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# FIRST-PRINCIPLES BAND STRUCTURE CALCULATION FOR ORGANIC MOLECULAR CRYSTALS

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Abstract The full-potentail LAPW band calculation in paramagnetic state is carried out for hypothetical square lattices of $H_2NO$ chains by assuming two kinds of stacking of $H_2NO$ molecule: face-to-face stacking and anti-phase alternating stacking. In the former case the ferromagnetic state is never expected to be realized, but in the latter case there is a possibility of appearance of ferromagnetic phase.

## INTRODUCTION

In recent decades much interest has been paid to molecular magnetism, in particular to synthesizing organic ferromagnets. As the results, very recently bulk ferromagnetism has been confirmed in several purely organic materils.[1–3] But their transition temperatures are quite low ($T_c \sim 1$ K) and hence continued effort has been maid to obtain organic ferromagnets with higher $T_c$. All the ferromagnetic or antiferromagnetic molecular crystals thus far discovered are well described in terms of Heisenberg Hamiltonian of localized $S$=1/2 spins. The exchange coupling $J$ has been discussed mainly in the framework of intermolecular charge transfer interaction based on McConnel model[4], and it has been clarified that the sign of $J$ can be positive (ferromagnetic) if the transfer between SOMO's is smaller compared with that between SOMO and NHOMO (or NLUMO). Low $T_c$ is ascribed to small magnitude of $J$ and it seems not so easy to realize positive and large $J$. Generally speaking, in 3$d$ magentic systems ferromagnets with quite high $T_c$ are realized in metallic systems. Then we expect that much higher $T_c$ would be obtained by synthesizing metallic organic ferromagnets.

Our purpose of this paper is to perform first-principles band calculations for hypothetical $H_2NO$ crystal as a first step to pursue the possibility of molecular metallic ferromagnets with high $T_c$. We have chosen the $H_2NO$ crystal because quantum chemical calculation of exchange interaction between two $H_2NO$ molecules has been done by Yamaguchi *et al.*[5] According to their results the sign of $J$ depends on stacking of the $H_2NO$ dimer. In case of syn-dimer (face-to-face stacking) $J$ is

negative (antiferromagnetic) while in case of anti-dimer (anti-phase stacking) it is positive (ferromagnetic). Thus it is quite interesting to study how the electronic band structure of $H_2NO$ crystals depends on the stacking of $H_2NO$ molecules.

## PROCEDURE OF BAND CALCULATION

For simplicity we have assumed square lattice of $H_2NO$ chains. For the $H_2NO$ chain we consider two kinds of stacking of $H_2NO$ molecules as shown in Figure 1: (A) face-to-face stacking and (B) anti-phase alternating stacking. The former corresponds to the syn-dimer and the latter to the anti-dimer. For the atomic distance within a $H_2NO$ molecule we use 1.04 Å for H-N and 1.23 Å for N-O, and the angle of H-N-H is taken to be 120°.[6]

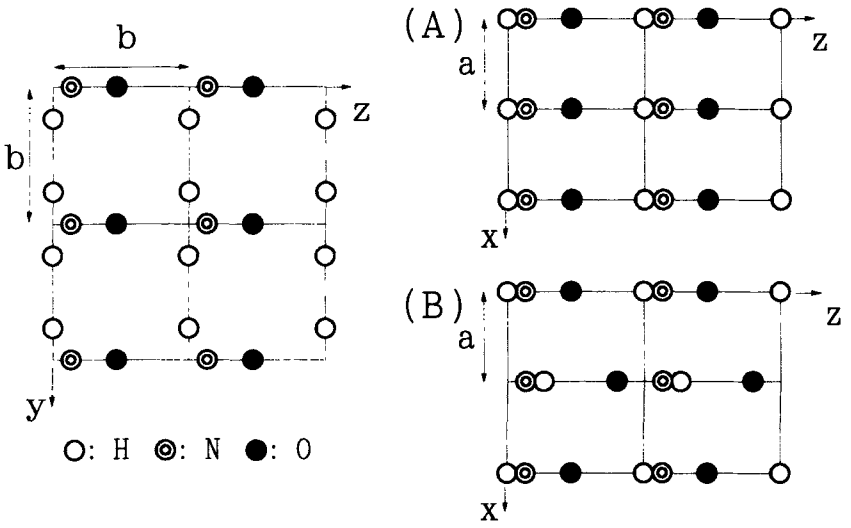


FIGURE 1 Two types of hypothetical structure of $H_2NO$ crystal.

