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REGULAR ARTICLE

Guidelines proposed for designing organic ferromagnets by using a quantum chemical approach

Shohei Onitsuka · Yuriko Aoki

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Abstract For predicting the characteristics of organic ferromagnetic substances, we have previously proposed a simple rule for conjugated organic molecules based on molecular orbital coefficients by the simple Hückel's nonbonding molecular orbital (NBMO) method. In this work, we extended the rule to systems including heteroatoms to become more widely applicable to various magnetic polymers. It was proven that the linkage between molecules having an NBMO conserves the original NBMO levels even for the supermolecule after the linkage. In addition, we have also proposed an index to estimate the amount of possessing ferromagnetic property. The reliability of the rule and index is examined by applying both the density functional theory (DFT) with functional methods, i.e., B3LYP, B3PW91, BLYP, PBEPBE, and PBEP86, and the complete active space SCF (CASSCF) calculations to several model molecules.

Keywords Organic ferromagnets · High spin · NBMO · Hückel method · MO method

1 Introduction

Recently, a large number of studies have been undertaken to design and elucidate organic ferromagnetic molecules both experimentally [1–6] and theoretically [7–19]. The methods for designing those molecules are roughly classified into two types: one is the syntheses of crystalline solids involving small radical molecules [20, 21] and the other is that of organic π-conjugated systems [22–26]. The transition temperature of crystalline solids composed of small radical molecules seems to be low because through-space interactions between radical molecules produce very weak exchange interactions. Therefore, ferromagnetic substances of that type are impractical.

In contrast, π-conjugated systems are theoretically predicted to have high transition temperatures due to the strong exchange interactions between radicals through bonds [27]. Therefore, those systems have received increasing interest as new organic magnets. Rajca et al. actually succeeded in synthesizing ultrahigh-spin π-conjugated systems in which the spin quantum number (S) is observed to be more than 5,000 [24].

Several principles were proposed for designing organic π-conjugated ferromagnetic systems, for example, the Longuet-Higgins (LH) algorithm [28] and the simple valence bond (SVB) approach [29]. Borden et al. predicted the spin state in the ground state by classification of the NBMOs of a non-Kekule hydrocarbon as being disjoint or non-disjoint and also discussed ferromagnetic coupling through exchange interactions in conjugated hydrocarbons and their derivatives using VB and MO theories [30–32]. Those principles are powerful tools in designing high-spin molecules and widely applied in pursuit of discovering new organic ferromagnetic materials. However, they cannot predict which molecules can provide more stable high-spin

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Dedicated to Professor Akira Imamura on the occasion of his 77th birthday and published as part of the Imamura Festschrift Issue.

S. Onitsuka
Department of Molecular and Material Sciences,
Interdisciplinary Graduate School of Engineering Sciences,
Kyushu University, 6-1 Kasuga-Park, Kasuga,
Fukuoka 816-8580, Japan

Y. Aoki (✉)
Department of Material Sciences, Faculty of Engineering
Sciences, Kyushu University, 6-1 Kasuga-Park,
Kasuga, Fukuoka 816-8580, Japan
e-mail: aoki@mm.kyushu-u.ac.jp

states compared with others without the performance of ab initio calculations or experiments. We intend to establish more convenient and systematic principles for designing high-spin molecules from the perspective of molecular orbital (MO) theory.

Previously, we proposed a simple rule for designing π-conjugated ferromagnetic molecules for alternant hydrocarbons and an index to predict the high-spin stabilities of those systems [33–35]. We call that simple rule the "0–* rule." The rule means that the linkage between an inactive carbon atom with zero coefficients (0) of the nonbonding molecular orbitals (NBMOs) in a molecule and an active carbon atom with a non-zero coefficient (*) of the NBMO in another molecule never changes the original two NBMO levels. This 0–* type combination results in a non-disjoint type of linkage in the system, thus providing a mixing between NBMOs that leads to a stable high-spin state through exchange interaction.

The index to predict the high-spin stabilities of π-conjugated systems is named the L_{ij} value, $L_{ij} = \sum_r (C_{ir}C_{jr})^2$, where C_{ir} is the coefficient of atomic orbitals (AOs) in the i-th NBMO in the linear combination of AO (LCAO) approximation. This index enables estimating the mixing between the two NBMOs. Unitary transformations can be possible between degenerate NBMOs while keeping their eigenvalues, and thus, we defined the L_{ij} value that provides the smallest value after those transformations as $L_{ij}^{\min}$. In the following discussion, we simply express $L_{ij}^{\min}$ as L_{ij} values.

The L_{ij} value is proportional to the value of K_{ij}. K_{ij} is the exchange integral between the i-th and the j-th NBMO, that is, $K_{ij} = \sum_r \sum_s \sum_t \sum_u C_{ir}C_{js}C_{it}C_{ju}(rs|tu)$ where r, s, t, and u indicate atomic orbitals and C_{ir} is the coefficient of atomic orbitals in the i-th NBMO in the LCAO approximation. The total energy difference between open singlet and triplet states is approximately expressed as $\Delta E = E(S) - E(T) = 2K_{ij}$ where $E(S)$ and $E(T)$ denote the total energies in singlet and triplet states, respectively. Therefore, the high-spin stability of the system can be efficiently predicted by evaluating the L_{ij} values. This treatment means that $L_{ij} = \sum_r (C_{ir}C_{jr})^2$ includes only $(rr|rr)$ terms in the exchange integrals, but the direct calculations of K_{ij} for large systems are troublesome especially for polymers. Since the purpose of our treatment is to provide a simple guideline with which experimentalists can do molecular design of high-spin molecules without performing calculations, we would like to provide a simple rule even by qualitative treatment. The reliability of simple K_{ij} including only $(rr|rr)$ contribution was examined as the ratio to the total Exchange integrals K_{ij} including all integrals, and it was found that the ratios are always in the range between 15 and 19% for several models at Hartree–Fock level. Semiempirical calculations that do not include overlap matrix would be suitable as another choice to prove the relationship between L_{ij} and K_{ij}. However, energy difference between singlet and triplet strongly depends on the electron correlation effects that cannot be described properly within semiempirical level. Therefore, we performed ab initio method including a part of electron correlation effects as well as DFT method to get energy differences between low-spin and high-spin states.

Although the 0–* rule is useful for designing organic ferromagnetic systems, it cannot be applied to systems including heteroatoms as is. In this work, the 0–* rule for hydrocarbons was extended to systems including heteroatoms with mathematical proof, and efficient calculations to find globally minimized L_{ij} values were implemented. Density functional theory (DFT) and complete active space self-consistent field (CASSCF) calculations were performed for several model molecules in order to verify the reliability of 0–* rule and the L_{ij} value. However, the $2K_{ij}$ energy separation between singlet and triplet states is defined at Hartree–Fock level of theory, and similar values are difficult to derive at post Hartree–Fock or DFT levels because of complicated or parameterized expression of exchange correlation energy terms. Moreover, the electron correlation effect is generally greater in singlet states than in triplet states, leading mostly to the stabilization in singlet state when we include electron correlation effects. Nevertheless, we performed CASSCF (and MP2 in previous paper [33]) and DFT calculations, because at least we can say that the greater is the L_{ij}, the higher possibility the system has in the triplet state than in the singlet state even including correlation effect. We need find a system that will exhibit large singlet and triplet separation as much as possible at Hartree–Fock levels, corresponding to the energy difference between two minimum energy points shown in FIGURE 5 of Ref. [33].

2 Theory

Our treatment is derived in the framework of the simple Hückel method. First, we showed which kind of molecule has an NBMO by a perspective different from the previous method [36–39]. Next, we proved that a specific combination of two molecules having NBMOs retains each NBMO level unchanged and results in completely maintaining the two degenerate NBMOs.

