Electron pairs’ sliding states in superconductivity

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A quantum-mechanical model of Cu-O-Cu-O four-center four-electron part of the copper-oxide plane embedded in a superconducting crystal La\textsubscript{2−x}Sr\textsubscript{x}CuO\textsubscript{4} (LSCO) is considered. It is shown that displacing the nearest-neighbor La(Sr)O plane lattice atoms off by a distance as small as \( \pm 0.1 \) Å, i.e. of the order of ground state vibrations dictated by the Heisenberg uncertainty principle, may trigger a dramatic change of the ground state electronic charge distribution in the CuOCuO system. This results in the electron pairs’ concerted sliding within the system over distances about 2 Å, i.e. close to the copper oxygen atomic distance. The effect depends crucially on the lattice crystal field and doping. The appearance of energy gaps associated with the electronic states’ avoided crossings points to a universal nature of the phenomenon. The results suggest a generalization of the models used up to now in description of strongly correlated electrons.

After 34 years from the discovery by Bednorz and Müller the mechanism behind the high-temperature superconductors (HTS) is still unclear (for a recent pedagogical review see [1]). There is a consensus that strong electronic correlation is to be taken into account [2] but the goal of finding and solving the proper model is not yet achieved (even though the magnetic properties are probably sufficiently well described by the Hubbard [3] or \( t-J \) models [4]). On the other hand the highest critical temperatures for cuprates correspond to a definite CuO distance equal to 1.923 Å - the discovery virtually unnoticed by the HTS community [6], confirming an earlier less accurate observation [2], indicates a sharp electronic instability with respect to lattice distances. The instability has been suggested first by Burdett [8] as an avoided crossing point of two hypothetical electronic states (a result of a low-energy conical intersection, see e.g. [5]). The present letter shows by explicit calculation the importance of ground state lattice vibrations on the presence of avoided crossings of electronic states.

Stable atomic and molecular structures represent a subject of most quantum chemical investigations. In the present letter the target is quite the opposite: to apply theory to find such an unstable electronic ground-state that, under some small changes of the nuclear framework, may produce dramatically different electronic density distribution with a kind of electronic pairs sliding (‘sliding states’) - a prerequisite of the resistance-free electron pairs’ flow.

Although the model presented is general we chose to focus on a particular lattice as an example, here taken as one of the first HTSs discovered: the La\textsubscript{2−x}Sr\textsubscript{x}CuO\textsubscript{4} crystal (LSCO), where \( x \) denotes the doping level. The model pertains to a fragment of the LSCO crystal, Fig.1.

An \textit{ab initio} Valence Bond (VB) method [10] of solving the Schrödinger equation for system I embedded in the LSCO crystal field produced by system II is applied, Fig.1 (the model allows also to mimic the doping by adding, removing, replacing and/or shifting some surrounding lattice ions of system II). The wave functions and energies are obtained by using Ritz variational approximation, with \( N = 10 \) normalized and mutually orthogonal resonance (or diabatic) structures \( \phi_i \) forming the basis set, \( \psi_n = \sum_{i=1}^{N} c_{ni}\phi_i \):

\[
\begin{align*}
\phi_1 &= |Cu\uparrow O Cu\downarrow\downarrow O\rangle \text{ ionic CuCu} \\
\phi_2 &= |Cu O\uparrow\downarrow Cu O\downarrow\rangle \text{ ionic OO} \\
\phi_3 &= |Cu O\uparrow\downarrow Cu\uparrow\downarrow O\rangle \text{ ionic OCu} \\
\phi_4 &= |Cu\uparrow\downarrow O Cu\downarrow\rangle \text{ ionic Cu...O} \\
\phi_5 &= |Cu\downarrow O\uparrow Cu\downarrow O\rangle \text{ antiferromagnetic 1} \\
\phi_6 &= |Cu\uparrow O\downarrow Cu\uparrow\downarrow O\rangle \text{ antiferromagnetic 2} \\
\phi_7 &= |Cu\uparrow\downarrow O Cu\uparrow\rangle \text{ ionic Cu/antiferro1} \\
\phi_8 &= |Cu\uparrow\downarrow O Cu\downarrow O\rangle \text{ ionic Cu/antiferro2} \\
\phi_9 &= |Cu O\downarrow Cu\uparrow O\rangle \text{ antiferro1/ionic O} \\
\phi_{10} &= |Cu O\uparrow Cu\downarrow O\rangle \text{ antiferro2/ionic O}. \quad (1)
\end{align*}
\]

