Changes in Ionic Electron Clouds in Cuprate Superconductor CaCuO2: A First-Principles Investigation of Electron Pairing

Authors: Tiege Zhou, Tiege Zhou

Date: 2019-07-02T00:00:00+00:00

Abstract

P. W. Anderson raised an important question in 2007: Is There Glue in Cuprate Superconductors? The author believes that the change of the electron clouds of ions is the glue in cuprate superconductors. The change of the electron clouds of the ions in the parent structure of the layered high-temperature superconductors CaCuO2 has been studied by the first-principles calculations. The electron clouds of Cu2+ and O2- ions change obviously under electric fields. It is also found, for the first time, the characteristic frequencies of the change of the electron clouds are 250 meV, 360 meV, and 100 meV, respectively, for the modes observed. The frequencies are low and close to that of lattice vibrations, indicating the change of the electron cloud of ions can be the electron-pairing medium in cuprate superconductors.

Full Text

Preamble

The Change of the Electron Clouds of Ions in Cuprate Superconductor CaCuO2: A First-Principles Investigation of the Electron-Pairing Mechanism

TieGe Zhou
zhoutg@nankai.edu.cn
College of Electronic Information and Optical Engineering, Nankai University, 300350 Tianjin, P. R. China

Abstract

In 2007, P. W. Anderson raised a fundamental question: Is There Glue in Cuprate Superconductors? The author proposes that changes in the electron

clouds of ions constitute this glue in cuprate superconductors. Using first-principles calculations, we have investigated the evolution of electron clouds in the parent structure of the layered high-temperature superconductor CaCuO2. The electron clouds of Cu2+ and O2- ions exhibit pronounced changes under electric fields. For the first time, we have identified characteristic frequencies of these electron cloud changes at 250 meV, 360 meV, and 100 meV for the observed modes. These frequencies are notably low and comparable to lattice vibrational frequencies, suggesting that changes in the electron clouds of ions can serve as the electron-pairing medium in cuprate superconductors.

Keywords: cuprate superconductors; time-dependent density functional theory; electron-pairing medium

1 Introduction

In 1986, J. G. Bednorz and K. A. Müller [1] discovered possible high-temperature superconductivity (HTS) in La-Ba-Cu-O oxides, leading to the subsequent discovery of numerous cuprate superconductors with transition temperatures exceeding 77 K [2][3][4]. However, the electron-lattice interaction cannot adequately explain the electron pairing mechanism in these materials, and the pairing mechanism for unconventional HTS remains under debate.

In 2007, P. W. Anderson [5] posed a critical question: Is There Glue in Cuprate Superconductors? The author proposes that changes in the electron clouds of ions may provide this glue. The mechanism operates as follows: when a free electron approaches a location, the electron clouds of nearby ions deform, reducing the charge density around the free electron. When the electron departs, the ionic electron clouds do not relax instantaneously, creating a charge-depleted region (equivalent to a positive charge region) that attracts another free electron. This generates an effective attraction between free electrons. This mechanism is essentially analogous to electron-phonon interaction, except that the mediating entity is the change of the electron cloud rather than ionic displacement.

According to the Born-Oppenheimer approximation [6], electrons move and respond to forces extremely rapidly because their masses are more than 1000 times smaller than nuclear masses. Consequently, electron density changes are considered too fast to be excited by free electrons, and it is generally believed that electron pairing cannot be achieved through electron cloud changes. But can electron density change as slowly as nuclei? If so, it could serve as an electron-pairing medium.

Based on this consideration, the author conducted an investigation using the parent structure of layered high-temperature superconductors CaCuO2 [7]. First, we studied charge density changes under electric fields. Second, we calculated the characteristic frequencies of these changes using the real-time TDDFT method [8, 9]. We have found, for the first time, that the characteristic frequencies of electron cloud changes are close to lattice vibrational frequencies, indicating that these changes can be excited by free electrons. This suggests

that electron cloud changes can indeed serve as the electron-pairing medium in cuprate superconductors. This paper reports our methods and results.