2.1 Molecules with heteroatoms having one NBMO ∼type A∼

Considering an odd alternant hydrocarbon, it is possible to divide carbon atoms into two sets in such a way that no two atoms of the same set are joined by a bond in the same way, as discussed in Ref. [40]. If we number all the atoms of one set from 1 to h (active carbon atoms are denoted by *) and all the atoms of the other set from $h+1$ to n (inactive carbon atoms are denoted by 0), then the secular equations are expressed by the following forms

$$\begin{cases} -\varepsilon C_r + \sum\limits_{s=h+1}^{n} \beta_{rs} C_s = 0 \quad (r = 1, 2, \ldots, h) \\ -\varepsilon C_r + \sum\limits_{s=1}^{h} \beta_{rs} C_s = 0 \quad (r = h+1, h+2, \ldots, n). \end{cases} \tag{1}$$

If one replaces all the active carbon atoms (*) by the same heteroatoms with a Coulomb integral $\alpha_x = \alpha + x\beta$ in the way of Tyutyulkov et al. [36], the secular equations become the following forms

$$\begin{cases} (-\varepsilon + x) C_r + \sum\limits_{s=h+1}^{n} \beta_{rs} C_s = 0 \quad (r = 1, 2, \ldots, h) \\ -\varepsilon C_r + \sum\limits_{s=1}^{h} \beta_{rs} C_s = 0 \quad (r = h+1, h+2, \ldots, n). \end{cases} \tag{2}$$

The secular determinant is therefore given by

$$\Delta(\varepsilon) = \begin{array}{c|c:c|} & *\text{-part} & 0\text{-part} \\ *\text{-part} & (-\varepsilon + x)I & \beta \\ \hdashline 0\text{-part} & \beta^T & -\varepsilon I \end{array} \tag{3}$$

where I is the unit matrix, and β has the form,

$$\beta = \begin{pmatrix} \beta_{1,h+1} & \beta_{1,h+2} & \cdots & \\ \beta_{2,h+1} & \beta_{2,h+2} & & \\ \vdots & & \ddots & \\ & & & \beta_{h,n} \end{pmatrix},$$

and β^{T} means the transposed matrix of β. Multiplying the first h columns (the columns of the *–part) of Eq. 3 by $1/(-\varepsilon + x)$ and multiplying the last $n - h$ rows (the rows of the 0–part) by $(-\varepsilon + x)$, one obtains the following identity,

$$\Delta(\varepsilon) = (-\varepsilon + x)^{2h-n} \left| \begin{array}{c:c} I & \beta \\ \hdashline \beta^T & \varepsilon(\varepsilon - x)I \end{array} \right| \tag{4}$$

In general, $\Delta(\varepsilon) = 0$ has $2h - n$ solutions corresponding to the NBMO with $\varepsilon = x$. For simplicity, if we take $2h - n = 1$, the molecules of this type have one NBMO with $\varepsilon = x$. The condition $2h - n = 1$ means that the molecule is an odd alternant molecule. Therefore, this condition is satisfied. We call this type of substitution (i.e., all of the active carbon atoms are changed to the same heteroatoms) type A.

2.2 Molecules with heteroatoms having one NBMO ∼type B∼

An alternate method of designing molecules that have an NBMO is to replace arbitrary inactive carbon atoms (0) by arbitrary heteroatoms. Arbitrary inactive carbon atoms (0) can be changed to arbitrary heteroatoms with a Coulomb integral $\alpha_x = \alpha + x_i\beta$ (x_i is an arbitrary parameter). The secular equations are given by

$$\begin{cases} -\varepsilon C_r + \sum\limits_{s=h_A+1}^{n_A} \beta_{rs} C_s = 0 \quad (r = 1, 2, \ldots, h_A) \\ -\varepsilon C_r + \sum\limits_{s=1}^{h_A} \beta_{rs} C_s = 0 \quad (\text{inactive carbon atoms}) \\ (-\varepsilon + x_i) C_r + \sum\limits_{s=1}^{h_A} \beta_{rs} C_s = 0 \quad (\text{hetero atoms}). \end{cases} \tag{5}$$

The secular determinant is therefore expressed as

$$\Delta(\varepsilon) = \begin{array}{c|c:ccccc|} & *\text{-part} & & & 0\text{-part} & & \\ *\text{-part} & -\varepsilon I & & & \beta & & \\ \hdashline 0\text{-part} & & -\varepsilon & & & & \\ & & & \ddots & & & \\ & \beta^T & & & -\varepsilon + x_i & & \\ & & & & & \ddots & \\ & & & & & & -\varepsilon \end{array}. \tag{6}$$

The following identity is obtained by multiplying the first h columns (the columns of the *–part) of Eq. 6 by $1/(-\varepsilon)$ and by multiplying the last $n - h$ rows (the rows of the 0–part) by $(-\varepsilon)$

$$\Delta(\varepsilon) = (-\varepsilon)^{2h-n} \left| \begin{array}{c:ccccc} I & & & \beta & & \\ \hdashline & \varepsilon^2 & & & & \\ & & \ddots & & & \\ \beta^T & & & \varepsilon(\varepsilon - x_i) & & \\ & & & & \ddots & \\ & & & & & \varepsilon^2 \end{array} \right| \tag{7}$$

where I is the unit matrix and β is the same as above. In general, $\Delta(\varepsilon) = 0$ has $2h - n$ solutions corresponding to the NBMO with $\varepsilon = 0$. For simplicity, if $2h - n = 1$ is selected, the molecules of this type have one NBMO with $\varepsilon = 0$. The substitution of this type (i.e., the substitution of arbitrary inactive carbon atoms (0) for arbitrary heteroatoms) is called type *B*.

The next step is to prove that a certain type of combination of molecules having NBMOs keeps each NBMO level unchanged and results in completely maintaining the two degenerate NBMOs.

2.3 General rule for obtaining degenerate NBMOs

Thus far, in the previous section, the condition that molecules including heteroatoms have one NBMO has been proposed as either type *A* or type *B* on the basis of the NBMO rule for pure hydrocarbons. Next, let us suppose that a bonding occurs between those two molecules. It will be proven in this section that when molecule *A* possessing an NBMO and molecule *B* also possessing an NBMO combine with each other in a certain manner, two NBMOs are maintained in the same energy level as that before combination. As well as the conditions in Sect. 2.2, $2h_A - n_A = 1$ and $2h_B - n_B = 1$ are imposed on molecules *A* and *B*. The whole system consists of *n* carbon atoms, that is, $n_A + n_B = n$.

In previous papers [33, 41], we derived mathematical proof for NBMO conservation by linkage between two NBMOs that belong to different atoms only for pure hydrocarbon systems by using MO-based secular equations. In this work, we derive a general rule for all hydrocarbons, type *A* and type *B* systems, by using atomic-orbital-based secular equations.

2.3.1 Hydrocarbon systems

Using the same method as Eq. 1, the secular equations for molecules *A* and *B* are written by

$$\begin{cases} -\varepsilon C_r + \displaystyle\sum_{s=h_A+1}^{n_A} \beta_{rs} C_s = 0 \quad (r = 1, 2, \ldots, h_A) \\ -\varepsilon C_r + \displaystyle\sum_{s=1}^{h_A} \beta_{rs} C_s = 0 \quad (r = h_A + 1, h_A + 2, \ldots, n_A) \end{cases} \tag{8}$$

and

$$\begin{cases} -\varepsilon C_r + \displaystyle\sum_{s=n_A+h_B+1}^{n} \beta_{rs} C_s = 0 \quad (r = n_A + 1, \ldots, n_A + h_B) \\ -\varepsilon C_r + \displaystyle\sum_{s=n_A+1}^{n_A+h_B} \beta_{rs} C_s = 0 \quad (r = n_A + h_B + 1, \ldots, n) \end{cases}, \tag{9}$$

respectively. If there is no linkage between molecule *A* and molecule *B*, then the secular determinant of the system is written as

$$\Delta(\varepsilon) = \begin{array}{r|c:c|c:c|} & \text{* -part of A} & \text{0 - part of A} & \text{* -part of B} & \text{0 - part of B} \\ \text{* -part of A} & -\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline \text{0 - part of A} & \beta_1^T & -\varepsilon I & 0 & 0 \\ \hline \text{* -part of B} & 0 & 0 & -\varepsilon I & \beta_2 \\ \hdashline \text{0 - part of B} & 0 & 0 & \beta_2^T & -\varepsilon I \end{array} \tag{10}$$

where

$$\beta_1 = \begin{pmatrix} \beta_{1,h_A+1} & \beta_{1,h_A+2} & \cdots & \\ \beta_{2,h_A+1} & \beta_{2,h_A+2} & & \\ \vdots & & \ddots & \\ & & & \beta_{h_A,n_A} \end{pmatrix}$$

and

$$\beta_2 = \begin{pmatrix} b_{n_A+1,n_A+h_B+1} & b_{n_A+1,n_A+h_B+2} & \cdots & \\ b_{n_A+2,n_A+h_B+1} & b_{n_A+2,n_A+h_B+2} & & \\ \vdots & & \ddots & \\ & & & b_{n,n} \end{pmatrix}.$$

Block matrices β_1 and β_2 show information about the intramolecular bonding of each molecule.

If there is a linkage between the inactive atom (0) of molecule *A* (the 0–part of *A*) and the inactive atom (0) of molecule *B* (the 0–part of *B*), the secular determinant has the following form

$$\Delta(\varepsilon) = \begin{array}{|c:c|c:c|} -\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & -\varepsilon I & 0 & P \\ \hline 0 & 0 & -\varepsilon I & \beta_2 \\ \hdashline 0 & P^T & \beta_2^T & -\varepsilon I \end{array} \tag{11}$$

where *P* has only one non-zero element. This is because only one bonding is assumed between molecules *A* and *B*.

