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REGULAR ARTICLE

Stability criterion for organic ferromagnetism

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Abstract Stability criterion for organic ferromagnetism is derived from crystal orbital method. For a given flat-band system, there exists a unique set of Wannier functions localized near each unit cell, which should be symmetric with respect to the lattice vector. The set of Wannier functions minimizes the exchange integral of the system within the freedom of degeneracy. When each Wannier function spans common atoms between the adjacent cells, the system becomes ferromagnetic. On the other hand, when each Wannier function spreads only at one unit cell, the system becomes antiferromagnetic. The proof of this rule is given by variational principle.

Keywords Organic ferromagnets · Flat bands · Wannier functions · Phase factor · Exchange integral

1 Introduction

Organic ferromagnetism is one of the most challenging themes in material sciences. One of the conventional strategies toward realization of organic ferromagnets has been based on Heisenberg Hamiltonian, which describes localized spin moments. The Hamiltonian has been applied for so-called bipartite lattices, in which the atomic sites are divided into two groups that are not adjacent to each other. In organic chemistry, such a classification has been applied as starred and unstarred atoms in alternant hydrocarbons. If number of starred atoms is larger than that of unstarred atoms, the system has a ferrimagnetic spin-polarized structure, in which plus spins and minus spins are induced at starred and unstarred atoms, respectively [1–3].

In view of molecular orbital methods, degenerate orbitals play an essential role for description of the ferromagnetic interactions. Degeneracy of molecular orbitals comes from topological linkage of the atomic orbitals, as well as molecular symmetries. In particular, non-bonding molecular orbitals (NBMOs), which result from zero-overlapping interactions of fragment moieties, are very important in chemistry of conjugated hydrocarbons. NBMOs are degenerate one-electron states, of which eigenvalues are zero with respect to the Coulomb integral in Hückel molecular orbital method. The number of NBMOs becomes $(N_c - 2T_d)$, where N_c and T_d are numbers of carbon atomic sites and classical double bonds, respectively [4]. Amplitude pattern of these orbitals cannot be determined within the Hückel level of theory, because there exists at least one degree of freedom within unitary transformations due to the degeneracy. However, when electron repulsions are explicitly included, recent studies on non-Kekulé hydrocarbons suggest that amplitude pattern of NBMOs are determined so that the exchange integrals between them are minimized. Then, each NBMO spreads as localized as possible. For biradicals, this was qualitatively pointed out by Borden and Davidson as disjoint/non-disjoint concept [5, 6]. That is, when the NBMOs can be made to span common atoms, which are non-disjoint type, triplet ground states are preferred. That is, two non-bonding orbitals contain non-zero amplitudes on the same atom. The resultant double occupation of electrons cause so-called ionic terms $\chi_r(\boldsymbol{x})\cdot\chi_r(\boldsymbol{x})$ in two-electron wavefunctions consisting of product of the two orbitals, where χ_r is the r-th atomic orbital, and $\boldsymbol{x}$ is a certain coordinate of electrons. This leads to simultaneous occupation of two electrons in the same

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atom, and thus, singlet states are relatively destabilized due to the Pauli principle. On the other hand, when the NBMOs cannot be made to span common atoms, which are disjoint type, singlet ground states are preferred. Recently, this has been mathematically proved for non-Kekulé biradicals by Aoki and Imamura [7]. They mathematically established the disjoint/non-disjoint concept of conjugated biradicals. That is, there exists a proper unitary transformation which minimizes the exchange interaction of the system, and thus, amplitude pattern of the degenerate orbitals are determined uniquely.

1 in Fig. 1 shows a famous triplet biradical trimethylenemethane and its NBMOs. The NBMOs span common atoms and lead to the triplet ground state, which has been established by ESR experiments [8] and PES spectra [9]. Many theoretical calculations also established the ground triplet state [6, 10, 11]. **2** in Fig. 1 is a singlet biradical cyclobutadiene. The NBMOs span no common atoms, and lead to the singlet ground state accompanied by pseudo Jahn–Teller effects [12–14]. **3** in Fig. 1 is another example of singlet biradical. Although a ferrimagnetic spin-polarization structure is expected by the Heisenberg model, the NBMOs also span no common atoms. The low-spin ground state was established by ESR studies on dinitroxide derivative of **3** [15, 16]. Thus, **3** is an exception for the conventional Heisenberg model and a good example for the Borden–Davidson rule. However, in polyradicals such as tri- or tetraradicals, the uniqueness of the NBMOs is not so evident due to difficulty in unitary transformation. Pranata guessed NBMOs of many polyradicals, but the uniqueness of the choice is somewhat ambiguous [17]. Instead, applications for polyradicals have been given for benzyl-radical oligomers by numerical extrapolation of the exchange integral [18, 19].

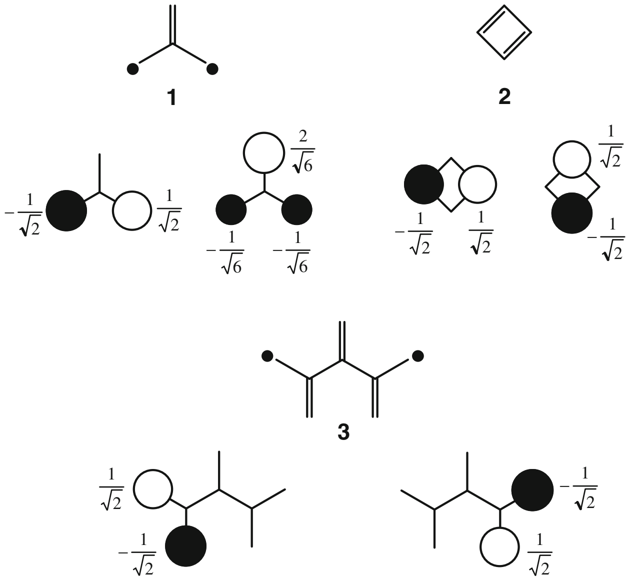


Fig. 1 Molecular structures of trimethylenemethane (**1**), cyclobutadiene (**2**), and pentamethylenepropane (**3**). NBMOs of them are also schematically shown

