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Ab initio calculation of the pair potentials of MgB_2

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Abstract

Ab initio calculations on model clusters of MgB_2 are presented to estimate the pairing potentials of superconductivity. The total energies of the clusters for the restricted Hartree–Fock (RHF) type and unrestricted Hartree–Fock (UHF) type singlet ground states and the triplet state are calculated by the hybrid DFT method of Gaussian G03 program. The energy difference between the UHF singlet state and the triplet state is correlated to the superconducting energy gap 2Δ. The highest occupied molecular orbital (HOMO) and the next HOMO are composed of mostly the $2p\sigma$ and the 3s orbitals of boron and $3p\sigma$ orbitals of magnesium. These orbitals constitute the spin polarized singlet state which represent the superconducting state. The vibrational frequencies of the singlet and the triplet states are calculated on a model cluster, $Mg_8B_{16}H_{10}$, to find vibrational frequencies, and the results are used to interpret the isotope effects of ^{10}B and ^{11}B for the transition temperatures.

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Keywords: Superconductivity mechanism; Pair potentials; MgB_2; Isotope effects; Model clusters of MgB_2

1. Introduction

Magnesium diboride is a marvelous superconductor discovered by Akimitsu et al. which show superconductivity at 39 K in spite of simple layered structure [1]. Recently the complex nature of superconductivity in MgB_2 is revealed by the total isotope effect including magnesium isotopes [2]. Previously the boron isotope effect as high as 1.0 K shift in T_c between $^{11}MgB_2$ and $^{10}MgB_2$ was regarded as favoring phonon mediated mechanism [3]. Presence of two energy gaps are reported by many experimentalists [4–6] and theoretical calculation by ab initio method has been presented [7].

In the previous papers, we have presented ab initio calculations on the model clusters of simple metals [8], LSCO [9], and Bi2201 [10]. We have shown that for some clusters the spin-polarized unrestricted Hartree–Fock type (UHF) singlet state are more stable than the restricted Hartree–Fock type (RHF) singlet state and the UHF triplet state. The UHF type singlet wavefunctions gives anti-ferromagnetic ground state. We have proposed that the superconducting state are composed of anti-ferromagnetic state and have shown that the superconducting pair potentials are correlated with the energy difference between the anti-ferromagnetic singlet state and the RHF type states. The superconducting transition is regarded as the transition from the normal metallic state to the anti-ferromagnetic metallic state.

In this paper, we will show similar calculation on MgB_2 model clusters. Furthermore, the isotope effect on the transition temperatures are analyzed by comparing the particular vibrational frequencies of the model clusters of $(MgB_2H_n)_m$ for two different electronic states, the singlet and the triplet states. We have assumed that the normal metallic state and the superconducting state are on different potential curves of nuclear coordinates, and particular

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vibration is involved to overcome the crossing point of the potential curve from the normal to the superconducting states. We have calculated the vibrational frequencies of several isotopic substituted species of $(MgB_2H_n)_m$ and attributed small difference of particular vibrational frequencies of the singlet and the triplet state to cause the change of transition temperatures.

2. Method of calculation

Among many physical properties of superconductors, the transition temperature is characteristic, but the energy gap 2Δ are more fundamental since the superconducting phase transition is second order and the transition temperature might be influenced by the entropy factors.

We used several different type model clusters to estimate the energy differences between the UHF type singlet and the triplet states and the RHF type states. To obtain useful result the size of the cluster should be reasonably large but the size is limited for computational time and accuracy. All calculations are done by Gaussian G03 programs [11], at Okazaki National Research Institutes. The RHF (restricted Hartree–Fock type) molecular orbitals and energies are calculated first by the hybrid HF-DFT method; the hybrid functionals of Perdew et al. (PBE1PBE of G03 program) was employed [12]. Then the UHF (unrestricted Hartee–Fock) type solutions are obtained by the HOMO (highest occupied MO) and the LUMO (lowest unoccupied MO) mixing method of G03 program [13]. Succeedingly, the triplet state is calculated by the same UHF wavefunctions.

Depending on the structure of clusters, a significant spin polarization appeared on each atom and some stabilization energies are found by a proper choice of geometries. In the model clusters of MgB_2 the spin polarizations are fairly large and we compared the energies of the UHF type singlet state to the triplet state (T) as the value compared to the pair potentials.

