

Spin–Spin Correlation Function and Magnetic Susceptibility of Quantum Ferrimagnetic Spin Chains as Models for Organic Molecule-Based Ferrimagnetics

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Spin–spin correlation function and temperature dependence of magnetic susceptibility were calculated for the finite-size Hamiltonian of an $S = 1$ and $S = 1/2$ antiferromagnetic Heisenberg chain. The $S = 1$ site in the chain is composed of two $S = 1/2$ spins coupled by finite ferromagnetic interaction. This is the simplest model Hamiltonian for organic molecule-based ferrimagnetics consisting of two kinds of molecules with different spin quantum numbers. The Hamiltonian possesses a magnetic degree of freedom in the $S = 1$ site and a multicentered nature of the intermolecular interactions, both of which are essential features of molecular magnetics. The low-temperature limit of susceptibility calculated by a quantum Monte Carlo simulation method was found to obey the Curie law of $S = N/2 = N(1-1/2)$ (N : the number of repeating units), indicating that the ground state of the chain is ferrimagnetic. A quasi-exponential decay, however, was found in the ground-state correlation function calculated from the numerical diagonalization of the Hamiltonian matrix, which implies that the ground state has no long-range order at the critical point of zero-temperature.

Introduction

Ferrimagnets have been attracting attention as one of the facile approaches to purely organic molecule-based ferromagnets after Buchachenko's proposal for organic ferrimagnetics in 1979.¹ The concept of organic ferrimagnetics is based on the tendency for organic molecules to have antiferromagnetic intermolecular interactions. The antiferromagnetic interactions would bring about antiparallel spin alignment between neighboring molecules with different magnetic moments to result in a possible ordered state with net magnetization.² Magnetic phase transition to a ferrimagnetic ordered state, however, has not been documented so far in organic molecular crystalline solids. This presents a remarkable contrast to the fact that genuinely organic molecular ferromagnets based on purely ferromagnetic intermolecular interactions³ and transition metal-based ferrimagnets⁴ have been discovered.

Some numerical studies have been reported on antiferromagnetic heterospin chains composed of different spin quantum numbers; e.g., an alternating chain of $S = 1$ and $S = 1/2$. Most of the studies assume "pure" $S = 1$ spins,^{5–7} i.e., the intramolecular ferromagnetic interaction is sufficiently large compared with both the thermal energy $k_B T$ and intermolecular interactions. These models are applicable to transition metal-based molecular ferrimagnets.⁴ In organic molecule-based magnetics, on the other hand, spin density is distributed over many atomic sites in an open-shell molecule and hence the intermolecular interaction has a multicentered nature. Furthermore, the intramolecular interaction is not robust compared with the intermolecular interactions. Therefore, the magnetic degree of freedom within the $S > 1/2$ molecules and spatial symmetry of intermolecular exchange interaction should be taken into account when considering magnetic properties of molecular assemblages

containing $S > 1/2$ molecules. These features make preceding theoretical studies invalid for the molecule-based heterospin assemblages as models for organic ferrimagnetics.

The difficulty in achieving a ferrimagnetic ordered state in purely organic systems would be underlain by some quantum effect due to the characteristics of the molecule-based materials described above. In our previous papers,^{8,9} we discussed the possibility of ferrimagnetic order occurring in organic molecular crystals both from numerical calculations⁸ of a Heisenberg spin Hamiltonian of an $S = 1/2$ and $S = 1$ alternating chain⁸ and from crucial experiments⁹ on only one model compound documented so far.¹⁰ In the chain, the intramolecular magnetic degree of freedom remains within the $S = 1$ site: The $S = 1$ site in the chain is composed of two $S = 1/2$ spins coupled by finite ferromagnetic interaction. The Heisenberg spin Hamiltonian for the chain under study is given as

$$H_{\text{chain}} = \sum_{i=1}^N [-2J_{\text{FM}} \mathbf{S}_{i,A} \cdot \mathbf{S}_{i,B} - 2J_{\text{AF}} (\mathbf{S}_{i,B} \cdot \mathbf{S}_{i,C} + \mathbf{S}_{i,C} \cdot \mathbf{S}_{i+1,B}) - 2aJ_{\text{AF}} (\mathbf{S}_{i,A} \cdot \mathbf{S}_{i,C} + \mathbf{S}_{i,C} \cdot \mathbf{S}_{i+1,A})] \quad (1)$$

