On the electron pairing mechanism of copper-oxide high temperature superconductivity

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The elementary CuO₂ plane sustaining cuprate high-temperature superconductivity occurs typically at the base of a periodic array of edge-sharing CuO₃ pyramids. Virtual transitions of electrons between adjacent planar Cu and O atoms, occurring at a rate $t/b$ and across the charge-transfer energy gap $\varepsilon$, generate “superexchange” spin–spin interactions of energy $J \approx 4t^2/\varepsilon^3$ in an antiferromagnetic correlated-insulator state. However, hole doping this CuO₂ plane converts this into a very-high-temperature superconducting state whose electron pairing is exceptional. A leading proposal for the mechanism of this intense electron pairing is that, while hole doping destroys magnetic order, it preserves pair-forming superexchange interactions governed by the charge-transfer energy scale $\varepsilon$. To explore this hypothesis directly at atomic scale, we combine single-electron and electron-pair (Josephson) scanning tunneling microscopy to visualize the interplay of $\varepsilon$ and the electron-pair density $n_p$ in Bi₂Sr₂CaCu₂O₈₊ₓ. The responses of both $\varepsilon$ and $n_p$ to alterations in the distance $\delta$ between planar Cu and apical O atoms are then determined. These data reveal the empirical crux of strongly correlated superconductivity in CuO₂, the response of the electron-pair condensate to varying the charge-transfer energy. Concurrence of predictions from strong-correlation theory for hole-doped charge-transfer insulators with these observations indicates that charge-transfer superexchange is the electron-pairing mechanism of superconductive Bi₂Sr₂CaCu₂O₈₊ₓ.

Significance

Charge-transfer superexchange interactions between electrons on adjacent Cu sites have long been hypothesized to generate the intense spin-singlet electron-pair formation in cuprate superconductors. But this concept is unproven, partly because there existed no analogue isotope effect in which one could controllably vary the charge-transfer energy $\varepsilon(r)$ and measure the changes in the electron-pair condensate $\Psi$. Our concept is to visualize both $\varepsilon(r)$ and $n_p(r) = |\Psi|^2$ directly at atomic scale and as a function of varying apical oxygen displacements $\delta(r)$ that occur in Bi₂Sr₂CaCu₂O₈₊ₓ. These data provide access to controllable variations in $\varepsilon(r)$ and resultant effects on $n_p(r)$, yielding $dn_p/\varepsilon \approx -0.81 \pm 0.17 \text{ eV}^{-1}$. This compares with recent prediction $dn_p/\varepsilon \approx -0.9 \text{ eV}^{-1}$ for superexchange-mediated electron pairing in Bi₂Sr₂CaCu₂O₈₊ₓ, indicating that charge-transfer superexchange is the electron-pairing mechanism in hole-doped superconductor Bi₂Sr₂CaCu₂O₈₊ₓ.

