



Theoretical direct evaluation of inter-dimer J values in BETS salts

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Abstract

Inter-dimer magnetic interactions ($J_{ab(D)}$) between BETS donors in the κ -BETS₂FeCl₄ crystal were studied theoretically by using of ab initio MO and DFT methods. These interaction parameters can describe spin properties. In cluster of four BETS molecules with two holes, more accurate $J_{ab(D)}$ values were evaluated directly, though such $J_{ab(D)}$ values were already evaluated from inter-molecular magnetic interaction ($J_{ab(M)}$) with the approximate equation $J_{ab(D)} = J_{ab(M)}/2$. In cluster of six molecules with three holes, competition of three antiferromagnetic interaction was discussed. Necessity of calculation under periodic condition and for surrounding cluster was introduced.

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1. Introduction

Past decades, many types of important donor-based organic superconductive salts have been reported. The scientific interest in molecular magnets and superconductors with strong electron correlation has been attracted. Many experimental and theoretical efforts have been made for elucidation of possible interplay between π - and d-electrons of transition-metal oxides [1–8]. In organic molecular systems it have been discovered in many crystals. Especially, some donor molecules, i.e., BEDT-TTF (= bis (ethylenedithio) tetrathiafulvalene) [6–8], BETS (= bis (ethylenedithio) tetraselenafulvalene) [1–5], TMTTF (= tetramethyl tetrathiafulvalene), TMTSF (= tetramethyl tetraselenafulvalene) and many other interesting species are very important to construct functional complex salts.

When we study conductivity, someone might say that MO-based approaches are not suitable, because only

few number of molecules can be taken into account. On the other hand, the extended Hückel band methods are usually powerful and can provide Fermi surfaces for organic conductors [9,10]. Thus, band pictures have been used for explanations of electronic properties. However, the band pictures often break down in strong correlating regions in organic conductors. In series of our studies, our group dare to employ these ab initio HF and DFT methods and try to determining effective parameters directly [11].

In this study, we employed mainly BETS salts in order to discuss electronic properties in BETS clusters. The series of κ -phase BETS₂FeCl₄ crystals show interesting magnetic behavior and are suitable systems for investigation of coexistence of magnetism and conductivity. Thus, in our previous studies, all magnetic parameters were theoretically evaluated [11]. For interaction in cluster ((BETS₂)⁺–(BETS₂)⁺), inter-molecular J_{ab} values ($J_{ab(D)}$) were simulated with the calculated inter-molecular J_{ab} values ($J_{ab(M)}$) with the approximate equation ($J_{ab(D)} = J_{ab(M)}/2$). This approximation must be improved and more accurate values will be discussed in this study. The recent remarkable

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progress in terms of faculty of quantum chemistry computation enables us to run large size calculations. Not only accretion of CPU speed but also evolution of parallel execution are enable us to run huge MO calculations easily. Thus, we can apply theoretical calculation to large number of cluster size with sufficient numerical accuracy.

2. Molecular structures and calculation detail

The TTF-based donor salts are very familiar and important. Here, we employ the κ -BETS₂FeCl₄ crystal as one of the very interesting crystals that have been reported by many scientists. The X-ray structural study was measured in room temperature ($T = 295$ K) as experimental condition, although we have to employ the structural data for lower temperature [1,12]. Simple representation of BETS layers in κ -phases crystal was depicted in Fig. 1. In this figure, dimerized BETS pairs in two-dimensional donor sheet are found. Roman-face numbers (1, 2, 3, ...) indicate each BETS molecule and italic-face alphabets (*A*, *B*, *p*, *q*) and numbers (*I*, 2, 3) indicate inter-molecule $J_{ab(M)}$ and inter-dimer $J_{ab(D)}$, respectively [13,14].

