

Theoretical study on electron correlation of 1-D (DCNQI)₂M (M = Li, Ag) salts

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Received 1 September 1998; in final form 13 October 1998

Abstract

We study electronic states of the (DCNQI)₂M (M = Li and Ag) salts based on the full configuration interaction (FCI) method using effective Hamiltonians derived from ab initio molecular orbital theory. FCI results of the DCNQI tetramer and octamer models indicate that the ground state has antiferromagnetic and charge ordering correlations. It corresponds to the 2k_F spin density wave and 4k_F charge density wave states (SDW and CDW, respectively). In the octamer model, it is also found that some low-lying excited states have similar spin-flipped CDW correlations and the antiferromagnetic correlation is weakened. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

(R1,R2-DCNQI)₂M (DCNQI = 2,5-disubstituted N,N'-dicyanoquinonediimine, M = Ag, Li) salts shown in Fig. 1 have unique physical properties. They show the strong one-dimensional (1-D) character of conductivity which originates from a 1-D column consisting of face-to-face stacking of DCNQI molecules. The DCNQI salts are the tetragonal crystals of space group I4₁/a as shown in Fig. 2. The formal charges of DCNQI and M are −1/2 and +1, respectively [1]. The conduction electrons therefore form a 1-D band with quarter filling. The physical properties of DCNQI salts are strongly influenced by the substituents, R1 and R2. For example, the ground state of (DI-DCNQI)₂Ag salt becomes

the 4k_F charge density wave (CDW) state of the charge modulation type below 200 K and becomes an antiferromagnetic (AF) state at 5.5 K, as observed by Hiraki and Kanoda [2,3]. The ground state of (DMe-DCNQI)₂Ag salt is the 4k_F CDW with lattice distortion below 100 K. It becomes a spin-Peierls state at 80 K [4]. Since the physical properties are very sensitive for the substituents of DCNQI molecules, which can be easily modified or synthesized experimentally, the ab initio method which allows us to obtain detailed information of electronic states on a molecular level is suitable to apply.

Seo and Fukuyama calculated the electronic states of the quasi-1-D quarter-filled band by the Hartree–Fock (HF) approximation [5]. They concluded that the nearest-neighbor Coulomb interactions introduce charge disproportion. Kobayashi et al. also used a HF model to a similar electronic system, (TMTSF)₂PF₆, and investigated a coexistence of the 2k_F spin density wave (SDW) and 2k_F CDW states

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considering electron–lattice interaction or the next-nearest neighbor Coulomb interaction [6,7]. Miyazaki et al. calculated the metallic states of DCNQI salts using the local density approximation or generalized gradient approximation (LDA or GGA, respectively) based on density functional theory [8–10]. They obtained the first-principles Fermi surfaces and dispersions of DCNQI-Cu/Ag salts. This problem was also studied by Yonemitsu from the renormalization-group approach [11]. Based on *ab initio* molecular orbital (MO) theory, we calculated the electronic structures of various DCNQI molecules and obtained *ab initio* parameters of DCNQI-Cu salts such as transfer integrals [12]. We found that the transfer integral correlates with the lattice parameter of the *c*-axis. However, there has been no *ab initio* study of DCNQI salts beyond mean-field approximations. Since these DCNQI salts have a 1-D character in which electron correlation is essential, it is expected that CI studies based on the *ab initio* effective Hamiltonian will convey important information on the electron correlation of various kinds of DCNQI salts. In Section 2, we present the computational details of CI calculations of the 1-D DCNQI salts. Parameterization is explained in Section 3. Results are shown in Section 4.

2. Method

The effective Hamiltonian is parametrized from *ab initio* MO calculations of the DCNQI tetramers. The calculations are at the HF level using the Ci symmetry with the Stevens–Basch–Krauss–Jasien (SBK) split valence basis sets and their effective

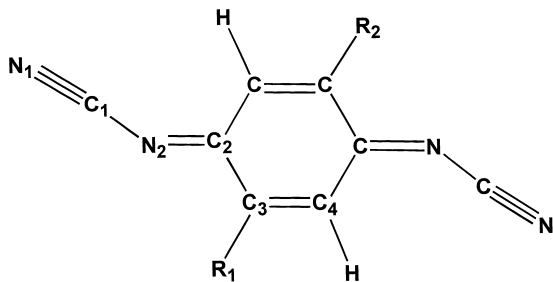


Fig. 1. The molecular structure of the 2,5-R₁,R₂-DCNQI molecule.