On the other hand, high-spin extended systems with infinite radical centers have been proposed by several workers. For example, non-Kekulé polymers have flat bands at the non-bonding level and have attracted many chemists. Tyutyulkov et al. proposed many one-dimensional non-Kekulé polymers in view of band theory [20–22]. They also showed ferrimagnetic spin polarization of non-Kekulé polymers by using UHF (unrestricted Hartree–Fock) wavefunctions. UHF wavefunctions of organic ferromagnets were well studied and related to the Heisenberg description by Yamaguchi et al. [23, 24]. Mataga also proposed a two-dimensional non-Kekulé polyradical based on 1,3,5-phenylene unit network [25]. Experimentally, Rajca et al. synthesized many polyradicals and established the high-spin ground states by ESR and magnetic susceptibility measurements [26–28]. Moreover, Iwamura et al. realized ferromagnetic interactions between face-to-face stacked polyradicals [29–32]. These experimental results are good examples for flat-band ferromagnetism.

In extended systems, the minimization of exchange interactions also seems to be essential, because Wannier functions, which are deduced by a special unitary transformation of the Bloch functions, well describe spin states of non-bonding-degenerate polymers or assemblies. This situation was first pointed out in our preceding works for one-dimensional and two-dimensional polyradicals [33, 34]. Magnetic ordering of organic-radical assemblies has also been established by using Wannier functions with minimal exchange integral [35, 36]. The minimization of exchange interactions should be considered as a fundamental principle to determine the amplitude pattern of the flat bands. In our preceding works, however, proof of the minimization theorem was not given, because little experimental results on low-spin non-Kekulé polymers have been reported. Nowadays, however, from theoretical point of view, the author believes that the minimization procedure should be regarded as a fundamental principle to determine the magnetic properties of flat-band systems, because the proof is given by simple variational principle, as described below.

In this article, it is shown that there exists a unique amplitude pattern in any flat band, which minimizes the exchange integral of the system. The unique orbitals are not Bloch- but Wannier-type crystal orbitals, in which the amplitudes are localized near each unit cell. Moreover, the best wavefunctions should be symmetrical with respect to the lattice vector. For practical use, a simple method to obtain the localized orbitals is also presented taking account of the uniqueness of the amplitude pattern. Such a procedure for determining the amplitude pattern of flat bands should hold in not only non-bonding bands of non-Kekulé systems but also general degenerate bands. The most important application of this principle is probably design and analysis for magnetic properties of extended systems. The phase factor of Bloch (Wannier) functions serves as a variational parameter for the exchange integral, and the resultant Wannier functions with minimal exchange integral coincide with maximally localized Wannier functions.

2 Theoretical

2.1 Phase-factor dependence of exchange integral

We discuss the uniqueness of Wannier functions in non-bonding extended systems. In view of molecular orbital theory, the high-spin states are deduced by exchange integrals between the non-bonding crystal orbitals (NBCOs). Figure 2 shows typical one-dimensional non-Kekulé polymers **4**, **5**, and **6**. While **4** and **5** have been analyzed as non-disjoint systems, **6** has been recognized as a disjoint system [33]. They have infinite number of degenerate NBCOs due to the non-Kekulé character, and the resultant flat bands are half (partially) occupied. The NBCOs are obtained by usual secular equations as Bloch functions. As mentioned above, the Bloch functions should be transformed into Wannier functions. Wannier functions are highly localized around each unit cell. We request that the exchange integrals between each adjacent cell are minimized, similar to the case of biradicals. Construction of the Wannier functions is as follows.

A certain Bloch function φ_k with wavenumber k is given as:

$$\phi_k = \frac{1}{\sqrt{N}} \sum_{\mu}^{N} \sum_{r}^{n} \exp(ik\mu) C_r(k) \chi_{\mu,r}, \tag{1}$$

where N and n are numbers of unit cells and atomic sites inside the cell, respectively. $\chi_{\mu,r}$ is the r-th atomic site in μ-th cell, and $C_r(k)$ is the cell-periodic moiety of Bloch coefficients. The v-th Wannier function is expressed by:

