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Theoretical studies of *d*–*d* and *d*–π–*d* magnetic interactions in $(EDT\text{-}TTFVO)_2FeBr_4$ crystals

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ABSTRACT

The effective exchange integrals (*J*(HB)) of the Heisenberg spin model have been evaluated by using the *ab initio* MO and based on Hartree–Fock (HF) and density functional theory (DFT) for organic magnetic metals, the $(EDT\text{-}TTFVO)_2FeBr_4$ crystal based on the X-ray crystallographic structures at 113 K. In order to study the magnetic properties, we proposed some of the pairs, where the direct (*d*–*d*) and indirect (*d*–π–*d*) magnetic couplings between Fe(III) *d*-spins ($S = 5/2$) without/with π-dimer spins ($S = 1/2$) were calculated, respectively. The effective exchange integrals were evaluated by using UB3LYP method, and principal *J* values were 0.5, −0.1 and 0.4 K. From these results, it is found that there were three dimensional spin arrangements of Fe(III) *d*-spins. The Quantum Monte Carlo (QMC) simulations had been carried out with our calculated *J* values to evaluate the magnetic susceptibility for this molecular crystal, reproducing the experimental tendency.

1. Introduction

For several years, the organic magnetic metals, where novel magnetism and conductivity coexist, have been reported. The typical constituent molecules in organic magnetic metals are TTF (tetrathiafulvalene) and its derivatives. Geometry of such TTF-derivatives is highly planar and they are excellent candidates for electronic donors. Various π-donor molecules have been synthesized on the basis of the TTF frame. Sugimoto and his co-workers reported the various crystals, which have novel magnetism and conductivity [1–4]. New π-donor molecule, EDT-TTFVO (ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide) (see Fig. 1) is one of important organic molecules to construct functional complex salts. Organic magnetic metals are composed of both this molecule as electronic donor and its counter ions as spin sources. In the $(EDT\text{-}TTFVO)_2FeBr_4$ (**1**) crystals, Sugimoto and his co-workers have reported the coexistence of ferromagnetism and conductivity. The ferromagnetic ordering temperature T_C was 1.0 K, and electrical conductivity exhibited a metallic property above 170 K and a semiconducting one below 170 K [2]. In the crystal, both layers of donor and acceptor are stacked alternately. It has been reported that the localized *d*-electrons of $FeBr_4^-$ anions play an important role in magnetism, and π-donor EDT-TTFVO layers contribute to conductivity.

The Fe(III) in $FeBr_4^-$ anions are spin sources ($S = 5/2$), because the spin state of five *d*-orbitals in a Fe(III) is half filling. Two types of magnetic interaction are expected to explain the experimental studies: *d*–*d* direct interaction between two $FeBr_4^-$ anions, and *d*–π–*d* indirect interaction among two $FeBr_4^-$ anions and EDT-TTFVO molecules. In this study, we have been interested in these magnetic interactions and magnetic parameters (for example, *J*) were calculated by using *ab initio* MO methods. Finally, the magnetic susceptibility of the $(EDT\text{-}TTFVO)_2FeBr_4$ crystal was simulated by the Quantum Monte Carlo (QMC) method with using our calculated *J* values, and compared with the experimental measurement.

2. Theoretical background

2.1. Effective exchange integrals (*J*(HB), *J*(Ising)) in Heisenberg and Ising spin models

In series of our studies, effective exchange integrals (*J*) successfully describe magnetic interactions. The magnetic interactions between two localized electrons are usually described by the Heisenberg-type spin coupling Hamiltonian

$$H(\mathrm{HB}) = -2J_{ab}\hat{S}_a \cdot \hat{S}_b, \qquad (1)$$

where J_{ab} is the orbital-averaged effective exchange integral between the *a*-th and *b*-th sites with total spin operators S_a and

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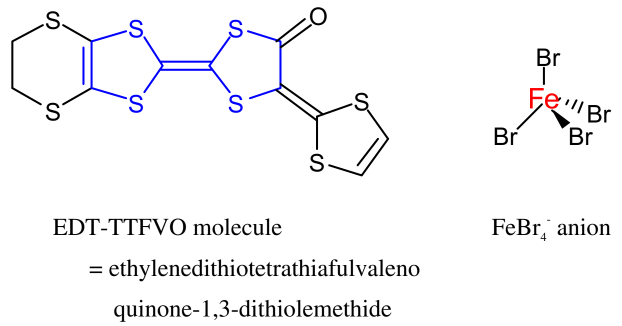

Fig. 1. EDT-TTFVO (ethylenedithiotetrathiafulvalenoquinone-1,3-dithiolemethide) molecule and FeBr$_4^-$ anion in the (EDT-TTFVO)$_2$FeBr$_4$ (**1**) crystal.

S_b. The physical meaning of J_{ab} is the energy difference between the lower spin state (LS) and the higher spin state (HS) in systems as illustrated in Fig. 2A. The positive value of J_{ab} means the ferromagnetic interaction in the ground state, while the negative value of J_{ab} means the antiferromagnetic interaction in the ground state. Recent development of the *ab initio* computational techniques has made it possible to calculate the J_{ab} values directly. Broken-symmetry (BS) approach with the spin projected scheme [5], which eliminates the spin contamination problem, can evaluate J_{ab} values with the following equation:

$$J_{ab} = \frac{{}^{LS}E(X) - {}^{HS}E(X)}{{}^{HS}\langle \hat{S}^2 \rangle (X) - {}^{LS}\langle \hat{S}^2 \rangle (X)}, \qquad (2)$$

where ${}^{Y}E(X)$ and ${}^{Y}\langle S^2 \rangle (X)$ denote, respectively, total energy and total spin angular momentum for the spin state Y by the computational methods X.