where $\mathbf{S}_{i,A}$, $\mathbf{S}_{i,B}$, and $\mathbf{S}_{i,C}$ denote the spin-1/2 operators. The periodic boundary condition $\mathbf{S}_{N+1,I} = \mathbf{S}_{1,I}$ ($I = A, B, C$) is imposed with N repeating units. $\mathbf{S}_{i,A}$ and $\mathbf{S}_{i,B}$ are coupled by the intramolecular ferromagnetic exchange interaction, $J_{\text{FM}} > 0$, to give the biradical site, or the two-spin site, which is coupled to a neighboring monoradical with $\mathbf{S}_{i,C} = 1/2$ by the antiferromagnetic exchange interactions, $J_{\text{AF}} < 0$ and $aJ_{\text{AF}} < 0$ ($a > 0$). In Figure 1 is schematically shown the Hamiltonian (eq 1). This is the simplest model Hamiltonian for molecular ferrimagnets possessing the above features; a biradical molecule with $\mathbf{S}_{i,A} + \mathbf{S}_{i,B}$ and a monoradical molecule with $\mathbf{S}_{i,C}$. The main issue of the calculations was the formation of a ground-state singlet ($S = 0$) pair between the biradical and the monoradical spins, which possibly competes against long-range ferrimagnetic spin–spin correlation. The system size of the previous study was too small

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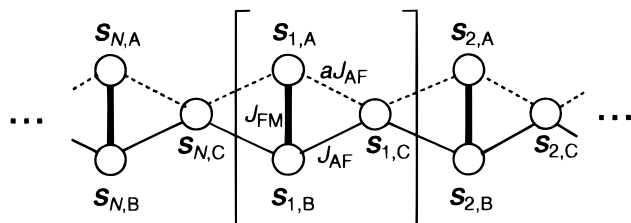


Figure 1. Heisenberg spin Hamiltonian of the molecule-based ferromagnetic chain with N repeating units. The periodic boundary condition ($S_{N+1,I} = S_{1,I}$; $I = A, B, C$) is imposed. The open circles denote the spin-1/2 operators. The thick solid line is the intramolecular ferromagnetic interaction J_{FM} , while the thin solid and dashed lines the intermolecular antiferromagnetic interactions, J_{AF} , aJ_{AF} .

to give a reliable solution to the occurrence of the long-range spin–spin correlation in the exchange-coupled systems. In the present study, the magnetic properties of the system of the Hamiltonian (eq 1) are numerically examined in terms of a quantum Monte Carlo simulation¹¹ and an exact numerical diagonalization¹² of the Hamiltonian with a larger number of spins for the longer chains in order to obtain the more reliable solution. A novel effect of intermolecular exchange interactions on the spin quantum number of the $S > 1/2$ site is presented. Real-space spin–spin correlation function and temperature dependence of magnetic susceptibility are calculated to show the existence of the ferrimagnetic spin alignment in the biradical–monoradical alternating chain.

Methods of Computation

The temperature dependence of magnetic susceptibility was calculated by the quantum Monte Carlo simulation method of the loop algorithm which was originally coded by M. Troyer at ETH Zurich.¹¹ The exact numerical diagonalization of the Hamiltonian matrix was done by the Lanczos method.¹² The largest system examined in this study consists of twenty-seven $S = 1/2$ spins with the matrix dimension of $2^{27} \times 2^{27} = 134217728 \times 134217728$. The matrix is block-diagonalized according to the conservation of the z -component of the total spin, giving submatrices with the dimension of ${}_{27}C_{13} \times {}_{27}C_{13} = 20058300 \times 20058300$. In the calculations, a parallelization procedure is used on an NEC supercomputer SX-5 at the Computer Center of the Institute for Molecular Science and on a HITACHI supercomputer HR8000 at the Computer Center of the University of Tokyo.

Results and Discussion

1. Three-Spin System of a Biradical–Monoradical Dimer.

Let us consider first a minimal system of interacting open-shell molecules with different spin quantum numbers; a molecular dimer of a biradical with the ground-state triplet ($S = 1$) and a monoradical molecule with $S = 1/2$. The spin Hamiltonian of the molecular dimer with three unpaired electrons is written as

$$H_{\text{dimer}} = -2J_{FM}\mathbf{S}_{1,A} \cdot \mathbf{S}_{1,B} - 2J_{AF}(\mathbf{S}_{1,B} \cdot \mathbf{S}_{1,C} + a\mathbf{S}_{1,C} \cdot \mathbf{S}_{1,A}) \quad (2)$$