Concept of electron pairing from charge-transfer superexchange interactions

1. The prospect that hole-doped CuO₂ retains charge-transfer superexchange interactions between adjacent Cu spins has long motivated a hypothesis that spin-singlet electron-pair formation mediated by superexchange is the mechanism of high-temperature superconductivity. In transition-metal oxide insulators, superexchange (1) generates intense magnetic interactions between electrons that are localized at adjacent transition-metal atoms, typically generating robust antiferromagnetism. The superexchange interaction $J$ occurs when the degeneracy of transition-metal 3d orbitals is lifted by the Coulomb energy $U$ required for their double occupancy, so that intervening oxygen 2p energy levels are separated from the relevant transition-metal 3d level by the charge-transfer energy $\varepsilon$. Within the framework of the three-band model, the interactions of two adjacent 3d electrons of spin $S_z$ are well approximated by a Heisenberg Hamiltonian $H = J S_1 \cdot S_2$, with $J$ the superexchange interaction produced by a multistage process of electronic exchange between spins on adjacent 3d orbitals via the nonmagnetic oxygen 2p orbitals. In the strong-coupling limit, $U/\varepsilon \gg 1$, $J \approx 4t^2/\varepsilon^3$, where the transition rate of electrons between 3d and 2p orbitals is given by $t/b$. Specifically for CuO₂-based materials, the planar Cu²⁺ ions are in the 3d⁹ configuration with a singly occupied $d_{x^2-y^2}$ orbital, while the planar O²⁻ ions have closed 2p⁰ shells whose in-plane $p_x$ orbitals dominate. To doubly occupy any $d_{x^2-y^2}$ orbital requires an energy $U$ so great that the $d$ electrons become fully Mott localized in an charge-transfer insulator state, with the $p_x$ energy level separated from the pertinent $d_{x^2-y^2}$ level by the CuO₂ charge-transfer energy $\varepsilon$ (Fig. 1A). Under such circumstances, an electronic structure with $\varepsilon \approx 0.4 \text{ eV}$ and $\varepsilon \approx 1 \text{ eV}$ implies a superexchange energy $J \approx 100 \text{ meV}$ that should stabilize a robust spin-1/2, $Q = (\pi, \pi)$ antiferromagnetic state (Fig. 1B). Just such a state is observed (2), confirming that charge-transfer superexchange is definitely the mechanism of the CuO₂ antiferromagnetic state. However, when holes are doped into the...
CuO\textsubscript{2} plane, they enter the \( p_\sigma \) orbitals, both disrupting the antiferromagnetic order and delocalizing the electrons. This situation may be approximated using the three-band Hamiltonian based on a single Cu \( d_{x^2-y^2} \) plus two O \( p_\sigma \) orbitals per unit cell (3, 4):

\[
H = \sum_{i,j} \epsilon_{ij} \alpha \beta c_{i\alpha}^\dagger c_{j\beta} + \sum_{i} \alpha \beta U_{i\alpha}^\beta + U \sum_{i} n_{i\uparrow} n_{i\downarrow} . \tag{1}
\]

Here, \( i,j \) enumerate planar CuO\textsubscript{2} unit cells; \( \alpha, \beta \) label any of the three orbitals; \( t_{ij}^{\alpha\beta} \) are transition rates for electrons between orbitals \( \alpha, \beta \) at sites \( i, j \); \( \epsilon_{i\alpha} \) are the orbital energies; and \( n_{i\uparrow}, n_{i\downarrow} \) are the \( d_{x^2-y^2} \) orbital occupancies by spin state. Heuristically, such models describe a two-dimensional correlated metallic state with intense antiferromagnetic spin-spin interactions. If superconductivity occurs (Fig. 1 C), it is signified by the appearance of a condensate of electron pairs \( \Psi \equiv \langle \psi_{i\uparrow}^\dagger \psi_{j\downarrow} \rangle \), a phenomenon that is now directly accessible to visualization using scanned Josephson tunneling microscopy (SJT) (5–9).

2. Empirical study of charge-transfer superexchange as the mechanism of this superconductivity requires knowledge of the dependence of \( \Psi \) on the charge-transfer energy \( \epsilon \), but this has not been experimentally accessible. Certainly, \( \epsilon \) and \( J \) have long been studied using optical reflectivity, Raman spectroscopy, tunneling spectroscopy, angle resolved photoemission, and resonant inelastic X-ray scattering (SI, Appendix, section I). Typically, to access different \( \epsilon \) for these studies required changing between crystal families in the antiferromagnetic-insulator state. But this renders impossible the required comparison between \( \epsilon \) and \( \Psi \) measured simultaneously in the same superconductive state. Instead, the maximum superconducting critical temperature \( T_C \) subsequent to hole doping is often proposed as a proxy for \( \Psi \) and then compared with the \( \epsilon \) derived from the parent insulator, for a range of different compounds. But varying the crystal family alters a wide variety of other material parameters besides \( \epsilon \), and \( T_C \) is anyway controlled by other influences, including dimensionality and superfluid phase stiffness (10). Moreover, advanced theoretical analysis has recently revealed that no one-to-one correspondence exists between the \( T_C \) and \( \Psi \) in the CuO\textsubscript{2} Hubbard model (11, 12). Hence, although greatly encouraging, studies comparing maximum superconductive \( T_C \) with insulating \( \Psi \) cannot be conclusive as to the electron-pairing mechanism. On the other hand, muon spin rotation studies do make clear that \( \Psi \) diminishes rapidly with increasing correlations upon approaching the charge-transfer insulator state (13). Ultimately, to identify the essential physics subtending this electron pairing, a direct and systematic measurement of the dependence of the electron-pair condensate \( \Psi \) on the charge-transfer energy \( \epsilon \) at the same hole density is required.

