Electron Pairing Mechanism in Unconventional Superconductors

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Abstract

The author put forward that the change of the electron clouds of the transition metal ions is the electron pairing medium in unconventional superconductors. It is just like the vibration of lattice is the electron pairing medium in conventional superconductors. Calculations with TDDFT method show that the frequency of the change of the electron clouds of the transition metal ions is close to that of the lattice. So, the change of the electron clouds can be excited by free electrons. Results of three copper oxide superconductors show that the higher the frequency, the higher the transition temperature. The difference between the change of the electron clouds and the lattice is also presented. The difference can explain special properties of unconventional superconductors, such as real space paring, pseudo energy gap, d symmetry and unconventional isotopy effect.

Key Words: high temperature superconductor; unconventional superconductor; electron pairing mechanism

1. Introduction

In 1911, Onnes [1] discovered superconductivity in Hg at 4.2K. In 1957, 44 years after the discovery of superconductivity, Bardeen, Cooper and Schlieffer put forward the famous BCS theory [2][3]. The theory can explain the superconductivity of conventional superconductors, such as Hg (T_c=4.2K) and Pb (T_c=7.2K). For conventional superconductors with lattice as the electron pairing medium, the critical temperature cannot exceed 40 K (McMillan limit) at normal pressures. The discovery of copper-oxide [4][5] and iron-based superconductors [6][7] challenged BCS theory seriously, because the critical temperatures are more than 40K. This indicates that electron-lattice interactions cannot explain the electron-pairing mechanism in unconventional superconductors.

The electron pairing mechanism for unconventional superconductors is still under debate. P. W. Anderson [8] has raised an important question in 2007: Is There Glue in Cuprate Superconductors?

The author believes that the change of the electron clouds of transition metal ions is the glue (medium) for electron pairing in unconventional superconductors. This idea is supported by the TDDFT calculation of real time evolution of charge density in metal Nb, iron-based superconductors and copper oxide superconductors. Special properties of unconventional high-temperature superconductors can also be explained by the change of the electron clouds of transition metal ions. This article will report the author's calculation methods and results.

2. Change of the electron clouds of the transition metal ions

The author has investigated 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 $Bi_2Sr_2Ca_2Cu_3O_{10}$) [9]. It is found that, under a static electric field, the electron clouds of transition metal ions change significantly. Figure 1 displays the crystal structure of $La_2Fe_2As_2O_2$ and the charge density difference with and without electric field. To introduce the electric field, one Li^+ ion was inserted. Detailed methods and results are given in reference [9].

The charge density around Fe^{2+} ions changes significantly. There are no similar change around other ions. The change is more like a rigid-body rotation rather than an elastic deformation, because the change is not entirely along the direction of the electric field. Some areas increase, while other areas decrease. Furthermore, the pattern of the change is like 3*d* electron clouds. It shows the importance of the change of the electron clouds of Fe^{2+} ions.

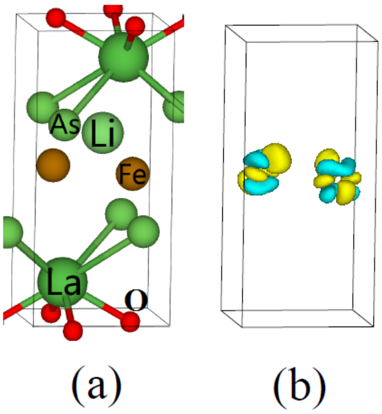

Figure 1 (a) Crystal structure of $La_2Fe_2As_2O_2$ with one Li^+ ion inserted; (b) Charge density change from Li^+ Insertion. The yellow color represents a positive value or increase of the charge density, while the blue color negative or decrease.

The author suggests that the change of the electron clouds of transition metal ions is the electron-pairing medium. The pairing mechanism is as follows. When a free electron comes to a new place, the electron clouds of the neighboring transition metal ions will change. In this way, the charge densities around the free electron will decrease. When the free electron leaves, the electron clouds of the transition metal ions will not relax immediately, so that there will be a region lack of charge. Another free electron will be attracted. An attraction between two free electrons appears. This mechanism is essentially the same as the electron-lattice interaction, except that the medium is the change of the electron clouds, not the displacement of the ions.

But, according to Born Oppenheimer approximation [10], the electrons are moving and responding to forces very quickly, because the electrons have much smaller masses than the nuclei (more than 1000 times). The electron density changes too fast and cannot be excited by free electrons. So, it is generally believed that electron pairing cannot be achieved by the change of the electron cloud.

But, can the electron density change as slowly as the nucleus?