In this figure, some of clusters (i), (ii), (iii) and (iv) are worth studying. Cluster (i) has four BETS molecules

with two holes and is a suitable model to investigate inter-dimer $J_{ab(D)}$ values. Clusters 56–78, 12–78 and 12–56 correspond to models for $J_{ab(D)}(n)$ ($n = 1, 2, 3$) values, respectively. In peculiar systems, triangular lattices with competitive antiferromagnetic J_{ab} values are important. Six BETS molecules with three holes are in cluster (ii), though spin frustration does not occur in this BETS complex. One-dimensional chain with periodic condition along this cluster is depicted in cluster (iii). This model is useful to investigate charge and spin density waves. For cluster (iv), larger size clusters are necessary, when eliminating edge-effects. If not only interacting pairs but also surrounding dimers are introduced in calculations, more accurate values can be given, though we encounter heavy calculations. As the following sections, we mainly discuss clusters (i) and (ii) and propose extended studies for clusters (iii) and (iv).

The effective exchange integrals based on Heisenberg Hamiltonian can describe spin properties. In series of our studies theoretical calculations by using of ab initio molecular orbital (MO) and density functional (DFT) methods were carried out [11]. Our calculations were carried out by GAUSSIAN-98 program packages, besides of periodic calculation by GAUSSIAN-03 Rev.C02 [15]. We used the simple basis sets included in Gaussian program packages. Moreover, our previous calculations

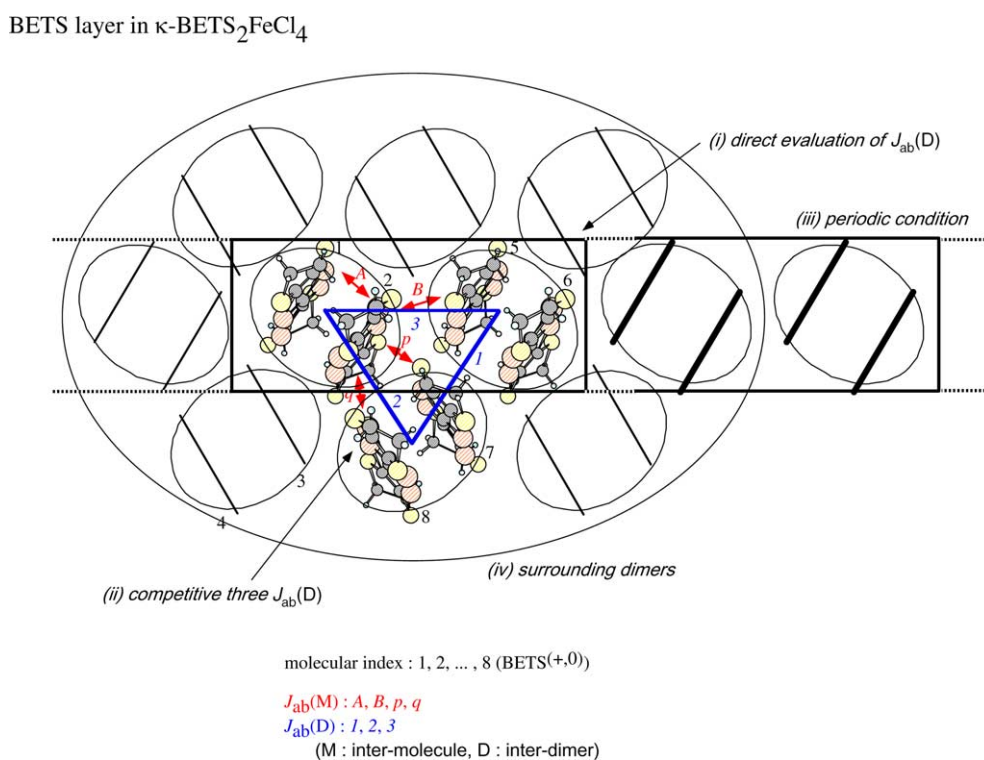


Fig. 1. Simple representation of BETS layers in κ -BETS₂FeCl₄ crystal. Roman-face numbers (1, 2, 3, ...) indicate each BETS molecule and italic-face alphabets (*A*, *B*, *p*, *q*) and numbers (*I*, 2, 3) indicate inter-molecule $J_{ab(M)}$ and inter-dimer $J_{ab(D)}$, respectively. Some of clusters (i), (ii), (iii) and (iv) are worth studying.

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