Ab initio MO studies of DCNQI molecules

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Abstract

We study electronic states of the one-dimensional $(DCNQI)_2M$ (M=Li and Ag) salts based on the full configuration interaction (CI) method using effective Hamiltonians from ab initio molecular orbital (MO) theory. In the tetramer and octamer models, the ground state has the antiferromagnetic (AF) and charge ordering correlations which correspond to the $2k_F$ spin density wave (SDW) and $4k_F$ charge density wave states (CDW). In the octamer model, it is found that some low-lying excited states have similar spin-flipped CDW correlations and the AF correlation is weakened.

Keywords: Ab initio quantum chemical methods and calculations, Organic conductors based on radical cation and/or anion salts, Metal-insulator phase transitions

1. Introduction

$(R1, R2 - DCNQI)_2M$ (M= Ag, Li) salts show the strong one-dimensional (1-D) character of conductivity because the DCNQI molecules are stacked face to face forming strong 1-D column [1–3]. The formal charges of DCNQI and M are -1/2 and +1, respectively. Therefore the electronic systems form a 1-D band with quarter filling. In these DC-NQI salts, substitution effects play an important role on the physical properties. For example, the electron correlation of $(DCNQI)_2M$ salts is changed by the substitutions of R1 and R2; For R1=R2=I, the ground state becomes the $4k_F$ CDW of the charge modulation type below 200 K and becomes an AF state at 5.5 K, as observed by Hiraki and Kanoda [4]. For R1=R2=Me, the ground state is the $4k_F$ CDW with lattice distortion below 100 K. It becomes a spin-Peierls state below 80 K [5]. The substituents of the organic molecules, which can be easily modified or synthesized experimentally, affect their physical properties. Therefore it is important to study such salts from ab initio method which is capable of analyzing the character of organic molecules. Seo and Fukuyama calculated the electronic states of the quasi-1-D quarter-filled band by the HF approximation [6]. They concluded that the nearest-neighbor Coulomb interactions introduce charge disproportion. Kobayashi et al. also used the HF model to the similar electronic system and investigated a coexistence of the $2k_F$ SDW and $2k_F$ CDW states considering the next-nearest Coulomb interaction [7]. From a first-principles approach, Miyazaki et al. calculated the first-principles Fermi surfaces and dispersions

using the generalized gradient approximation (GGA) based on the density functional theory (DFT) [8]. But, there has been no ab initio study of the DCNQI salts beyond mean-field theory. As these DCNQI salts have the 1-D characters, electron correlation is essential. Therefore an ab initio-based CI study will convey important information of the electron correlation of various kinds of DCNQI salts.

2. Method

The effective Hamiltonian is parametrized from ab initio MO calculations of DCNQI tetramer. The calculations are at the Hartree-Fock (HF) level using the Ci symmetry with the Stevens-Basch-Krauss-Jasien valence split basis sets and their effective core potentials [9]. Structural parameters of the $(DMe - DCNQI)_2Ag$ from the X-ray diffraction (XRD) experiments are used [10]. We calculated only DC-NQI molecules because of the strong 1-D character. The obtained LUMO1-4 are localized by Boys localization procedure [11]. For the effective Hamiltonian over localized molecular orbitals (LMO),

$$H_{eff} = \sum_{ij} < \phi_i|h|\phi_j > E_{ij} \qquad (1)$$

$$+ \frac{1}{2} \sum_{ijkl} < \phi_i\phi_k|\phi_j\phi_l > (E_{ij}E_{kl} - \delta_{jk}E_{il}) \qquad (2)$$

where $E_{ij} = c_{i\uparrow}^{\dagger}c_{j\uparrow} + c_{i\downarrow}^{\dagger}c_{j\downarrow}$. $c_{i\sigma}^{\dagger}(c_{i\sigma})$ is the electron creation(annihilation) operator of the i-th LMO. σ is the index of spin and h represents the one-electron Hamiltonian. The Dirac notation is used for the two electron integrals. Transfer integral is regarded as the off-diagonal element $< \phi_i|h|\phi_j >$. On site and nearest neighbor Coulomb interactions are defined as $< \phi_i\phi_i|\phi_i\phi_i >$ and $< \phi_i\phi_j|\phi_i\phi_j >$

