Can electrons move as slowly as nuclei? Something about the Born Oppenheimer Approximation and electron-pairing medium in high temperature copper-oxide superconductors

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June 30, 2019

Abstract

Real-time evolution of the electron densities under excitations in La_2CuO_4 was calculated by the time-dependent density functional theory (TDDFT). The author found, for the first time, the electrons (the electron cloud of Cu^{2+}) in high temperature copper-oxide superconductors (La_2CuO_4) can move as slowly as nuclei. Under excitations, the electron cloud of Cu^{2+} changes obviously and the characteristic frequencies are 83 meV and 36 meV, respectively, for two different modes. The results are unexpected and close to that of lattice vibrations, because the change of the electron density should be very quick according to the Born Oppenheimer Approximation. The results show that the electron cloud of Cu^{2+} (just like the lattice) can be the electron-pairing medium in high temperature copper oxide superconductors.

Keywords: Born Oppenheimer Approximation; high temperature copper-oxide superconductors; time-dependent density functional theory; electron-pairing medium

1 Introduction

In 1986, J. G. Bednorz and K. A. Müller discovered that there may be high-temperature superconductivity (HTS) in La-Ba-Cu-O oxides [1], which revealed a new chapter in the research of superconductivity. In 1987, M. K. Wu et al. [2] and Z. X. Zhao et al. [3] synthesized Y-Ba-Cu-O superconductors, respectively, almost at the same time. The critical temperature (T_c) for superconductivity reached 90K and achieved a breakthrough above the liquid nitrogen temperature. The T_c of Hg-1223 can reach 153 K under a high pressure [4]. The electron-lattice interaction cannot explain the electron pairing mechanism in copper oxide superconductors. According to the BCS theory [5, 6], the superconducting transition temperature (T_c) caused by

electron-lattice interaction (at normal pressures) cannot be higher than 40K. The main reason is that the frequency of the lattice vibration at normal pressure is low, so T_c cannot be high. From the formula of T_c below, the higher the vibration frequency of the medium, the higher the transition temperature (under certain other conditions).

$$T_c = \frac{\langle \omega \rangle}{1.20} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

Recent advances in superconducting transition temperatures at high pressures [7][8][9] have taken advantage of the higher frequency of lattice vibration at high pressures. Table 1 gives the maximum phonon frequencies and T_c of three typical conventional superconductors. The higher the vibration frequency of the medium, the higher the transition temperature.

Table 1 Maximum phonon frequencies and T_c of three typical conventional superconductors.

	Pb [10]	MgB_2 [10]	H_3S [11]
ω / meV	9	90	250
T_c / K	7	39	164

Mr. Anderson [12] has raised an important question in 2007: Is There Glue in Cuprate Superconductors? The author believes that, if there does exist a glue in high temperature superconductors, the frequency should be close to that of the lattice vibration.

The author raises the question: Can the change of the electron densities be used as a pairing medium for superconducting electrons? The mechanism is as follows. When a free electron comes to a new place, the electron densities around the free electron will decrease. When the free electron leaves, another free electron will be attracted. An attraction appears. This mechanism is essentially the same as the electron-lattice interaction, except that the medium is the change of the electron density, not the displacement of the ions.

According to Bonn Oppenheimer approximation [13], the electrons have much smaller masses than the nuclei (more than 1000 times), consequently, the electrons are moving and responding to forces very quickly. The electron density changes too fast and can not be excited by free electrons. So, it is generally believed that electron pairing cannot be achieved by the change of the electron densities.

But can the electron density change as slowly as the nucleus does? If it is, then it can be the pairing medium.

Based on the above consideration the author made an investigation, exploring the frequencies of the change of the electron densities. The real-time evolution of charge densities under some excitation of La_2CuO_4 has been calculated by TDDFT [14, 15] method. The author found, for the first time, the change of the electron density of Cu^{2+} can be as slow as lattice vibration. This paper will report the methods and results.

2 Methods

Calculations were conducted within the Octopus package [16, 17]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation energy. The GGA+U method [18, 19] was considered to deal with the strong correlation of the 3*d* electrons. HSCV pseudopotentials [20] were adopted. Approximated Enforced Time-Reversal Symmetry (AETRS) algorithm was used to approximate the evolution operator and the time step is 0.002 $\hbar$/eV. $5p^6d^16s^2$ of La, $3p^6d^{10}4s^1$ of Cu and $2s^2p^4$ of O are taken as valence electrons. The *k*-point setting is 4×4×2. The real space spacing is 0.35 Bohr. The change of charge densities is induced by a time-dependent electric field:

$$f(t) = F_0 \cos(\frac{\pi}{2}\frac{t-2\tau_0-t_0}{\tau_0})\cos\omega t \qquad If\ |t-t_0| > \tau_0\ ,\ then\ f(t) = 0.$$

where F_0 = 1.0 eV/angstrom, τ_0 = 5.0/eV and t_0 = 5.0/eV. The electric field is along the [111] direction. Fig.1 shows the time dependence of the electric filed. The excitation vanishes after 5000 steps and the charge densities vibrate freely thereafter.

