vec{j}) n_{i\sigma} (n_{j\sigma'} - \delta_{ij} \delta_{\sigma\sigma'}), \\ \epsilon \mathcal{H}_{\text{int}}^{(1)} &= \sum_{\langle \vec{i}, \vec{j} \rangle = \text{n.n.}} \sum_{\vec{\ell}; \sigma, \sigma'} V(\vec{i}\vec{\ell}/\vec{j}\vec{\ell}) (n_{\ell\sigma'} - \delta_{i\ell} \delta_{\sigma\sigma'}) a_{i\sigma}^+ a_{j\sigma'}, \\ \epsilon^2 \mathcal{H}_{\text{int}}^{(2)} &= \sum_{\langle \vec{i}, \vec{j} \rangle = \text{n.n.n.}} \sum_{\vec{\ell}; \sigma, \sigma'} V(\vec{i}\vec{\ell}/\vec{j}\vec{\ell}) n_{\ell\sigma'} a_{i\sigma}^+ a_{j\sigma} + \\ &+ \frac{1}{2} \sum_{\substack{\langle \vec{i}, \vec{i}' \rangle = \text{n.n.} \\ \langle \vec{j}, \vec{j}' \rangle = \text{n.n.} \\ \sigma, \sigma'}} V(\vec{i}\vec{j}/\vec{j}'\vec{i}') a_{i\sigma}^+ a_{j\sigma'}^+ a_{j'\sigma'} a_{i'\sigma}. \end{aligned} \quad (3)$$

The Hamiltonian (2), (3) has a very complicated form to be treated. Further in this paper we restrict ourselves to the most strong on-site Coulomb repulsion $V(\vec{i}\vec{i}/\vec{i}\vec{i}) \equiv V_{d,p}$. In this case the Hamiltonian reduces to a generalized two-sublattice Hubbard model with hopping terms being considered as a perturbation $\mathcal{H} \rightarrow H = H_0 + \epsilon H_1 + \epsilon^2 H_2$, where

$$\begin{aligned} H_0 &= E_d \sum_{\vec{f}, \sigma} n_{f\sigma} + E_p \sum_{\vec{g}, \sigma} n_{g\sigma} + \frac{1}{2} V_d \sum_{\vec{f}, \sigma} n_{f\sigma} n_{f-\sigma} + \\ &+ \frac{1}{2} V_p \sum_{\vec{g}, \sigma} n_{g\sigma} n_{g-\sigma}, \quad H_1 = t_{fg} \sum_{\langle \vec{f}, \vec{g} \rangle, \sigma} (a_{f\sigma}^+ a_{g\sigma} + \text{h.c.}), \quad (4) \\ H_2 &= t_{ff} \sum_{\langle \vec{f}, \vec{f}' \rangle, \sigma} a_{f\sigma}^+ a_{f'\sigma} + t_{gg} \sum_{\langle \vec{g}, \vec{g}' \rangle, \sigma} a_{g\sigma}^+ a_{g'\sigma}. \end{aligned}$$

We choose the parameters of the model to be such that, first, an initial undoped state belongs to a manifold L of state vectors $|\phi_0(\{N_i\})\rangle^{(\text{undop.})}$ with single occupied \vec{f} -sites and double occupied \vec{g} -sites, i.e. $|\phi_0(\{N_i\})\rangle^{(\text{undop.})} = |\phi_0(\{N_f=1, N_g=2\})\rangle$ and, second, doping

creates holes at \vec{g} -sites rather than at \vec{f} -sites, i.e. $|\phi_0(\{N_i\})\rangle \xrightarrow{(\text{dop. } \frac{1}{2})} = |\phi_0(\{N_f = 1, N_g = 2, 1\})\rangle$. This is true when $(E_p + V_p) - E_d \equiv \xi > 0$ and $(E_d + V_d) - (E_p + V_p) = V_d - \xi > 0$. To be more definite, we assume also that $\epsilon t_{fg}, \epsilon^2 t_{ff}, \epsilon^2 t_{gg} \ll V_d, \xi, V_d - \xi$, and do not constrain a value of V_p . A similar model was proposed by Emery^{/5/} and investigated by several authors^{/6,7/}.