This Hamiltonian is regarded as the unit cell of the chain Hamiltonian (eq 1) and is solvable analytically. The Hamiltonian H_{dimer} is block-diagonalized in the ket space spanned by the set of direct product $\{|\sigma_A\sigma_B\sigma_C\rangle\}$ defined as

$$S_I^z|\sigma_A\sigma_B\sigma_C\rangle = \pm 1/2|\sigma_A\sigma_B\sigma_C\rangle \quad (3)$$

where σ_I is the spin function α or β ($I = A, B, C$). The block matrices are labeled in terms of the z -component of the total

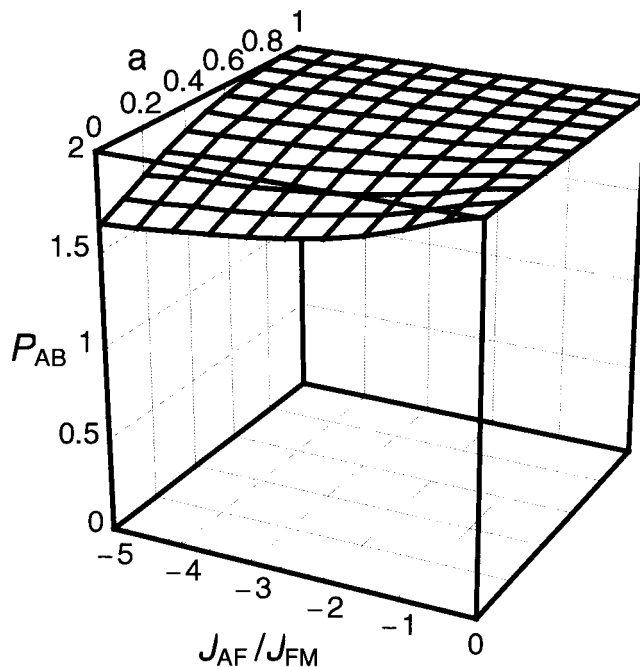


Figure 2. Expectation value of the biradical spin $P_{AB} = \langle (S_{1,A} + S_{1,B})^2 \rangle$ in the biradical–monoradical dimer as a function of the interaction ratio J_{AF}/J_{FM} and the asymmetry parameter a .

spin operator

$$(\sum_I S_I^z)|\sigma_A\sigma_B\sigma_C\rangle = M_S|\sigma_A\sigma_B\sigma_C\rangle \quad (M_S = \pm 3/2, \pm 1/2) \quad (4)$$

As mentioned above, the spatial symmetry of the intermolecular exchange interactions should be taken into account in considering magnetic properties of molecular assemblages containing $S > 1/2$ molecules. The spatial symmetry is signified by the parameter a in the Hamiltonian. Let us elucidate the significance of the spatial symmetry by evaluating the spin value of the biradical site, $S_{AB}^2 \equiv (S_{1,A} + S_{1,B})^2$. In the ket space of eq 3, the commutator $[H_{\text{dimer}}, S_{AB}^2]$ is given by

0	0	0	0	0	0	0	0	$\alpha\alpha\alpha$
0	0	$(a-1)J_{AF}$	$(1-a)J_{AF}$	0	0	0	0	$\beta\alpha\alpha$
0	$(1-a)J_{AF}$	0	$(a-1)J_{AF}$	0	0	0	0	$\alpha\beta\alpha$
0	$(a-1)J_{AF}$	$(1-a)J_{AF}$	0	0	0	0	0	$\alpha\beta\beta$
0	0	0	0	0	$(a-1)J_{AF}$	$(1-a)J_{AF}$	0	$\beta\alpha\beta$
0	0	0	0	0	$(a-1)J_{AF}$	$(1-a)J_{AF}$	0	$\beta\beta\alpha$
0	0	0	0	0	0	0	0	$\beta\beta\beta$

(5)

where the basis kets are shown in the right side of the matrix. It is found from the matrix elements of $[H_{\text{dimer}}, S_{AB}^2]$ that the expectation value of S_{AB}^2

$$P_{AB} \equiv \langle S_{AB}^2 \rangle = \langle (S_{1,A} + S_{1,B})^2 \rangle \quad (6)$$

takes a definite value of 2 for the eigenkets with $M_S = \pm 3/2$, $|\alpha\alpha\alpha\rangle$ and $|\beta\beta\beta\rangle$: $S_{AB} = 1$ is a good quantum number. The P_{AB} value in the subspace of $M_S = \pm 1/2$, on the other hand, is equal to 2 ($S_{AB} = 1$) or 0 ($S_{AB} = 0$) only when $a = 1$ or $J_{AF} = 0$.