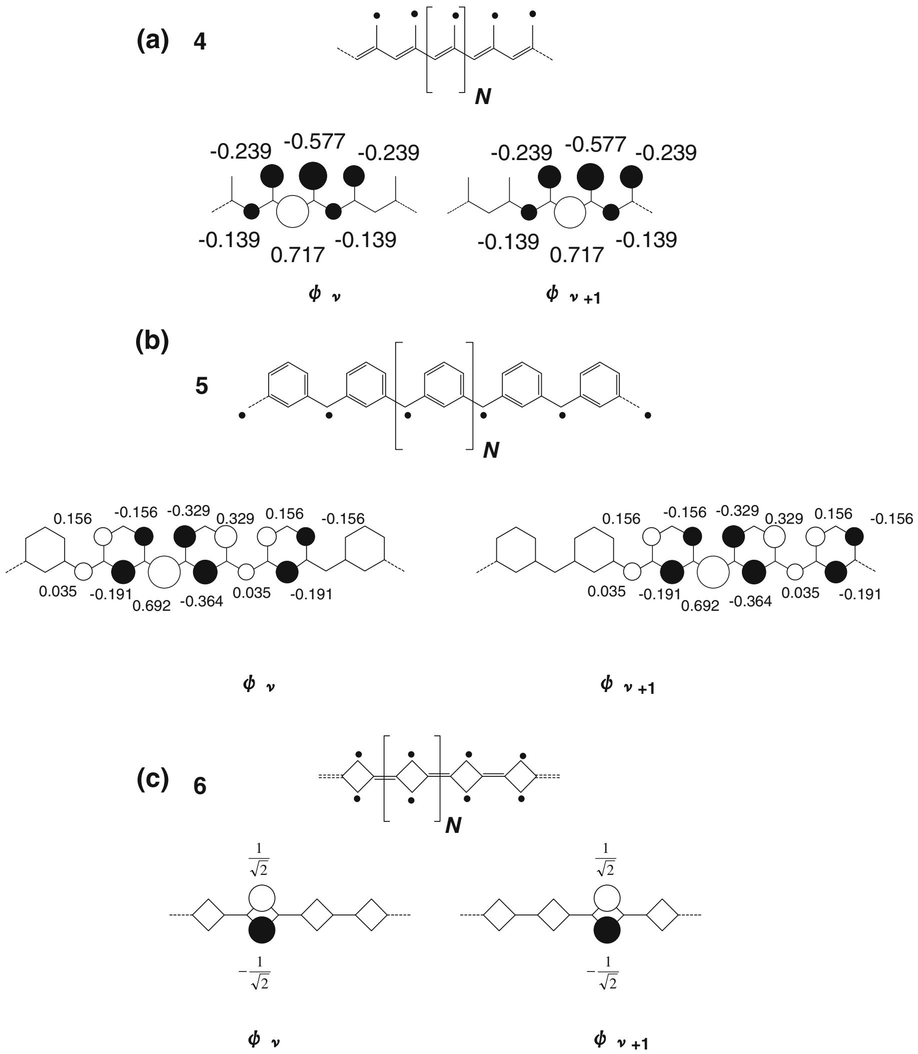


Fig. 2 Molecular structures of non-Kekulé polymers **4**, **5**, and **6**. Wannier functions of them are also schematically shown

$$\psi_v = \sum_{\mu}^{N} \sum_{r}^{n} a_r(\mu - v)\chi_{\mu,r}, \tag{2}$$

where

$$a_r(\mu - v) = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\{i(\mu - v)k\} C_r(k) dk, \tag{3}$$

$$\tau = \mu - v. \tag{4}$$

τ is difference between the μ-th and v-th cells. Bloch functions φ_k have degree of freedom expressed by phase factor $\exp(i \cdot \theta(k))$, and

$$\phi'_k = \exp\{i \cdot \theta(k)\}\phi_k \tag{5}$$

are also Bloch functions. Here, the phase factor $\exp(i \cdot \theta(k))$ is expanded by Fourier series:

$$\exp\{i \cdot \theta(k)\} = \sum_{m=-\infty}^{\infty} A_m \exp(-imk). \tag{6}$$

A_m are the Fourier coefficients. Then, the new Wannier function coefficients become:

$$\begin{aligned} a'_r(\tau) &= \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp\{i\tau k\} \sum_{m=-\infty}^{\infty} A_m \exp(-imk) C_r(k) dk \\ &= \sum_{m=-\infty}^{\infty} A_m a_r(\tau - m). \end{aligned} \tag{7}$$

The total exchange integral K is obtained by all summation of each exchange integral K_{ij} between the i-th and j-th cells ($i < j$). Taking account of only one-centered electron-repulsion integrals $(rr|rr)$ in common, K becomes:

$$\begin{aligned} K &= \sum_{i<j} K_{ij} \\ &\cong \sum_{i<j} \left[\begin{aligned} &\sum_{r}^{i\text{–thcell}} \left\{ a'_r 0)^2 a'_r(i-j)^2 \right\} \\ &+ \sum_{r}^{(i+1)\text{–thcell}} \left\{ a'_r(1)^2 a'_r(i-j+1)^2 \right\} \\ &+ \sum_{r}^{(i+2)\text{–thcell}} \left\{ a'_r(2)^2 a'_r(i-j+2)^2 \right\} + \cdots \\ &+ \sum_{r}^{(j-2)\text{–thcell}} \left\{ a'_r(j-i-2)^2 a'_r(-2)^2 \right\} \\ &+ \sum_{r}^{(j-1)\text{–thcell}} \left\{ a'_r(j-i-1)^2 a'_r(-1)^2 \right\} \\ &+ \sum_{r}^{j\text{–thcell}} \left\{ a'_r(j-i)^2 a'_r(0)^2 \right\} \end{aligned} \right] (rr|rr) \\ &\cong \sum_{i<j} \left[\sum_{r}^{i\text{–thcell}} \left\{ a'_r(0)^2 a'_r(i-j)^2 \right\} + \sum_{r}^{j\text{–thcell}} \left\{ a'_r(j-i)^2 a'_r(0)^2 \right\} \right] (rr|rr) \\ &\geq 2 \times \sum_{i<j} \left[\sum_{r}^{n} a'_r(0)^2 |a'_r(i-j)| |a'_r(j-i)| \right] (rr|rr). \end{aligned} \tag{8}$$

The equality holds only when

$$a'_r(i-j) = \pm a'_r(j-i). \tag{9}$$

This means that the Wannier coefficients are even or odd functions with respect to the cell index τ, that is, symmetric $(a_r(\tau) = a_r(-\tau))$ or antisymmetric $(a_r(\tau) = -a_r(-\tau))$ around each unit cell. Then, the exchange integral is minimized. If one requests that $a'_r(0)$ is not zero, which means localization of amplitudes around the central cell, only the even-function solutions are suitably adopted. This is reasonable in that the most localized Wannier function is given by the delta function localized at one unit cell, which is an even function of cell index τ, as discussed later.