3. Results and discussion

In Fig. 1, a typical results on $(Mg_7B_{12})^{2+}$ are illustrated on the spin polarization and the change of HOMOs and the next HOMOs by mixing. Before mixing the α and the β-HOMOs are the same shape with higher symmetry. They are distorted by the HOMO–LUMO mixing and the spin polarization appears as shown on the top of Fig. 1. The large and small arrows show up and down spins of 0.7 and 0.28 in Bohr unit. The stabilization energy of the mixed singlet state to the triplet state is 12 meV which is reasonably in agreement with the experimental value (14 meV) of 2Δ [4–6]. The composition of the atomic orbitals of HOMOs and NHOMOs show that the contribution of $2p\sigma$ and 3s orbitals of B and $3p\sigma$ orbitals of Mg are dominant rather than the $2p\pi$ orbitals of B and 3s orbitals of Mg.

In the next part, we will discuss the phonon contribution to the pair potential by calculating the vibrational frequencies of the model cluster $Mg_8B_{16}H_{10}$, which is a minimum size cluster of $(MgB_2)_n$ whose geometry can be optimized by adding extra H atoms to satisfy the residual valence of B. Fig. 2 illustrates the fully optimized structure,where all frequencies for the RHF type singlet state and the UHF type triplet states are calculated for four isotopic species of $Mg_8B_{16}H_{10}$. Among 96 frequencies, a particular mode which extends the ring of boron is illustrated in Fig. 2 since this mode will be effective for the spin polarization and the superconducting transition. The calculated values of the frequency are shown in Table 1. We actually need the frequencies for the mixed singlet state, but the geometry optimization for the mixed state is very difficult, hence we used the values of the triplet state for comparison with the singlet state as a substitute for the structure of superconducting and normal state.

Fig. 3 illustrates the idea of evaluating the changes of the transition temperatures for isotopic substitution. We assume that the experimentally observed energy gap is a sum of the purely electronic origin $2\Delta_0$ and contribution from a particular vibrational energy. The curve for N is a

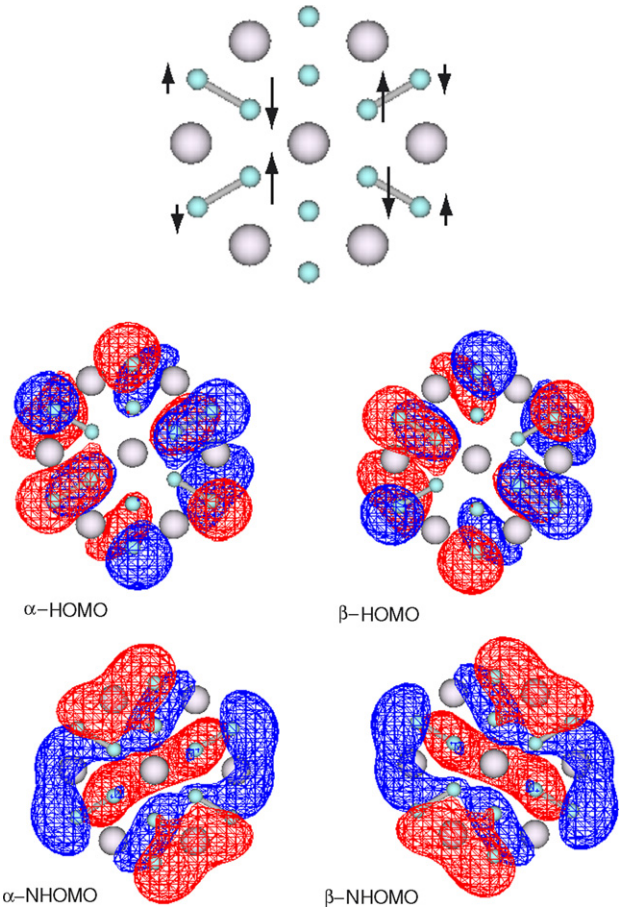

Fig. 1. Spin polarizations and the shape of wave funcions of the α and the β-HOMOs and NHOMOs of the model cluster, $Mg_7B_{12}^{(2+)}$ in the mixed orbitals (UHF type). On the top figure, small blue circles are boron atoms and large grey ball are magnesium atoms which are on the boron plane. Large and small arrows indicate 0.7 and 0.28 spins in Bohr unit with positive (up) and negative (down) sign.