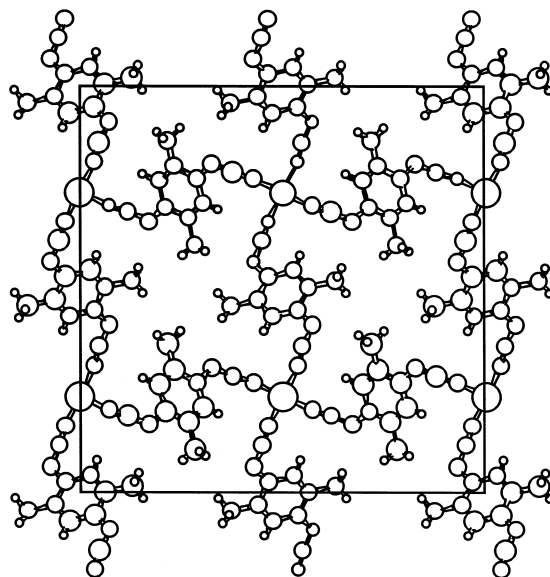


Fig. 2. The *c*-axis projection of the crystal structure of (DMe-DCNQI)₂Ag at room temperature.

core potentials (ECPs) [13]. The previous theoretical and experimental studies suggest Ag and Li metallic ligands hardly contribute to the conduction bands [3,9]. Therefore, we neglect the metals and treat only the DCNQI molecules. Structural parameters of the (DMe-DCNQI)₂Ag [14], (DMe-DCNQI)₂Li [15] and (DI-DCNQI)₂Li [3] salts from X-ray diffraction (XRD) experiments are used to carry out calculations as shown in Fig. 2. The obtained LUMO1–4 which referred to those of the neutral molecules are localized by the procedure of Boys [16] such that the localized molecular orbitals (LMOs) are located on each DCNQI molecule. To check the charge separation effect due to the finite cluster model, results with two different formal charges, 0 and –2, are compared.

Henceforward, the spatial orbital indices, *i, j, k, l...* and *p, q...* are used for the doubly occupied and localized molecular orbitals, respectively. For the effective Hamiltonian over LMOs,

$$H_{\text{eff}} = \sum_{pq} \langle p | f | q \rangle E_{pq} + \frac{1}{2} \sum_{pqrs} \langle pq | rs \rangle \times (E_{pr} E_{qs} - \delta_{qr} E_{ps}), \quad (1)$$

where f and E are respectively defined as

$$\langle p|f|q\rangle = \langle p|h|q\rangle + \sum_i [2\langle ip|i q\rangle - \langle ip|qi\rangle], \quad (2)$$

and

$$E_{pq} = a_{p\uparrow}^+ a_{q\uparrow} + a_{p\downarrow}^+ a_{q\downarrow}, \quad (3)$$

where transformed one- and two-electron integrals are used as the matrix elements, h represents the one-electron Hamiltonian, and we employed the Dirac notation for the two-electron integrals. In this particular work, we use two different effective Hamiltonians, $H_{\text{eff}}(1)$ and $H_{\text{eff}}(2)$. In $H_{\text{eff}}(1)$, the one-electron part consists of diagonal elements and off-diagonal elements over nearest-neighbor LMOs, and the two-electron part is of four type integrals, $\langle pp|pp\rangle$, $\langle pq|pq\rangle$, $\langle pq|qp\rangle$ and $\langle pp|pq\rangle$, where p and q represent nearest neighboring LMOs. In $H_{\text{eff}}(2)$, the one-electron part includes diagonal elements and off-diagonal elements over LMOs up to the third nearest-neighbor orbitals, and the two-electron part includes transformed two-electron integrals over LMOs up to the third nearest-neighbor orbitals. In $H_{\text{eff}}(1)$ and $H_{\text{eff}}(2)$, one- and two-electron integrals up to nearest-neighbor orbitals are obtained from the middle two DCNQI LMOs of a DCNQI tetramer. In $H_{\text{eff}}(2)$, one- and two-electron integrals over LMOs of the second and third nearest-neighbor orbitals are obtained from DCNQI tetramer calculations. We take an average of multiplied integrals which correspond to one matrix element of $H_{\text{eff}}(2)$ to maintain the translational symmetry. The transfer integral is regarded as a one-electron off-diagonal element:

$$t \equiv \langle p|f|q\rangle. \quad (4)$$

Besides the transfer integrals, on-site and nearest-neighbor Coulomb interactions, $\langle pp|pp\rangle$ and $\langle pq|pq\rangle$, respectively, are estimated, where p and q represent the nearest neighboring LMOs. We solve the FCI secular problem using the Slater-determinant-based direct CI algorithm proposed by Knowles and Handy [17]. We use the periodic and anti-periodic boundary conditions for the DCNQI tetramer and octamer models, respectively, so that the ground state does not become an artificial high multiplet state due to the finite-size effect. We analyzed the

electronic phases of the obtained states using the spin correlation function,

$$\Delta_{p\sigma, q\sigma'} = \langle n_{p\sigma} n_{q\sigma'} \rangle / N^2, \quad (5)$$

where $n_{p\sigma} = a_{p\sigma}^+ a_{p\sigma}$ and $N = \langle n_{p\sigma} \rangle$.