The author made a further investigation. Real-time evolution of charge densities of unconventional superconductors has been calculated by TDDFT method. Detailed method and results are given in [11][12][13][14][15][16]. Figure 2 shows the crystal structure $La_2Fe_2As_2O_2$ and the real-time evolution of the charge density. 100 represents the charge density difference of the 8100th step and that of the 8000th step and the same below. The change of the electron clouds of the Fe^{2+} ions become obvious gradually with the evolution steps. After 100 steps, almost no change can be seen, and after 500 steps, the change has been obvious. The charge density change reaches its maximum after 800 steps, and the corresponding time is 1.6 $\hbar$/eV. It is the time from zero to the maximum. The time of one period should be 4×1.6 $\hbar$/eV and the frequency is about 160 meV.

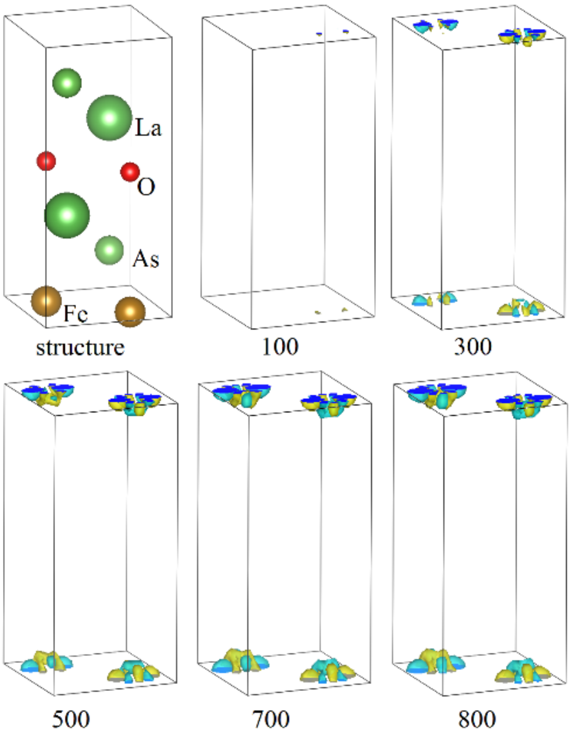

Figure 2 Crystal structure and the charge density evolution of $La_2Fe_2As_2O_2$.

For comparison, Table 1 gives the maximum phonon frequencies and T_c of three typical conventional superconductors. It can be clearly seen from the comparison that the frequency (160meV) of the change of the electron cloud of Fe^{2+} ion close to the lattice vibration frequency, which completely violates the Bonn-Oppenheimer approximation. It shows that the change of the electron cloud can be excited by free electrons to become the pairing medium of superconducting electrons.

Table 1 Maximum phonon frequencies and T_c of three typical conventional superconductors. H_3S is under a 250GPa pressure.

	Pb [17]	MgB_2 [17]	H_3S [18]
ω / meV	9	90	250
T_c / K	7	39	164

Why can the electron cloud of transition metal ions change significantly, and the frequency is low (it is close to the lattice vibration frequency), while the electron cloud of other ions fails to change significantly? This is because the outer electron configuration of Fe^{2+} ion in LaOFeAs is $3d^6$, and the $3d$ shell is not completely filled. In this way, the Fe^{2+} ion does not possess spherical symmetry, so it rotates under the influence of electric fields. An equivalent explanation is that the $3d$ orbital of the Fe^{2+} ion is reorganized and the electrons are refilled, so the electron cloud changes. Other ions, due to their full shells, exhibit spherical symmetry. Although they can also change, but greater electric field is required. The vibration frequency will be much higher than that of lattice vibration.

In addition to iron-based superconductors, the authors also observed the same phenomenon in copper oxide superconductors and metal elemental Nb. Figure 3 shows the change of the Nb electron clouds. The electron clouds of three Nb atoms has changed significantly, and the frequency is about 160 meV (it is a coincidence that the frequency is the same as that of $La_2Fe_2As_2O_2$). The difference from Fe^{2+} is that the 4d electron cloud of Nb has a more complex shape. We know that Nb does not conform to the isotope effect, indicating that the superconducting electron pairing medium is the change of the electron cloud not the lattice vibration.

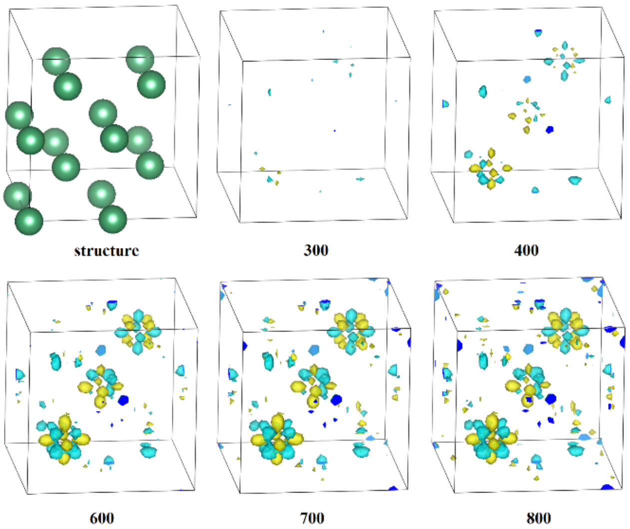

Figure 3 Crystal structure of Nb and the charge density evolution. The isosurface is 0.02