One multiplies the first h columns (the columns of the *–part of A) and the columns from $n_A + 1$ to $n_A + h_B$ (the columns of the *–part of B) of Eq. 11 by $1/(-\varepsilon)$. Additionally, the rows from $h_A + 1$ to n_A (the rows of the 0–part of A) and the last $n_B - h_B$ rows (the rows of the 0–part of B) are multiplied by $(-\varepsilon)$. As a result, Eq. 11 becomes

$$\Delta(\varepsilon) = (-\varepsilon)^{2h_A - n_A + 2h_B - n_B} \left| \begin{array}{c:c|c:c} I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & \varepsilon^2 I & 0 & -\varepsilon P \\ \hline 0 & 0 & I & \beta_2 \\ \hdashline 0 & -\varepsilon P^T & \beta_2^T & \varepsilon^2 I \end{array} \right|$$
$$= \varepsilon^2 |H_{0-0}| \qquad (12)$$

where

$$|H_{0-0}| = \left| \begin{array}{c:c|c:c} I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & \varepsilon^2 I & 0 & -\varepsilon P \\ \hline 0 & 0 & I & \beta_2 \\ \hdashline 0 & -\varepsilon P^T & \beta_2^T & \varepsilon^2 I \end{array} \right|$$

Therefore, $\Delta(\varepsilon) = 0$ has two solutions for $\varepsilon = 0$. We can call this type of linkage as “Disjoint type” molecules, because no interaction occurs between the original two NBMOs.

Next, another type of linkage is examined. That is, bonding between the inactive atom (0) of molecule A (the 0–part of A) and the active atom (*) of molecule B (the *–part of B). It is also possible to prove the case that a linkage between the active atom (*) of molecule A and the inactive atom (0) of molecule B exists, as given by the following secular determinant

$$\Delta(\varepsilon) = \left| \begin{array}{c:c|c:c} -\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & -\varepsilon I & P & 0 \\ \hline 0 & P^T & -\varepsilon I & \beta_2 \\ \hdashline 0 & 0 & \beta_2^T & -\varepsilon I \end{array} \right|. \qquad (13)$$

The same multiplication as before is performed on Eq. 13. Then, the following equation is obtained by

$$\Delta(\varepsilon) = \varepsilon^2 |H_{0-*}|, \qquad (14)$$

where

$$|H_{0-*}| = \left| \begin{array}{c:c|c:c} I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & \varepsilon^2 I & P & 0 \\ \hline 0 & P^T & I & \beta_2 \\ \hdashline 0 & 0 & \beta_2^T & \varepsilon^2 I \end{array} \right|$$

Therefore, the equation $\Delta(\varepsilon) = 0$ provides two solutions of $\varepsilon = 0$. We can call this type of linkage “Non-disjoint type” molecules, because interaction occurs between the original two NBMOs even though the original NBMOs are reserved.

As well as references [33] and [41], it has been proven that two NBMOs are maintained in both the 0–0 bonding and the 0–* bonding. We consider that it is similarly possible to prove the case in which the system has more NBMOs.

2.3.2 *Type A system*

Next, the system including heteroatoms is examined. First, a type *A* system is examined as to whether degenerate NBMOs can be obtained. All of the active atoms (*) in molecule *A* and molecule *B* have been changed to the same heteroatoms. Then, the secular determinant is written for the case where there is no bonding between molecule *A* and molecule *B* as

$$\Delta(\varepsilon)=\begin{array}{r|cc|cc|}
 & \text{*-part of A} & \text{0 - part of A} & \text{*-part of B} & \text{0 - part of B}\\
\text{*-part of A} & (-\varepsilon+x)I & \beta_1 & 0 & 0\\
\text{0 - part of A} & \beta_1^T & -\varepsilon I & 0 & 0\\
\hline
\text{*-part of B} & 0 & 0 & (-\varepsilon+x)I & \beta_2\\
\text{0 - part of B} & 0 & 0 & \beta_2^T & -\varepsilon I
\end{array} \tag{15}$$

where β_1 and β_2 have the same definition as in Eq. 10.

When a bonding between the inactive atom (0) of molecule *A* (the 0–part of *A*) and the inactive atom (0) of molecule *B* (the 0–part of *B*) occurs, the secular determinant has the following form

$$\Delta(\varepsilon)=\left|\begin{array}{cc|cc}
(-\varepsilon+x)I & \beta_1 & 0 & 0\\
\beta_1^T & -\varepsilon I & 0 & P\\
\hline
0 & 0 & (-\varepsilon+x)I & \beta_2\\
0 & P^T & \beta_2^T & -\varepsilon I
\end{array}\right| \tag{16}$$

where *P* has the same definition as that in Eq. 11. By multiplying the first *h* columns (the columns of the *–part of *A*) and the columns from n_A+1 to n_A+h_B (the columns of the *–part of *B*) of Eq. 16 by $1/(-\varepsilon+x)$ and multiplying the rows from h_A+1 to n_A (the rows of the 0–part of *A*) and the last n_B-h_B rows (the rows of the 0–part of *B*) by $(-\varepsilon+x)$, one can obtain the following identity

$$\Delta(\varepsilon)=(-\varepsilon+x)^2|A_{0-0}|, \tag{17}$$

where

$$|A_{0-0}|=\left|\begin{array}{cc|cc}
I & \beta_1 & 0 & 0\\
\beta_1^T & \varepsilon(\varepsilon-x)I & 0 & (-\varepsilon+x)P\\
\hline
0 & 0 & I & \beta_2\\
0 & (-\varepsilon+x)P^T & \beta_2^T & \varepsilon(\varepsilon-x)I
\end{array}\right|$$

Therefore, $\Delta(\varepsilon)=0$ has two solutions with $\varepsilon=x$. As well as with the hydrocarbon systems, the linkage in this type is supposed to form disjoint molecules that will be verified in Sect. 3 by using the L_{ij} values.

Next, it is shown that two NBMOs are preserved under the situation that a linkage between the inactive atom (0) of molecule *A* (the 0–part of *A*) and active atom (*) of molecule *B* (the *–part of *B*) exists. The secular determinant in that case is written by

$$\Delta(\varepsilon)=\left|\begin{array}{cc|cc}
(-\varepsilon+x)I & \beta_1 & 0 & 0\\
\beta_1^T & -\varepsilon I & P & 0\\
\hline
0 & P^T & (-\varepsilon+x)I & \beta_2\\
0 & 0 & \beta_2^T & -\varepsilon I
\end{array}\right|. \tag{18}$$

The multiplications were implemented in the same manner that was applied to Eq. 16 and then Eq. 18 becomes

$$\Delta(\varepsilon)=(-\varepsilon+x)^2|A_{0-*}|, \tag{19}$$

where

$$|A_{0-*}|=\left|\begin{array}{cc|cc}
I & \beta_1 & 0 & 0\\
\beta_1^T & \varepsilon(\varepsilon-x)I & P & 0\\
\hline
0 & P^T & I & \beta_2\\
0 & 0 & \beta_2^T & \varepsilon(\varepsilon-x)I
\end{array}\right|$$

This is the reason why $\Delta(\varepsilon) = 0$ has two solutions of $\varepsilon = x$. This type of linkage is also considered to form non-disjoint molecules. This proof can be generalized to systems having more than three NBMOs.

2.3.3 Type B system

Next, the case in which two molecules in type B having NBMOs combine with each other is examined and verified. In this type, arbitrary inactive atoms (0) of molecule A and molecule B is changed to arbitrary heteroatoms. In the same manner as Eqs. 5 and 6, the secular determinant is written by

$$\Delta(\varepsilon) = \begin{array}{c|c:c|c:c|}
 & \text{*-part of A} & \text{0 - part of A} & \text{*-part of B} & \text{0 - part of B} \\
\text{*-part of A} & -\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline
\text{0 - part of A} & \beta_1^T & A_1 & 0 & 0 \\ \hline
\text{*-part of B} & 0 & 0 & -\varepsilon I & \beta_2 \\ \hdashline
\text{0 - part of B} & 0 & 0 & \beta_2^T & B_1
\end{array} \tag{20}$$

where

$$A_1 = \begin{pmatrix} -\varepsilon & & & & & & \\ & \ddots & & & & & \\ & & -\varepsilon + x_i & & 0 & & \\ & & & \ddots & & & \\ & & 0 & & -\varepsilon + x_j & & \\ & & & & & \ddots & \\ & & & & & & -\varepsilon \end{pmatrix}$$

and

$$B_1 = \begin{pmatrix} -\varepsilon & & & & & & \\ & \ddots & & & & & \\ & & -\varepsilon + x_k & & & & \\ & & & \ddots & & & \\ & & & & -\varepsilon + x_l & & \\ & & & & & \ddots & \\ & & & & & & -\varepsilon \end{pmatrix}$$

in the case that there is no bonding between molecule A and molecule B. A_1 and B_1 indicate that a part of the inactive carbon atoms (0) are changed to arbitrary heteroatoms. β_1 and β_2 are the same as before.

