Unconventional High-Temperature Superconductivity Electron Pairing Mechanism: Variations in Transition Metal Ion Electron Clouds

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Date: 2020-10-21T00:00:00+00:00

Abstract

This paper proposes that variations in the electron clouds of transition metal ions serve as the pairing mechanism for electrons in unconventional high-temperature superconductivity, analogous to how lattice vibrations act as the pairing mechanism in conventional superconductivity. Calculations employing the TDDFT method reveal that the vibration frequencies of transition metal ion electron clouds are close to lattice vibration frequencies and can be excited by free electrons. Results from computations on three copper oxide high-temperature superconductors demonstrate that the superconducting transition temperature is highly correlated with the frequency of electron cloud vibrations. The paper also elaborates on the distinctions between electron cloud variations and lattice vibrations, and how the unique characteristics of electron cloud vibrations can account for real-space electron pairing, the pseudogap, d-wave symmetry, and isotope effects in unconventional superconductivity.

Full Text

Electron Pairing Mechanism in Unconventional High-Temperature Superconductors: Changes in the Electron Clouds of Transition Metal Ions

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Abstract

This paper proposes that changes in the electron clouds of transition metal ions serve as the pairing medium for electrons in unconventional high-temperature superconductors, analogous to how lattice vibrations mediate pairing in conventional superconductors. Time-dependent density functional theory (TDDFT) calculations reveal that the vibration frequency of transition metal ion electron clouds approaches that of lattice vibrations and can be excited by free electrons. Calculations for three copper oxide high-temperature superconductors demonstrate a strong correlation between the superconducting transition temperature and the frequency of electron cloud oscillations. The paper also elaborates on the differences between electron cloud changes and lattice vibrations, showing that the unique characteristics of electron cloud vibrations can explain phenomena in unconventional superconductors such as real-space pairing, pseudogaps, d-wave symmetry, and isotope effects.

Keywords: high-temperature superconductor; unconventional superconductor; electron pairing mechanism

1. Introduction

In 1911, Onnes first discovered superconductivity in mercury at 4.2 K. In 1957, Bardeen, Cooper, and Schrieffer developed the renowned BCS theory, which successfully explained superconductivity in materials like mercury and lead. In BCS theory, electrons achieve pairing through the lattice as a mediating medium, and the theory predicts that superconductivity arising from electron-lattice interactions cannot exceed a critical temperature of 40 K. However, the discovery of copper oxide high-temperature superconductors and iron-based superconductors, with transition temperatures surpassing 40 K, has seriously challenged BCS theory, demonstrating that electron-lattice interactions cannot explain electron pairing in unconventional high-temperature superconductors. The pairing mechanism for electrons in unconventional high-temperature superconductors remains unresolved and continues to be vigorously debated. Anderson explicitly posed a crucial question in 2007: Is there a pairing glue in copper oxide superconductors?

The author has investigated various unconventional high-temperature superconductors using TDDFT methods and proposes for the first time that changes in the electron clouds of transition metal ions can replace lattice vibrations as the electron pairing medium, capable of explaining the electron pairing mechanism and other special properties of unconventional high-temperature superconductors. This paper introduces these findings.

2. Changes in the Electron Clouds of Transition Metal Ions

The author studied eight typical unconventional superconductors (Fe_2KSe_2, $La_2Fe_2As_2O_2$, $Nd_2Fe_2As_2O_2$, $Ba_2Fe_4As_4$, $YBa_2Cu_3O_7$, $HgBa_2Ca_2Cu_3O_9$, $Tl_2Ba_2CaCu_2O_8$, and $Bi_2Sr_2Ca_2Cu_3O_{10}$) under static electric fields and observed significant changes in the electron clouds of transition metal ions [9]. [Figure 1: see original paper] shows the crystal structure of $La_2Fe_2As_2O_2$

and the charge density difference with and without an electric field, where the field was applied by inserting a Li^+ ion. Detailed calculation methods and results are available in reference [9]. The results reveal that the charge density around Fe^{2+} ions changes noticeably, increasing in some regions and decreasing in others, exhibiting clear rotational characteristics with shapes resembling d-orbital electron clouds—indicating that the electron clouds of Fe^{2+} ions have undergone transformation. No significant electron cloud changes were observed for La^{3+}, As^{3-}, and O^{2-} ions, highlighting the unique nature of Fe^{2+} ion electron cloud changes.

The author proposes that changes in transition metal ion electron clouds can serve as the pairing medium for superconducting electrons. The simple physical picture is as follows: when a free electron arrives at a certain position, the electron clouds of nearby transition metal ions change, reducing the density of non-free electrons around the free electron (equivalent to creating a positive charge). When the free electron departs, the electron clouds of the transition metal ions do not relax extremely rapidly (as detailed TDDFT calculations will show), thereby attracting another free electron and creating an attractive force between the two electrons. This mechanism is essentially similar to electron-lattice interactions, except the medium changes from ion displacement to changes in ion electron clouds.