The ground state belongs to the subspace of $M_S = \pm 1/2$ for $J_{FM} > 0$ and $J_{AF} < 0$. P_{AB} in the ground state is shown in Figure 2 as a function of J_{AF}/J_{FM} and a . P_{AB} substantially deviates from 2 as the ratio $|J_{AF}/J_{FM}|$ is larger and the parameter a approaches zero. We find $P_{AB} = 2$ ($S_{AB} = 1$) for any value of J_{AF}/J_{FM} along

the $a = 1$ line, indicating that symmetrical intermolecular interactions give pure triplets ($S_{AB} = 1$) at the biradical site. The pure triplet is also found in the vicinity of the $J_{AF}/J_{FM} = 0$ line. When intraatomic or intramolecular exchange interaction is sufficiently large compared with intermolecular interactions, as in transition metal ions, the spatial symmetry of the intermolecular interaction has little effect on the spin state of the $S > 1/2$ site: $S = 1$ is always a good spin quantum number for a two-spin site. The deviation of the spin quantum number of the $S > 1/2$ site as found above for the biradical spin site $S_{AB} < 1$ occurs when intermolecular interaction has a multi-centered nature and the intramolecular interaction is not robust compared with the intermolecular interactions, both of which are characteristic of molecule-based spin assemblages composed of molecules with different spin quantum numbers. In a previous theoretical study,⁷ the finite ferromagnetic interactions within the two-spin sites are taken into account by setting S_{AB} either to 0 or 1. From the above results, this is found to be oversimplified.

2. Extended Chains. (a) *Spin Quantum Number of the Biradical Site.* The expectation value P_{AB} for an extended chain with N repeating units

$$\begin{aligned} P_{AB}(N) &\equiv \langle (S_{1,A} + S_{1,B})^2 \rangle = 2 \langle S_{1,A} S_{1,B} \rangle + \langle S_{1,A}^2 \rangle + \langle S_{1,B}^2 \rangle \\ &= 2 \langle S_{1,A} \cdot S_{1,B} \rangle + 3/2 \end{aligned} \quad (7)$$

is calculated from an exact diagonalization of the spin Hamiltonian (eq 1) of length N with $J_{AF}/J_{FM} = -1$. Only the biradical at the "origin" of the chain $S_{1,A} + S_{1,B}$ is considered, because P_{AB} is independent of the site number owing to the translational symmetry of the Hamiltonian (eq 1). The bracket denotes the expectation value for the eigenvector of the ground state. The Hamiltonian (eq 1) is, as eq 2 for the three-spin system, written in the ket space spanned by the set of direct product $\{|\sigma_{1,A}\sigma_{1,B}\dots\sigma_{N,C}\rangle\}$ defined as

$$S_I^\pm |\sigma_{1,A}\sigma_{1,B}\dots\sigma_{N,C}\rangle = \pm 1/2 |\sigma_{1,A}\sigma_{1,B}\dots\sigma_{N,C}\rangle \quad (3')$$

for $\sigma_I = \alpha$ or β ($I = 1, A, 1, B, \dots, N, C$). All of the calculations are made for a spin subspace with the z -component of the total spin

$$\left(\sum_I S_I^z \right) |\sigma_{1,A}\sigma_{1,B}\dots\sigma_{N,C}\rangle = M_S |\sigma_{1,A}\sigma_{1,B}\dots\sigma_{N,C}\rangle \quad (4')$$

where $M_S = 0$ for even $3N$ and $M_S = +1/2$ for odd $3N$, respectively. The $P_{AB}(N)$ values for $a = 0, 0.5$, and 1 are plotted as functions of N in Figure 3. $P_{AB}(N)$ takes a constant of 2 when $a = 1$ as expected from the calculations for the minimal three-spin system of the biradical–monoradical dimer. For $a = 0$ and 0.5 , $P_{AB}(N)$ is reduced from the value of pure triplet ($S = 1$) but it makes a gradual recovery as N increases. For the chain with most asymmetric intermolecular interactions ($a = 0$), 98% ($= \sqrt{1.923/2}$) of spin contraction is found at $N = 9$.¹³ Although the spin contraction is overestimated owing to a finite-size effect of the chain length, it is obvious from the calculation that the contraction depends substantially on the degree of asymmetry of intermolecular interactions. This is characteristic of a molecule-based spin chain having multicentered intermolecular interactions and nonrobust intramolecular magnetic coupling.