The HF calculations and integral transformations are performed using the GAMESS [18] and GAUSS-IAN94 [19] program packages.

3. Parametrization of a model Hamiltonian

We calculate DCNQI tetramers using the structural parameters of DCNQI-Ag/Li salts with different formal charges, $q_d = 0$ and -2 . The calculated parameters are shown in Table 1. Transfer integrals, t , on-site and nearest-neighbor Coulomb interactions are obtained from the middle two DCNQI LMOs of the DCNQI tetramer. We obtain one on-site Coulomb interaction by the symmetry C_i of the DCNQI tetramer. For (DMe-DCNQI)₂Ag salt at room temperature, on-site and nearest-neighbor Coulomb interactions with $q_d = -2$ are 6.23 and 3.28 eV, respectively. Those parameters are scarcely changed by the formal charge. For (DMe-DCNQI)₂Ag, the transfer integral, t , is 0.370 eV with $q_d = -2$ which is larger than the previous one (-0.22 eV) [9]. Reasons are discussed in another paper [12]. On the other hand, for (DI-DCNQI)₂Li, t is 0.274 and 0.226 eV with $q_d = 0$ and -2 , respectively. This difference in t for R1 = R2 = Me and R1 = R2 = I affects dimensionality which is determined by the ratio of the intracolumn to intercolumn interactions. Therefore it may be the cause of different physical properties as explained in Section 1. Large transfer integrals enhance the screenings of Coulomb interactions. Therefore the difference in t for DMe- and DI-DCNQI salts may also affect their correlations of charge ordering. We find for (DMe-DCNQI)₂Ag/Li salts that the formal charge dependence on t is small, whereas, for (DI-DCNQI)₂Li, it is large.

4. Electron correlation

We study electron correlation of the H_{eff} extracted from transformed LMO integrals of (DMe-DCNQI)₂Ag salt with $q_d = -2$. For the $H_{\text{eff}}(1)$ of

Table 1

Ab initio parameters from the HF/SBK split valence basis sets and ECPs calculations

	Temperature	Cluster	Charge	Basis set	Lattice parameter, <i>c</i> (Å)	Transfer integral (eV)	On-site Coulomb interaction (eV)	Nearest-neighbor Coulomb interaction (eV)
(DMe-DCNQI) ₂ Li	RT ^a	tetramer	0	SBK	3.849 ^d	0.368	6.265	3.240
(DMe-DCNQI) ₂ Li	RT	tetramer	−2	SBK	3.849	0.374	6.233	3.283
(DI-DCNQI) ₂ Li	RT	tetramer	0	SBK	4.076 ^e	0.274	6.162	3.138
(DI-DCNQI) ₂ Li	RT	tetramer	−2	SBK	4.076	0.226	6.156	3.131
(DMe-DCNQI) ₂ Ag	RT	tetramer	0	SBK	3.818 ^f	0.361	6.258	3.247
(DMe-DCNQI) ₂ Ag	RT	tetramer	−2	SBK	3.818	0.370	6.227	3.283
(DMe-DCNQI) ₂ Cu	RT	dimer	−1	DZP ^b	3.849 ^g	0.380	6.545	3.323
(DI-DCNQI) ₂ Cu	RT	dimer	−1	DZP ^b	4.077 ^d	0.292	6.395	3.242
(DMe-DCNQI) ₂ Ag	RT			theory ^c	3.818	−0.22		

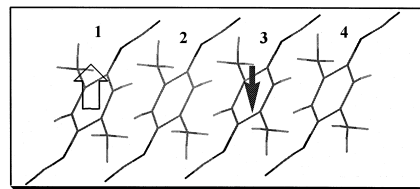
^aRoom temperature.^bRef. [12].^cRef. [9].^dRef. [15].^eRef. [3].^fRef. [14].^gRef. [20].

the tetramer model, the ground state and first singlet excited states have the AF and charge ordering correlations between the first and third sites as shown in Fig. 3. The spin correlation function, $\Delta_{1\uparrow,3\downarrow}$, is 3.65 and $\Delta_{p\sigma,q\sigma'}$ among another sites are < 0.02 . This state corresponds to the $2k_F$ SDW and $4k_F$ CDW states. For the second singlet excited state, the up spin in the second site and down spin in the third site are correlated in Fig. 3. This state corresponds to the $2k_F$ SDW and $2k_F$ CDW states. For the triplet state, the up spin in the first and third sites are correlated.