The \( i \)\textsuperscript{th} resonance structure \( \phi_i \) represents a normalized Slater determinant built of four orthonormal atomic spinorbitals. To minimize the termini effects the symmetric orthogonalization [11] has been performed for nine atomic orbitals (AOs): \( 3d_{xy}^2 \) (for copper atoms, \( xy \) is a CuO\textsubscript{2} plane) and \( 2p_x^2 \) (for oxygen atoms) centered, respectively, along the \( O_{-1}, Cu_{0}, O_{1}, Cu_{1}, O_{2}, Cu_{2}, O_{3}, O_{3} \) axis (\( x \)), see the inset of Fig.1. Due to the symmetric orthogonalization the resulting orthogonal orbitals (OAOs) have the least possible deviation from the starting AOs. The four OAOs that are to be used to build \( \phi_i \) functions are centered on four consecutive Gaussian spherical atomic cores symbolized by the centers \( Cu_{1}, O_{1}, Cu_{2}, O_{2} \) (system I).

The present approach uses a superposition of the diabatic structures to describe the electron transfer, and

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FIG. 1: The LSCO crystal fragment considered: system I treated quantum-mechanically is embedded in the electrostatic field of system II. In system I, the inner electronic shells of an atom together with its nucleus, are modeled as a spherical Gaussian pseudo-nucleus, with the exponent coefficients 0.577 $u$ and 0.115 $u$ for the oxygen and copper atoms, respectively (the corresponding mean radii are chosen to be equal to the atomic ones, the core charges 1.05 and 0.95 are used for the copper and the oxygen atoms, respectively. The $3d_{Cu}$ and $2p_{O}$ orbitals are taken as composed of Gaussian type spherical lobes, with the nucleus-lobe distance equal to 0.5 $u$ and the lobe’s exponent values: $a_{3d} = 0.04$ and $a_{2p} = 0.16$ for which the effect is most pronounced.

The model’s calculated electronic states depend in an important way on the lattice ions’ displacements in system II (off their lattice positions) $d \equiv d_{O} = d_{La}$. In order to be on the safe side we have reduced this coupling by a factor of $\frac{1}{2}$ and modeled this effect by $\Delta a_{3d}/a_{3d} = 0.15 \text{tanh}(10d_{O}\bar{q}_{Cu})$ and $\Delta a_{2p}/a_{2p} = 0.30 \text{tanh}(10d_{La}\bar{q}_{O})$, where $\bar{q}_{Cu}$ and $\bar{q}_{O}$ are the mean values of the nearest-neighbor ions’ charge for the copper and the oxygen atoms of system I, respectively. The nominal ionic charges of system II are scaled by $\eta = \frac{1}{3}$.

thus, in a general sense, goes along with the heuristic Marcus two-parabolas picture of electron transfer \cite{11} and its three-parabolas extensions by Larsson \cite{12}. The electronic Hamiltonian ($\hat{H}$) of system I contains all the (non-relativistic) terms: the kinetic energy and Coulombic interaction operators of the four electrons with themselves, with the cores and the core-core-interaction of system I, as well as four electrons with 102 point-like ions of system II. The model presented (when modified with other types of AOs) shows the sliding effect to appear also for the $\pi$ states coming from the $3d_{Cu}$ and $2p_{O}$ interaction, as well as for the interacting $1s$ - type orbitals ($\sigma$ state).

Fig. 2 and schematic Fig. 3 show the dependence of the ground- and the first excited electronic singlet states as functions of the ions’ lattice displacement $d$. Along the curves the corresponding values of the dipole moment are given (in Debye units, D). The values of the dipole moments reflect the presence of the avoided crossings: between the highly polarized ionic CuCu and low-polarity antiferromagnetic states (left) and between the antiferromagnetic and the oppositely polarized ionic OO states (right).