If a connection between an inactive atom (0) of molecule A (the 0–part of A) and an inactive atom of molecule B (the 0–part of B) exists, the secular determinant is written by

$$\Delta(\varepsilon) = \begin{array}{|c:c|c:c|}
-\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline
\beta_1^T & A_1 & 0 & P \\ \hline
0 & 0 & -\varepsilon I & \beta_2 \\ \hdashline
0 & P^T & \beta_2^T & B_1
\end{array}, \tag{21}$$

where P has the same definition as that in Eq. 11. One multiplies the first h columns (the columns of the *–part of A) and the columns from $n_A + 1$ to $n_A + h_B$ (the columns of the *–part of B) of Eq. 21 by $1/(-\varepsilon)$. Additionally, the rows from $h_A + 1$ to n_A (0–part of A) and the last $n_B - h_B$ rows (0–part of B) are multiplied by $(-\varepsilon)$. As a result, Eq. 21 becomes

$$\Delta(\varepsilon) = \varepsilon^2 |B_{0-0}|, \tag{22}$$

where

$$|B_{0-0}| = \begin{array}{|c:c|c:c|}
I & \beta_1 & 0 & 0 \\ \hdashline
\beta_1^T & -\varepsilon A_1 & 0 & -\varepsilon P \\ \hline
0 & 0 & I & \beta_2 \\ \hdashline
0 & -\varepsilon P^T & \beta_2^T & -\varepsilon B_1
\end{array}$$

Therefore, the equation $\Delta(\varepsilon) = 0$ has two solutions of $\varepsilon = 0$. Two degenerate NBMOs are maintained after 0–0 bonding, as well as the hydrocarbon systems, forming disjoint molecules.

Next, the case in which there is a bond between an inactive atom (0) of molecule A (the 0–part of A) and an active atom (*) of molecule B (the *–part of B) is examined. The secular determinant is written by

$$\Delta(\varepsilon)=\left|\begin{array}{c:c|c:c} -\varepsilon I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & A_1 & P & 0 \\ \hline 0 & P^T & -\varepsilon I & \beta_2 \\ \hdashline 0 & 0 & \beta_2^T & B_1 \end{array}\right|, \tag{23}$$

where P has only one non-zero element. The same multiplications as before are performed to Eq. 23. Then, the identical equation is obtained as

$$\Delta(\varepsilon)=\varepsilon^2|B_{0-*}|, \tag{24}$$

where

$$|B_{0-*}|=\left|\begin{array}{c:c|c:c} I & \beta_1 & 0 & 0 \\ \hdashline \beta_1^T & -\varepsilon A_1 & P & 0 \\ \hline 0 & P^T & I & \beta_1 \\ \hdashline 0 & 0 & \beta_1^T & -\varepsilon B_1 \end{array}\right|$$

Therefore, $\Delta(\varepsilon)=0$ has two solutions of $\varepsilon=0$, that is, 0–* bonding has no effect on the two degenerate NBMOs, resulting in maintaining two degenerate NBMOs. Similar to the hydrocarbon systems, it is considered that the linkage of this type forms non-disjoint molecules.

In addition, this proof can be also generalized to the mixed systems of the hydrocarbon and type B systems. This is because Eqs. 22 and 24 become the equations that express the relationship between the hydrocarbon and the type B system if parameter x_i and x_j are put at zero. Therefore, two degenerate NBMOs are maintained even after 0–0 bonding and 0–* bonding occur in those hybridized systems.

Finally, for all the cases, we can summarize the results for three types of systems (hydrocarbons, A- and B-types) with two types of linkages of disjoint (0–0 linkage) non-disjoint (0–* linkage) as follow,

Linkage	System		
	Hydrocarbons	Type A (Hetero on active atoms)	Type B (Hetero on inactive atoms)
0–0	$\varepsilon^2\lvert H_{0-0}\rvert$	$(-\varepsilon+x)^2\lvert A_{0-0}\rvert$	$\varepsilon^2\lvert B_{0-0}\rvert$
0–*	$\varepsilon^2\lvert H_{0-*}\rvert$	$(-\varepsilon+x)^2\lvert A_{0-*}\rvert$	$\varepsilon^2\lvert B_{0-*}\rvert$

where each determinant was shown in the text above. One can see that, for both 0–0 and 0–* linkages between two molecules, we have always degenerate two solutions with $\varepsilon=0$ for hydrocarbons and B-type and with $\varepsilon=x$ for A-type in which x is defined as coulomb parameter depending on the kind of hetero atom on starred positions.

3 Results and discussion

In order to demonstrate the utility of the L_{ij} value and 0–* rule, DFT and CASSCF computations were performed by using the Gaussian 03 program package [42]. In the DFT calculations, unrestricted calculations were executed for triplet states and the broken symmetry (BS) approach was used to obtain the wave functions of the open-shell singlet state; unrestricted DFT calculations were performed for the singlet states.

We obtained the energy differences ΔE between the singlet and triplet states, that is, E(singlet)–E(triplet). A positive ΔE value means that the molecule is energetically stable in the triplet ground state. The geometries for both the low- and high-spin states of the molecules in Figs. 1, 5, and 7 were optimized by the energy gradient techniques at B3LYP/6-311G(d, p). In those calculations, the geometries were constrained to be planar to conserve their distinct π-electrons because we have to constrain the planarity for all the models for checking if our prediction at Hückel level is reasonable or not. If we fully optimized them, some of the models should have non-planar structures, but we cannot apply L_{ij} index for these non-planar structures in the present stage of development. As an another work, we are considering this effect by projecting L_{ij} value to the plane by the transformation using the dihedral angles for three atoms set in general, then we can compare the high-spin stability of non-planar structure to

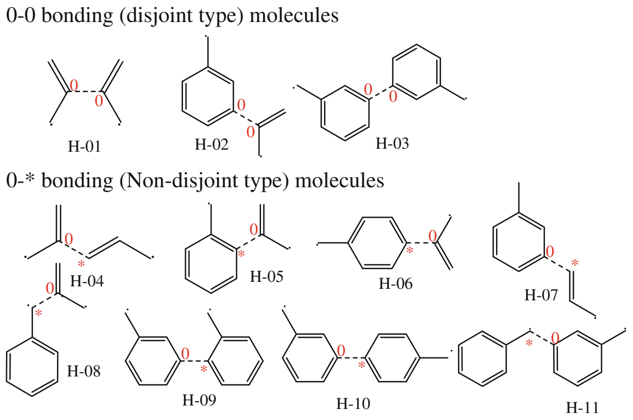

Fig. 1 (Color online) 0–0 and 0–* bonding molecules calculated for hydrocarbon systems

the transformed L_{ij} even at Hückel level. Consequently, it is reasonable that all of the spins originate from these individual π-electrons.

Using the geometries obtained, CASSCF calculations were performed for singlet and triplet states, in which all the π-orbitals and π-electrons are selected as the active space. That is, full configuration interaction (CI) calculations for π-electrons and π-orbitals were implemented. We assume that all of the spins originate from π-electrons. Therefore, the molecular properties about the spin state, for instance whether the ground state is singlet or triplet, can be appropriately predicted at least qualitatively within this assumption. However, the above CASSCF calculations include no electron correlation effects for σ-electrons, so the ΔE values obtained by the B3LYP calculations were also used.

There is another way to use L_{ij} from semi-empirical MO method instead of Hückel method to get better comparison with ab initio energy separation between low-spin and high-spin states. To get minimum value of L_{ij}, however, geometrical parameters of the system including heteroatoms sometimes show non-negligible difference from those by higher accurate calculations. So, using L_{ij}, minimized at poor geometries at semi-empirical level is doubtful in comparison with high-spin state stability optimized by CASSCF or DFT level. Therefore, in this paper, we compared the energy stabilization in high-spin state only to L_{ij} values from Hückel method.

3.1 Hydrocarbon system

The model molecules of the hydrocarbon system are shown in Fig. 1. H-01, H-02, and H-03 are 0–0 bonding (disjoint type) molecules and the others are 0–* bonding (non-disjoint type) molecules.

The total energies, ΔE values, and L_{ij} values of the molecules in Fig. 1 are listed in Table 1. The L_{ij} values are obtained by both the simple Hückel molecular orbital (HMO) and the restricted open-shell Hartree–Fock (ROHF) methods. The results of the B3LYP and the CASSCF calculations indicate that all the 0–* model molecules have positive ΔE values, while 0–0 model molecules have negative ΔE values (i.e., 0–* molecules have triplet ground states and 0–0 molecules have singlet ground states). Therefore, we consider that the 0–* rule is appropriate for hydrocarbon systems.