(b) *Temperature Dependence of Magnetic Susceptibility.* In realizing molecule-based ferrimagnetics, most important is

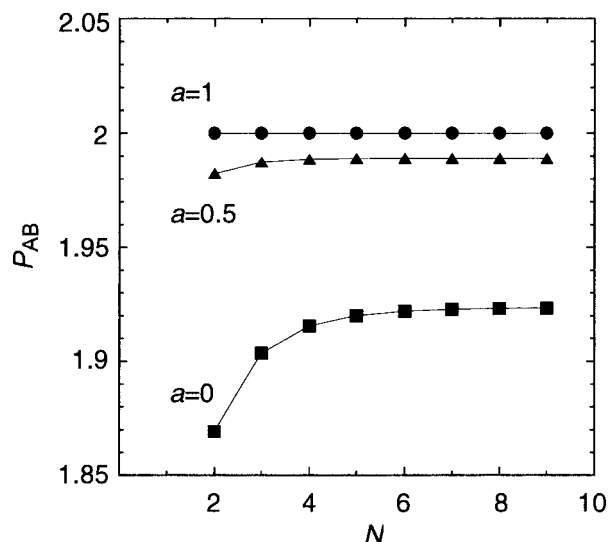


Figure 3. Expectation value of the biradical spin $P_{AB}(N) = (S_{1,A} + S_{1,B})^2$ in the extended chain as a function of the chain length N for the asymmetry parameters of $a = 0, 0.5$, and 1 . The solid lines are to guide the eye.

whether the antiferromagnetic spin chain of the Hamiltonian (eq 1) has a ground state with ferrimagnetic spin alignment. Although purely one-dimensional Heisenberg spin systems has no long-range order at finite temperatures, $T > 0$ K,¹⁴ the ferrimagnetic state at zero-temperature is a prerequisite for bulk ferrimagnetism. We calculate the temperature dependence of magnetic susceptibility χ by the quantum Monte Carlo simulation method¹¹ in order to give a solution to the occurrence of the ferrimagnetic spin alignment in the chain.

Figure 4 shows the temperature dependence of the product χT for the rings of the Hamiltonian ($J_{AF}/J_{FM} = -1$) with length up to $N = 20$ as a function of reduced temperature $k_B T/J_{FM}$ in the two limiting cases of the spatial symmetry of intermolecular interaction, $a = 0$ (Figure 4a) and $a = 1$ (Figure 4b). The number of Monte Carlo updating steps of spin configurations is 10 000, which gives a statistical error of 1% in χ at the lowest temperature $k_B T/J_{FM} = 0.004$. The error decreases at higher temperatures; 0.4% at $k_B T/J_{FM} = 0.1$ and 0.06% at $k_B T/J_{FM} = 1$. The high-temperature limit of χT is 0.375 emu K per spin, which is consistent with the Curie law of $S = 1/2$ with the g -value of 2.0. As T lowers, χT exhibits a rounded minimum both for $a = 0$ ($k_B T/J_{FM} \approx 0.26$) and $a = 1$ ($k_B T/J_{FM} \approx 0.62$). The appearance of minimum in χT is characteristic of one-dimensional ferrimagnetic chains.^{4,6,8,10} At the lowest temperatures ($k_B T/J_{FM} \leq 0.01$), χT approaches finite values depending on the system size N . The low-temperature value of χT corresponds to the Curie law for the spin quantum number $S = N/2$ of the whole chain

$$\chi T(T \rightarrow 0) = \frac{1}{3N} \times \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B} = \frac{N_A g^2 \mu_B^2 (N+1)}{36k_B} \quad (8)$$

where N_A , g , μ_B , and k_B stand for Avogadro constant, g -factor, Bohr magneton, and Boltzmann constant, respectively. The spin quantum number $S = N/2$ is acceptable by assuming that N pairs of $S = 1$ and $S = 1/2$ spins are aligned in an antiparallel fashion. From the quantum Monte Carlo calculations, the antiferromagnetic chain (eq 1) is found to have a ferrimagnetic ground state, even if the intramolecular magnetic degree of freedom remains in the biradical sites. This finding is consistent with the Lieb–Mattis theorem.¹⁵

