

Slow change of the electron clouds of ions: a common medium for electron pairing in LaOFeP, Nb and TlBa₂CaCu₂O₇

Tiege Zhou

College of Electronic Information and Optical Engineering, Nankai University, 300350 Tianjin, P. R. China

zhoutg@nankai.edu.cn

Abstract

The author proposes that the change of the electron clouds of ions can be a new electron-pairing medium in unconventional superconductors. Real-time evolution of the electron clouds of ions in LaOFeP, Nb and TlBa₂CaCu₂O₇ was calculated by the time-dependent density functional theory (TDDFT). The natural frequencies of the change of the electron clouds were obtained. The author found, for the first time, the frequencies are close to those of the lattice vibrations. The characteristic frequencies are 280 meV, 160 meV, 208 meV and 140 meV, respectively, for different ions, showing that the change of the electron clouds of the ions can be the electron-pairing medium. Iron-based superconductors, copper-based superconductors and superconductors which do not conform to isotope effects or cannot be explained by electron-phonon interactions may all have a common electron-pairing medium: the change of the electron clouds of ions.

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

1 Introduction

It is well known that the superconductivity in copper-oxides [1, 2] and iron-based [3, 4] superconductors cannot be explained by the electron-lattice interaction. In addition, Nb is a well-known superconductor. Nb does not conform to the isotope effect and cannot be fully explained by the electron-lattice interaction. There may be other electron-pairing mechanisms.

Is there a common electron-pairing medium in copper-oxides, iron-based superconductors and Nb?

The author proposes that the change of the electron clouds of ions can be a new pairing medium for superconducting electrons. The mechanism is as follows. When a free electron comes to a new place, the electron clouds of ions nearby will change and the electron densities around the free electron will decrease. When the free electron leaves, the electron density will not relax immediately, so there will be a region lack of charge. 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 clouds, not the displacement of the ions.

But according to Bonn Oppenheimer approximation^[5], 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 clouds change too fast and relax immediately. So, it is generally believed that electron pairing cannot be achieved by the change of the electron clouds.

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

To test the author's idea, real-time evolution of the electron clouds of LaOFeP, Nb and TlBa₂CaCu₂O₇ has been calculated by TDDFT^[6, 7] method. The author found, for the first time, the electron clouds can change as slowly as the nucleus. This paper will report the methods and results.

2 Methods

Calculations were conducted within the Octopus package^[8, 9]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation energy. The GGA+U method^[10, 11] was considered to deal with the strong correlation of the 3d electrons of Fe and Cu. HSCV pseudopotentials^[12] 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.

3 Results and Discussions

3.1 LaOFeP

The k -point setting is $4 \times 4 \times 2$ and $5p^6d^16s^2$ of La, $3p^6d^64s^2$ of Fe, $3d^{10}4s^2p^3$ of As and $2s^2p^4$ of O are taken as valence electrons in the calculation. The real space spacing is 0.35 Bohr. The change of charge densities is induced by a time-dependent electric field:

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

where $F_0 = 1.0$ eV/angstrom, $\omega = 1.8$ eV, $\tau_0 = 10$ /eV and $t_0 = 10$ /eV. The electric field is along the [111] direction. The excitation vanishes after 10000 steps and the charge densities vibrate freely thereafter. After 15000 steps, the change of the charge densities is recorded. At this stage, the charge densities vibrate freely without any external influence and the positions of all atoms are fixed. Fig. 1 shows the crystal structure and the real-time evolution of the charge densities. 100 represents the charge density

difference between the 15100th step and the 15000th step and the same below. The change of the electron clouds of Fe ions become obvious gradually with the evolution steps. After 100 steps, almost no change can be seen, while after 400 steps, the change has been obvious. To give a better illustration, Fig. 2 shows the maximum value of the charge density change as a function of the evolution steps. The charge density change reaches its maximum after about 450 steps, and the corresponding time is $0.9 \hbar/eV$. It is the time from zero to the maximum. The time of one period should be $4 \times 0.9 \hbar/eV$, so the frequency is about 280 meV.