Our band calculations are based on a scalar-relativistic version of the full potential linearized APW (FLAPW) method, *i.e.* relativistic effects other than the spin-orbit interaction are included. We introduce practically the muffin-tin (MT) sphere around each atom, but the potential is determined fully self-consistently through the whole crystal (both inside and outside the MT spheres). For the exchange-correlation potential we have used the Gunnarsson-Lundqvist type.[7] The core electrons are treated as relaxed. The basis function and the potential inside the MT sphere are expanded up to $\ell_{max}$=7 and $\ell_{max}$=2, respectively. The potentail outside the MT spheres is expanded in Fourier series of reciprocal lattice vectors $\boldsymbol{G}$ up to $|\boldsymbol{G}|_{max}$=7.8 Å$^{-1}$. The number of used basis functions are about 360 (720) for the

case (A) (case (B)). We have determined self-consistently the charge density of the crystal using eight $\boldsymbol{k}$ points in the iteration process. The density of states (DOS) has been calculated with a linearly energy-interpolated tetrahedron method.

## RESULTS AND DISCUSSION

Actual calculations are performed for the lattice parameters: $a$=2.75 Å and $b$=4 Å. Here $a$ denotes the distance between adjacent $H_2NO$ molecules along the chain direction and $b$ is the lattice constant of the square lattice. The electronic DOS's obtained for (A) and (B) cases are shown in Figure 2 (A) and (B), respectively.

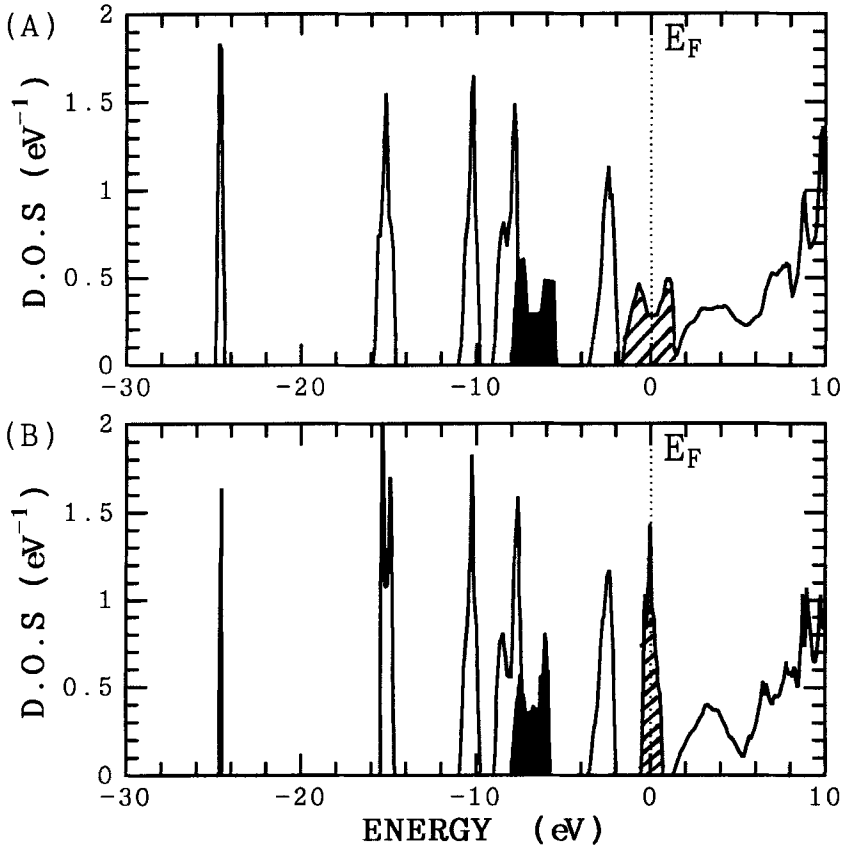


FIGURE 2 The density-of-states (DOS) calculated for the case (A) (face-to-face stacking) and for the case (B) (antiphase alternating stacking). The hatched region denotes the band arising from the anti-bonding states of the $\pi$-orbitals of N and O (SOMO) whereas the shaded region that arising from the bonding states.

The electronic band structures of the respective case are characterized as follows:

(A). Antibonding states of $\pi$-orbitals of N and O (SOMO) form a one-dimensional like band and the Fermi level $E_F$ lies at the center of this band. Good nesting is realized for wave vector $(00\pi)$ and therefore a possible magnetic state would be antiferromagnetic, or the system would undergo a CDW (Peierls) transition.