In general, Wannier functions deduced from a given set of Bloch functions are asymmetry with respect to the cell index τ. In order to obtain symmetric Wannier functions, it is convenient to adopt the real part of $C_r(k)$ and transform them into Wannier functions. That is, the following Bloch coefficients

$$C'_r(k) = \frac{C_r(k) + C_r(k)^*}{2} = \frac{C_r(k) + C_r(-k)}{2} \tag{10}$$

give the symmetric Wannier functions. The resultant Wannier functions should be renormalized by proper scalars, because Wannier functions derived by Eq. (10) are not always normalized to unity. Within the simple Hückel approximation, we can adopt the following renormalization factor:

$$C' = \frac{1}{\sqrt{\sum_{\tau} \sum_{r} |a_r(\tau)|^2}}. \tag{11}$$

Apart from the renormalization factors, Eq. (10) is a general procedure to give the symmetric Wannier functions. Such a choice minimizes the exchange integral of the system. In general, Wannier functions decay very rapidly with respect to the distance, that is, τ. Therefore, for practical use, we can neglect the terms $a_r(\tau)$ with $|\tau| \geq 2$. Then, the exchange integrals K_{ij} are non-trivial only when $|i - j| = 1$. Though some Wannier functions were not renormalized in the previous works [33–35, 41], here we consider the renormalized Wannier functions.

The set of renormalized symmetric Wannier functions is unique. Even if another set of symmetric Wannier functions exists, the phase factor $\exp(i \cdot \theta(k))$ relative to the original should be unity, because the Wannier functions are real and symmetric. That is, once the symmetric Wannier functions are renormalized, the resultant exchange integrals are minimized, as derived by the inequality (8). Similar to biradicals, there are two important cases. One is non-disjoint Wannier function which spans common atoms, and another is disjoint Wannier function which spans no common atoms. The former leads to ferromagnetic, and the latter leads to antiferromagnetic ground states.

2.2 Ferromagnetic interactions between non-disjoint Wannier functions

Figure 2a shows the renormalized Wannier functions of **4**, which is symmetric with respect to the lattice vectors. The amplitudes $a_r(\tau)$ with $|\tau| \geq 2$ are neglected due to the triviality. Figure 2b also shows similar Wannier functions of **5**, which is also a famous ferromagnetic polymer. In **4** and **5**, it can be seen that each Wannier function at a certain cell spreads over the adjacent cells as well as the central cell. The common spanned atoms cause ionic terms in the two-electron wavefunctions consisting of product of adjacent Wannier functions ψ_v and ψ_{v+1}. Thus, the exchange interaction between the adjacent cells becomes significantly positive due to the Pauli principle. Indeed, the high-spin stabilities of **4** and **5** have been established by many calculations. For example, for **4**, ab initio studies on the oligomers [17] and UHF band calculations [20] revealed the ferromagnetism. For **5**, DFT (density-functional theory) band calculations strongly supported the ferromagnetic interactions [37].

2.3 Antiferromagnetic interactions between disjoint Wannier functions

When Bloch coefficients $C'_r(\mathrm{k})$ are independent of wavenumbers k, it can be seen from Eq. (3) that the corresponding Wannier functions become Kronecker delta functions with respect to the cell index τ:

$$a'_r(\mu - v) = \frac{1}{2\pi}\int_{-\pi}^{\pi} \exp\{i(\mu - v)k\}C'_r(k)dk = \delta_{\mu v} \times \text{const.} \quad (\mu - v = \tau) \tag{12}$$

This is a special case of the symmetric Wannier functions. In such a case, exchange integral of the system becomes zero due to the extreme localization, and thus, the system cannot be ferromagnetic. On the contrary, antiferromagnetic interactions due to through-space interactions between the separated amplitudes may be dominant. At least, high-spin and low-spin states should be nearly degenerate. **6** in Fig. 2c is the typical example, of which Wannier functions can be chosen to spread only at each unit cell. Indeed, cyclobutadiene oligomers with methylene terminal groups have been proved to be antiferromagnetic except for the terminal two spins [38].

2.4 Two-dimensional systems

Figure 3 shows Wannier functions of so-called Mataga polymer **7**. This polymer has 1,3,5-phenylene units and the resultant NBCOs forms a half-filled flat band. The Wannier functions are obtained by double integral

$$a_r(\mu_1 - v_1, \mu_2 - v_2) = \frac{1}{4\pi^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi} \exp\{i(\mu_1 - v_1)k_1 + i(\mu_2 - v_2)k_2\}C'_r(k_1, k_2)dk_1dk_2, \tag{13}$$