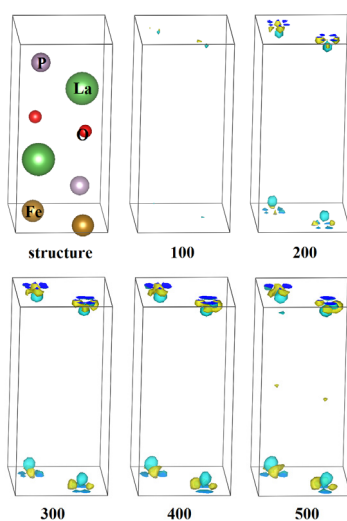


Fig. 1 Crystal structure and the charge density evolution of LaOFeP. Plots were generated using VESTA^[13] (the same below). The isosurface is 0.01 e/bohr^3 . The yellow color represents an increase of the charge density, while the blue a decrease (the same below).

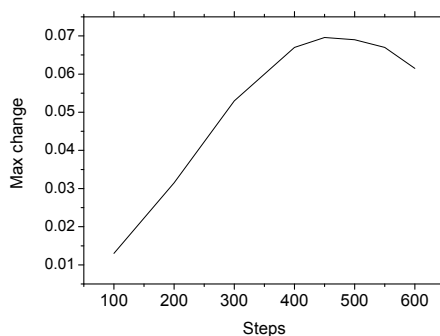


Fig. 2 The relationship between the maximum value of charge density change and the evolution steps.

The electron clouds of Fe^{2+} ions ($3p^6d^6$) have changed significantly, while La^{3+} , O^{2-} and P^{3-} ions have not changed significantly. This is because the 3d shell of Fe^{2+} ions are not fully filled, while shells of La^{3+} , O^{2-} and P^{3-} ions are fully filled. For Fe^{2+} ions, the electron clouds possess no spherical

symmetry, so they can change significantly. It's like the rotation of a polar molecule. Of course, there is another way of interpretation. The 3d orbitals are re-hybridized and the electron clouds change.

3.2 Nb

Fig. 3 shows crystal structure and the charge density evolution of Nb. The k -point setting is $2 \times 2 \times 2$ and $4p^6 4d^4 5s^1$ of Nb are taken as valence electrons. The real space spacing is 0.35 Bohr. After 15000 steps, the change of the charge densities is recorded. The change of the electron clouds reaches its maximum after about 800 steps and the frequency is about 160 meV.

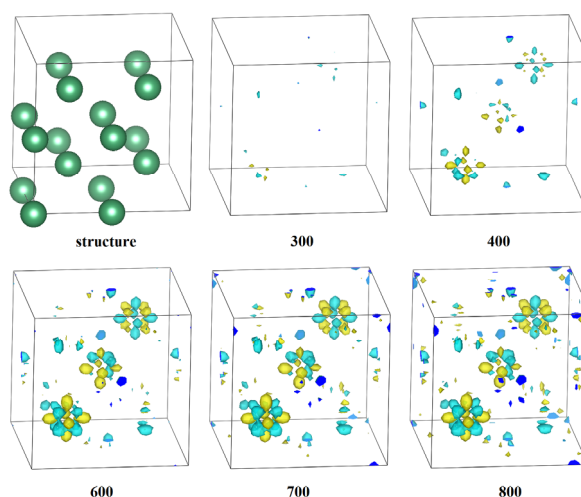


Fig. 3 Crystal structure and the charge density evolution of Nb. The excitation is the same as above. The isosurface is 0.02.

For Nb atoms ($4p^6 4d^4 5s^1$), the 4d shell is not fully filled and the electron clouds possess no spherical symmetry. Electron clouds of three Nb atoms changed significantly. Not all Nb atoms were activated. Calculation with $4 \times 4 \times 4$ k -points give consistent results.