To investigate the long-range effects of Coulomb interactions, we extend the model to the octamer. For the $H_{\text{eff}}(2)$ of the octamer model, the ground state also has the AF and charge ordering correlations as shown in Fig. 4. The spin correlation functions, $\Delta_{1\uparrow,3\downarrow}$ ($\Delta_{1\uparrow,7\downarrow}$), $\Delta_{1\uparrow,5\uparrow}$ and $\Delta_{1\uparrow,5\downarrow}$, are 2.75, 2.27 and 1.15, respectively. $\Delta_{1\uparrow,q\sigma'}$ ($q = 2, 4, 6$ and 8 ; $\sigma = \uparrow$ and $\downarrow$) are < 0.4 . So, in this model, the localization is weaker than in the tetramer model. Some low-lying excited states have similar spin-flipped CDW correlations. So, it is elucidated that the spin correlation is weak for this octamer model. The charge ordering of these states is in good agreement with the $4k_F$ CDW state observed experimentally for the 1-D DCNQI salts [2–4].

For the tetramer and octamer models, we found that the ground state is an AF type state. This state corresponds to the $4k_F$ CDW and $2k_F$ SDW states

Ground state



2nd singlet excited state

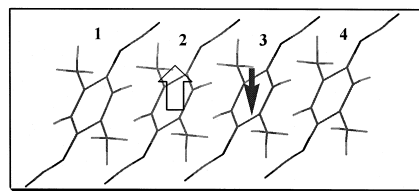
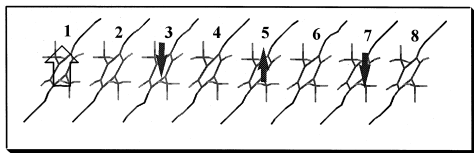
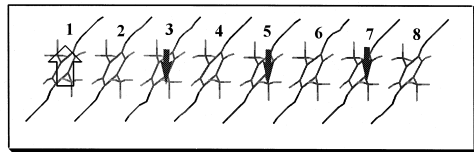


Fig. 3. The spin configurations of the ground state and the 2nd singlet excited state for the periodic tetramer model. Arrows pointing upward (downward) represent up (down) spins and solid arrows indicate the *j*th LMO where spin correlation function has strong amplitude toward the *i*th LMO indicated by open arrows.

Ground state



1st quintet excited state



1st singlet excited state

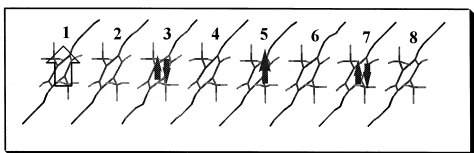


Fig. 4. The spin configurations of the ground state and some low-lying excited states for the anti-periodic octamer model. The definitions of arrows follow those in Fig. 3.

calculated by Kobayashi et al. and Seo and Fukuyama by the HF approximation [5–7]. In the case of the tetramer model, the second singlet excited state corresponds to the $2k_F$ SDW and $2k_F$ CDW states calculated by Kobayashi et al. Actually, Pouget and Ravy suggested by XRD experiments that the ground state for a similar electronic system, $(\text{TMTSF})_2\text{PF}_6$, is the coexistence of $2k_F$ SDW and $2k_F$ CDW states [21].

We have investigated the spin correlation based on FCI calculations of the 1-D octamer and tetramer models. In these calculations, we neglect the effect of intercolumn interactions. Basically, for DCNQI-Ag/Li salts, we think that these effects are small due to the strong 1-D character. For DI-DCNQI salt, however, intercolumn interaction is large [9] and intracolumn interaction is small in comparison with other DCNQI salts. Relatively, this system has a 3-D character. In such a case, it may be necessary to include intercolumn interactions. The long-range behavior will be inspected by extending the size of the model. We are proceeding with employing the method like the density-matrix renormalization group approach to treat large-scale models.

5. Conclusions

We performed the DCNQI tetramer calculations using the XRD structural parameters at the HF level with the SBK split valence basis sets and their ECPs. The parameters for the model Hamiltonian were obtained and compared with the formerly calculated parameters. We constructed the H_{eff} for the tetramer and octamer models under the periodic and anti-periodic boundary conditions, respectively, and calculated the spin correlation function. In both models, the ground state has the AF and charge ordering correlations which correspond to the $2k_F$ SDW and $4k_F$ CDW states. In the octamer model, however, we observed that the spin correlation is weak. The ground state and some low-lying excited states have the correlation of charge ordering which corresponds to the $4k_F$ CDW state observed experimentally for the 1-D DCNQI salts.

Acknowledgements

We thank Hayao Kobayashi for fruitful discussions and useful suggestions. We are grateful to Kouichi Hiraki, Hiroshi Sawa and Akiko Kobayashi for giving the crystal structures of DCNQI salts. One of authors (YI) is indebted for the fellowship from the Japan Society for the Promotion of Science. The numerical calculations were performed at the computer center of Institute for Molecular Science.

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