Possible new electron-pairing medium in superconductors: A TDDFT study of Nb, Nb_3Ge, Pb and MgB_2

Tiege Zhou

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

zhoutg@nankai.edu.cn

Abstract

Besides the electron-lattice interaction, the author proposes that the change of the electron clouds of ions can be a new electron-pairing medium in superconductors. Real-time evolution of the charge densities in Nb, Nb_3Ge, Pb and MgB_2 was calculated by the time-dependent density functional theory (TDDFT). The electron clouds of Nb atoms change significantly in Nb and Nb_3Ge. The natural frequencies are 125 meV and 156 meV, respectively. The frequencies are close to those of lattice vibrations, showing that the change of the electron clouds of the ions can be the electron-pairing medium. For Pb and MgB_2, no similar result was obtained.

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

1 Introduction

Nb, Nb_3Ge, Pb and MgB_2 are well-known superconductors. Electron pairing in Pb and MgB_2 can be explained by the electron-lattice interaction. But Nb and Nb_3Ge don't conform to the isotope effect and cannot be fully explained by the electron-lattice interaction. Furthermore, the superconductivity in copper-oxides [1, 2] and iron-based [3, 4] superconductors cannot be explained by the electron-lattice interaction.

So, besides the electron-lattice interaction, there may be another electron-pairing medium. The author thinks that, if a new medium does exist, the medium should change under excitations and the characteristic frequency should be close to that of the lattice vibration.

To test the author's idea, real-time evolution of the electron clouds in Nb, Nb_3Ge, Pb and MgB_2 been calculated by TDDFT [5, 6] method. This paper will report the methods and results.

2 Methods

Calculations were conducted within the Octopus package [7, 8]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation energy. The GGA+U method [9, 10] was considered to deal with the strong correlation of the 3*d* electrons of Fe and Cu. HSCV pseudopotentials [11] were adopted. Approximated Enforced Time-Reversal Symmetry (AETRS) algorithm was used to approximate the evolution operator and the time step is 0.002 ħ/eV. Reference [12] gives detailed calculation methods and key parameters.

3 Results and Discussions

3.2 Nb

Fig. 1 shows the results of Nb. The vibration was excited by a time dependent electric field (Reference [12]). The excitation vanished after 10000 steps, the charge density vibrates freely thereafter, and the charge density change were recorded. The *k*-point setting is 4×4×4 and $4p^6 4d^4 5s^1$ of Nb are taken as valence electrons. The real space spacing is 0.35 Bohr. The change of the electron clouds of the Nb atom indicated by an arrow reaches its maximum after about 1000 steps and the frequency is about 125 meV.

The change of the electron clouds of Nb is more like a rigid rotation rather than an elastic deformation, because the change is not entirely along the direction of the electric field. Some areas increase, while some areas decrease. Furthermore, the pattern of the change is like 4d electron clouds.

This is because the 4d shell of Nb is not fully filled, 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 4d orbitals are re-hybridized and the electron clouds change.

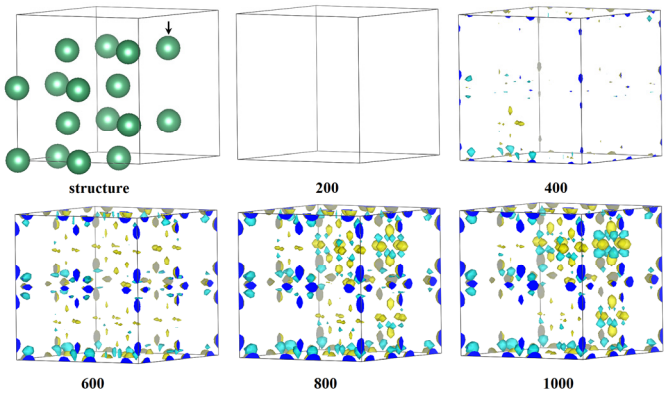

Fig. 1 Crystal structure and the charge density evolution of Nb excited by a time dependent electric field. Plots were generated using VESTA [13] (the same below). The isosurface is 0.01 e/bohr^3. 600 represents the charge density difference between the 15600th step and the 15000th step and the same below. The yellow color represents an increase of the charge density, while the blue a decrease (the same below).

3.2 Nb_3Ge

$3d^{10}4s^24p^2$ of Ge and $4p^64d^45s^1$ of Nb are taken as valence electrons. The *k*-point setting is 4×4×4 The real space spacing is 0.35 Bohr. Fig. 2 shows the crystal structure and the real-time evolution of the charge density. The charge density change reaches its maximum after about 800 steps, and the frequency is about 156 meV. The change of the electron clouds in Nb_3Ge is like in Nb.