2 Methods

We employed VASP [10][11] and QE [12] to investigate charge density changes under electric fields. In VASP calculations, the projector augmented plane wave (PAW) method [13][14] described the interaction between valence electrons and ion cores, while the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [15] was used for the exchange-correlation potential. To account for strong correlation among 3d electrons, we applied the GGA+U method with Ueff = 6.5 eV for Cu 3d orbitals [16][17]. Plane waves expanded the valence electron wave functions with a cutoff energy of 400 eV, chosen to balance accuracy and computational cost. Valence electron configurations for the pseudopotentials were 3s23p64s2 for Ca, 3p63d104s1 for Cu, and 2s22p4 for O. Additional calculations using the Heyd, Scuseria, and Ernzerhof (HSE) [18] hybrid functional were performed for cross-validation. In QE calculations, norm-conserving pseudopotentials were employed to calculate changes under uniform electric fields.

We studied the characteristic frequencies of charge density changes using the real-time TDDFT method within the Octopus package [19, 20]. Valence electrons were treated as 3p64s2 for Ca, 3p6d104s1 for Cu, and 2s2p4 for O. The GGA-PBE functional described the exchange-correlation energy, with GGA+U [21, 22] applied to handle strong 3d electron correlation. HSCV pseudopotentials [23] were adopted, and the Approximated Enforced Time-Reversal Symmetry (AETRS) algorithm approximated the evolution operator with a time step of 0.002 /eV.

3 Results and Discussions

[Figure 1: see original paper] displays the crystal structure and charge density difference (CDD) with and without electric fields. Yellow indicates positive values or charge density increase, while blue indicates negative values or decrease. The charge density around Cu2+ ions changes significantly, whereas no comparable change occurs around Ca2+ ions. The deformation resembles a rigid rotation rather than elastic distortion because it is not entirely aligned with the electric field direction; some regions show increased density while others show decreased density. Furthermore, the pattern resembles 3d electron clouds. Why do electron clouds change in this manner?

Transition metal ions possess incompletely filled 3d orbitals, giving their electron clouds non-spherical symmetry. Like polar molecules, these clouds deform under electric fields. The charge density around O2- ions also changes substantially, suggesting that the O2- valence is not strictly -2 (which would remain unchanged like Ca2+ ions). We have also studied eight other unconventional superconductors (Fe2KSe2, La2Fe2As2O2, Nd2Fe2As2O2, Ba2Fe4As4, YBa2Cu3O7,

HgBa2Ca2Cu3O9, Tl2Ba2CaCu2O8, and Bi2Sr2Ca2Cu3O10) [24], finding significant electron cloud changes in transition metal ions under static electric fields.

To study the real-time evolution of charge density changes, we employed two excitation methods: applying a time-dependent electric field and slightly displacing atomic positions. [Figure 2: see original paper] shows the crystal structure and real-time evolution of charge density excited by a time-dependent electric field with = 1.8 eV and F0 = 1.0 eV/angstrom. The excitation ceases after 5000 steps, after which charge densities vibrate freely. Densities were recorded after 7000 steps; "100" represents the charge density difference between the 7100th and 7000th steps (similar notation applies below). The electron cloud changes in O2- ions (marked with arrows) become progressively evident with evolution steps. The charge density change reaches its maximum after approximately 500 steps, corresponding to a time of 1.0 /eV from zero to maximum. The period is 4×1.0 /eV, yielding a frequency of about 250 meV.

[Figure 3: see original paper] shows the crystal structure and real-time evolution of charge density excited by a time-dependent electric field with = 1.8 eV and F0 = 10 eV/angstrom. The excitation vanishes after 5000 steps, after which charge densities vibrate freely. Densities were recorded after 18000 steps; "50" represents the charge density difference between the 18050th and 18000th steps. The charge density change in the Cu2+ ion (marked with an arrow) reaches its maximum after about 350 steps, corresponding to a frequency of approximately 360 meV.

[Figure 4: see original paper] shows the crystal structure and real-time evolution of charge density excited by slightly displacing a Ca atom. To excite charge vibrations, we moved a Ca atom from its original coordinate (0, 0.5, 0.5) to (0.02, 0.52, 0.5)—a displacement of 0.15 Å in the (001) direction. After calculating the ground state, we restored the coordinate to (0, 0.5, 0.5) for TDDFT calculations. Charge densities were recorded after 13000 steps. The electron cloud of the Cu2+ ion (marked with an arrow) changes gradually, reaching its maximum after 1300 steps, with a frequency of about 100 meV.