It can also be seen from Table 1 that the higher the frequency of the electron pairing medium (the frequency cannot be too high, and it cannot be excited by free electrons), the higher the transition temperature of superconductor. Of course, this is only an approximation, and it can only be established when other parameters are approximately the same.

Copper oxide high-temperature superconductors all have copper-oxygen planes, and their structures have very high similarities. It is expected that the higher the frequency of the electron cloud, the higher the superconducting transition temperature. Table 2 shows the critical temperature of three copper oxide superconductors and the frequency of electron cloud calculated by the author. There is indeed an approximate relationship, which strongly illustrates that the change of the electron cloud is the unconventional superconducting electron pairing medium.

Table 2 Transition temperatures of three copper oxide superconductors and the frequencies calculated by the author. LaCuO gives the transition temperature of $La_{2-x}Sr_xCuO_4$ with $x = 0.15$. The author observes different modes with different frequency in LaCuO and $TlBa_2CaCu_2O_7$.

	LaCuO	$TlBa_2CaCu_2O_7$	$HgBa_2Ca_2Cu_3O_8$
T_c/K	38	91	133
ω/meV	36, 83 [13]	140, 208 [15]	250 [11]

Table 3 shows the frequencies of the electron clouds of five iron-based superconductors calculated by the author. The calculation objects are ideal structures with strict chemical ratio (actual superconductors are all doped). The frequencies are close to the lattice vibration frequencies, but the approximate relationship between the transition temperature and the frequency cannot be observed. This is because there are many types of iron-based superconductors, the chemical composition is complex, and the transition temperature is relatively close.

Table 3 The calculated frequencies of five iron-based superconductors, -2e means the reduction of two valence electrons. Different modes with different frequencies are observed in some systems.

Iron based	ω/meV
LaOFeP	280
$BaFe_2As_2$	150, 160, 250, 200
$La_2Fe_2As_2O_2$	160
$K_2Fe_4Se_4$-2e	250, 100
FeSe sheet	230, 90

It is also meaningful to compare the frequencies and transition temperatures of different types of superconductors. H_3S is a conventional superconductor by electron-phonon coupling. It has a transition temperature of 164K under ultra-high pressure, and its highest lattice vibration frequency is 250 meV. The electron cloud change frequency of $HgBa_2Ca_2Cu_3O_8$ also happens to be 250 meV, and its transition temperature is as high as 133K. Both have high transition temperature and high frequency, which is in line with the expectation that the higher the frequency of the pairing medium, the higher the transition temperature. At the same time, the fundamental reason why the copper oxide high-temperature superconductor can achieve a transformation temperature far exceeding 40K under normal pressure is also given. That is the frequency of the electron pairing medium (electron cloud change) is much higher than the frequency of the lattice vibration under normal pressure.

In short, from the perspective of frequency, the change of the electron clouds of transition metal ions can be used as a pairing medium for superconductivity. The high correlation between the frequency of the electron cloud and transition temperature observed in three typical copper oxide high-temperature superconductors is a strong proof.

3. The difference between the change of the electron cloud and lattice vibration

As electron pairing mediums, the electron cloud of transition metal ions and crystal lattice have similar vibration frequencies, which is where they coincide. But there are also important differences between the two, which can explain the difference between unconventional high-temperature superconductivity and conventional superconductivity.

It can be seen from Figure 1 that the change of the electron cloud is more like a rotation, where the charge density increases in some places and decreases in other places. When a free electron comes to a new position, the density of non-free electrons around it will decrease due to the change of the electron cloud (the electron cloud are also non-free electrons), which is equivalent to the appearance of a positive charge ('positive charge' is used in the following). Compared with the lattice change, the positive charge area formed by the electron cloud is smaller and the charge is more concentrated. When this free electron leaves, this positively charged region will form a strong attraction to other free electrons. But also, because the change of the electron cloud is like a rotation, the charge increases in some places and decreases in other places, which will form a shield for the positive charge area formed by itself, and therefore cannot attract the electrons farther away. Therefore, the attraction between electrons caused by the electron cloud is characterized by strong force, but short-range. Furthermore, the shielding of the positive charge area is directional. This is not the case with lattice vibration. The positive charge area caused by lattice vibration is very large (see Figure 4), and the attraction to electrons near the positive charge area is weak, but there is no shielding effect. It is long-range and isotropic. Such a difference leads to the special properties of unconventional high-temperature superconductivity.