The 0–0 bonding molecules have zero L_{ij} values, that is, the two degenerate NBMOs have no mixing with each other. As a result, the 0–0 bonding forms disjoint molecules. In contrast, 0–* bonding molecules, for example H-04, have non-zero L_{ij} values and the two degenerate NBMOs are mixed. Non-disjoint molecules are formed by

Table 1 Total energies, ΔE values by B3LYP and CASSCF methods, and L_{ij} values by both Hückel and ROHF methods of the molecules in Fig. 1

	Method	Triplet	Singlet	ΔE	L_{ij} (HMO)	L_{ij} (ROHF)
H-01	B3LYP	−233.3831	−233.3876	−0.0045	0.0000	0.0000
	CASSCF	−231.8602	−231.8662	−0.0060		
H-02	B3LYP	−387.0738	−387.0759	−0.0021	0.0000	0.0000
	CASSCF	−384.6013	−384.6046	−0.0033		
H-03	B3LYP	−540.7641	−540.7651	−0.0011	0.0000	0.0000
	CASSCF	−537.3423	−537.3440	−0.0018		
H-04	B3LYP	−233.4047	−233.3929	0.0117	0.1000	0.0170
	CASSCF	−231.8793	−231.8594	0.0199		
H-05	B3LYP	−387.0612	−387.0583	0.0029	0.0333	0.0003
	CASSCF	−384.5851	−384.5797	0.0054		
H-06	B3LYP	−387.0794	−387.0746	0.0048	0.0333	0.0003
	CASSCF	−384.6060	−384.5981	0.0079		
H-07	B3LYP	−387.0951	−387.0879	0.0072	0.0394	0.0003
	CASSCF	−384.6199	−384.6058	0.0141		
H-08	B3LYP	−387.0854	−387.0731	0.0123	0.1111	0.0185
	CASSCF	−384.6100	−384.5884	0.0216		
H-09	B3LYP	−540.7499	−540.7481	0.0019	0.0139	0.0001
	CASSCF	−537.3242	−537.3204	0.0037		
H-10	B3LYP	−540.7689	−540.7659	0.0029	0.0139	0.0001
	CASSCF	−537.3462	−537.3408	0.0054		
H-11	B3LYP	−540.7761	−540.7686	0.0075	0.0430	0.0013
	CASSCF	−537.3507	−537.3355	0.0152		

Energy difference is defined as $\Delta E = E(\text{singlet}) - E(\text{triplet})$; ΔE values are shown in a.u.

ROHF/6-311G(d, p) optimized geometries for triplet states were used to obtain the L_{ij} values by the ROHF method

Table 2 Total energies, ΔE values by B3LYP and CASSCF methods, and L_{ij} values by both Hückel and ROHF methods of the molecules in Fig. 5

	Method	Triplet	Singlet	ΔE	L_{ij} (HMO)	L_{ij} (ROHF)
A-01	B3LYP	−297.5624	−297.5656	−0.0032	0.0000	0.0000
	CASSCF	−295.8896	−295.8941	−0.0044		
A-02	B3LYP	−483.3310	−483.3324	−0.0014	0.0000	0.0000
	CASSCF	−480.6318	−480.6339	−0.0021		
A-03	B3LYP	−669.0893	−669.0900	−0.0006	0.0000	0.0000
	CASSCF	−665.3644	−665.3658	−0.0014		
A-04	B3LYP	−297.5645	−297.5521	0.0124	0.1000	0.0025
	CASSCF	−295.8886	−295.8694	0.0191		
A-05	B3LYP	−483.3379	−483.3320	0.0059	0.0394	0.0001
	CASSCF	−480.6339	−480.6235	0.0104		
A-06	B3LYP	−483.3320	−483.3168	0.0152	0.1111	0.0026
	CASSCF	−480.6276	−480.6038	0.0238		
A-07	B3LYP	−669.0871	−669.0794	0.0077	0.0430	0.0004
	CASSCF	−665.3573	−665.3442	0.0131		

Energy difference is defined as $\Delta E = E(\text{singlet}) - E(\text{triplet})$; ΔE values are shown in a.u.

ROHF/6-311G(d,p) optimized geometries for high-spin states were used to obtain the L_{ij} values by the ROHF method

Table 3 (a) Total energies, ΔE values by B3LYP and CASSCF methods, and L_{ij} values by both Hückel and ROHF methods of the molecules in Fig. 7a, (b) Total energies, ΔE values by B3LYP and CASSCF methods, and L_{ij} values by both Hückel and ROHF methods of the molecules in Fig. 7b

	Method	Triplet	Singlet	ΔE	L_{ij} (HMO)	L_{ij} (ROHF)
a						
B-01	B3LYP	−403.1128	−403.1148	−0.0021	0.0000	0.0000
	CASSCF	−400.6012	−400.6045	−0.0032		
B-02	B3LYP	−249.4457	−249.4342	0.0115	0.1000	0.0186
	CASSCF	−247.8802	−247.8610	0.0193		
B-03	B3LYP	−403.1082	−403.1055	0.0027	0.0333	0.0002
	CASSCF	−400.5935	−400.5883	0.0051		
B-04	B3LYP	−419.1529	−419.1500	0.0029	0.0333	0.0002
	CASSCF	−416.6003	−416.5945	0.0058		
B-05	B3LYP	−403.1240	−403.1193	0.0047	0.0333	0.0002
	CASSCF	−400.6112	−400.6033	0.0079		
B-06	B3LYP	−419.1695	−419.1649	0.0046	0.0333	0.0002
	CASSCF	−416.6178	−416.6108	0.0070		
B-07	B3LYP	−403.1364	−403.1294	0.0070	0.0394	0.0003
	CASSCF	−400.6211	−400.6070	0.0141		
B-08	B3LYP	−403.1334	−403.1262	0.0072	0.0394	0.0003
	CASSCF	−400.6190	−400.6050	0.0141		
B-09	B3LYP	−419.1739	−419.1668	0.0070	0.0394	0.0003
	CASSCF	−416.6195	−416.6056	0.0140		
B-10	B3LYP	−403.1239	−403.1115	0.0124	0.1111	0.0186
	CASSCF	−400.6093	−400.5875	0.0218		
B-11	B3LYP	−419.1663	−419.1538	0.0125	0.1111	0.0186
	CASSCF	−416.6131	−416.5911	0.0220		
b						
B-12	B3LYP	−556.8030	−556.8040	−0.0011	0.0000	0.0000
	CASSCF	−553.3420	−553.3435	−0.0015		
B-13	B3LYP	−572.8415	−572.8426	−0.0010	0.0000	0.0000
	CASSCF	−569.3416	−569.3432	−0.0017		

Table 3 continued

	Method	Triplet	Singlet	ΔE	L_{ij} (HMO)	L_{ij} (ROHF)
B-14	B3LYP	−556.7985	−556.7968	0.0018	0.0139	0.0001
	CASSCF	−553.3339	−553.3302	0.0038		
B-15	B3LYP	−556.7896	−556.7878	0.0018	0.0139	0.0001
	CASSCF	−553.3246	−553.3211	0.0035		
B-16	B3LYP	−572.8435	−572.8417	0.0018	0.0139	0.0001
	CASSCF	−569.3403	−569.3368	0.0035		
B-17	B3LYP	−572.8372	−572.8355	0.0018	0.0139	0.0001
	CASSCF	−569.3339	−569.3301	0.0038		
B-18	B3LYP	−588.8814	−588.8796	0.0018	0.0139	0.0001
	CASSCF	−585.3398	−585.3358	0.0041		
B-19	B3LYP	−556.8142	−556.8113	0.0029	0.0139	0.0001
	CASSCF	−553.3521	−553.3469	0.0051		
B-20	B3LYP	−556.8078	−556.8048	0.0030	0.0139	0.0001
	CASSCF	−553.3460	−553.3406	0.0053		
B-21	B3LYP	−572.8603	−572.8575	0.0028	0.0139	0.0001
	CASSCF	−569.3594	−569.3544	0.0051		
B-22	B3LYP	−572.8521	−572.8493	0.0028	0.0139	0.0001
	CASSCF	−569.3513	−569.3458	0.0055		
B-23	B3LYP	−588.8984	−588.8956	0.0028	0.0139	0.0001
	CASSCF	−585.3586	−585.3535	0.0050		
B-24	B3LYP	−556.8147	−556.8071	0.0076	0.0430	0.0013
	CASSCF	−553.3501	−553.3351	0.0150		
B-25	B3LYP	−556.8148	−556.8073	0.0076	0.0430	0.0012
	CASSCF	−553.3500	−553.3350	0.0150		
B-26	B3LYP	−572.8572	−572.8496	0.0076	0.0430	0.0013
	CASSCF	−569.3541	−569.3383	0.0158		
B-27	B3LYP	−572.8528	−572.8452	0.0076	0.0430	0.0012
	CASSCF	−569.3491	−569.3335	0.0155		
B-28	B3LYP	−588.8950	−588.8874	0.0077	0.0430	0.0012
	CASSCF	−585.3527	−585.3372	0.0155		

Energy difference is defined as $\Delta E = E(\text{singlet}) - E(\text{triplet})$; ΔE values are shown in a.u

ROHF/6-311G(d, p) optimized geometries for high-spin states were used to obtain the L_{ij} values by the ROHF method

0–* bonding. From Tables 2 and 3, type *A* and type *B* molecules have the same tendency. For example, A-01 has an L_{ij} value of 0.0000 and forms a disjoint molecule. In contrast, A-04 has an L_{ij} value of 0.1000 and shows the non-disjoint property. These results demonstrate the reliability for designing non-disjoint molecules by 0–* bonding and disjoint molecules by 0–0 bonding.

In addition, if the L_{ij} value of a molecule is zero, the molecule is stabilized in the singlet ground state. For instance, H-01 has an L_{ij} value of 0.0000 by HMO and $\Delta E = -0.0060$ (i.e., the ground state of that molecule is singlet) by CASSCF calculations. When the L_{ij} value provides a non-zero value, the molecule is stabilized in the triplet ground state. For example, H-11 has L_{ij} value = 0.0430 by HMO and $\Delta E = 0.0152$ by the same method as above. This tendency is similar using L_{ij} values by ROHF (see Table 1). Therefore, by the use of the L_{ij} values, molecules that have a high-spin ground state can be predicted.

