Characteristic frequency of the orbital fluctuation in the unconventional iron-based superconductor BaFe2As2: A TDDFT investigation of the electron pairing mechanism

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Abstract

It has been proposed that the electron-pairing medium in iron-based superconductors may be orbital fluctuations of transition metal ions. However, the characteristic frequency of orbital fluctuations has not been previously reported. For the first time, the author has calculated the real-time evolution of electron clouds of transition metal ions in BaFe2As2 under excitations using time-dependent density functional theory (TDDFT). Multiple fluctuation modes have been identified. The characteristic frequencies for the observed modes are 150 meV, 160 meV, 250 meV, and 200 meV, respectively. These results are unexpected, as the general consensus holds that changes in electron density occur extremely rapidly, with frequencies much higher than lattice vibrations. The frequencies obtained by the author are comparable to those of lattice vibrations in conventional superconductors under ambient and high pressures, indicating that orbital (or electron cloud) fluctuations can serve as the electron-pairing medium. Based on these calculation results, the author proposes a new electron pairing mechanism.

Full Text

Preamble

Characteristic Frequency of Orbital Fluctuation in the Unconventional Iron-Based Superconductor BaFe As : A TDDFT Investigation of the Electron Pairing Mechanism

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Abstract

It has been proposed that the electron-pairing medium in iron-based superconductors may be the orbital fluctuation of transition metal ions, yet the characteristic frequency of this orbital fluctuation remains unknown. For the first time, the author has calculated the real-time evolution of the electron clouds of transition metal ions in BaFe As under excitations using time-dependent density functional theory (TDDFT). Multiple distinct fluctuation modes were observed, with characteristic frequencies of 150 meV, 160 meV, 250 meV, and 200 meV, respectively. These results are unexpected, as the general view holds that changes in electron density occur extremely rapidly, with frequencies much higher than lattice vibrations. However, the frequencies obtained in this work are close to those of lattice vibrations in conventional superconductors at normal and high pressures, indicating that orbital (or electron cloud) fluctuation could serve as the electron-pairing medium. Based on these calculations, the author proposes a new electron pairing mechanism.

Keywords: iron-based superconductor; time-dependent density functional theory; electron-pairing medium; orbital fluctuation

1 Introduction

The electron-lattice interaction cannot explain the electron-pairing mechanism in unconventional copper-oxide [**?**, **?**] and iron-based [**?**, **?**] superconductors. Orbital fluctuation has been extensively studied as a new electron pairing mechanism [**?**, **?**, **?**, **?**], but its characteristic frequency has not yet been determined. If this frequency is too low or too high, orbital fluctuation is unlikely to serve as an effective electron-pairing medium. Table 1 provides the maximum phonon frequencies and Tc values for three typical conventional superconductors, suggesting that the characteristic frequency should reasonably fall in the range of 100–250 meV. Based on this consideration, the author has investigated the characteristic frequency of orbital fluctuation by calculating the real-time evolution of charge densities in BaFe As under excitations using the TDDFT method [**?**, **?**]. This paper reports the methods and results of that investigation.

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

Pb [9]	MgB	H S [10]
/ meV	Tc / K	

2 Methods

All calculations were conducted using the Octopus package [**?**, **?**]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was em-

ployed to describe the exchange-correlation energy, with the GGA+U method [**?**, **?**] applied to handle the strong correlation of 3d electrons. HSCV pseudopotentials [**?**] were adopted, and the Approximated Enforced Time-Reversal Symmetry (AETRS) algorithm was used to approximate the evolution operator with a time step of 0.002 /eV. The valence electron configurations were 3p 3d $4s^2$ for Fe, $3d^1$ $4s^2 4p^3$ for As, and 5p $6s^2$ for Ba. The real-space grid spacing was set to 0.35 Bohr. Charge density vibrations were excited using two distinct methods. The first applies a time-dependent electric field along the [111] direction. The second involves slight displacement of an atom; in these TDDFT calculations, the ions remain fixed while the electron densities vibrate freely.