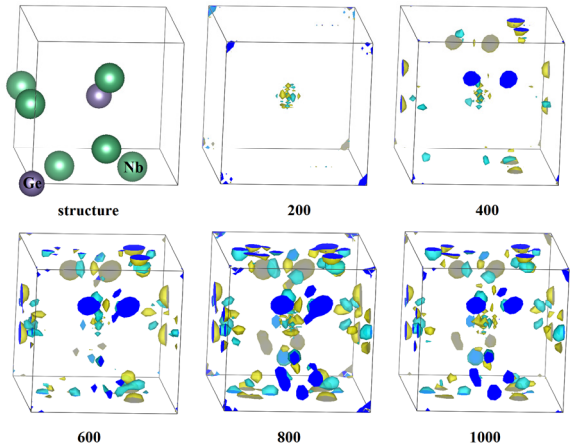

Fig. 2 Crystal structure and the charge density evolution of Nb_3Ge. The isosurface is 0.005.

3.3 Pb

The *k*-point setting is 2×2×2 and $5d^{10}6s^26p^2$ of Pb are taken as valence electrons. Fig. 3 shows the results. The change of charge density is different from Fig. 1 and Fig. 2. The electron cloud does not change, while the charge density of the whole system changes. This is because the shells are fully filled.

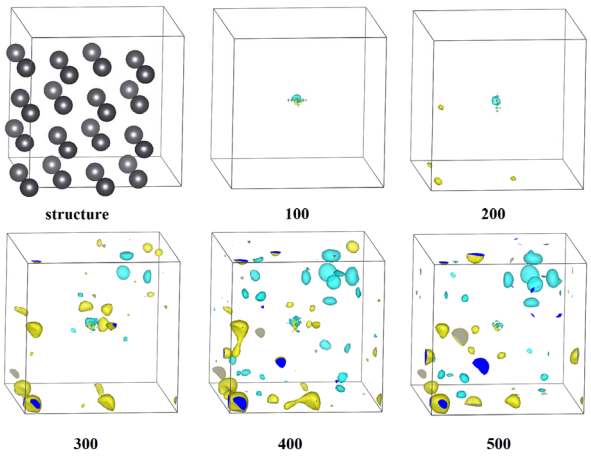

Fig. 3 Crystal structure and evolution of the charge density of Pb. The isosurface is 0.002.

3.4 MgB_2

The *k*-point setting is 2×2×2 and $2p^63s^2$ of Mg and $2s^22p^1$ of B are taken as valence electrons. Fig. 4 shows the results. It is like Fig.3. The electron cloud does not change. The charge density of the whole system changes.

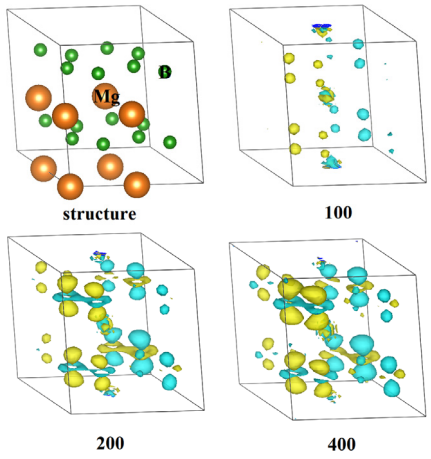

Fig. 4 Crystal structure and real time evolution of the charge density of MgB_2. The isosurface is 0.002.

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_3S [15]
ω / meV	9	90	250
T_c / K	7	39	164

The frequencies the author obtained in Nb and Nb_3Ge are close to that of the lattice vibration, so the change of the electron clouds can be a new electron pairing medium. The author has also studied

other systems [16] [17][18][19]. Similar results were obtained.

P. W. Anderson [20] 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 Nb, Nb_3Ge, Pb and MgB_2 was calculated by the TDDFT method. The frequencies of evolution of electron clouds in Nb and Nb_3Ge 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.

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] 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).

[6] Marques, M. A. L., Gross, E. K. U.: Time-dependent density functional theory, Annu. Rev. Phys. Chem. 55 427-455 (2004).

[7] 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).

[8] 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).

[9] 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).

[10] 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).

[11] Vanderbilt, D.: Optimally smooth norm-conserving pseudopotentials. Phys. Rev. B 32, 8412-8115 (1985).

[12] 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

[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., Szczęśniak, R.: First-principles study of superconducting hydrogen sulfide at pressure up to 500 Gpa. Sci. Rep. 7, 4473 (2017).

[16] 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] 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

[18] Tiege Zhou. Slow Change of the Electron Clouds of Ions: a Common Medium for Electron Pairing in Laofep,

Nb and Tlba2cacu2o7. http://vixra.org/abs/1908.0615

[19] 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

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