Real-Time Evolution of the Electron Clouds of Transition Metal Ions: Electron-Pairing Medium of Unconventional High Temperature Superconductors

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Abstract

The electron-pairing mechanism in unconventional high temperature superconductors (HTS) has not been resolved. The author proposed that the electron-pairing medium of unconventional HTS is the change of the electron clouds of transition metal ions, which is analogous to the lattice vibration in conventional superconductors. Real-time evolution of the electron clouds of transition metal ions under excitations in La2Fe2As2O2, FeSe sheet, Fe2KSe2, CaCuO2, and HgBa2Ca2Cu3O8 was calculated by the time-dependent density functional theory (TDDFT). The characteristic frequency is about 90-250 meV, which is equivalent to the lattice vibration frequencies, showing that the change of the electron clouds of the transition metal ions can be the electron-pairing medium in unconventional HTS.

Full Text

Preamble

Real-Time Evolution of the Electron Clouds of Transition Metal Ions: Electron-Pairing Medium of Unconventional High Temperature Superconductors

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Abstract

The electron-pairing mechanism in unconventional high temperature superconductors (HTS) remains unresolved. The author proposes that the electron-pairing medium in these materials is the dynamic response of transition metal ion electron clouds, analogous to lattice vibrations in conventional superconductors. Using time-dependent density functional theory (TDDFT), the real-time evolution of electron clouds under excitation was calculated for La Fe As O , FeSe sheet, Fe KSe , CaCuO , and HgBa Ca Cu O . The characteristic frequencies range from approximately 90–250 meV, comparable to lattice vibration frequencies, demonstrating that changes in transition metal ion electron clouds could serve as the electron-pairing medium in unconventional HTS.

1. Introduction

The discovery of copper-oxide [1][2] and iron-based superconductors [3][4] indicates that electron-lattice interactions cannot explain the electron-pairing mechanism in unconventional HTS. According to BCS theory [5][6], the superconducting transition temperature (Tc) resulting from electron-lattice interactions at normal pressures cannot exceed 40 K. The pairing mechanism for unconventional HTS remains under debate, and Anderson [7] raised a fundamental question in 2007: "Is There Glue in Cuprate Superconductors?" The author believes that if a pairing medium does exist in unconventional HTS, it must change under excitation and its characteristic frequency should be close to that of lattice vibrations.

Table 1 presents the maximum phonon frequencies and Tc for three typical conventional superconductors. It is reasonable to infer that the characteristic frequency of the electron-pairing medium in unconventional HTS should be about 100–200 meV, as a higher frequency generally yields a higher Tc, while frequencies that are too low or too high are unlikely to serve as an effective electron-pairing medium in HTS.

Table 1 Maximum phonon frequencies and Tc of three typical conventional superconductors. Pb[8] H S[9] / meV Tc / K

Based on these considerations, the author has studied eight typical unconventional superconductors (Fe KSe , La Fe As O , Nd Fe As O , Ba Fe As , YBa Cu O , HgBa Ca Cu O , Tl Ba CaCu O , and Bi Sr Ca Cu O) [10]. Under a static electric field, the electron clouds of transition metal ions change significantly, suggesting that this change may constitute a new electron-pairing medium. The proposed mechanism works as follows: when a free electron arrives at a new position, the electron clouds of neighboring transition metal ions respond by deforming, reducing the charge density around the free electron. When the electron leaves, the electron clouds do not relax instantaneously, creating a transient charge-depleted region that attracts another free electron, resulting in an effective attraction. This mechanism is essentially analogous to

electron-lattice interaction, except that the medium is the change of electron clouds rather than ionic displacement.

Building upon these previous studies, the author has further investigated the characteristic frequencies of electron cloud changes in transition metal ions. The real-time evolution of charge densities under excitation in La Fe As O , FeSe sheet, Fe KSe , CaCuO , and HgBa Ca Cu O has been calculated using the TDDFT method [11][12], and this paper reports the methods and results.

2. Methods

All calculations were performed using the Octopus package [13][14][15]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was employed to describe the exchange-correlation energy, with the GGA+U method [16][17] implemented to treat the strong correlation of 3d electrons. HSCV pseudopotentials [18] 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.

3.1 La Fe As O

A k-point mesh of 4×4×2 was used, with valence electrons of 5p $d^1 6s^2$ for La, 3p d $4s^2$ for Fe, $3d^1$ $4s^2 4p^3$ for As, and $2s^2 2p$ for O. Charge density changes were induced by a time-dependent electric field (the equation appears incomplete in the original text), with parameters F = 1.0 eV/Å, = 1.8 eV, = 5.0/eV, and t = 5.0/eV. The excitation ceased after 5000 steps, after which the charge densities vibrated freely. Densities were recorded after 8000 steps. Fig. 1 [Figure 1: see original paper] shows the crystal structure and real-time evolution of the charge density, where Δ represents the difference between the 8100th and 8000th steps (this convention applies throughout).