3 Results and Discussions

Electric Field Excitation at = 1.8 eV

When an electric field with = 1.8 eV was applied, Figure 1 Figure 1: see original paper shows its time dependence. The excitation ceases after 5000 steps, after which the charge densities vibrate freely. The charge densities were recorded after 8000 steps of evolution. Figure 1(b) illustrates the crystal structure and the real-time evolution of charge density changes, where "100" represents the difference between the 8100th and 8000th steps (with analogous notation used throughout). The changes in the electron clouds of Fe ions (marked 3 and 4) become progressively more pronounced with evolution steps. For clarity, Figure 1(c) plots the maximum value of charge density change as a function of evolution steps. The charge density change reaches its maximum after approximately 850 steps, corresponding to a time of 1.7 /eV from zero to maximum. The period of one complete oscillation should be 4×1.7 /eV, yielding a frequency of about 150 meV. This result is unexpected, as conventional wisdom suggests that electron density changes occur extremely rapidly at frequencies much higher than lattice vibrations. However, the author' s results are comparable to lattice vibration frequencies, providing evidence—though not highly precise—that orbital fluctuation could serve as the electron-pairing medium in unconventional superconductors.

Electric Field Excitation at = 0.9 eV

When the applied electric field frequency was reduced to = 0.9 eV, Figure 2 Figure 2: see original paper shows its time dependence, while Figure 2(b) displays the crystal structure and real-time evolution of charge density changes. The change in Fe ions (marked 3 and 4) reaches its maximum after 800 steps, corresponding to a frequency of about 160 meV. Comparison with Figure 1(b) reveals significant differences in the pattern of charge density changes between the two excitation frequencies.

Atomic Displacement Excitation

The second excitation method involved slight displacement of an As atom from its original coordinate (0.0000, 0.0000, 0.3585) to (0.0000, 0.0000, 0.3685)—a shift of 0.13 Å along the (001) direction. After calculating the ground state, the coordinate was restored to (0.0000, 0.0000, 0.3585) for the TDDFT calculation. Charge densities were recorded after 5000 and 8000 steps, respectively. Figure 3 Figure 3: see original paper shows the charge density change after 5000 steps of evolution; the change in the Fe ion marked by the arrow reaches its maximum after 500 steps, yielding a frequency of 250 meV. Figure 3(b) shows the charge density change after 8000 steps; the change in the Fe ion marked by the arrow reaches its maximum after 600 steps, corresponding to a frequency of 200 meV. These results demonstrate that different patterns of charge density change can emerge from the same excitation method.

Other Materials and General Observations

The author has investigated other unconventional superconductors, obtaining similar results. For La Fe As O , FeSe sheets, and HgBa Ca Cu O , the characteristic frequencies are 160 meV, 190 meV, and 250 meV, respectively [**?**]. Orbital (charge density of Fe or Cu ions) fluctuation may also serve as the electron pairing mechanism for copper oxide superconductors. It is noteworthy that changes in the electron clouds of transition metal ions are highly complex, potentially exhibiting different modes corresponding to different frequencies.

The underlying reason for this behavior lies in the incomplete filling of the 3d shell in transition metal ions. The resulting electron clouds lack spherical symmetry and are therefore susceptible to distortion under electric fields.

Proposed Electron Pairing Mechanism

Based on these results, the author proposes an electron pairing mechanism for both iron-based and copper-oxide superconductors. When a free electron arrives at a new location, the electron clouds of neighboring transition metal ions undergo deformation, causing a decrease in charge density around the free electron. When the free electron departs, the electron clouds of the transition metal ions do not relax instantaneously—analogous to lattice vibrations—creating a region of electron deficiency that attracts another free electron. This mechanism is essentially identical to electron-phonon interaction, except that the mediating medium is the deformation of the electron cloud rather than ionic displacement.

4 Summary

The real-time evolution of electron clouds of transition metal ions in unconventional superconductors was calculated using the TDDFT method. The frequencies of electron cloud evolution match well with lattice vibration frequencies in conventional superconductors at normal and high pressures. Although the

frequencies obtained by this method are not highly accurate, they provide significant evidence that changes in electron clouds can serve as the electron-pairing medium in unconventional superconductors.

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Note: Figure translations are in progress. See original paper for figures.