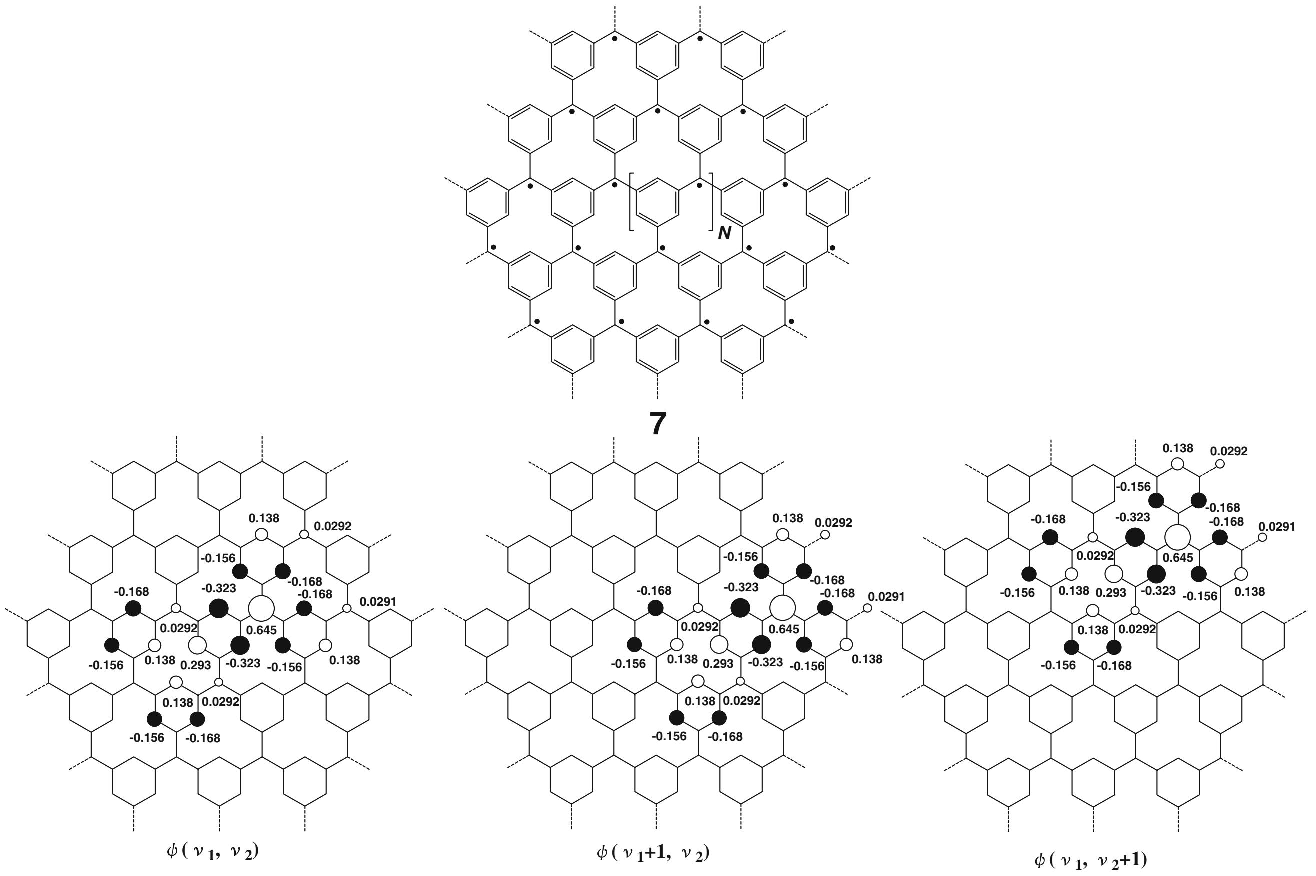
$$\tau_1 = \mu_1 - v_1, \quad \tau_2 = \mu_2 - v_2, \tag{14}$$

instead of single integral Eq. (3), where $C'_r(k_1, k_2)$ is Bloch coefficients with two wavenumbers and τ_1 and τ_2 are two indices of the Wannier coefficients. The Wannier functions spread at the adjacent cells as well as the central unit cell, and thus, the common spanned atoms lead to ferromagnetic interactions due to the ionic terms in the two-electron wavefunctions consisting of product of adjacent Wannier functions.

2.5 Organic-radical assemblies toward three dimensional systems

Figure 4 shows two allyl-radical assemblies **8** and **9**. These assemblies have been analyzed as extended non-Kekulé systems within the Hückel approximation [35]. We note that there are two independent non-bonding bands in **8**, because there are two radical centers in each unit cell. On the other hand, when only the topological linkage is considered, there exists only one independent non-bonding band in **9** [35]. While **8** is predicted to be ferromagnetic due to the common spanned atoms between each Wannier function, **9** is predicted to be antiferromagnetic due to the delta-function-type localization of the Wannier functions. Indeed, DFT calculations supported ferromagnetic ground state of **8** and antiferromagnetic ground state of **9**, and the total exchange integral is approximately proportional to number of unit cells [35]. **9** is an important example for violation of the spin-polarization rule, similar to **3**. That is, although one can describe a ferrimagnetic spin alignment by Heisenberg model, actual ground state is antiferromagnetic due to the extremely localized Wannier functions.

In principle, three-dimensional ferromagnets based on non-bonding degeneracy are possible, when non-Kekulé systems are stacked so that the starred and unstarred atoms are adjacent. For example, Fig. 5 shows three-dimensionally stacked Mataga polymers, in which two layers A and B are interacted so as to cause the non-bonding degeneracy. Orientation of A and B are different by the rotation angle $\pi/3$. The resultant three-dimensional crystal should have half-filled non-bonding bands, though the resonance integrals are different between intra- and interlayer bondings. Then, the Wannier functions should be localized only near the unit cell, as schematically shown by sphere in Fig. 5.



