The 3d-to-4s-by-2p highway to superconductivity in cuprates

T. M. Mishonov, J. O. Indekeu, and E. S. Penev
\textsuperscript{1}Laboratorium voor Vaste-Stoffysica en Magnetisme, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium\textsuperscript{2}Faculty of Physics, Sofia University "St. Kliment Ohridski", 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria
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High-temperature superconductors are nowadays found in great variety and hold technological promise. It is still an unsolved mystery that the critical temperature $T_c$ of the basic cuprates is so high. The answer might well be hidden in a conventional corner of theoretical physics, overlooked in the recent hunt for exotic explanations of new effects in these materials. A forgotten intra-atomic $s$-$d$ two-electron exchange in the Cu atom is found to provide a strong ($\sim$ eV) electron pairing interaction. A Bardeen-Cooper-Schrieffer approach can explain the main experimental observations and predict the correct $d_{x^2-y^2}$ symmetry of the gap.

The discovery of high-temperature superconductivity in cuprates and the subsequent “research rush” have led to the appearance of about 100,000 papers to date. Virtually every fundamental process known in condensed matter physics was probed as a possible mechanism of this phenomenon. Nevertheless, none of the theoretical efforts resulted in a coherent picture. For the conventional superconductors the mechanism was known to be the interaction between electrons and crystal-lattice vibrations, but the development of its theory lagged behind the experimental findings. The case of cuprate high-$T_c$ superconductivity appears to be opposite: we do not convincingly know which mechanism is to be incorporated in the traditional Bardeen-Cooper-Schrieffer (BCS) theory. Thus the path to high-$T_c$ superconductivity in cuprates, perhaps carefully hidden or well-forgotten, has turned into one of the long-standing mysteries in physical science.

In contrast with all previous proposals, we advance the exchange of two electrons between the 4$s$ and $3d_{x^2-y^2}$ shells of the Cu atom as the origin of high-$T_c$ superconductivity in the layered cuprates and show that the basic spectroscopic, thermodynamic and kinetic experiments can be explained by it. This process has been familiar since the dawn of quantum mechanics and is known to be responsible for the magnetism of transition metals. Its energetic characteristic is referred to as the $s$-$d$ exchange amplitude (or integral) $J_{sd}$. The gist of this two-electron correlation is sketched in Fig. 1. The question then naturally arises as to how this exchange process can trigger pairing between electrons with opposite momenta and spins, the so-called Cooper pairs.

The underlying idea is analogous to Heitler and London’s reasoning which led to their celebrated model for the valence bonding of the H$_2$ molecule: The strong electron correlation brought about by the ubiquitous Coulomb repulsion lowers the energy when the two electrons have opposite spins (the singlet state). In quantum mechanics, according to the Hellmann-Feynman theorem, this energy decrease “drives” the attractive interatomic force. Reverting to the Cu atom, Fig. 1, one can think of the $s$-$d$ exchange as an “intra-atomic valence bond”. We shall further argue that it is the specific crystal structure of the cuprates that renders this intensive process macroscopically observable, “disguised” as the phenomenon of superconductivity for temperatures lower than some critical value $T < T_c$.

Superconducting cuprates have as their main structural detail the copper-oxygen plane shown in Fig. 2 (a). It has previously been demonstrated that its normal-phase electronic properties can be understood on the basis of Bloch’s tight-binding formalism (chemists would call it an extended Hückel method) applied to the set of atomic orbitals indicated in Fig. 2 (b). This plane behaves much like a two-dimensional metal. Electronic

FIG. 1: Pairing two-electron exchange amplitude $J_{sd}$ “hidden” in the Cu atom. (a) Classical Bohr-Sommerfeld representation of the $s$-$d$ two-electron exchange process. The inset shows how the Coulomb scattering leads to an effective electron spin exchange. (b) Electron charge distribution for Cu 4$s$ and Cu 3$d$ orbitals: the dashed line marks the Cu-O distance in the CuO$_2$ plane.
Bloch states of quasi-momentum $\mathbf{p} = (p_x, p_y) \in (0, 2\pi)$ are described by a four-component tight-binding wave function $\psi_\mathbf{p} = (D_\mathbf{p}, S_\mathbf{p}, X_\mathbf{p}, Y_\mathbf{p})$. At $T = 0$ these states are occupied up to the Fermi energy $E_F$. The corresponding energy level is comprised in a single conduction band $\varepsilon_\mathbf{x}$ of dominant Cu 3$d_{x^2-y^2}$ character, Fig. 2 (a). Thus, the amplitude for a conduction electron to be Cu 4$s$ is $S_\mathbf{p}$. $D_\mathbf{p}$ corresponds to Cu 3$d_{x^2-y^2}$, $X_\mathbf{p}$ to O 2$p_x$, and $Y_\mathbf{p}$ to O 2$p_y$, Fig. 2 (b).