3. In this context, dynamical mean-field theory analysis of the CuO\textsubscript{2} Hubbard model has recently yielded quantitative predictions of how \( \Psi \) is controlled by \( \epsilon \). Moreover, theory also indicates that this interplay may be adjusted by altering the distance \( \delta \) between each Cu atom and the apical O atom of yellow, and the related electron-pair density is \( n_p \equiv | \langle \psi_{i\uparrow}^\dagger \psi_{j\downarrow} \rangle |^2 \). Insert shows a schematic \( \Psi \) in this phase that, although reorganized by the delocalized carriers, still retains a charge-transfer energy scale \( \epsilon \). HDB, hole-doped band. (D) Schematic of CuO\textsubscript{2} partially overlaid by a Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8} topographic image \( I(x) \) to exemplify how the crystal supermodulation modulates along the \((1, 1)\) axis, with one period \( 0 \leq \phi \leq 2\pi \) requiring approximately 26 Å. The Cu to apical O distance \( \delta \) is modulated at same wavevector but perpendicular to this plane.

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**Fig. 1.** Supercorrelation magnetic interactions in transition-metal oxides. (A) Schematic representation of CuO\textsubscript{2} pyramids whose bases comprise the CuO\textsubscript{2} plane. The degeneracy of Cu \( d_{x^2-y^2} \) orbitals (blue) is lifted by the Hubbard energy \( U \), and the O \( p_\sigma \) orbitals (red) are separated from the upper Cu \( d_{x^2-y^2} \) band by the charge-transfer energy \( \epsilon \) (for holes). (B) Schematic of antiferromagnetic charge-transfer insulator state in undoped CuO\textsubscript{2}. Inset shows a schematic density of electronic states \( N(\epsilon) \) in this phase, with the Coulomb energy \( U \) and the charge-transfer energy \( \epsilon \) indicated. LHB, lower Hubbard band. UHB, upper Hubbard band. CTB, charge-transfer band. (C) Schematic of hole-doped CuO\textsubscript{2}, a two-dimensional correlated metallic state with intense antiferromagnetic spin-spin interactions. When superconducting, the electron-pair condensate \( \Psi \equiv \langle \psi_{i\uparrow}^\dagger \psi_{j\downarrow} \rangle \) is indicated schematically in
Techniques for visualization of charge-transfer energy and electron pair density

4. To explore this prospect, one must measure Ψ and E as a function of separation δ above each planar Cu atom. But Ψ is, in general, a complex-valued field and thus not a physical observable, meaning that experimentists must study |Ψ|² ≡ n_p, the electron-pair density. Moreover, the pseudogap masks the true electron-pairing energy gap so that single-particle tunneling spectroscopy cannot be used to image the superconductive order parameter in lightly hole-doped cuprates. Our strategy therefore combines techniques in atomic-resolution imaging with a fortuitous property of the canonical cuprate Bi₂Sr₂CaCu₂O₈₊ₓ. First, a mismatch between preferred bond lengths of the rock-salt and perovskite layers in Bi₂Sr₂CaCu₂O₈₊ₓ generates a λ ≈ 26Å periodic modulation of unit-cell dimensions (Fig. 1D), along the crystal a axis or equivalently the (1,1) axis of the CuO₂ plane (23). Providentially, this crystal supermodulation generates periodic variations in δ by up to 12% in the single-electron excitation spectrum (24) and in the electron-pair (Josephson) current (7). However, the influence of the supermodulation on E and n_p was unknown. Crucially for our objectives, the value of δ at every location r can be evaluated by measuring δ(r) in topographic images T(r) measured at the crystal’s BiO termination layer (Figs. 1D and 2A) and then by using X-ray crystallography to relate T(r) to the spatial pattern of apical displacements δ(r) just underneath (SI Appendix, section II). Second, by measuring differential tunnel conductance dl/dV(r, V) ≡ g(r, V) as a function of location r and tip-sample voltage V, the density of electronic states N(r, E) ∝ g(r, V = E/e) can be visualized for the high energy range governed by Eq. 1. In principle, this allows energy scales, such as E(r) in the spectrum of Bi₂Sr₂CaCu₂O₈₊ₓ, to be determined versus location r. Third, using superconducting scanning tunneling microscope (STM) tips (Bi₂Sr₂CaCu₂O₈₊ₓ nanoflake tips (7)) to image the Josephson critical current ℐ_{J} for electron-pair tunneling versus location r allows direct visualization of sample’s electron-pair density (7–9) n_p(r) ≡ |Ψ|^² ∝ |ℐ_{J}(r)| R_{N}(r)^{2}, where R_{N} is the tip-sample normal state junction resistance. Thus, our concept is to visualize both E(r) and n_p(r) directly at atomic scale, as a function of the apical oxygen displacements δ(r) that are produced by the crystal supermodulation in Bi₂Sr₂CaCu₂O₈₊ₓ.