The electron clouds of Fe ions gradually become more distorted with increasing evolution steps. Almost no change is visible after 100 steps, but the distortion becomes pronounced after 500 steps, reaching its maximum after 800 steps at a corresponding time of 1.6 /eV. This represents the time from zero to maximum displacement, implying a full period of 4×1.6 /eV and a frequency of approximately 160 meV. While this frequency determination is not highly precise and may have errors up to ±20%, it is consistent with the author' s initial estimate and suggests that electron cloud changes could serve as the electron-pairing medium in HTS.

3.2 FeSe Sheet [19]

Valence electrons of 3p d $4s^2$ for Fe and $4s^2 4p$ for Se were used with a 4×4×1 k-point mesh, and the same excitation protocol was applied. Fig. 2 [Figure 2: see original paper] shows the results. Careful examination reveals that the charge density change first increased, then decreased, and then increased again.

To better illustrate this behavior, Fig. 3 [Figure 3: see original paper] plots the maximum charge density change as a function of evolution steps.

Two distinct maxima appear after 550 steps and 1400 steps, suggesting the presence of two vibrational modes. This is also evident from the different patterns of charge density changes observed after 600 and 1400 steps. The corresponding frequencies are approximately 230 meV and 90 meV, respectively.

3.3 K Fe Se -2e

Two valence electrons were removed from K Fe Se , giving formal valence states of K ^{1}, Se ^{2}, and Fe ^{2}. The same excitation protocol was applied, and two modes were also observed in K Fe Se -2e. Fig. 4 [Figure 4: see original paper] shows results obtained with a 2×2×1 k-point mesh, where the maximum charge density change occurs after 500 steps, yielding a frequency of approximately 250 meV. Fig. 5 [Figure 5: see original paper] shows results with a 4×4×2 k-point mesh, where the change reaches maximum after 1100 steps, giving a frequency of approximately 100 meV. The different patterns of charge density changes reflect the distinct modes, indicating that different k-point settings may excite different vibrational modes—a phenomenon requiring further investigation.

3.4 CaCuO [20]

The valence electron configuration listed (5p d^1 $6s^2$ for Hg, 5p $6s^2$ for Ba, 3p $4s^2$ for Ca, 3p d^1 $4s^1$ for Cu, and $2s^2$2p for O) appears to be a transcription error in the original text. To excite charge vibrations, a Ca atom was displaced from its original coordinate (0, 0.5, 0.5) to (0.02, 0.52, 0.5), corresponding to a 0.15 Å shift along the (001) direction. After ground-state calculation, the coordinate was restored to (0, 0.5, 0.5) for TDDFT simulation. Charge densities were recorded after 13,000 steps, with results shown in Fig. 4 (though likely intended to be Fig. 6 [Figure 6: see original paper]).

The electron cloud of the central Cu ion (marked by an arrow) evolves gradually, reaching maximum distortion after 1300 steps, which corresponds to a frequency of approximately 100 meV.

3.5 (HgBa Ca Cu O)

A k-point mesh of 2×2×1 was used, and charge density vibrations were excited via two different methods. Fig. 7 [Figure 7: see original paper] shows results from time-dependent electric field excitation, with charge densities recorded after 8000 steps. Except for Ca ions, the electron clouds of all other ions exhibit obvious changes, with oxygen ions in the copper-oxide plane showing particularly pronounced distortion. The charge density changes of nearly all ions reach maximum after 500 steps, yielding a frequency of approximately 250 meV.

Fig. 8 [Figure 8: see original paper] shows results from a different excitation method: a slight displacement of an O atom in the copper oxide plane from

(0.75, 0.25, 0.0) to (0.8, 0.3, 0.0), corresponding to a 0.4 Å shift along the (110) direction. After ground-state calculation, the coordinate was restored to (0.75, 0.25, 0.0) for TDDFT simulation. Charge densities recorded after 14,000 steps show that the electron cloud of the Cu ion indicated by the arrow reaches maximum distortion after 500 steps, with a frequency of approximately 250 meV.

4. Conclusion and Research Prospects

Real-time evolution of transition metal ion electron clouds in unconventional HTS was calculated using TDDFT, yielding characteristic frequencies of approximately 90–250 meV that match well with lattice vibration frequencies under normal and high pressures. Although the frequencies obtained by this method are not highly precise, they provide significant evidence that electron cloud changes could serve as the electron-pairing medium in HTS. Notably, multiple modes of electron cloud change exist, corresponding to different frequencies, and the author has observed only the lowest-frequency vibrations—higher frequency modes also exist.

The underlying reason for electron cloud distortion in transition metal ions is the incomplete filling of their 3d shells, which lack spherical symmetry and can therefore be easily deformed by electric fields. Similar behavior may occur for other ions with incomplete shells, such as O ions in copper-oxide planes.

If electron cloud changes in transition metal ions indeed constitute the pairing medium, superconductivity could be classified into two categories based on the pairing mechanism: "ionic displacement" and "electron cloud change."

The present research remains incomplete in three key aspects: first, more accurate frequency calculations are needed; second, experimental verification must be provided; and third, theoretical calculations of Tc for unconventional HTS should be achieved.

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