The relationship between the ΔE values and the L_{ij} values of the molecules in Fig. 1 is plotted in Figs. 2 and 3. The ΔE values increase with an increase in the L_{ij} value. Particularly, ΔE values are proportional to the L_{ij} value obtained by the Hückel method, that is, $\Delta E = 0.2234 \times L_{ij}$ (HMO) − 0.0004 with $R^2 = 0.8459$ for linear fitting in CASSCF.

In molecules H-05 and H-10, the ΔE values remain unchanged with an increase in the L_{ij} values. For example, H-10 has $\Delta E = 0.0054$ by CASSCF calculation and an L_{ij} value of 0.0139 by HMO, while H-05 also has

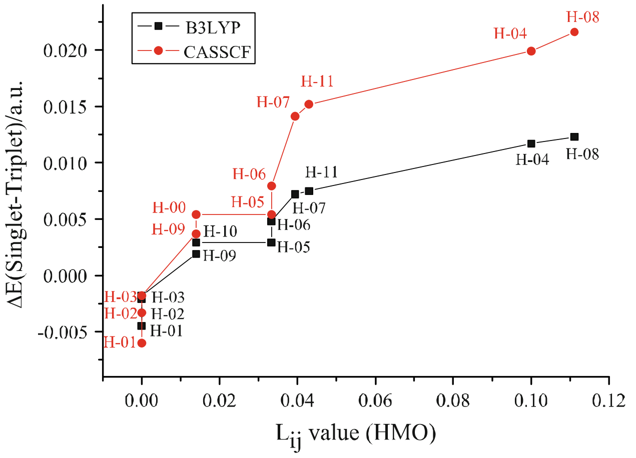

Fig. 2 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP and CASSCF/6-311G(d,p) methods for the molecules in Fig. 1 versus L_{ij} values (HMO)

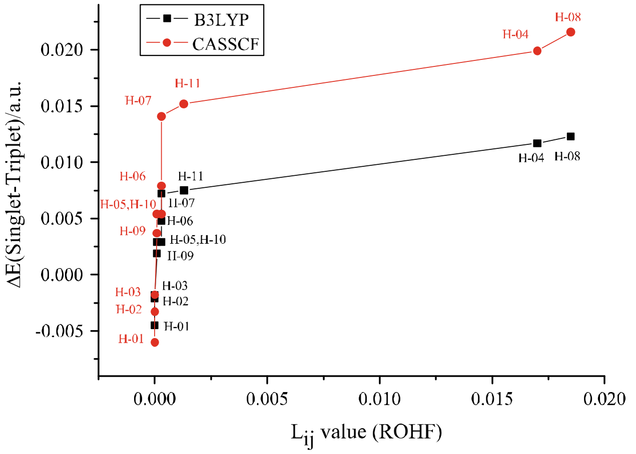

Fig. 3 (Color online) Plots of ΔE (Singlet–Triplet)/a.u. by B3LYP and CASSCF/6-311G(d,p) methods for the molecules in Fig. 1 versus L_{ij} values (ROHF)

$\Delta E = 0.0054$ by CASSCF and an L_{ij} value of 0.0333 by HMO. However, in general, there is a proportional connection between the values of ΔE and L_{ij}.

Figure 4 shows the relationship between L_{ij} values by HMO and those by ROHF. A proportional connection is shown, that is, L_{ij} (ROHF) $= 0.1711 \times L_{ij}$ (HMO) $-$ 0.0026 with $R^2 = 0.8529$. Additionally, type A and type B molecules have the same tendency. Consequently, the L_{ij} values obtained by HMO are used in the following discussion.

The absolute values of ΔE obtained by CASSCF calculations are larger than those obtained by B3LYP calculations (see Table 1). However, Fig. 2 shows that these two methods give the same tendency to the relationship between the ΔE and L_{ij} values. Although the accuracy of the ΔE values of the molecules is not determined, it is possible to discuss the relative stability of the triplet states in terms of the L_{ij} value, that is, about which molecules have large ΔE values.

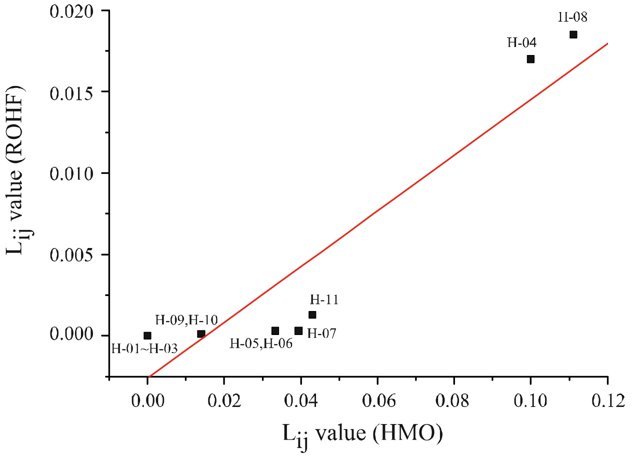

Fig. 4 (Color online) Correlation between L_{ij} (ROHF) and L_{ij} (HMO) for the molecules in Fig. 1

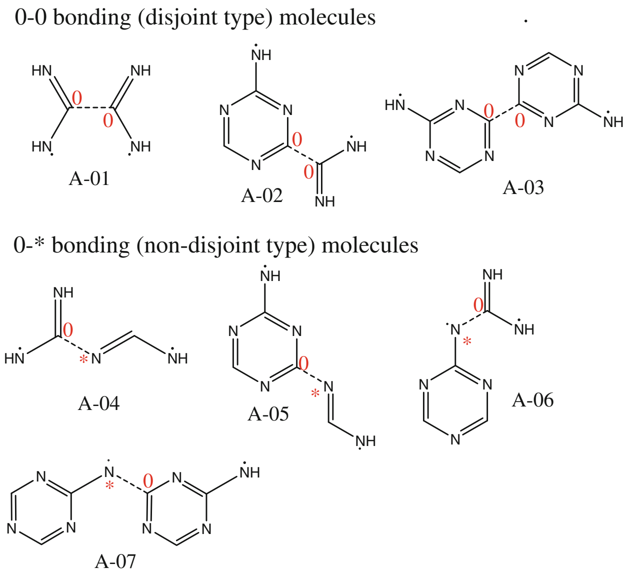

Fig. 5 (Color online) 0–0 and 0–* bonding molecules calculated for type A systems

3.2 Type A system

Next, the type A molecules in Fig. 5 are examined. These are the molecules whose active atoms (*) are changed by the same heteroatoms on all of the starred atoms. In Sect. 2.3, we proved that they have two $\varepsilon = x$ solutions corresponding to NBMOs. In this section, we examine the relationship between the ΔE and the L_{ij} values, and the reliability of the 0–* rule for type A molecules. Neutral molecules were chosen as model molecules, and the nitrogen atom was chosen as the replaced heteroatom.

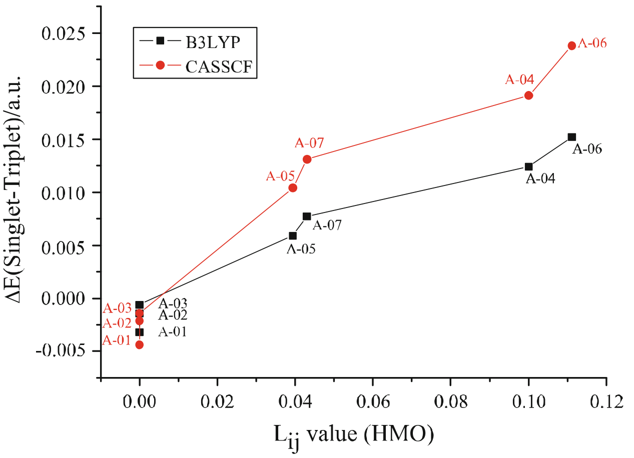

Fig. 6 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP and CASSCF/6-311G(d, p) methods for the molecules in Fig. 5 versus L_{ij} values (HMO)

In Fig. 5, molecules A-01, A-02, and A-03 are 0–0 bonding (disjoint type) molecules. The others are 0–* bonding (non-disjoint type) molecules. Table 2 lists the total energies, ΔE values, and L_{ij} values of the molecules in Fig. 5. All the B3LYP and CASSCF calculations indicate that all the 0–* model molecules have positive ΔE values, whereas the 0–0 model molecules have negative ΔE values. Therefore, it seems appropriate that the 0–* bonding molecules have the triplet ground state and the 0–* rule can predict stable spin states. Additionally, when a molecule has a zero L_{ij} value, the molecule has the singlet ground state. In contrast, if the L_{ij} value of a molecule gives a non-zero value, the molecule has a triplet ground state. For example, A-01 has L_{ij} value = 0.0000 and $\Delta E = -0.0044$ by CASSCF level, while A-07 has L_{ij} value = 0.0430 and $\Delta E = 0.0131$ by the same method.