7

$\phi(\nu_1, \nu_2)$ $\phi(\nu_1+1, \nu_2)$ $\phi(\nu_1, \nu_2+1)$

Fig. 3 Molecular structure and Wannier functions of Mataga polymer (**7**)

By using the real part of the Bloch coefficients $C'_r(k_1, k_2, k_3)$, the Wannier functions should be represented by the triple integral with three lattice vectors μ_1, μ_2, and μ_3,

$$a_r(\mu_1 - \nu_1, \mu_2 - \nu_2, \mu_3 - \nu_3) = \frac{1}{8\pi^3} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \times \exp\{i(\mu_1 - \nu_1)k_1 + i(\mu_2 - \nu_2)k_2 + i(\mu_3 - \nu_3)k_3\} \times C'_r(k_1, k_2, k_3)dk_1dk_2dk_3, \tag{15}$$

$$\tau_1 = \mu_1 - \nu_1,\ \tau_2 = \mu_2 - \nu_2,\ \tau_3 = \mu_3 - \nu_3. \tag{16}$$

Each sphere represents the Wannier function localized near at the cell. Though the Wannier functions are too complex to calculate at present, each localized orbital should span common atoms after the Wannier transformation because of the starred-unstarred linkages. We note that expansion of non-bonding degeneracy to three-dimensional systems above is possible only when all the linkages are made between the starred and unstarred atoms. This is the same situation of π-stacked benzyl radicals [36]. Then, there appear ionic terms in the two-electron wavefunction consisting of the product between the adjacent Wannier functions. The Wannier functions should be spread as symmetric as possible with respect to the lattice vectors μ_1, μ_2, and μ_3.

3 Discussions

If adjacent Wannier functions span common atoms, ferromagnetic ground states are expected, because exchange interactions arise from ionic terms in two electron wavefunctions consisting of product of the adjacent Wannier functions. This is expansion of non-disjoint orbitals. In biradicals, unitary transformation minimizes the exchange integrals, and resulting NBMOs are not canonical. The degree of freedom due to the degeneracy is rotational parameter. Similarly, in extended systems such as non-Kekulé polymers, the phase factor $\exp(i \cdot \theta(k))$ in Eq. (5) or its Fourier series serve as degree of freedom. The corresponding Wannier transformations become symmetric with respect to the lattice vectors when the exchange integrals are minimized.

Here, we consider the highest-spin and lowest-spin states with open-shell configurations. Strictly speaking, closed-shell low-spin states should be also considered, but

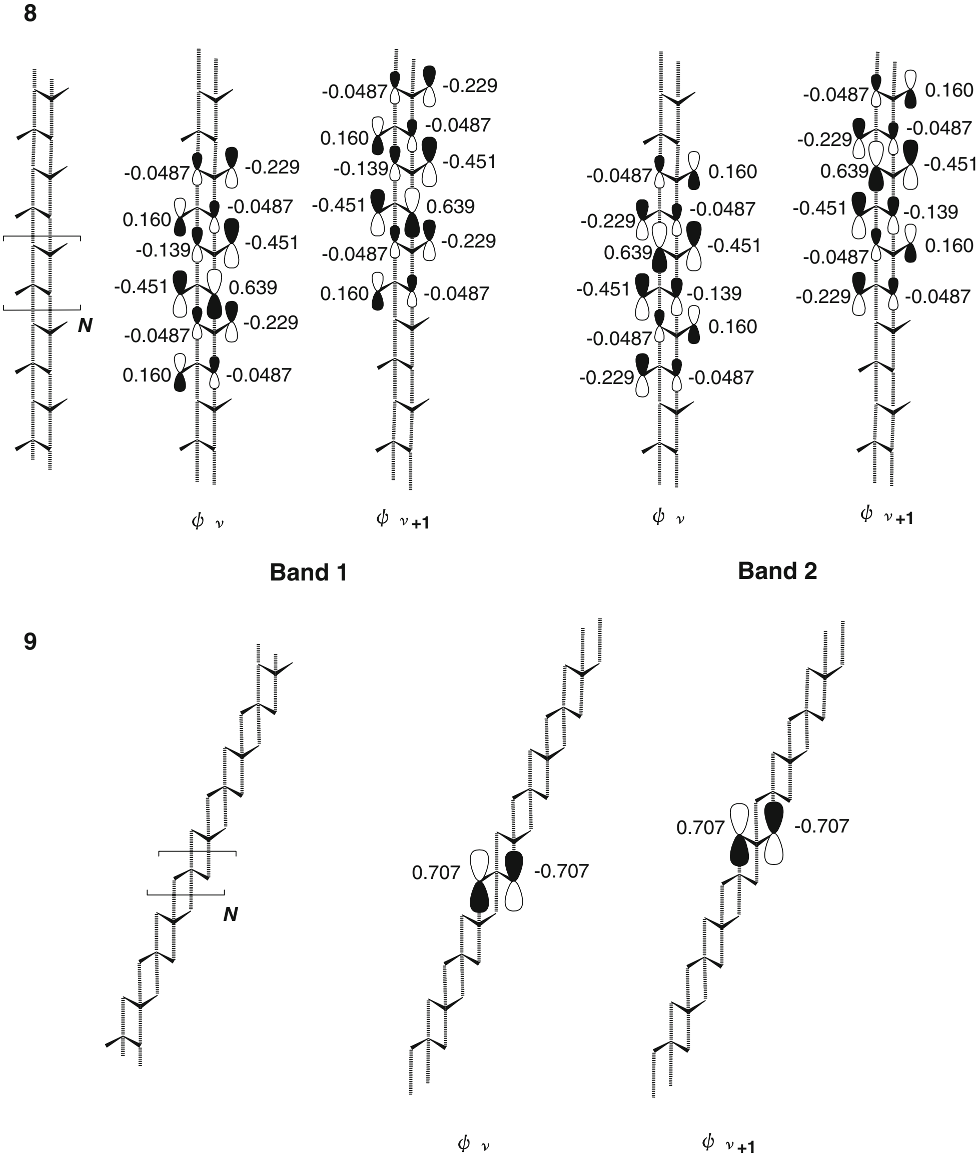


Fig. 4 Molecular structures of allyl-radical assemblies **8** and **9**. Wannier functions of them are also schematically shown