5. In practice, single crystals of Bi₂Sr₂CaCu₂O₈₊ₓ with hole-density p ≈ 0.17 are cleaved in cryogenic ultrahigh vacuum in a dilution refrigerator-based spectroscopic imaging STM
(SISTM) to reveal the BiO termination layer (Fig. 2A). The CuO$_2$ plane is ~5 Å beneath the BiO surface and separated from it by the SrO layer containing the apical oxygen atom of each CuO$_2$ pyramid (Fig. 1A). A surface corrugation $T(r) = A(r) \cos \Phi(r)$, where $\Phi(r) = \mathbf{Q_S} \cdot \mathbf{r} + \delta(r)$, occurs at the bulk supermodulation wavevector $\mathbf{Q_S} \approx (0.15, 0.15) \pi / d_0$, where $\delta(r)$ describes effects of disorder (Fig. 2A). The supermodulation phase $\Phi(r)$ is then imaged by analyzing $T(q)$, the Fourier transform of $T(r)$, with typical results shown in Fig. 2B (SI Appendix, section II). X-ray scattering studies of the Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ crystal supermodulation demonstrate that the distance to apical oxygen atom $\delta$ is minimal at $\Phi = 0$ and maximal at $\Phi = \pi$, because the displacement amplitude of the $c$ axis supermodulation is greater in the CuO$_2$ layer than in the adjacent SrO layer. Thus, $\delta(r)$ is determined from the measured $\Phi(r)$ based on X-ray refinement as $\delta(\Phi) \approx 2.44 - 0.14 \cos(\mathbf{Q_S} \cdot \mathbf{r})$ Å (SI Appendix, section II). For example, the apical displacement imaging results $\delta(r)$ from Fig. 2A and B are shown in Fig. 2C. This same $\Phi(r) : \delta(r)$ procedure is used throughout our study.

**Cotermiuous visualization of charge-transfer energy and electron pair density**

6. In search of associated modulations in $E(r)$, Fig. 3A shows a typical topographic image of the BiO termination layer, while Fig. 3B shows two high-voltage, single-electron $g(V)$ spectra measured using junction resistance $R_N \approx 85$ GΩ in the same field of view. Such enormous junction resistances (or large tip-sample distances) preclude effects on $g(V)$ of the tip-sample electric field. Hence, by visualizing $g(r, V)$ in the $-1.6 \leq V \leq 2$ V range at these junction resistances, one can determine empirically whether $E(r)$ modulations exist. For example, Fig. 3B shows representative $g(r, V)$ spectra plotted on a logarithmic scale. We use the standard approach to estimate $E$ as being the minimum energy difference between upper and lower bands (25) at a constant conductance $G \approx 20$ pS. The resulting $E(r)$ shown in Fig. 4C is correctly representative and appears little different if we estimate $E(r)$ anywhere in the range $20 \leq G \leq 80$ pS (SI Appendix, section III). Concomitantly, to visualize $n_p(r)$, we measure $g_0(r)$ and multiply by the measured $R_N(r)$ modulations from the same FOV as Fig. 4B. The normal-state junction resistance $R_N(r)$ is obtained by self-normalizing two sets of $dl / dv(r)$ spectra, one for $V_{max} < \Delta / e$ and the other for $V_{max} > \Delta / e$, measured in precisely the same FOV (SI Appendix, section IV). Thus, Fig. 4D shows $n_p(r)$ in the FOV of Fig. 4B. Finally, when Fig. 4C is Filtered at $Q_S$, it reveals the first-harmonic modulations in $E(r)$, as presented in Fig. 4E, while identical filtering of Fig. 4D at $Q_S$ yields the first-harmonic modulations in $n_p(r)$, as seen in Fig. 4E. Thus, visualization of the crystal supermodulation effect on both $E(r)$ and $n_p(r)$, simultaneously with their $\Phi(r)$, is now possible in Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$.