However, according to the Born-Oppenheimer approximation [10], since electron mass is far smaller than nuclear mass, changes in electron density occur much faster than nuclear motion. Consequently, electron clouds might relax too quickly to serve as an electron pairing medium. The equivalent statement is that electron cloud changes cannot be excited by free electrons due to excessively high frequency. But could there be circumstances where electron cloud change frequencies violate the Born-Oppenheimer approximation and approach lattice vibration frequencies? If so, electron cloud changes could potentially act as an electron pairing medium.

To explore this possibility, the author employed TDDFT methods to study multiple unconventional superconductors for the first time; specific research objects, methods, and results are detailed in references [11][12][13][14][15][16]. [Figure 2: see original paper] illustrates the structure of $La_2Fe_2As_2O_2$ and the time evolution of charge density with a time step of 0.002 $\hbar$/eV. The electron cloud changes of Fe^{2+} ions become increasingly apparent with each step: at 100 steps, almost no change is visible, while after approximately 800 steps the charge density change reaches maximum, corresponding to a time of about 1.6 $\hbar$/eV. Considering this is only the time from zero to maximum, the oscillation period should be 4×1.6 $\hbar$/eV, yielding a frequency of about 160 meV. Electron clouds of other ions show no significant change, consistent with the results in [Figure 1: see original paper].

presents the highest lattice vibration frequencies and superconducting transition temperatures for three typical conventional superconductors. Comparison clearly shows that the 160 meV frequency of Fe^{2+} ion electron cloud changes approaches lattice vibration frequencies, completely violating the Born-Oppenheimer approximation. This demonstrates that electron cloud changes can be excited by free electrons and thus serve as a pairing medium for superconducting electrons.

Why can the electron clouds of transition metal ions change significantly with frequencies close to lattice vibration frequencies, while other ions' electron clouds cannot? In $La_2Fe_2As_2O_2$, the Fe^{2+} ion has an outer electron configuration of $3d^6$, with the 3d shell not completely filled. Consequently, Fe^{2+} ions lack spherical symmetry and thus rotate under electric field influence; equivalently, the 3d orbitals of Fe^{2+} ions undergo recombination with electrons redistributing, causing electron cloud changes. Other ions, having filled shells with spherical symmetry, can also change but require much stronger electric fields and exhibit vibration frequencies far higher than lattice vibration frequencies.

Beyond iron-based superconductors, the author observed the same phenomenon in copper oxide superconductors and elemental metal Nb. [Figure 3: see original paper] shows the electron cloud changes in Nb, where three Nb atoms exhibit significant changes with a frequency of about 160 meV (coincidentally the same as $La_2Fe_2As_2O_2$). Unlike Fe^{2+}, Nb involves 4d electron clouds with more complex shapes. Since Nb does not conform to isotope effects, its superconducting electron pairing medium is likely electron cloud changes rather than lattice vibrations.

also shows that higher lattice vibration frequencies (but not excessively high, as overly high frequencies cannot be excited by free electrons) correspond to higher superconducting transition temperatures. This is only approximate, however, and holds when other parameters are roughly consistent.

In unconventional copper oxide high-temperature superconductors, which all feature copper-oxygen planes as their core with highly similar structures, one would expect to observe an approximate relationship where higher electron cloud frequencies correspond to higher superconducting transition temperatures. gives the critical temperatures and calculated electron cloud change frequencies for three copper oxide superconductors. The relationship is indeed observed, providing strong evidence that electron cloud changes constitute the electron pairing medium in unconventional superconductors.

presents the electron cloud change frequencies calculated by the author for five iron-based superconductors, with calculations performed on ideal stoichiometric systems (whereas actual superconductors are doped). The frequencies all approach lattice vibration frequencies, but no clear relationship between transition temperature and frequency was observed. This is because iron-based superconductors have diverse types and complex stoichiometry, with transition temperatures that are relatively close.

Comparing the frequencies of pairing media and transition temperatures across different superconductor types also holds significance. H_3S is a conventional superconductor with electron-phonon coupling, achieving a transition temperature of 164 K under ultrahigh pressure of 250 GPa, with a highest lattice vibration frequency of 250 meV. $HgBa_2Ca_2Cu_3O_8$ has an electron cloud change frequency of exactly 250 meV and a transition temperature as high as 133 K. Both exhibit high transition temperatures and high frequencies, consistent with the expectation that higher pairing medium frequency yields higher transition temperature. This also explains why copper oxide high-temperature superconductors can achieve transition temperatures far exceeding 40 K at ambient pressure—the frequency of the electron pairing medium (electron cloud changes) is higher than lattice vibration frequencies at ambient pressure.

In summary, from a frequency perspective, the frequency of transition metal ion electron cloud changes approaches lattice vibration frequencies, enabling them to serve as a pairing medium for superconducting electrons. The strong correlation observed between electron cloud change frequencies and transition temperatures in three typical copper oxide high-temperature superconductors provides compelling evidence for this mechanism.