We have also studied electron cloud changes in other superconductors [26]. For La2Fe2As2O2, FeSe sheets, and HgBa2Ca2Cu3O8, TDDFT studies yield characteristic frequencies of 160 meV, 190 meV, and 250 meV, respectively [27]. For BaFe2As2, we observed modes at 150 meV, 160 meV, 250 meV, and 200 meV [28]. presents the maximum phonon frequencies and Tc for three typical conventional superconductors. The characteristic frequencies of electron cloud changes are comparable to lattice vibrational frequencies.

These results are unexpected because conventional wisdom holds that electron density changes occur too rapidly, with frequencies much higher than lattice vibrations. Our obtained frequencies are close to phonon frequencies, indicating they can be excited by free electrons. Therefore, changes in the electron clouds of transition metal ions can serve as the electron-pairing medium. W. A. Little

[31] reported similar results, but with excessively high frequencies (> 1000 meV) whose excitability by free electrons requires justification.

Why do transition metal ion electron clouds exhibit such behavior? The primary reason is that these electron clouds lack spherical symmetry and are therefore easily deformable under electric fields.

4 Summary

Using first-principles methods, we studied electron cloud changes in CaCuO2. For the first time, we demonstrated that ionic electron clouds can change slowly, with evolution frequencies matching lattice vibrational frequencies. This contradicts the Born-Oppenheimer approximation. Although our method' s frequency accuracy is limited, it provides significant evidence that electron cloud changes can serve as the electron-pairing medium in HTS. The change of electron clouds can indeed function as a pairing medium for superconducting electrons.

References

[1] Bednorz, J. G., Müller, K. A.: Possible high TC superconductivity in the Ba-La-Cu-O system. Zeitschrift für Physik B 64, 189-193 (1986)
[2] Wu, M. K., Ashburn, J. R., Torng, C. J., Hor, P. H., Meng, R. L., Gao, L., Huang, Z. J., Wang, Y. Q., Chu, C. W.: Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. Physical Review Letters 58, 908-910 (1987)
[3] Zhao, Z. X., Chen, L. Q., Yang, Q. S., Huang, Y. Z., Chen, G. H., Tang, R. M., Liu, G. R., Cui, C. G., Chen, L., Wang, L. Z., Guo, S. Q., Li, S. L., Bi, J. Q.: Superconductivity above liquid-nitrogen temperature in Ba-Y-Cu oxides. Chinese Science Bulletin 6, 412-414 (1987)
[4] Chu, C. W., Gao, L., Chen, F., Huang, Z. J., Meng, R. L., Xue, Y. Y.: Superconductivity above 150 K in HgBa2Ca2Cu3O8+ at high pressures. Nature 365, 323-325 (1993).
[5] Anderson, P. W.: Is There Glue in Cuprate Superconductors? Science 22, 1705-1707 (2007)
[6] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," Ann. Physik 84, 457-484 (1927).
[7] Siegrist, T., Roth, R.S., Zahurak, S.M., Murphy, D.W.: The parent structure of the layered high-temperature superconductors, Nature 334, 231-232 (1988).
[8] Castro, A., Marques, M.A.L., Alonso, J.A., Rubio, A.: Optical properties of nanostructures from time-dependent density functional theory, J. Comp. Theoret. Nanoscience 1, 231-255 (2004).
[9] Marques, M.A.L., Gross, E.K.U.: Time-dependent density functional theory, Annu. Rev. Phys. Chem. 55 427-455 (2004).
[10] Kresse, G., Hafner, J.: Ab initio molecular dynamics for liquid metals. Physical Review B 47, 558–561 (1993).