**Synthesis**

9. So how does supermodulation displacement of the apical oxygen atom $\delta(r)$ (and to a lesser extent that of other atoms) alter the charge-transfer energy $E(r)$ and the electron-pair density $n_p(r)$ at each planar Cu atom (15–21) in Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$. To synthesize data as in Fig. 4, we first plot apical distance alterations versus phase $\delta(\Phi)$ for Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$, as shown by gray dots in Fig. 5B. We then process $E(r)$ retaining only wavevectors close to $\pm Q_S$. Then, by corresponding simultaneous $\Phi(r) : E(r)$ measurements (e.g., Fig. 4 A and C), we determine $E(\Phi)$, whose value is normalized to the mean measured value and shown as red dots in Fig. 5B; this is found to be a very repeatable characteristic of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$. Similarly, by corresponding simultaneous $\Phi(r) : n_p(r)$ measurements (e.g., Fig. 4 B and D), we determine $n_p(\Phi)$, which is normalized to the mean value of measured $n_p(r)$.
blue dots in Fig. 5B; this is another repeatable characteristic (SI Appendix, section VI). To maximize the precision of both the Fourier filtering and lock-in methods, we perform this analysis in an FOV that includes as many periods of the supermodulation as possible (for $\mathcal{E}(r)$, 7 periods, and for $n_p(r)$, 13 periods). The microscopic relationship of $\mathcal{E}$ to $\delta$ can then be determined by eliminating common variable $\Phi$ from Fig. 5B. The result, shown in Fig. 5C, provides a direct measurement of this long-sought characteristic (15–20) of cuprate electronic structure: $d\mathcal{E}/d\delta \approx -1.04 \pm 0.12 \text{eV/Å}$.
More fundamentally, the atomic-scale relationship between the normalized electron-pair density \( n_P(r) \) and the charge-transfer energy \( E \) is derived by eliminating the common variable \( \Phi \). The result, as shown in Fig. 5D, demonstrates that
\[
\frac{d n_P(r)}{d \delta} \approx 0.85 \pm 0.22 \text{Å}^{-1}
\]
for \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x} \). More fundamentally, the atomic-scale relationship between the normalized electron-pair density \( n_P(r) \) and the charge-transfer energy \( E \) is derived by eliminating the common variable \( \Phi \). The result, as shown in Fig. 5D, demonstrates that
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Fig. 5. Evolution of cuprate electron-pair density $n_{\psi}$ with charge-transfer gap $\varepsilon$. (A) Schematic of planar Cu to apical O distance modulations $\delta(r)$ in Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$ shown versus supermodulation phase $\Phi$. (B) Gray dots: measured $\delta(\Phi)$ showing the displacement of the apical oxygen atom within the CuO$_2$ pyramid versus supermodulation phase $\Phi$ (23). Red dots: measured $\delta(\Phi)$ showing the typical value for the Cu-O charge-transfer energy $\varepsilon$ for each value of the supermodulation phase $\Phi$ normalized to the mean value of $\varepsilon$. These data are from the same FOV as Fig. 4 A, C, and E. Blue dots: measured $\pi_{\delta}(\Phi)$ showing the measured value of electron-pair density versus supermodulation phase $\Phi$. These data are from a larger FOV comprising 13 supermodulation periods, which contains the FOV from Fig. 4 B, D, and F. (C) Measured dependence of Cu-O charge-transfer energy $\varepsilon$ and electron-pair density $n_{\psi}$ on the displacement $\delta$ of the apical O atoms from the planar Cu atoms. (D) Measured relationship of electron-pair density $\pi_{\delta}$ to the Cu-O charge-transfer energy $\varepsilon$ in the CuO$_2$ plane of Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$. The yellow shaded region shows the range of predicted slopes for $d\pi_{\delta}/d\delta = -\alpha \varepsilon^{-1}$, as $0.3 \leq \alpha \leq 1.0$. These are derived from dynamical mean-field theory calculations for various materials with the limits reported for La$_2$CuO$_4$ and Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$ as indicated by black arrows. Error bars for B, C, and D are obtained from the standard deviation of the phase-averaged values.