FIG. 2: The energies (parameters as in the text) of the ground- and the first excited electronic singlet states as functions of the ions’ lattice displacement $d$. As we can see the ions’ displacements of system II may lower the energy of an excited large-polarity state to such an extent that it becomes the ground state, instead of the low-polarity and usually lowest-energy antiferromagnetic state, thus changing profoundly the character of the ground state. It should be emphasized, as explained below, that the displacements needed (about 0.1 Å) are of the order of the ground state amplitude of vibrations of the lattice. The two avoided crossings gaps appear, $\Delta_{cross1}$ and $\Delta_{cross2}$: for the parameters assumed in this letter they are equal to $\Delta_{cross1} \approx 1.5$ eV and $\Delta_{cross2} \approx 0.92$ eV.

The calculated ground-state electron density distribution $\rho_0 (\mathbf{r}) = \langle \psi_0 | \sum_{i=1}^4 \delta(\mathbf{r} - \mathbf{r}_i) \psi_0 \rangle$, $\mathbf{r}_i$ being the $i^{th}$ electron position, as a function of the ions’ displacement $d$, shows the details of the two quite abrupt changes

FIG. 3: Schematic representation (‘letter A’) of the ground and excited states illustrating electron pairs’ sliding states

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at two consecutive avoided crossings during a vibration of a certain amplitude corresponding to a long-distance concerted sliding of the two interacting electron pairs by about the CuO distance 1.92 Å.

The model used allows to study doping effects. At a chosen doping \(x \sim 0.125\) (in an example, Fig.1: two Sr ions replacing two La ions, with appropriate changes in charges of two O ions to keep charge neutrality) and optimizing orbital parameters the two avoided crossings have been within a reasonable vibrational amplitude. If the doping have been chosen bigger then the avoided crossings are still present but the \(d_{\text{cross}}\) values shift by about a hundredth of Å per an added/removed dopant atom. Therefore, if initially the values of \(d_{\text{cross}}\) correspond to the physical range of the ions’ vibrations, the doping exceeding some degree may lead to going outside of an effective vibrationally-allowed \(d\). The disappearance of the sliding effect with the excessive doping explains two puzzles: why doping is necessary for cuprates to obtain a HTS and why there exists an optimal doping. On the other hand the fact that the energy levels in the CuO plane depend very little on the oxygen mass and only parametrically on the vibrations of the La(Sr)O plane may explain the observation that the isotopic effect in HTS is very small, in distinction to the BCS theory.

It is also important to note that the vibrations of the lattice, crucial for the proposed effect, are for \(T \to 0\) given by (an average displacement squared in one direction of a single atom of mass \(M\) in a crystal in the Debye theory with Debye temperature \(\theta_D\) [14])

\[
\langle \zeta^2 \rangle = \frac{3kT}{4Mk_B\theta_D} \left(1 + \frac{2\pi^2T^2}{3\theta_D^2} + O\left(\frac{T}{\theta_D^3}\right)\right).
\]

(2)

As we see, the amplitudes of vibrations are dominated by ground state vibrations (existing for \(T = 0\) as a result of the Heisenberg uncertainty principle) and the thermal excitations start to be important only at high temperatures, comparable to \(\theta_D\). These ground state vibrations have larger amplitudes for smaller Debye temperature.

In view of the effect described in this letter, it appears not accidental that the best known HTS materials have lattices based on elements with very low Debye temperatures – mercury (72 K), thallium (78 K), barium (111 K), bismuth (120 K) or lanthanum (135 K). It is consistent with the fact that experimentally, and unlike the BCS theory, the critical temperature for the HTSs increases with decreasing Debye temperature [15]. Plugging in the numbers for lanthanum oxide we get \(\sqrt{\langle \zeta^2 \rangle^0} \approx 0.06\) Å for the ground state average displacements and it is approximately the value where the electronic ground state of system I changes its character from antiferromagnetic to ionic as seen in Fig.2.