3. Differences Between Electron Cloud Changes and Lattice Vibrations

As an electron pairing medium, transition metal ion electron clouds share similar vibration frequencies with the lattice. However, important differences exist that can explain the distinctions between unconventional high-temperature superconductors and conventional superconductors.

As shown in [Figure 1: see original paper], electron cloud changes resemble a type of rotation, with charge density increasing in some regions and decreasing in others. When a free electron arrives at a position, the density of non-free electrons in its vicinity decreases due to electron cloud changes (also non-free electrons), equivalent to the appearance of positive charge (hereinafter referred to as positive charge). Compared with lattice changes, the positive charge region formed by electron cloud changes is smaller and more concentrated. When this free electron departs, the positive charge region strongly attracts other free electrons. However, because electron cloud changes resemble rotation with charge increasing in some places and decreasing in others, they create a screening effect on their own positive charge region, preventing attraction of more distant electrons. Therefore, the attractive force between electrons caused by electron cloud changes is characterized by strong strength but short range, and may possess directionality because screening is weaker in some directions than others. Lattice vibrations differ fundamentally: the positive charge region created by lattice vibrations is large (see [Figure 4: see original paper]), exerting weaker attraction on nearby electrons but lacking the screening effect caused by electron cloud changes, resulting in a long-range force capable of attracting electrons at greater distances. This distinction leads to the special properties of unconventional high-temperature superconductors.

First, comparing elemental superconducting metals Pb and Nb: Pb is a conventional superconductor that can be satisfactorily explained by electron-phonon interactions, whereas Nb does not exhibit isotope effects and cannot be fully explained by electron-phonon interactions. The author proposes that electron cloud changes constitute the primary pairing medium in Nb. However, Pb has a transition temperature of 7 K and a highest lattice frequency of 9 meV, while Nb' s electron cloud change frequency is 160 meV—far higher than Pb' s highest frequency—yet its transition temperature is only 9.2 K. Why? For Nb, the 4d orbitals are involved, with electron cloud shapes more complex than 3d electron clouds, making it difficult to form large positive charge regions during interaction with free electrons. This results in weaker coupling between free electrons and electron clouds, leading to lower transition temperature. High frequency is a necessary but not sufficient condition for high transition temperature.

Heavy fermion superconductors such as $CeCu_2Si_2$ (Tc = 0.6 K) [19] can also be explained by electron cloud changes, where the pairing medium is the 4f electron cloud with highly complex shapes and even weaker electron-electron cloud interactions, resulting in lower transition temperatures.

Properties of unconventional high-temperature superconductors—including superconducting electron coherence length, real-space local pairing, pseudogaps, and d-wave symmetry—can all be explained using electron cloud changes as the electron pairing medium.

In conventional superconductors, the coherence length of superconducting electron pairs is on the order of 100 nm, whereas in unconventional superconductors it is on the order of 1 nm. This is because the attractive force between free electrons caused by electron cloud changes is short-range, resulting in short average distances between the two electrons in a superconducting pair. The coherence length of elemental superconductor Nb is 38 nm, which is also very short compared to traditional low-temperature superconductors, further supporting electron cloud changes as the pairing medium in Nb.

In 2007, K. K. Gomes [20] presented images of real-space local pairing in unconventional superconductors, where local pairing persists even above Tc. Again, because the force is short-range, it can only attract nearby electrons, enabling only real-space local pairing. For unconventional superconductors, as temperature decreases to a certain point, electrons begin to pair, but due to strong locality and few electron pairs, a coherent state cannot form and macroscopic superconductivity cannot emerge. Consequently, local pairing remains above Tc, creating a pseudogap. The anisotropy of the pseudogap in momentum space [21] and the d-wave symmetry of superconducting electron pairs [22] also originate from the complexity of electron cloud changes. First, electrons with different wave vectors may excite different changes in transition metal ion electron clouds; second, after forming positive charge regions, screening effects may be anisotropic, resulting in different attractions for electrons with different wave vectors.

Finally, regarding isotope effects: unconventional superconductors have more complex structures and compositions with more atomic species, making isotope effects very complicated. In copper oxide high-temperature superconductors, although electron-phonon interactions cannot explain electron pairing, existing experimental results have proven that phonons significantly influence electron pairing in high-temperature superconductors [23][24]. This is easily explained by electron cloud changes: because the frequency of electron cloud changes approaches lattice vibration frequencies, lattice vibrations greatly influence electron cloud changes, thereby affecting electron pairing and superconducting transition temperature.

The author proposes that electron clouds constitute an electron pairing medium similar to the lattice. Calculations show that electron cloud change frequencies approach lattice vibration frequencies and exceed lattice vibration frequencies at ambient pressure, enabling higher transition temperatures at ambient pressure. Simultaneously, electron cloud changes differ importantly from lattice vibrations: their force is short-range and directional, capable of explaining the special phenomena of unconventional superconductors.

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