The remarkable success of the CuO$_2$ plane in mediating high-$T_c$ superconductivity is due to the following reasons. (i) The quasi-two-dimensional $d$-band $\varepsilon_\mathbf{x}$ created by $p$-$d$ hybridization is relatively narrow and the density of states rather high. The wide $s$-band resulting mainly from $s$-$p$ hybridization is empty, which is why up to now the $s$-$d$ model has not been applied. (ii) In order for the $s$-$d$ exchange process to become a pairing mechanism the $s$- and $d$-levels must be close. A virtual population of the $s$-level by band hybridization is needed in order to make the $J_{sd}$ amplitude operative. Indeed, the conduction $d$-band is the result of an $s$-$p$-$d$ hybridization in the CuO$_2$ plane. Another favorable factor for hybridization is the proximity of the O 2$p_x$ and Cu 3$d_{x^2-y^2}$ levels. As the 3$d$ and 4$s$ states are orthogonal the hybridization requires a go-between, the O 2$p$ orbital. Hence this theory can be nicknamed “3$d$-to-4$s$-by-2$p$ highway to high-$T_c$ superconductivity in cuprates”.

The foregoing discussion can be put in mathematical form. The central entity is the many-particle Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_\text{int}$. Here $\hat{H}_0$ describes $\hat{S}$ self-consistent motion of independent Fermi particles in Bloch-Hückel approximation, and $\hat{H}_\text{int}$ specifies the interaction. Following the seminal works by Schubin and Wonsowsky [7], Vonsovskii [8], and Zener [9], cf. the Feynman lectures on physics [10], we set up the $s$-$d$ pairing Hamiltonian for the CuO$_2$ plane

$$\hat{H}_\text{int} = -J_{sd} \sum_{\mathbf{n}, \alpha, \beta} \hat{S}^\dagger_{\mathbf{n}\alpha} \hat{D}^\dagger_{\mathbf{n}\beta} \hat{S}_{\mathbf{n}\beta} \hat{D}_{\mathbf{n}\alpha}, \quad \alpha, \beta = \uparrow, \downarrow. \quad (1)$$

This Hamiltonian is written in the language of second quantization but one can easily trace the connection with the classical Bohr-Sommerfeld picture, Fig. 2 (a). $\hat{D}_{\mathbf{n}\alpha}$ is the Fermi operator for annihilating a 3$d_{x^2-y^2}$ electron with spin projection $\alpha$ in the nth unit cell. The electron is then recreated without spin flip in the 4$s$ state by the Fermi creation operator $\hat{S}^\dagger_{\mathbf{n}\alpha}$. Simultaneously, another electron with spin $\beta$ makes a reverse hop, from 4$s$ to 3$d_{x^2-y^2}$ in the same Cu atom. Thus, the $\hat{S}^\dagger \hat{D}^\dagger \hat{S} \hat{D}$ product in Eq. (1) represents the two-electron exchange drawn as a double arrow in Fig. 2 (b) and shown in Fig. 2 (a).

A model which incorporates a Hamiltonian of the form $\hat{H} = \hat{H}_0 + \hat{H}_\text{int}$ implies the validity of the Fermi-liquid picture for the cuprates. That is, we assert that an electron is merely a Fermi quasiparticle and not a composite object displaying spin-charge separation. Two key experiments [11, 12] have shown that this is correct. The long-sought bilayer splitting in the electronic structure of the cuprates was observed [11] for overdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (BSCCO). Furthermore, the overdoped Tl$_2$Ba$_2$CuO$_{6+\delta}$ was found [12] to obey the 150-years-old Wiedemann-Franz law to a remarkable accuracy of the Sommerfeld’s value for the Lorentz ratio. Let us stress also that the linear temperature dependence of the normal-state resistivity is an intrinsic property [13] of the “layered” electron gas and cannot be used as an argument in favor of non-Fermi-liquid behavior.