3.3 $TlBa_2CaCu_2O_7$

The k -point setting is $2 \times 2 \times 1$ and $5d^{10} 6s^2 6p^1$ of Tl, $5p^6 6s^2$ of Ba, $3p^6 4s^2$ of Ca, $3p^6 d^{10} 4s^1$ of Cu and $2s^2 p^4$ of O are taken as valence electrons. The real space spacing is 0.39 Bohr. Fig. 4 shows the results excited by a slight change in the position of an Tl atom. The original coordinate of the Tl ion is (0.5, 0.5, 0.0), and modified to (0.52, 0.51, 0.0), The ground state was calculated. Then modify the coordinate back to (0.5, 0.5, 0.0) and conduct TDDFT calculations. In the evolution, the charge densities vibrate freely without any external influence and the positions of all atoms are fixed. After 15000 steps, charge densities were recorded. The change of the electron cloud of the Cu^{2+} ion indicated by an arrow reaches its maximum after about 600 steps. The frequency is approximately 208 meV. The 3d shell of Cu^{2+} ions ($3p^6 d^9$) is not fully filled and the electron clouds possess no spherical symmetry.

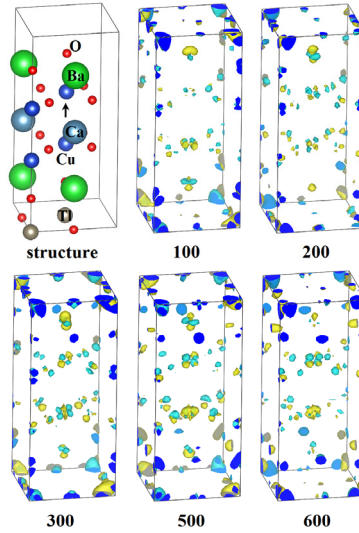


Fig. 4 Crystal structure and evolution of the charge density of $(\text{TlBa}_2\text{CaCu}_2\text{O}_7)$ excited by changing an Tl atom.

The isosurface is 0.05.

Fig. 5 gives the change of charge densities of $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ induced by a time-dependent electric field. The charge densities are recorded after 18000 steps. For the O^{2-} ion indicated by an arrow, the change of the charge density research its maximum after 900 steps and the characteristic frequency is about 140meV. For this, the change of the charge density is very complicated, and the author only carefully observed one of the oxygen ions. The author believes that the valence of the oxygen is not strictly -2, which has been introduced in other literatures. Then its electron clouds can change significantly.

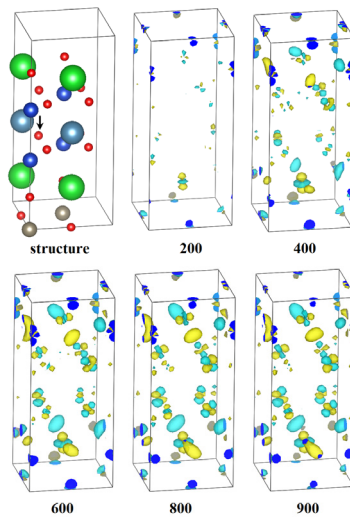


Fig. 5 Crystal structure and evolution of the charge density of $(\text{TlBa}_2\text{CaCu}_2\text{O}_7)$ excited by a time-dependent

electric field. The isosurface is 0.02.

The obtained characteristic frequencies of the change of the electron clouds are 280 meV, 160 meV, 208 meV and 140 meV, respectively, for different ions. Table 1 gives the maximum phonon frequencies and T_c of three typical conventional superconductors.

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

	Pb [14]	MgB ₂ [16]	H ₃ S [15]
ω / meV	9	90	250
T_c / K	7	39	164

The frequencies the author obtained are close to that of the lattice vibration. 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, so the change of the electron clouds of ions can be the electron-pairing medium.