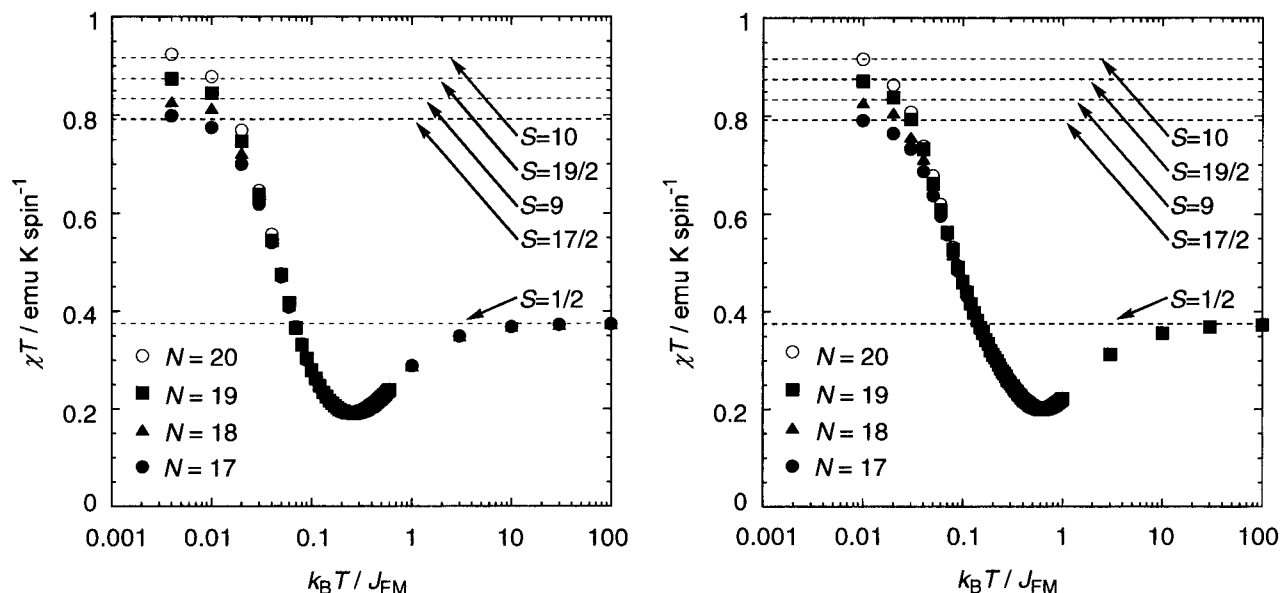


Figure 4. Temperature dependence of the product of susceptibility χ and temperature T calculated for the chains of length $N = 17, 18, 19$, and 20 with the asymmetry of the intermolecular interactions, $a = 0$ (left) and $a = 1$ (right). The dashed lines denote the χT values of the Curie law for $S = 10, 19/2, 9$, and $17/2$, and $1/2$, respectively. The g -factor of 2.0 and $J_{AF}/J_{FM} = -1$ are assumed.

(c) *Spin-Spin Correlation in the Ground State.* The real-space spin-spin correlation function $\omega(N, L)$ for the rings of length N

$$\omega(N, L) = \frac{\langle (S_{1,A} + S_{1,B}) \cdot S_{L,C} \rangle}{\sqrt{\langle (S_{1,A} + S_{1,B})^2 \rangle} \times \sqrt{\langle S_{L,C}^2 \rangle}} \quad (9)$$

is calculated in terms of the eigenvectors obtained from the exact diagonalization of the Hamiltonian (eq 1) in the subspaces with $M_S = 0$ (even $3N$) or $M_S = +1/2$ (odd $3N$). The brackets in eq 9 denote the expectation value for the eigenvector of the ground state. The numerator represents the spin-spin correlation between the biradical at the “origin” of the chain $S_{1,A} + S_{1,B}$ and the monoradical $S_{L,C}$ in the L th unit cell. The correlation function is normalized with the expectation values $\sqrt{\langle (S_{1,A} + S_{1,B})^2 \rangle}$ and $\sqrt{\langle S_{L,C}^2 \rangle}$.