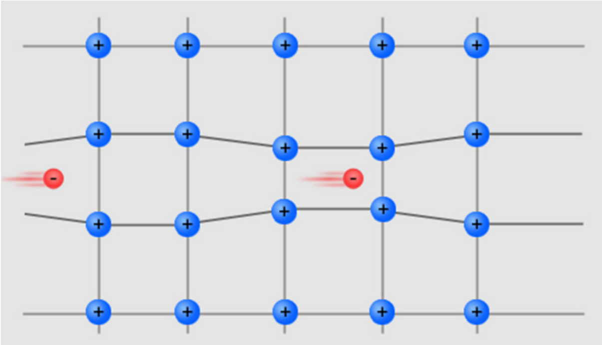

Figure 4 Schematic diagram of attraction of electrons caused by lattice

First, compare the superconducting metal element Pb and the superconducting metal element Nb. Pb is a conventional superconductor that can be fully explained by the electron-phonon interaction, while Nb does not conform to the isotope effect and cannot be fully explained by the electron-phonon interaction. The author believes that the change of the electron cloud is medium for electronic pairing in Nb. However, the transition temperature of Pb is 7K, and the highest lattice frequency is 9meV. The electron cloud change frequency of Nb is 160meV, which is much higher than the highest frequency of Pb, but the transition temperature is only 9.2K. Why? Because for Nb, it is the 4d orbital that plays a role, and the shape of the electron cloud is more complicated than that of the 3d electron cloud. It is difficult to form a large positive charge area in the interaction with free electrons, so the coupling between the free electrons and the electron cloud is weak, so the transition temperature is low. High frequency is a necessary condition for high transition temperature, but not a sufficient condition.

Heavy fermion superconductors, such as $CeCu_2Si_2$, T_c=0.6 K [19], can also be explained by the electron cloud change. The electron pairing medium is the 4f electron cloud. The shape of the electron cloud is very complex. The interaction between a free electron and the electron cloud is weak, so the transition temperature is low.

The coherence length, real-space pairing, pseudo-energy gap and d-wave symmetry in unconventional high-temperature superconductors can all be explained by the change of electron cloud as the electron pairing medium.

In conventional superconductors, the coherence length of superconducting electron pairs is on the order of 100 nm, but in unconventional superconductors, the coherence length is on the order of 1 nm. This is because the attraction between free electrons caused by the change of the electron cloud is short-range, and the average distance between two electrons in a superconducting electron pair is very short. The coherence length of the metallic elementary superconductor Nb is only 38nm, which is also very short compared to the traditional low-temperature superconductor. It suggests that the electron cloud change is the electron pairing medium of Nb.

In 2007, K. K. Gomes [20] gave an image of the local pairing of electrons in unconventional superconductors. When the temperature is above T_c, local electron pairing remains. Because the force caused by the change of the electron cloud is short-range, a free electron can only attract nearby electrons. Therefore, electrons can only be paired locally in real space. For unconventional superconductors, when the temperature drops to a certain level, the electrons will start to pair. But a coherent state of macroscopic superconducting cannot be achieved, because the electron pair is highly local and the number of the electron pairs is small. Above T_c, the local electron pairing remains, forming a pseudo-energy gap. The anisotropy of the pseudo-energy gap in the *k*-space [21] and the d-wave symmetry [22] of the superconducting electron pair also come from the complexity of the change of the electron cloud. Firstly, electrons with different wave vectors may cause different excitations of the electron cloud; secondly, after the formation of a positive charge region, due to the anisotropy of the screening effect, the attraction to the electrons with different wave vectors will be different.

In the end, the author wants to briefly talk about the isotope effect. The structure and composition of unconventional superconductors are more complex. The isotope effect is very complicated compared with low temperature conventional superconductors. In copper oxide high-temperature superconductivity, although the electron-phonon interaction cannot explain the electron pairing problem, experimental results have proved that phonon has an important influence on the electron pairing [23][24]. This is easy to explain using the change of the electron clouds. Because the frequency of the change of the electron cloud is close to the lattice vibration frequency, the vibration of the crystal lattice will affect the change of the electron cloud, which affects the pairing of electrons.

4. Conclusion

The author proposed that the electron cloud is an electron pairing medium like crystal lattice. The calculation results show that the frequency of the electron cloud is close to that of the lattice vibration, and higher than the lattice vibration frequency under normal pressure. Therefore, the electron cloud can be the electron pairing medium to obtain a higher transition temperature under normal pressure. There are important differences between the change of the electron cloud and the lattice vibration. The force caused by the change of the electron cloud is short-range and directional. This can explain the special phenomenon in unconventional superconductors.

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