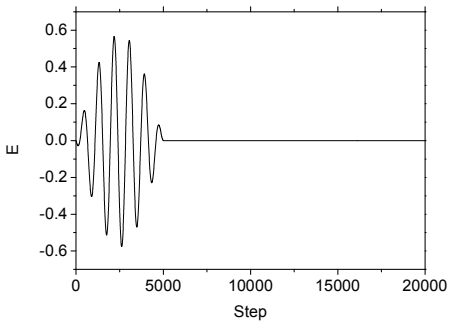

Fig. 1 Time dependence of the electric field applied

3 Results and Discussions

After 10000 steps' evolution, the charge densities are recorded. Fig. 2 shows the crystal structure and the real-time evolution of the charge density. 500 represents the charge density difference between the 10500th step and the 10000th step and the same below. The change of the electron clouds of Fe ions become obvious gradually with the evolution steps. For Cu1, the change of the charge density reaches its maximum after about 1500 steps, and the corresponding time is 3.0 $\hbar$/eV. It is the time from zero to the maximum. The time of one period should be 4×3.0 $\hbar$/eV and the frequency is about 83 meV. For Cu2, the change of the charge density reaches its maximum after about 3500 steps, and the corresponding frequency is about 36 meV. The frequency given in this way is not very accurate and may have an error as large as ±20%, but the frequency is close to that of the lattice vibration.

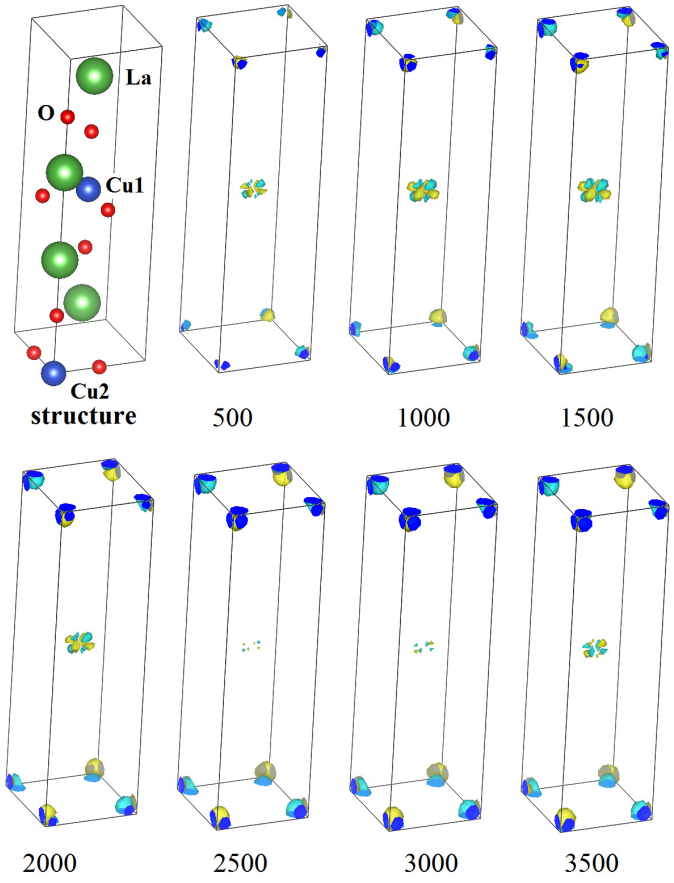

Fig.2 Crystal structure and the charge density evolution of La_2CuO_4. Plots were generated using VESTA [21]. The isosurface is 0.05 e/bohr^3. The yellow color represents an increase of the charge density, while the blue a decrease.

The authors also studied other superconductors. For $La_2Fe_2As_2O_2$, FeSe sheet and $HgBa_2Ca_2Cu_3O_8$, the characteristic frequencies are 160 meV, 190meV, and 250meV, respectively [22]. For $BaFe_2As_2$, the characteristic frequencies are 150 meV, 160 meV, 250 meV, and 200 meV, respectively, for the modes the author observed [23]. It is worth noting that the change of the electron clouds of transition metal ions is very complicated. There may be different modes, corresponding to different frequencies. The results are unexpected, because the general view is that the change of the electron density is very quick and the frequency is much higher than the lattice vibration. The frequencies the author obtained are close to that of the lattice vibration, indicating it can be excited by free electrons. So, the change of the electron clouds of transition metal ions can be the electron-pairing medium. W. A. Little [24] gave similar results, but the frequencies are too high. Whether it can be excited by free electrons should be justified.

Why do the electron clouds of transition metal ions change this way? The main reason is that the 3*d* shell of transition metal ions is not fully filled. The electron clouds possess no spherical symmetry, and easy to change under electric fields.

4 Summary

Real-time evolution of the electron clouds of transition metal ions in La_2CuO_4 was calculated by the TDDFT method. For the first time, the author found that the electron cloud of transition metal ions can change slowly. The frequencies of evolution of electron clouds match well with the frequencies of the lattice vibrations. This is contrary to Bonn Oppenheimer approximation. Though the frequencies obtained by this method are not accurate, it can give a significant evidence that the change of electron clouds can be the electron-pairing medium in HTS. The change of electron cloud can be used as a pairing medium for superconducting electrons.

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