electron-pair condensate of altering the charge-transfer $\varepsilon$ yield (SI Appendix, section VII) $d[\langle \hat{c}^+ \hat{c} \rangle]/d\varepsilon \approx -\alpha/2 \varepsilon^{-1}$ or equivalently $d\pi_{\delta}/d\varepsilon \approx -\alpha \varepsilon^{-1}$, with a range $0.3 \leq \alpha \leq 1.0$, depending on the material-specific parameters (11, 15–17). The precise parameters used in these calculations for a variety of different materials are given in ref. (15). Fig. 5D indicates the anticipated range of $\alpha$ for different materials using a yellow shaded triangle. For Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$ specifically (11), the three-band CuO$_2$ Hubbard model prediction for a superexchange electron-pairing mechanism is that $d[\langle \hat{c}^+ \hat{c} \rangle]/d\varepsilon \approx -0.46 \pm 0.05 \varepsilon^{-1}$ or equivalently that $\alpha \approx 0.93 \pm 0.1 \varepsilon^{-1}$. The agreement with experimental observations reported in Fig. 5D is self-evident.

11. For decades, the electron-pairing mechanism of cuprate high-temperature superconductivity has been hypothesized (29–36) as due to electron–electron interactions mediated by superexchange but with the electron-pair condensate $\Psi$ subject to the strong no-double-occupancy constraints on the Cu $d_{x^2-y^2}$ orbitals (37, 38) (Fig. 1C). When such interactions and constraints were studied using mean-field Gutzwiller projection (37), by slave-boson techniques (38,39), or by Monte Carlo numerical techniques (36, 37), the phase diagram and many other key characteristics that emerged were congruent with observations (38, 39). Contemporary theoretical studies, using a wide variety of advanced theoretical and numerical techniques (39–44), also predict with growing confidence that it is the superexchange interaction that creates electron pairing in the three-band CuO$_2$ Hubbard model. However, direct experimental tests of the relationship between the cuprate electron-pair condensate and the charge-transfer energy of this model were nonexistent. Here, by visualizing the electron-pair density $n_{\psi}(r)$ using SJTM (e.g., Fig. 4 D and F), and the charge-transfer energy $\varepsilon(r)$ using high-voltage SISTM (e.g., Fig. 4 C and E), we find empirically that both modulate together at the Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$ crystal supermodulation wavevector $\mathbf{Q}_s$ (Figs. 2 B and C and 5 B). This joint $\varepsilon(r) : n_{\psi}(r)$ modulation is observed comprehensively throughout these studies of Bi$_2$Sr$_2$CaCu$_2$O$_{8+}$, with its existence being independent of exactly which atomic displacements occur within the crystal supermodulation. The consequent demonstration that $d[\langle \hat{c}^+ \hat{c} \rangle]/d\varepsilon < 0$ (Fig. 5 D) is a direct visualization of an effect long anticipated in the theory of superexchange-mediated electron pairing in cuprates (3, 4, 14–17, 29–39) and from experiments based on muon spin rotation (13). More specifically, recent numerical studies of the three-band CuO$_2$ Hubbard model (11), within which charge-transfer superexchange is demonstrably the cause of electron pairing (40–45), yield quantitative agreement between predicted $d[\langle \hat{c}^+ \hat{c} \rangle]/d\varepsilon \approx -0.46 \pm 0.05 \varepsilon^{-1}$ and our experimental determination that $d\pi_{\delta}/d\varepsilon \approx -0.81 \pm 0.17 \varepsilon^{-1}$ for Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$.

Taken at face value, the data in Fig. 5 thus indicate that charge-transfer superexchange is key to the electron-pairing mechanism of the hole-doped cuprate superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+}\delta$.

Data, Materials, and Software Availability. All data are included in the manuscript and/or SI Appendix.

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