The correlation functions $\omega(N, L)$ calculated for the rings of length up to $N = 9$ ($L = 1, 2, 3, 4, 5$) are extrapolated to $N \rightarrow \infty$ for each L by assuming the convergence proportional to $1/N^3$ to yield the thermodynamic limit $\omega(\infty, L)$. In Figure 5 are plotted $\omega(\infty, L)$ and $\omega(9, L)$ for $J_{AF}/J_{FM} = -1$ as a function of the distance L between the biradical $S_{1,A} + S_{1,B}$ and the monoradical $S_{L,C}$. The correlation function $\omega(\infty, L)$ is compared with that of the pure $S = 1/2$ antiferromagnetic Heisenberg chain, which has power law decaying with divergent correlation length¹⁶

$$\omega'(\infty, L') \equiv \frac{\langle S_1 \cdot S_{L'} \rangle}{2\sqrt{\langle S_1^2 \rangle}} \propto (-1)^{L'}/L' \quad (10)$$

in the limit of $L' \rightarrow \infty$ at the critical point of zero-temperature, where L' is defined as the distance between the $S = 1/2$ spin at the origin and that in the L' th unit cell. For the pure $S = 1/2$ chain, $\omega'(\infty, L')$ values for the short distance L' have also been reported.^{17–19} As depicted in Figure 5, we see quasi-power-law dependence of $\omega'(\infty, L')$ for the pure $S = 1/2$ antiferromagnetic chain, even in the very short distance L' . The absence of power-law dependence of $\omega(\infty, L)$ on L is obvious and a quasi-exponential decaying is found. This finding for the ground state

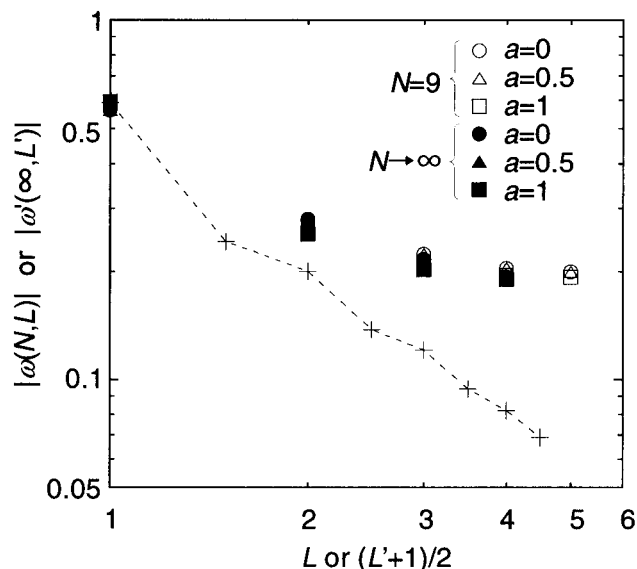


Figure 5. Real-space spin-spin correlation function $|\omega(N, L)|$ of the ferrimagnetic chain as a function of the distance L between the biradical spin ($S_{1,A} + S_{1,B}$) at the origin of the chain and the monoradical spin $S_{L,C}$ in the L th unit cell. The open symbols denote $|\omega(9, L)|$ for the longest chains ($N = 9$) in our calculations. The solid symbols are extrapolated values ($1/N^3 \rightarrow 0$) of the correlation function, $|\omega(\infty, L)|$. The crosses connected by the dashed lines represent the two-spin correlation function $|\omega'(\infty, L')|$ of the $S = 1/2$ antiferromagnetic chain as a function of the spin-spin distance L' (from ref 17).

indicates that our molecule-based ferrimagnetic chain has no long-range spin-spin correlation at zero-temperature.

For the chain composed of $S = 1/2$ and “pure” $S = 1$ spins with $J_{FM} = +\infty$ corresponding to the transition metal-based ferrimagnets, both the correlation function in short spin-spin distances L'' and the leading term in the limit of $L'' \rightarrow \infty$ have been reported:⁵ The long-distance correlation has an exponential decay

$$\omega''(\infty, L'') \propto \exp(-L''/\xi) \quad (11)$$

with the correlation length $\xi = 1/\ln 2 \approx 1.44$ in the limit of $L'' \rightarrow \infty$.⁵ The distance L in our calculations for the finite J_{FM} is

too short to determine the leading behavior of long-distance decay in the correlation function. At present, it can be stated that the correlation function under study seems to decay more slowly than that of the "pure" $S = 1$ and $S = 1/2$ chain in the short distance L .⁵ To elucidate the physical meaning of the apparently longer correlation length in the molecule-based ferrimagnetic chains compared with the ferrimagnetic chain of "pure" $S = 1$ and $S = 1/2$, longer distance (L) behavior of $\omega(\infty, L)$ in longer chains is needed, which is beyond the scope of this work. The quasi-exponential decay of the correlation function suggests a quantum mechanically disordered ground state resulting from quantum fluctuation due to the singlet pair formed between the $S = 1/2$ spins coupled by nearest-neighbor exchange interactions.