We now apply the traditional BCS approach [3] to the Hamiltonian $\hat{H}$ and derive an equation for the basic characteristic of superconductors—the energy gap $\Delta_p(T)$ (the energy needed to break up a Cooper pair is $2\Delta$). The local, intra-atomic character of the pairing interaction tremendously simplifies the BCS gap equation and the solution has the plain form

$$\Delta_p(T) = \Xi(T)e_p, \quad e_p = S_p D_p. \quad (2)$$

The order parameter $\Xi(T)$, which satisfies the standard BCS gap equation, is maximal at $T = 0$ and vanishes for $T \rightarrow T_c$. The $S_p D_p$ product is the amplitude of the
for the Fermi velocity. It is a direct consequence of the electron band hybridization. The mediator O 2p orbitals transmit the symmetry of the Cu 3d_{x^2−y^2} orbital to the momentum dependence of the Bloch wave amplitude S_p and the superconducting gap $\Delta_p(T)$. This is why the pairing state has d-wave symmetry directly coming from the Cu 3d_{x^2−y^2} orbital.

The angle-resolved photoemission spectroscopy (ARPES) provides a straightforward method for measuring $\Delta_p$. We have fitted our theoretical result Eq. (2) to the recent precise ARPES data [16] for BSCCO and the outcome is given in Fig. 3 (c). It is the first demonstration that the theory provides a satisfactory description of overdoped cuprates.

We mentioned some normal state properties [11, 12, 13] of overdoped cuprates which are governed by conventional physics. The point to be stressed now is that not only the normal phase but even the superconducting phase at optimal doping, for which the $T_c$ is the highest, can be explained by conventional theory, since there is overwhelming evidence for the applicability of the Landau quasiparticle picture.

The quantitative analysis of the thermal conductivity [14] of optimally doped Bi_2Sr_2CaCu_2O_8 gave values for the Fermi velocity $v_F$ and derivative of the gap function with respect to the momentum component tangential to the Fermi contour, $v_{\Delta} = \partial \Delta / \partial p_t$, within 10% of the values found in independent ARPES experiments, as emphasized in a recent review [18]. Furthermore, measurements of heat transport, specific heat, and superfluid density through the penetration depth also strongly support the existence of low-energy Fermi excitations of the conventional BCS ground state for a d-wave superconductor. Moreover, the quality of the quasiparticles is astonishing since their mean-free path in some high-quality crystals can reach 2500 Å at 15 K, as reviewed by Lee [14].

Our calculations consist of solving the gap equation in the framework of the BCS theory using linear combination of atomic orbitals for the electron band structure. In contrast with theoretical explanations advanced so far our results indicate that the extraordinarily large pairing amplitude together with the correct gap symmetry cannot be explained by any interatomic or even interlayer exchange interaction. Instead it must be due to the powerful intra-atomic two-electron exchange process, which incidentally is responsible for the magnetism of the transition metals as well. The superconductivity of the optimally doped cuprates, most important for practical applications, can now be understood. The pairing amplitude we uncover is so strong that the high $T_c$ is robust to many other new effects discovered in optically doped cuprates, including the existence of a weak pseudo-gap [20], the appearance of stripes [21, 22], and the confluence of superconductivity and magnetism [23]. Although these new effects can be considered to make the physics of cuprates revolutionary, and require novel the-
oretical ideas for their explanation, our point is that all these effects are irrelevant to the main issue of explaining the high \( T_c \) of high-\( T_c \) superconductors \[24\].

The proposed model contains energies and hopping parameters which have to be determined by fits to experimental data or by first-principles calculations. Predicting thermodynamic properties close to \( T_c \) constitutes a strongest test of the model. For example, let us recall that the BCS result for the jump of the specific heat in isotropic-gap superconductors, \( \Delta C \), at \( T = T_c \), relative to the specific heat of the normal phase \( C_n \), is given by

\[
\frac{\Delta C}{C_n} = \frac{12}{7\zeta(3)} \approx 1.43
\]

(\( \zeta \) is the Riemann zeta function). For the overdoped samples we find that this ratio is renormalized by the gap anisotropy according to the relation

\[
\frac{\Delta C}{C_n} = 1.43 \frac{\langle |\Delta_p|^2 \rangle^2}{\langle 1 \rangle \langle |\Delta_p|^4 \rangle} \quad (3)
\]

Here \( \langle \ldots \rangle \) denotes averaging over the Fermi surface and \( \langle 1 \rangle \) is the density of states. This simple expression provides another direct means for experimental verification of the model’s validity for overdoped samples.

As a fundamental microscopic process the two-electron s-d exchange has been known in the physics of magnetism long before \[7, 8, 9\] the advent of the BCS theory \[3\]. So it is not surprising that an exchange-driven superconductivity was attempted shortly after \[25\] the BCS theory. Reventuring this idea we have shown how the two paradigms (s-d & BCS) can be reconciled to obtain a coherent traditional theory of high-\( T_c \) superconductivity in the cuprates. Magnetism of transition metals and high-\( T_c \) superconductivity of cuprates seem to be two faces of the same ubiquitous two-electron exchange amplitude.

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