respectively. In this particular work, we use two different
effective Hamiltonians, $H_{eff}(1)$ and $H_{eff}(2)$. The $H_{eff}(1)$
and $H_{eff}(2)$ include one- and two-electron parts over LMOs
up to nearest neighbor and third nearest neighbor orbitals
respectively. We analyzed the electronic phases of the ob-
tained states using the spin correlation function,

$$\Delta_{i\sigma 1 j\sigma 2} = <n_{i\sigma 1} n_{j\sigma 2}> /N^2 \tag{3}$$

where $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ and $N = <n_{i\sigma}>$.

3. Results

We calculate DCNQI tetramer with the formal charge -
2 at the HF level. In this calculation, on site and nearest
neighbor Coulomb interactions are calculated as 6.23 and
3.28 eV. Transfer integral is 0.37 eV which is larger than
that of -0.22 eV calculated from DFT [8]. We construct and
diagonalize the $H_{eff}(1)$ under the periodic boundary condi-
tion. In Fig. 1-2, arrows pointing upward (downward) rep-
resent up (down) spins and solid arrows indicate the LMO
where the spin correlation function has strong amplitude to-
ward the LMO indicated by open arrows. The ground state
and 1 st singlet excited states have the AF and charge or-
dering correlations between the 1 st and 3 rd sites in Fig. 1.
They correspond to the 2 k_F SDW and 4 k_F CDW states.
For the 2 nd singlet excited state, the up spin in the 2 nd site
and down spin in the 3 rd site are correlated in Fig. 1. This
state corresponds to the $2k_F$ SDW and $2k_F$ CDW states.
For the triplet state, the up spin in the 1 st and 3 rd sites are
correlated. We extend the model to the octamer to inves-
tigate the range-dependent spin correlation. We construct
and diagonalize the octamer $H_{eff}(2)$ under the anti-periodic
condition. The ground state also has the AF and charge or-
dering correlations in Fig. 2. Some low-lying excited states
have similar spin-flipped CDW correlations in Fig. 2. The
excitation energies of these excited states are very small.
Therefore, it is elucidated that the spin correlation is weak
for the octamer model. The correlation of charge ordering
for the ground states and some low-lying excited states is in
good agreement with the $4k_F$ CDW state observed experi-
mentally for 1-D DCNQI salts [4,5].
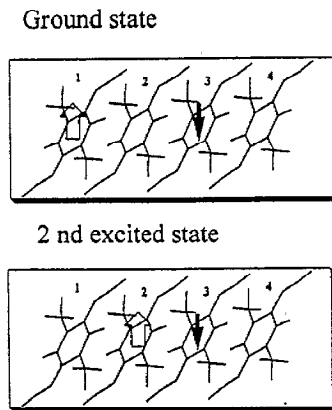
Ground state

2 nd excited state

Fig. 1. The spin structure of DCNQI tetramer for the
periodic model.

For the tetramer and octamer models, we find that the
ground state is an AF type state. This state corresponds to
the $4k_F$ CDW and $2k_F$ SDW states calculated by Kobayashi
et al. and Seo and Fukuyama by the HF approximation
in k-space to consider the crystal effect. For the $H_{eff}(1)$
of the tetramer model, the 2 nd singlet excited state may
correspond to the $2k_F$ SDW and $2k_F$ CDW states calcu-
lated by Kobayashi et al.. Actually, Pouget and Ravy sug-
gested by the XRD experiments that the ground state for
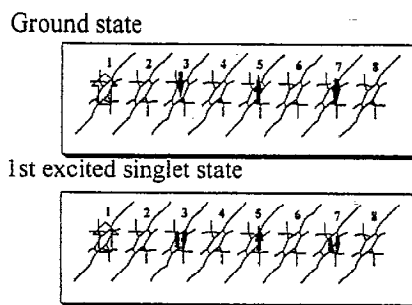$(TMTSF)_2PF_6$ is the coexistence of the $2k_F$ SDW and $2k_F$
CDW states [12].

Ground state

1st excited singlet state

Fig. 2. The spin structure of DCNQI octamer for the
anti-periodic model.

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