Now we are interested in the ground state and low-lying excited states which clearly belong to the above-defined manifold L of single occupied \vec{f} -site states. Let us introduce the operator P projecting an arbitrary state vector $|\phi\rangle$ of the system onto L, i.e. $P|\phi\rangle = |\phi_0\rangle$. Note that $H_0 P|\phi\rangle = E_0 P|\phi\rangle$ and thus the energy level E_0 is strongly degenerated. In its turn the projection operator $(1 - P)$ gives highly excited, polar, states of the system separated from the E_0 -level by energies $V_d, V_d - \xi$ and ξ . To remove the degeneracy mentioned, we find an effective Hamiltonian $\tilde{H}P$ which operates in the L subspace, instead of initial H (from (4)). The operator form of perturbation theory developed in^{/1-2/} permits us to obtain the following expansion

$$\tilde{H}P = P\tilde{H}_0P + \sum_{n=1}^{\infty} \epsilon^n P\tilde{H}_n P. \quad (5)$$

The problem will be treated to the fourth order in ϵ . Let us introduce the operator $R = (H_0 - E_0)^{-1} \times (1 - P)$ which involves the excited polar states to the theory as virtual ones and write the necessary expressions

$$(1) \quad P\tilde{H}_0P = P(E_d \sum_{\vec{f}, \sigma} n_{\vec{f}\sigma} + E_p \sum_{\vec{g}, \sigma} n_{\vec{g}\sigma} + \frac{1}{2} V_p \sum_{\vec{g}, \sigma} n_{\vec{g}\sigma} n_{\vec{g}-\sigma})P, \quad (6)$$

$$(\epsilon) \quad P\tilde{H}_1P = PH_1P, \quad (7)$$

$$(\epsilon^2) \quad P\tilde{H}_2P = P\tilde{H}_2^{(1)}P + P\tilde{H}_2^{(2)}P, \quad (8)$$

$$P\tilde{H}_2^{(1)}P = -PH_1RH_1P, \quad P\tilde{H}_2^{(2)}P = PH_2P,$$

$$(\epsilon^3) \quad P\tilde{H}_3P = P\tilde{H}_3^{(1)}P + P\tilde{H}_3^{(2)}P, \quad (9)$$

$$P\tilde{H}_3^{(1)}P = PH_1RH_1RH_1P, \quad P\tilde{H}_3^{(2)}P = -PH_1RH_2P - PH_2RH_1P,$$

$$(\epsilon^4) \quad P\tilde{H}_4P = \sum_{i=1}^4 P\tilde{H}_4^{(i)}P, \quad (10)$$

$$\begin{aligned}
\tilde{P}H_4^{(1)}P &= -PH_1RH_{1\downarrow}RH_1RH_1P, & \tilde{P}H_4^{(2)}P &= -PH_2RH_2P, \\
\tilde{P}H_4^{(3)}P &= PH_1RH_2RH_{1\downarrow}P, \\
\tilde{P}H_4^{(4)}P &= PH_1RH_{1\downarrow}RH_2P + PH_2RH_{1\downarrow}RH_1P.
\end{aligned} \tag{10}$$

Below we follow ^{1/} and treat various perturbative contributions (6)-(10) as exchange spin Hamiltonians. We present some principal results gained in this way without details.

One can see that $\tilde{P}H_1P = \tilde{P}H_3P = 0$ holds both in the undoped ($N_f = 1, N_g = 2$) and doped ($N_f = 1, N_g = 2, 1$) system. Proceeding to even terms let us start with the former case. Then one can get

$$\tilde{P}H_2^{(1)}P = J'_{fg} \sum_{\langle \vec{f}, \vec{g} \rangle} \vec{S}_{\vec{f}} \vec{S}_{\vec{g}}. \tag{11}$$

Here $J'_{fg} = 2t_{fg}^2 / (V_d - \mathcal{E})$ and \vec{S}_i is the spin operator at an i -th site. Since $\langle \phi_0 | \vec{S}_i | \phi_0 \rangle$ (undop.) = 0 and $\tilde{P}H_2^{(2)}P = 0$, the second order contribution does not remove the spin degeneracy of f -sites. The next approximation $\sim \epsilon^4$ yields

$$\tilde{P}H_4^{(1)}P + \tilde{P}H_4^{(2)}P = (J'_{ff} + J''_{ff}) \sum_{\langle \vec{f}, \vec{f}' \rangle} \vec{S}_{\vec{f}} \vec{S}_{\vec{f}'}, \tag{12}$$