Though the effective exchange integrals based on Heisenberg Hamiltonian can describe spin properties of two spin systems exactly, the treatment based on Ising spin Hamiltonian is more convenient to decompose all magnetic interactions in many spin systems. Ising spin Hamiltonian is usually employed in order to investigate spin properties at anisotropic spin limits. Here, let us propose another calculation J scheme for many spin sites systems. For example, we assume 3-sites/3-spins triangle systems and its Hamiltonian can be described as

$$H(\text{Ising}) = -2J_{12}\hat{S}_1^z \cdot \hat{S}_2^z - 2J_{23}\hat{S}_2^z \cdot \hat{S}_3^z - 2J_{31}\hat{S}_3^z \cdot \hat{S}_1^z \qquad (3)$$

where three J(Ising) values (J_{12}, J_{23} and J_{31}) are magnetic coupling constants between any two sites. All spin structures in total system can be classified into four variations as Fig. 2B. Here only collinear spins are realized because of employing Ising spins. If we calculate the total energies of each spin structure, the following simultaneous equations can be constructed. Resolving these equations consistently produces all J(Ising) values.

$$\begin{cases} E_{LS3} = -2J_{12}S_1S_2 - 2J_{23}S_2(-S_3) - 2J_{31}(-S_3)S_1 \\ E_{LS2} = -2J_{12}S_1(-S_2) - 2J_{23}(-S_2)S_3 - 2J_{31}S_3S_1 \\ E_{LS1} = -2J_{12}(-S_1)S_2 - 2J_{23}S_2S_3 - 2J_{31}S_3(-S_1) \\ E_{HS} = -2J_{12}S_1S_2 - 2J_{23}S_2S_3 - 2J_{31}S_3S_1 \end{cases} \qquad (4)$$

In series of our studies, the effective exchange integrals based on Heisenberg and Ising spin Hamiltonians can describe spin properties. Nowadays, many types of theoretical MO calculations by using both Hartree–Fock (HF) and Kohn–Sham (KS)-DFT methods are feasible. Especially in this study, the J values were evaluated on the basis of spin-polarized HF (UHF), DFT (UDFT) and hybrid DFT approximations. In order to involve electron correlation correction effectively, several post-HF methods, i.e., Møller-Plesset (MP)-4, Coupled-Cluster (CC) methods were employed. As useful DFT's functional, Becke's three parameter exchange [6], and Lee, Yang, and Parr's correlation functional [7] (UB3LYP) have been chosen for our calculations in GAUSSIAN-98 program packages [8] and the energy convergence criterion was 10^{-6} au for SCF calculation, since they are expected to produce feasible solutions judged from the results of our former studies [9]. In addition to calculation methods, we have to examined basis set dependency. From our previous results all basis sets except for the STO-3G basis sets can reproduce magnetic interaction correctly [9]. Polarization functions and diffuse functions improve magnetic interaction slightly. Thus, we used the simple basis sets included in GAUSSIAN-98 program packages; 4-31G(p) for EDT-TTFVO molecule, 6-31G for Fe atom and 6-31+G for Br atom. Implications of the calculated results are discussed in relation to magnetic structure in BDT-TTFVO salts.

2.2. Magnetic susceptibility in quantum spin systems

To obtain macroscale measurements, for example magnetic susceptibility, magnetization, specific heat and so on, we must know

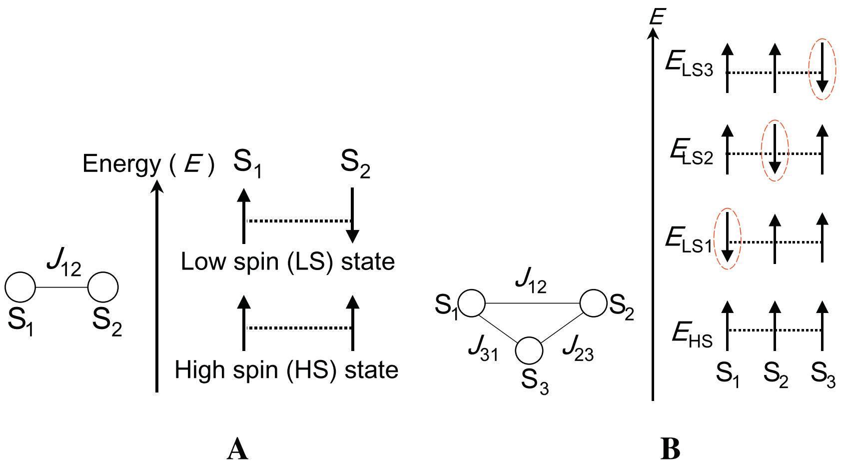

Fig. 2. (A) Effective exchange integrals (J_{ab}) between the a-th and b-th sites are evaluated by the Eq. (3), which is based on Heisenberg spin Hamiltonian. The physical meaning is the energy difference between the lower spin state (LS) and the higher spin state (HS) in systems. (B) Though the effective exchange integrals based on Heisenberg spin Hamiltonian can describe spin properties of two spin systems exactly, the treatment based on Ising spin Hamiltonian is more convenient to decompose all magnetic interactions in many spin systems. When we assume 3-sites/3-spins triangle systems, all spin structures in total system can be classified into four variations.