the energies should be close to that of the open-shell case due to the degeneracy. The energy for the highest-spin state (ferromagnetic state) is expressed as follows:

$$E_H = \sum_{n}^{N} h_n + \sum_{i<j}^{N} (J_{ij} - K_{ij}), \tag{17}$$

where h_n is the expectation value of one-electron operator for the degenerate orbitals, and J_{ij}, K_{ij} are the Coulomb and exchange integral, respectively. All the h_n are invariant with respect to any Wannier transformation, because the orbitals are degenerate. Both $\Sigma_{i<j}J_{ij}$ and $\Sigma_{i<j}K_{ij}$ are not invariant, but the difference $\Sigma_{i<j}(J_{ij} - K_{ij}) = (1/2)\Sigma_{i,j}(J_{ij} - K_{ij})$ is invariant, because the self-repulsion terms J_{ii} and K_{ii} are cancelled each other. Thus, the energy for the highest-spin state is invariant with respect to the Wannier transformation. However, energy for the lowest-spin state (antiferromagnetic state) is not invariant, and energy gap between the highest-spin and lowest-spin states should be proportional to minimum of the exchange integrals. In non-disjoint systems, the ground states should be ferromagnetic due to the positive exchange integrals. Schematic diagram for this situation is shown in Fig. 6. The energy for ferromagnetic state is invariant with respect to the phase factor $\exp(i \cdot \theta(k))$, but the energy for the antiferromagnetic state has a minimum. That is, the phase factor $\exp(i \cdot \theta(k))$, (or the Fourier coefficients A_m) serves as a variational parameter and the lowest-spin state energy is optimized when the Wannier functions become symmetric. It is noteworthy that the choice of the Wannier functions is

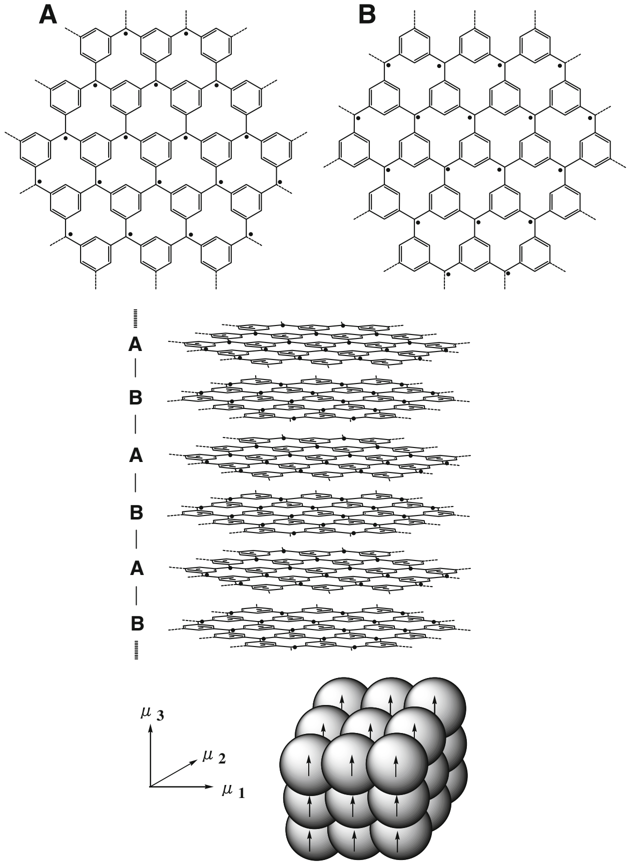


Fig. 5 Stacked Mataga polymer as a three-dimensional organic ferromagnet. μ_1, μ_2, and μ_3 denote coordinates for the lattice vectors. The sphere-like Wannier functions span common atoms between the adjacent cells

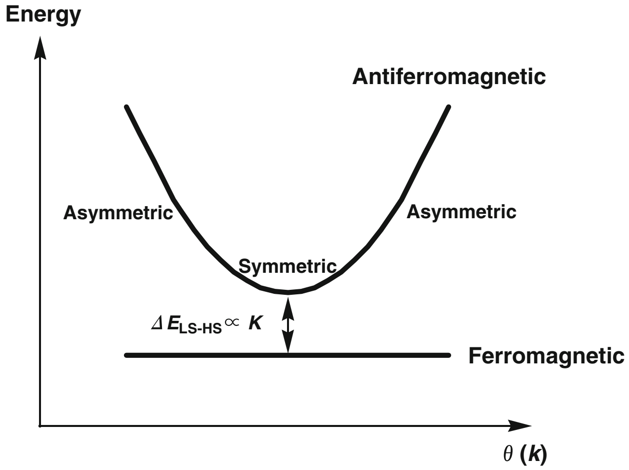


Fig. 6 Energetics for variational principle in flat-band ferromagnetism

unique in spite of the degeneracy. This means that degree of freedom due to the degeneracy coincides with phase factor of the best Wannier functions, which minimizes the energy of antiferromagnetic states.

The minimization of the exchange integrals is based on variational principle, as described above. In view of degree of localization, this implies that NBMOs or NBCOs should be maximally localized so that the wave packets of the orbitals are spatially separated as much as possible. In the field of physics, existence of maximally localized Wannier functions itself has been shown for one or composite bands [39, 40]. However, their treatment is based on closed-shell configurations of non-degenerate systems, and thus, unitary-transformation invariance of ground-state energies is almost evident. In general, energy of each Wannier function is different from that of the Bloch functions. For example, in valence band of polyacetylene, the energy of each Wannier function lies in the middle of the band. Therefore, to estimate chemical properties relating to the frontier bands such density of states, reactivities and so on, one had better use the Bloch functions at special wavenumbers k in the high-energy region. In degenerate or nearly degenerate bands, however, energy of each Wannier function is identical to that of the Bloch functions at all the k points. Therefore, each Wannier function itself is suitable for description of magnetic orbitals, surface states, edge states, and so on. For example, Wannier analysis on edge states of methylene-substituted graphenes has been performed to show the magnetic ground states [41].