The author has also studied other systems ^{[16][17][18]}. Similar results were obtained. It is worth noting that the change of the electron clouds of transition metal ions is very complicated. For the same superconductor, there may be different modes, corresponding to different frequencies.

Why do the electron clouds of transition metal ions change slowly? The main reason is that the shell of the ions is not fully filled. The electron clouds possess no spherical symmetry, and easy to change under electric fields. Because it is easy to change, the frequency is low and close to the frequency of lattice vibrations.

P. W. Anderson ^[19] 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. It is not only the glue in cuprate superconductors, but also the glue in iron-based superconductors, Nb and other superconductors which cannot be explained by electron-lattice interaction. It can also be the glue in heavy fermion superconductors. Because these superconductors have ions with shells that are not fully filled.

4 Summary

Real-time evolution of the electron clouds of ions in LaOFeP, Nb and TlBa₂CaCu₂O₇ was calculated by the TDDFT method. The frequencies of evolution of electron clouds match well with the frequencies of the lattice vibrations in conventional superconductors. Though the frequencies obtained by this method are not accurate, it can give a significant evidence that the change of electron clouds can

be a new electron-pairing medium.

Acknowledgements The author sincerely thanks Xu Zuo, Xu Zhang, Xiaoguang Luo, Min Wang, Feng Lu, Hong Dong, Jian Zhou and Yu Bai for useful discussions.

References

- [1] Bednorz, J. G., Müller, K. A.: Possible high T_C 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. *Phys. Rev. Lett.* 58, 908-910 (1987)
- [3] Kamihara, Y., Hiramatsu, H., Hirano, M., Kawamura, R., Yanagi, H., Kamiya, T., Hosono, H.: Iron-Based Layered Superconductor: LaOFeP. *J. Am. Chem. Soc.* 128(31), 10012-10013 (2006).
- [4] Kamihara, Y., Watanabe, T., Hirano, M., Hosono, H.: Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs ($x = 0.05-0.12$) with $T_c = 26$ K. *J. Am. Chem. Soc.* 130, 3296-3297 (2008).
- [5] M. Born and R. Oppenheimer, "Zur Quantentheorie der Molekeln," *Ann. Physik* 84, 457-484 (1927)..
- [6] 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).
- [7] Marques, M. A. L., Gross, E. K. U.: Time-dependent density functional theory, *Annu. Rev. Phys. Chem.* 55 427-455 (2004).
- [8] 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).
- [9] 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).
- [10] 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).
- [11] 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).
- [12] Vanderbilt, D.: Optimally smooth norm-conserving pseudopotentials. *Phys. Rev. B* 32, 8412-8115 (1985).
- [13] Momma, K., Izumi, F.: VESTA: a three-dimensional visualization system for electronic and structural analysis. *J. Appl. Cryst.* 41, 653-658 (2008).
- [14] 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).
- [15] Durajski, A.P., Szczyński, R.: First-principles study of superconducting hydrogen sulfide at pressure up to 500 Gpa. *Sci. Rep.* 7, 4473 (2017).
- [16] Tieg Zhou. Is There Glue in Cuprate Superconductors? The Change of the Electron Clouds of Ions. <https://dx.doi.org/10.13140/RG.2.2.20629.78561>
- [17] Tieg Zhou, et al. Real-Time Evolution of the Electron Clouds of Transition Metal Ions: Possible

Electron-Pairing Medium in Unconventional High-Temperature Superconductors.
<https://dx.doi.org/10.1007/s10948-019-05205-6>

[18] Tiegeng Zhou. Can electrons move as slowly as nuclei? Something about the Born Oppenheimer Approximation and electron-pairing medium in high temperature copper-oxide superconductors.
<https://dx.doi.org/10.13140/RG.2.2.17090.84160>

[19] Anderson, P. W.: Is There Glue in Cuprate Superconductors? *Science* 22, 1705-1707 (2007)