Since the dipole moments can be very large (up to \(\sim \pm 20\) D) the dipole-dipole interactions may make the electron sliding mechanism to become a coherent motion of many electron pairs within the CuO_2 planes. The motion might spread throughout the whole lattice, especially along the dipole alignment lines (‘stripes’). At a given temperature, it may be viewed as a frustrating competition of the charge density waves (CDW) vs the spin density waves (SDW). Such a spontaneous polarization [16] would additionally lower the ground-state energy, thus increasing the gap by \(\Delta_{\text{coh}}\).

The method used in this letter has several differences with respect to usual approaches. The first difference comes from the VB method’s real-space material-dependent insight into the electronic correlation: the electron pairs’ formation, interaction and dissociation, also with appearance of chemical bonds. Secondly, in the tight-binding and band structure pictures crystal orbitals describe only the exchange part of the electron-electron correlation and take into account only the ground state. The question which model should be used within the latter approach to simulate the mechanism of superconductivity described in this letter requires a comment. In the undoped case (antiferromagnetic) the presence of ionic states is irrelevant since they correspond to too large amplitudes of the LaO plane oscillations and then we expect that the Heisenberg-like model should adequately describe the case. In the appropriately doped case both the Cu and O orbitals should be taken into account and then we should use the Emery three-band model [17, 18]. However, the effect described in this letter shows that the parameters used in the model (or its simplified versions) should depend on the position of La(Sr)O planes and even the most general models considered up to now did not take into account the time dependence of parameters induced by the La(Sr)O oscillations. It follows that the effective models aiming to describe HTS should be generalized to time dependent (oscillating) parameters. In the three-band model the mechanism described in this letter could be approximately simulated by a generalization in which the Coulomb repulsion terms on oxygen \(U_p\) and on copper \(U_d\) (treated in the previous models as constants) depend on time with the opposite phase, schematically

\[
U_d(t) \sim U_0^d + \Delta_p \cos(\omega_s t), \quad U_p(t) \sim U_0^p - \Delta_d \cos(\omega_s t).
\]

(3)

\(\omega_s\) is related to oscillation frequencies in the La(Sr)O plane and can be estimated from the Heisenberg uncertainty principle \(\sqrt{\Delta \zeta^2 \Delta \rho^2} \geq \hbar/2\) as

\[
\omega_s \sim \frac{\hbar}{2M(\Delta \zeta^2)} \sim 1.3 \cdot 10^{13} \text{ s}^{-1}.
\]

(4)

for the lanthanum atom mass and \(\sqrt{\Delta \zeta^2} \approx 0.06\) Å(from [2] we see that \(\omega_s = 2k_B\theta_D/3h\)). \(U_0^d\) and \(U_0^p\) are estimated as 5-6 eV and 2-3 eV, respectively [17]. The depths of the oscillation \(\Delta s\) depend on the doping – they can be estimated as half of the gaps \(\Delta_{\text{cross}}\) and \(\Delta_{\text{cross}}^2\) so for our case of \(x = 0.125\) it gives \(\Delta_p \approx 0.8\) eV and \(\Delta_d \approx 0.5\) eV. One could also add the dependence of the hopping parameters \(t\) on time with frequency \(\omega_c\) related to the oscillation frequencies in the CuO plane. Such time dependences required by the presented mechanism may significantly change the properties of the models. As mentioned
earlier, because of very large electric dipole moments in ionic states, one should also add dipole-dipole interactions extending over larger distances than just nearest neighbors.

The described mechanism indicates a possible general nature of the electron pairs’ sliding appearance whenever the electronic instability (avoided crossing) can be reached by a suitable choice of materials (elements, lattice structure, doping) and external conditions (like pressure). It leads to a necessity, in the three-band model or its simplified versions, to introduce time dependence of the parameters. The mechanism is also an example of the quantum ground state vibrations (of the La(Sr)O plane) coupled to a quantum system (electronic states in the CuO planes) strongly enough to significantly modify its properties. In conclusion, electron pairs’ sliding states described in this letter may possibly provide an explanation of the presence of high temperature superconductivity in copper-oxide planes surrounded by very special lattice structures.

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