While the Heisenberg model describes completely localized spin moment at each atomic site, Wannier functions describe itinerant characters of magnetic electrons, because the amplitudes spread over the adjacent cells. Indeed, one-dimensional and two-dimensional non-Kekulé polymers with half-filled bands have been already synthesized by many chemists, and their ground states have been established as ferromagnetic. While in one-dimensional systems some defects destroy the exchange interactions, in two-dimensional or three-dimensional systems, there exist many paths for realizing exchange interactions. For example, porous graphenes are promising precursor of two-dimensional ferromagnets [42], and heterocyclic thia/selenazyl radicals are three-dimensional organic ferromagnets, of which magnetisms are realized through the π-slipped stacking arrays [43]. For the given phase factor $\exp(i \cdot \theta(k))$, amplitude pattern of Wannier functions is independent of the cell number, and thus, the total exchange integral K is proportional to the number of unit cell N. Thus, as a rough estimation, energy difference $\Delta E_{LS\text{-}HS}$ between the lowest-spin and highest-spin states is proportional to K and N. In one-dimensional systems, $\Delta E_{LS\text{-}HS}$ becomes:

$$\Delta E_{LS-HS} = 4NK_{ij}s_is_j, \tag{18}$$

where s_i and s_j are spins within the i-th and j-th unit cell (not atomic orbital). In the present cases, $s_i = s_j = 1/2$. This is identical to that of Ising model under the periodic boundary condition. In the case of chain oligimers, N should be substituted by ($N-1$). The linearity can be confirmed by ab initio calculations for the high-spin oligomers. Here, we show an example for DFT calculation by using the simplest model **4**. Figure 7 shows the high-spin stability $\Delta E_{LS\text{-}HS}$ for chain oligomers of **4** up to 24mer, which was calculated by using the Vosko-Wilk-Nusair (VWN) functional [44] under the 6-31G* basis set. The C–C and C–H bond lengths were fixed at 1.40 and 1.09 Å, respectively, and all the bond angles were fixed to be 120°. The reference was constructed by the restricted method, and thus, all the spin symmetries were satisfied. The calculations were done by GAMESS program [45]. It can be seen from Fig. 7 that the system shows robust ferromagnetism and the linearity holds very well. This supports invariance of exchange integral between adjacent Wannier functions, as discussed above.

In two-dimensional and three-dimensional systems, the linearity is also expected with respect to the number of nearest-neighbor cells, rather than N, in the Ising sense. However, in view of multi-configuration molecular orbital theory, spin-symmetry-satisfied low-spin states are not described only by one configuration. In such a situation, analytical expressions of energy of the lowest-spin states are too complex, and the mathematical proof toward the N dependence is not clear at present. Instead, Yamaguchi et al. suggested a useful method for estimation of $\Delta E_{LS\text{-}HS}$ by using the spin-squared expectation values of the highest-spin and lowest-spin states [23, 24]. In general, N dependence on $\Delta E_{LS\text{-}HS}$ is not always linear. The analytical expression depends on the spin-squared expectation values and the spin-correlation term, and the spin states are often contaminated by broken-symmetry calculations such as UHF method. In non-periodic systems, the effective exchange integral as an average also depends on the size of systems, shape of edges, and topology of the linkage. Anyway, recent experimental and theoretical developments shows that magnetic ordering in organic degenerate systems is determined only by exchange integral in NBMOs or NBCOs, rather than the spin-polarization rule. The author believes that whether adjacent localized orbitals span common atoms or not determines the ground spin state of the system. From a given flat band, we can construct a unique set of Wannier functions which minimizes the exchange interaction of the system, and the best Wannier functions should be symmetric with respect to the lattice vectors. The description of magnetic ordering is consistent with recent experiments and theoretical calculations.

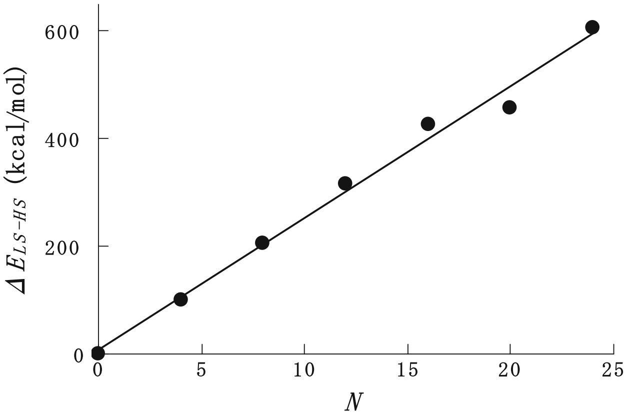


Fig. 7 High-spin stability $\Delta E_{LS\text{-}HS}$ for chain oligomers of **4** calculated by restricted VWN/6-31G* level of theory. The total energy for the high-spin state of 4mer is –387.287048 a.u

4 Conclusions

Origin of organic ferromagnetism was deduced from crystal orbital method. For a given flat-band, the degree of freedom within the degeneracy serves as a variational parameter, and a unique set of Wannier functions minimizes the exchange integrals. The best Wannier functions should be symmetric with respect to the lattice vectors. Stability of the ferromagnetic state is determined by whether or not the Wannnier functions span common atoms.

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