[11] Kresse, G., Furthmüller, J.: Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Physical Review B 54, 11169–11186 (1996).
[12] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G. L., Cococcioni, M., Dabo, I., Corso, A. D., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A. P., Smogunov, A., Umari, P., Wentzcovitch, R. M.: QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter 21, 395502 (2009)
[13] Blöchl, P.E.: Projector augmented-wave method. Physical Review B 50, 17953–17979 (1994)
[14] Kresse, G., Joubert, D.: From ultrasoft pseudopotentials to the projector augmented-wave method. Physical Review B 59, 1758–1775 (1999)
[15] Perdew, J. P., Burke, K., Ernzerhof, M.: Generalized Gradient Approximation Made Simple. Physical Review Letters 77, 3865 (1996)
[16] Qian, M. C., Hu, W. Y., Zheng, Q. Q.: Electronic structure of PrBa2Cu3O7 and YBa2Cu3O7: A local spin density approximation with the on-site Coulomb interaction study. Journal of Applied Physics 85, 4765-4767 (1999)
[17] Blaha P., Schwarz, K., Novák, P.: Electric Field Gradients in Cuprates: Does LDA+U Give the Correct Charge Distribution? International Journal of Quantum Chemistry 101, 550–556 (2005)
[18] Heyd, J., Scuseria, G. E., Ernzerhof, M.: Hybrid functionals based on a screened Coulomb potential. Journal of Chemical Physics 118, 8207–8215(2003)
[19] Andrade, X., Strubbe, D.A., De Giovannini, U., Larsen, A.H., Oliveira, M.J.T., Alberdi-Rodriguez, J., Varas, A., Theophilou, I., Helbig, N., Verstraete, M., Stella, L., Nogueira, F., Aspuru-Guzik, A., Castro, A., Marques, M. A. L., Rubio, A.: Real-space grids and the Octopus code as tools for the development of new simulation approaches for electronic systems. Phys. Chem. Chem. Phys. 17, 31371-31396 (2015)
[20] Marques, M.A.L., Castro, A., Bertsch, G.F., Rubio, A: Octopus: a first-principles tool for excited electron-ion dynamics. Comput. Phys. Commun. 151 60-78 (2003)
[21] Agapito, L.A., Curtarolo, S., Nardelli, M.B.: Reformulation of DFT + U as a Pseudohybrid Hubbard Density Functional for Accelerated Materials Discovery. Phys. Rev. X 5(1), 011006 (2015)
[22] Tancogne-Dejean, N., Oliveira, M.J.T., Rubio, A.: Self-consistent DFT+U method for real-space time-dependent density functional theory calculations. Phys. Rev. B 96, 245133 (2017)
[23] Vanderbilt, D.: Optimally smooth norm-conserving pseudopotentials. Phys. Rev. B 32, 8412-8115 (1985)
[24] Zhou, T.G.: Rotation of Transition Metal Ions under Electric Fields: Possible New Superconducting Electron Pairing Mechanism. http://vixra.org/abs/1804.0338 (2018)

[25] Momma, K., Izumi, F.: VESTA: a three-dimensional visualization system for electronic and structural analysis. J. Appl. Cryst. 41, 653-658 (2008).
[26] Tiege Zhou: Rotation of Transition Metal Ions under Electric Fields: Possible New Superconducting Electron Pairing Mechanism. http://vixra.org/abs/1804.0338 (2018)
[27] Tiege zhou: Real-Time Evolution of the Electron Clouds of Transition Metal Ions: Electron-Pairing Medium of Unconventional High Temperature Superconductors, http://vixra.org/abs/1904.0447 (2019)
[28] Tiege Zhou: Characteristic Frequency of the Orbital Fluctuation in the Unconventional Iron-Based Superconductor Bafe2as2: a TDDFT Investigation of the Electron Pairing Mechanism. http://vixra.org/abs/1906.0205 (2019)
[29] Poncé, S., Margine, E.R., Verdi, C., Giustino, F.: EPW: Electron–phonon coupling, transport and superconducting properties using maximally localized Wannier functions. Comput. Phys. Commun. 209, 116-133 (2016)
[30] Durajski, A.P., Szczęśniak, R.: First-principles study of superconducting hydrogen sulfide at pressure up to 500 Gpa. Sci. Rep. 7, 4473 (2017)
[31] Little, W. A., Holcomb, M. J., Ghiringhelli, G., Braicovich, L., Dallera, C., Piazzalunga, A., Tagliaferri, A., Brookes, N. B.: A determination of the pairing interaction in the high Tc cuprate superconductor Tl2Ba2CaCu2O8 (Tl2212). Physica C 460–462, 40-43 (2007).

Note: Figure translations are in progress. See original paper for figures.