where $J'_{ff} = 2t_{fg}^4 / V_d (V_d - \mathcal{E})^2 > 0$, $J''_{ff} = 2t_{ff}^2 / V_d > 0$; besides

$$\tilde{P}H_4^{(3)}P = I_{ff} \sum_{\langle \vec{f}, \vec{f}' \rangle} (S_{\vec{f}}^+ S_{\vec{f}'}^- + S_{\vec{f}}^- S_{\vec{f}'}^+), \tag{13}$$

where $I_{ff} = t_{fg}^2 t_{ff} / (V_d - \mathcal{E})^2$ and the final term is $\tilde{P}H_4^{(4)}P = 0$. Thus, the behaviour of f -sites electron spins is governed by the anisotropic Heisenberg Hamiltonian with exchange constants $J_{ff}^z = J'_{ff} + J''_{ff}$, $J_{ff}^x = J_{ff}^y = J_{ff}^z + I_{ff}$. In particular, concerning CuO_2 layers in the La CuO_4 compound ^{8/} one may deduce that the parameters of the model considered are such that they make an antiferromagnetic ground state preferable.

Now let us turn to the doped system. The second-order contribution now gives more complicated Hamiltonian forms:

$$\begin{aligned}
\tilde{P}H_2^{(1)}P &= (J'_{fg} + J''_{fg}) \sum_{\langle \vec{f}, \vec{g} \rangle} \vec{S}_{\vec{f}} \vec{S}_{\vec{g}} \rightarrow + \\
&+ \frac{J'_{fg} + J''_{fg}}{2} \sum_{\langle \vec{f}, \vec{g} \neq \vec{g}' \rangle} (S_{\vec{f}}^- a_{\vec{g}\uparrow}^+ a_{\vec{g}'\downarrow} + S_{\vec{f}}^+ a_{\vec{g}\downarrow}^+ a_{\vec{g}'\uparrow}) - \\
&- \frac{J'_{fg}}{2} \sum_{\langle \vec{f}, \vec{g} \neq \vec{g}' \rangle} (n_{\vec{f}\downarrow} a_{\vec{g}\uparrow}^+ a_{\vec{g}'\uparrow} + n_{\vec{f}\uparrow} a_{\vec{g}\downarrow}^+ a_{\vec{g}'\downarrow}) + \\
&+ \frac{J''_{fg}}{2} \sum_{\langle \vec{f}, \vec{g} \neq \vec{g}' \rangle} (n_{\vec{f}\uparrow} a_{\vec{g}\uparrow}^+ a_{\vec{g}'\uparrow} + n_{\vec{f}\downarrow} a_{\vec{g}\downarrow}^+ a_{\vec{g}'\downarrow}), \quad (14)
\end{aligned}$$

$$PH_2^{(2)}P = t_{gg} \sum_{\langle \vec{g}, \vec{g}' \rangle} a_{\vec{g}\sigma}^+ a_{\vec{g}'\sigma} \quad (15)$$

Here $J'_{fg} = 2t_{fg}^2 / (V_d - \epsilon)$, $J''_{fg} = 2t_{fg}^2 / \epsilon$, and $\langle \vec{f}, \vec{g} \neq \vec{g}' \rangle$ implies summation over pairs of $\vec{g} \neq \vec{g}'$ sites with a common intervening \vec{f} site under summation too. Of course, one should keep in mind that derived expressions (14), (15) are applicable in the L subspace where $N_f = 1$, $N_g = 2, 1$. The next fourth-order terms retain the spin forms (12), (13) provided that a small doping causes a weak renormalization of exchange constants. The derived expressions give us a starting point for further studies of electronic and magnetic properties of layered superconductors.

Emery^{5/}, treating this model (with $\epsilon_{H_2} = 0$) actually on a similar perturbative basis, proposed a mechanism of superconducting pairing of O(2p) holes through O(2p) - Cu(3d) exchange. We note that the present formally strict approach excludes the virtual process underlying the antiferromagnetic pairing mechanism proposed by Emery. On the other hand, the qualitative suggestion made by Hirsh^{6/} seems to us very attractive. Hamiltonians (14), (15) and (12), (13) derived in this paper may serve as a quantitative basis in developing this suggestion.

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