(B). Compared with the case (A) the electron transfer between SOMO's along the chain direction is much reduced and hence one-dimensionality weakens considerably. Furthermore band degeneracy increases. Thus the density of states at $E_F$ increases remarkably and good nesting condition is destroyed. Therefore there is a possibility of appearance of ferromagnetic phase.

The quite different character of the SOMO band in the cases (A) and (B) may be explained as follows. We first note that in each SOMO the amplitude of O $\pi$ orbital is larger than that of N $\pi$ orbital. Then the relative spatial configuration between two nearest neihgboring SOMO's can be illustrated for the cases (A) and (B) as shown in Figure 3 (A) and (B), respectively. We easily understand from Figure 3 that the electron transfer between two nearest neighboring SOMO's in case (B) is much smaller than that in case (A). This difference in the electron transfer is regarded as the main origin for the different character of the SOMO bands in the cases (A) and (B).

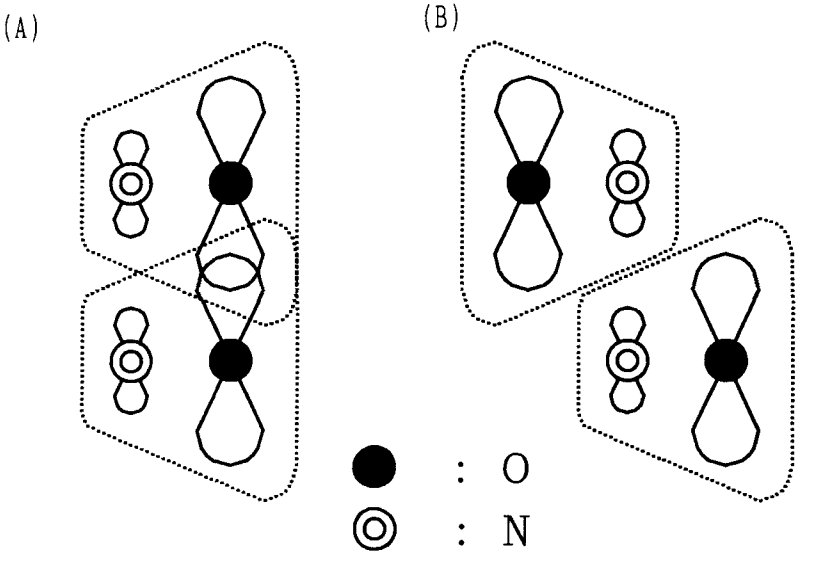


FIGURE 3 The schematic illustration of two SOMO's of the nearest neighboring $H_2NO$ molecules for the case (A) (left) and for the case (B) (right).

By investigating the instability of paramagnetic phase within the HF-RPA approximation we have determined the mangetic phase diagram of the extended Hubbard system in which each atom (molecule) has two different molecular orbitals.[8] According to our results the ferromagnetic phase may be realized when electron filling is $\frac{1}{4}$ (or $\frac{3}{4}$) and if the transfer between the different orbitals is much larger than that between the same orbitals. The calculated band structure of the case (B) seems to satisfy this condition for ferromagentism. Now we are calculating the spin-polarized (ferromagnetic) band structure for the case (B). The results will be reported elsewhere.

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## REFERENCES

1. M.Tamura, Y.Nakazawa, D.Shiomi, K.Nozawa, Y.Hosokoshi, M.Ishikawa, M. Takahashi and M.Kinoshita, Chem. Phys. Lett., 186, 401 (1991); Y.Nakazawa, M.Tamura, N.Shirakawa, D.Shiomi, M.Takahashi, M.Kinoshita and M.Ishikawa, Phys. Rev. B, 46, 8904 (1992).
2. R.Chiarelli, M.A.Novak, A.Rassat and J.L.Tholence, Nature, 363, 147 (1993).
3. T.Nogami, K.Tomioka, T.Ishida, H.Yoshikawa, M.Yasui, F.Iwasaki, H.Iwamura, N.Takeda and M.Ishikawa, Chem. Lett., 29 (1994).
4. H.M.McConnell, J. Phys. Chem. Soc., 39, 1910 (1963).
5. K.Yamaguchi, M.Okumura, J.Maki, T.Noro, H.Namimoto, M.Nakano, T.Fueno and K.Nakasuji, Chem. Phys. Lett., 190, 353 (1992).
6. R.Zahradnik and P.Čársky, Theoret. Chim. Acta (Berl.), 27, 121 (1972).
7. O.Gunnarsson and B.I.Lundqvist, Phys.Rev.B, 13, 4274 (1976).
8. T.Kawamoto, M.Shirai and N.Suzuki, Synthetic Metals, to be published.