Conclusion

From the exact numerical diagonalization of the finite-size spin Hamiltonian for the biradical–monoradical alternating chain, the spin magnetic moment of the biradical is shown to be reduced by the quantum spin contraction. The spin contraction should occur in the metal-based ferrimagnetic chains.^{20,21} The contraction in our molecule-based chain is, however, due to the asymmetric intermolecular antiferromagnetic interactions. This novel effect tells us that the spin state of a molecule is affected by the spatial symmetry of intermolecular magnetic interactions, when the intermolecular interaction has a multi-centered nature. Although the ground state of the chain has no long-range pair correlation at zero-temperature, the chain exhibits a minimum in χT characteristic of one-dimensional ferrimagnetic systems. The χT obeys the Curie law of spin quantum number $S = N/2$ (N is the number of unit cells) at the lowest temperatures examined in the quantum Monte Carlo simulation. The spin quantum number proportional to the system size N is indicative of possible ferrimagnetic ordered states occurring in real molecule-based materials with higher dimensional, e.g., interchain, exchange interactions.

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References and Notes

- (1) Buchachenko, A. L. *Dokl. Akad. Nauk. Eng. Ed.* **1979**, *244*, 107.
- (2) In this paper, we mean by "ferrimagnetic" that the intermolecular interaction is primarily antiferromagnetic but net magnetization arises from the differing moments ordered in the sublattices.
- (3) (a) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401. (b) Nakazawa, Y.; Tamura, M.; Shirakawa, N.; Shiomi, D.; Takahashi, M.; Kinoshita, M.; Ishikawa, M. *Phys. Rev. B*, **1992**, *46*, 8906.
- (4) For example, see: (a) Kahn, O.; Pei, Y.; Verdager, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782. (b) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976. (c) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866.
- (5) Pati, S. K.; Ramasesha, S.; Sen, D. *Phys. Rev. B* **1997**, *55*, 8894 and references therein.
- (6) Yamamoto, S. *Phys. Rev. B* **1999**, *59*, 1024 and references therein.
- (7) Niggemann, H.; Uimin, G.; Zittartz, J. *J. Phys.: Condens. Matter*. **1997**, *9*, 9031.
- (8) Shiomi, D.; Nishizawa, M.; Sato, K.; Takui, T.; Itoh, K.; Sakurai, H.; Izuoka, A.; Sugawara, T. *J. Phys. Chem. B* **1997**, *101*, 3342.
- (9) Nishizawa, M.; Shiomi, D.; Sato, K.; Takui, T.; Itoh, K.; Sawa, H.; Kato, R.; Sakurai, H.; Izuoka, A.; Sugawara, T. *J. Phys. Chem. B* **2000**, *104*, 503.
- (10) Izuoka, A.; Fukada, M.; Kumai, R.; Itakura, M.; Hikami, S.; Sugawara, T. *J. Am. Chem. Soc.* **1994**, *116*, 2609.
- (11) Troyer, M.; Ammon, B.; Heeb, E.; Caromel, D. *Lecture Notes in Computer Science*; Springer: Berlin, 1999; p 191.
- (12) We have modified the routines of the Lanczos method in the program package "TITPACK" version 2 supplied by H. Nishimori at Tokyo Institute of Technology.
- (13) Spin contraction effect in a finite-size organic high-spin molecular system has been discussed: Teki, Y.; Kinoshita, T.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst.* **1997**, *306*, 447.
- (14) Mermin, N. D.; Wagner, H. *Phys. Rev. Lett.* **1966**, *17*, 1133.
- (15) Lieb, E.; Mattis, D. *J. Math. Phys.* **1962**, *3*, 749.
- (16) Luther, A.; Peschel, I. *Phys. Rev. B* **1975**, *12*, 3908.
- (17) Betsuyaku, H.; Yokota, T. *Phys. Rev. B* **1985**, *33*, 6505.
- (18) Takahashi, M. *J. Phys. C* **1977**, *10*, 1289.
- (19) Hulthen, L. *Ark. Mater. Astron. Phys. A* **1938**, *26*, 1.
- (20) Kolezhuk, A. K.; Mikeska, H.-J.; Yamamoto, S. *Phys. Rev. B* **1997**, *55*, R3336.
- (21) Srinivasan, B.; Kahn, O.; Ramasesha, S. *J. Chem. Phys.* **1998**, *109*, 5770.