The relationships between the ΔE and L_{ij} values are plotted in Fig. 6. We used the L_{ij} values obtained by the Hückel method mentioned above. The ΔE values increase with an increase of the L_{ij} value. Note that there is a proportional relationship, which is similar to the straight line $\Delta E = 0.229 \times L_{ij}$ (HMO) − 0.0013 with $R^2 = 0.9406$ by CASSCF. Therefore, we can assume that the L_{ij} values are effective in predicting the stability of high-spin states for these types of molecules.

3.3 Type *B* system

Next, let us consider type *B* molecules, shown in Fig. 7. These are molecules whose arbitrary inactive atoms (0) are changed to arbitrary heteroatoms. In Sect. 2.3, we proved that they have two $\varepsilon = 0$ solutions corresponding to NBMOs. In this section, we examine the relationship between the ΔE and L_{ij} values, as well as the reliability of the 0–* rule regarding the type *B* system. In this article, nitrogen is chosen as the replaced atom.

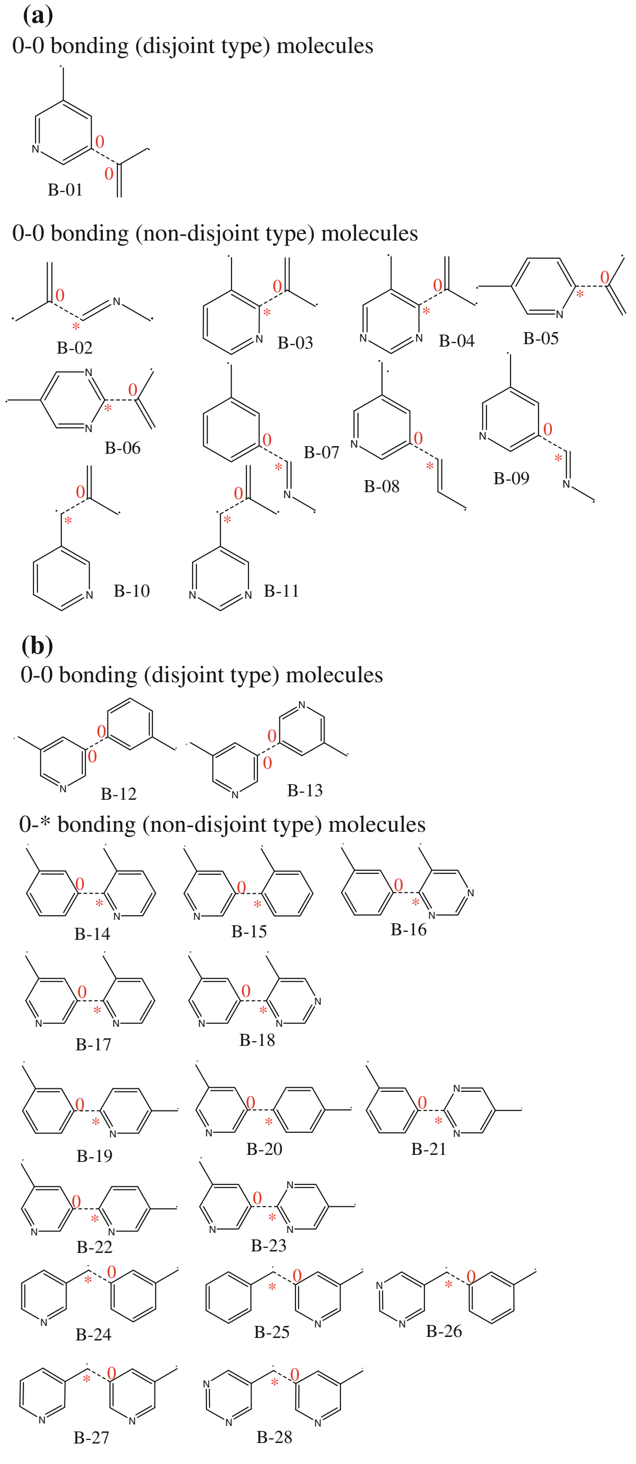

Fig. 7 (Color online) **a** 0–0 and 0–* bonding (6π and 10π) molecules calculated for type *B* systems. **b** 0–0 and 0–* bonding (14π) molecules calculated for type *B* systems

B-01 in Fig. 7a and B-12 and B-13 in Fig. 7b are 0–0 bonding (disjoint type) molecules; the rest are 0–* bonding (non-disjoint type) molecules. The total energies,

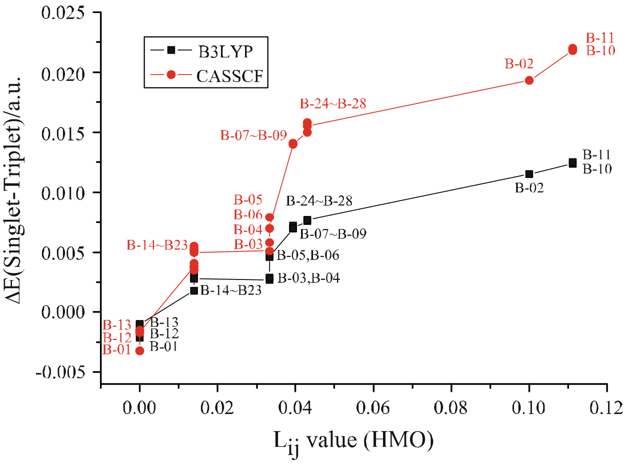

Fig. 8 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP and CASSCF/6-311G(d,p) methods for the molecules in Fig. 7 versus L_{ij} values (HMO)

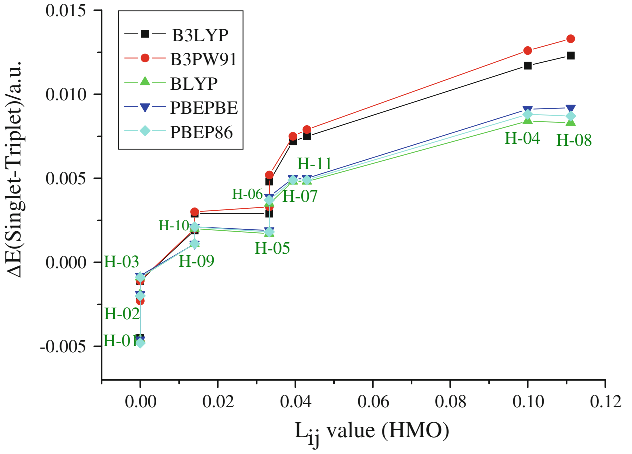

Fig. 9 (Color online) Plots of ΔE (LS-HS)/a.u. by various functionals with 6-311G(d, p) basis sets for the molecules in Fig. 1 versus L_{ij} values (HMO)

ΔE values, and L_{ij} values of the molecules in Fig. 7a, b are listed in Table 3a, b, respectively. The results of the two types of calculations indicate that all the 0–* model molecules have positive ΔE values (i.e., the ground state of these molecules is triplet), while the 0–0 model molecules have negative ΔE values (i.e., the ground state of these molecules is singlet). We can see from these results that the 0–* rule appropriately predicts the ground spin state. In addition, if the L_{ij} value of a molecule is non-zero, the molecule has the singlet ground state. In contrast, if the L_{ij} value of a molecule is non-zero, the molecule has the triplet ground state. Therefore, the L_{ij} value can be a useful index for predicting the ground spin states of molecules.

The relationships between the ΔE and L_{ij} values are plotted in Fig. 8. Here, we used the L_{ij} values obtained by HMO, as discussed above. In general, the ΔE values increase with an increase in the L_{ij} value, although Table 3 shows a few exceptions such as that B-20 has $\Delta E = 0.0030$ by B3LYP calculation and an L_{ij} value of 0.0139, while B-03 has $\Delta E = 0.0027$ by the same method and an L_{ij} value of 0.0333. Therefore, we can conclude that the L_{ij} value can be an effective tool for these types of molecules. Additionally, a molecular group that has nearly the same molecular shape gives almost the same ΔE values in the hydrocarbon and type *B* systems. For instance, H-08 has $\Delta E = 0.0123$ by B3LYP calculations, and B-10 has $\Delta E = 0.0124$.

3.4 Functional dependence

In Sects. 3.1–3.3, it was found that the ΔE values increase with an increase in the L_{ij} values and B3LYP and CASSCF calculations provide a similar tendency. However, DFT calculations depend on the functionals used. In order to examine the functional dependence of the DFT, the calculations for the molecules in Figs. 1, 5, and 7 were performed using the B3PW91, BLYP, PBEPBE, and PBEP86 functionals.

Figure 9 shows the relationship between the ΔE and L_{ij} values of all molecules in Fig. 1 (the hydrocarbon system) by functional. In B3LYP and B3PW91 (hybrid functionals), ΔE increases with an increasing L_{ij} value. In contrast, in BLYP, PBEPBE, and PBEP86 (GGA functionals), there are some points at which ΔE decreases with an increasing L_{ij} value. Two examples are H-10 ($\Delta E = 0.0020$ by BLYP and L_{ij} value $= 0.0139$) and H-05 ($\Delta E = 0.0017$ by BLYP and L_{ij} value $= 0.0333$). However, this tendency is corrected with improved functionals. In addition, the ΔE values mostly increase with an increase in the L_{ij} values.

The relationships between the ΔE and L_{ij} values of the molecules in Fig. 5 (type *A* system) are shown in Fig. 10. It

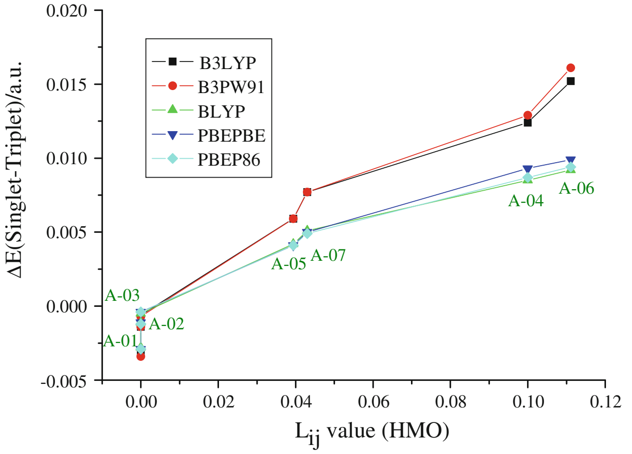

Fig. 10 (Color online) Plots of ΔE (singlet–triplet)/a.u. by various functionals with 6-311G(d, p) basis sets for the molecules in Fig. 5 versus L_{ij} values (HMO)

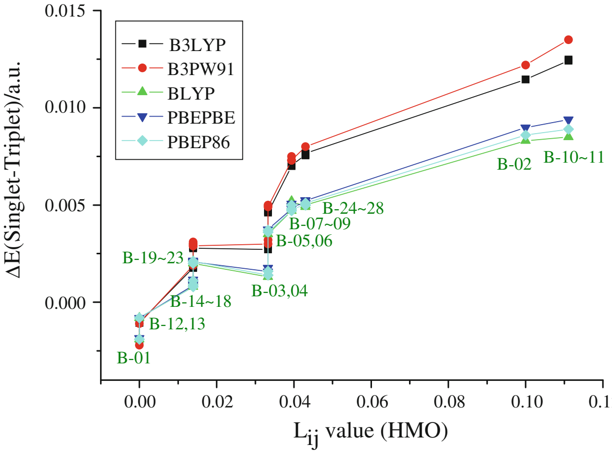

Fig. 11 (Color online) Plots of ΔE (singlet–triplet)/a.u. by various functionals with 6-311G(d, p) basis sets for the molecules in Fig. 7 versus L_{ij} values (HMO)

can be seen that the ΔE value increases with an increase in the L_{ij} value and there is no functional dependence on ΔE.

The relationships between the ΔE and L_{ij} values of the molecules in Fig. 7 (type *B* system) by functional are shown in Fig. 11, where for several molecules, the same L_{ij} value corresponds to a wide range of Singlet–Triplet separations. The reason is that Hückel model is nearest neighbor approximation and the coefficients are determined by the connecting information only between two atoms even though the structures are different. Therefore, it happens the case that L_{ij} value sometimes provides same value even for different structure. This comes from the limitation of simple Hückel method, but we expect this point will be improved when we use extended Hückel method. In principle, however, the ΔE values increase with an increase in the L_{ij} values although the tendency similar to that of the hydrocarbon systems (i.e., the ΔE value decreases with an increase in the L_{ij} value) is also observed in the BLYP, PBEPBE, and PBEP86 functionals. For example, B-21 has $\Delta E = 0.0020$ by BLYP and L_{ij} value $= 0.0139$, whereas B-03 has $\Delta E = 0.0013$ by BLYP and L_{ij} value $= 0.0333$. However, as well as in the case of the hydrocarbon systems, it can be concluded that there generally is a proportional connection between the ΔE and L_{ij} values. Although there was little functional dependence on the relationship between the ΔE and L_{ij} values, ΔE generally increases with increasing L_{ij} values.

3.5 Basis set dependence

DFT calculations with the B3LYP functional are executed using the 6-311G, 6-31G(d,p), 6-31G, and 3-21G basis functions in order to examine basis set dependence in the relationship between the ΔE and L_{ij} values. The results are shown in Figs. 12, 13, and 14. The relationships between

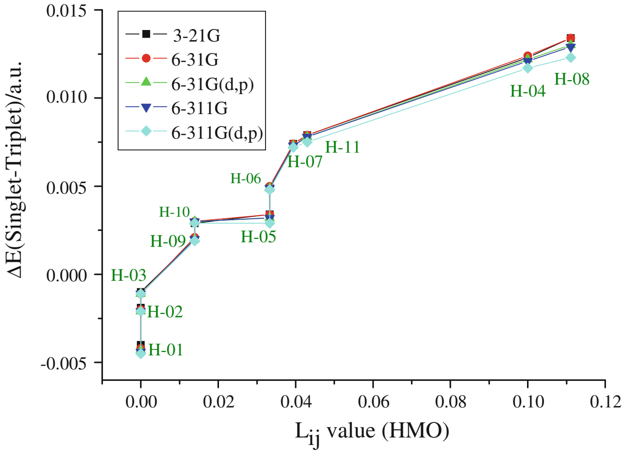

Fig. 12 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP functional with various basis sets for molecules in Fig. 1 versus L_{ij} values (HMO)

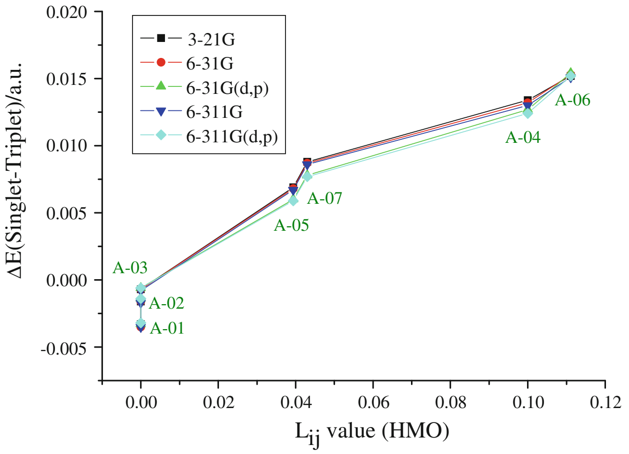

Fig. 13 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP functional with various basis sets for the molecules in Fig. 5 versus L_{ij} values (HMO)

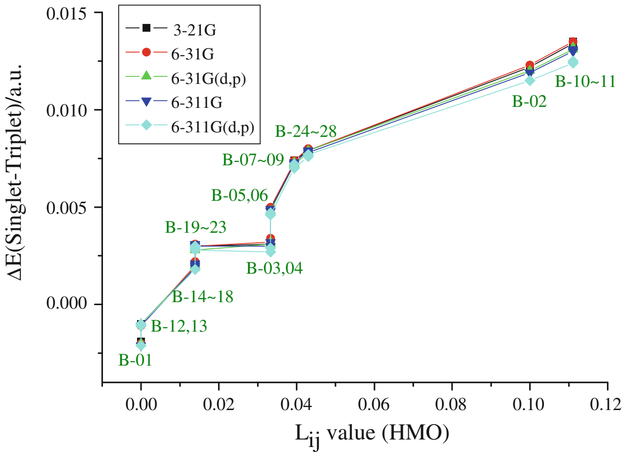

Fig. 14 (Color online) Plots of ΔE (singlet–triplet)/a.u. by B3LYP functional with various basis sets for the molecules in Fig. 7 versus L_{ij} values (HMO)

the ΔE values by each basis set and the L_{ij} values of the molecules in Fig. 1 (the hydrocarbon systems) are plotted in Fig. 12. In general, it was found that the ΔE values are proportional to the L_{ij} values in all basis sets. The ΔE values tend to be proportional to the L_{ij} values in all basis sets as a whole, although the ΔE values in H-05 and H-10 by 6-311G (d,p) basis sets are slightly not proportional to the L_{ij} values, as discussed in Sect. 3.1.

The relationships between the ΔE and L_{ij} values of the molecules in Fig. 5 (type *A* system) are shown in Fig. 13. The ΔE values increase with an increase in the L_{ij} values and there is no basis set dependence in the ΔE values. For example, A-07 has $\Delta E = 0.0086$ by 6-311G basis set and L_{ij} value $= 0.0430$, and A-04 has $\Delta E = 0.0130$ by 6-311G basis set and L_{ij} value $= 0.1000$.

The relationships between the ΔE and L_{ij} values of the molecules in Fig. 7 (type *B* system) by basis set are plotted in Fig. 14. The ΔE values also increase with increases in the L_{ij} values, and the tendency similar to that of the hydrocarbon systems (i.e., the ΔE value decreases with an increase in the L_{ij} value at some points) is also observed in the 6-311G(d, p) and 6-311G basis sets. For example, B-03 has $\Delta E = 0.0030$ by 6-311G and L_{ij} value $= 0.0333$, and B-21 has $\Delta E = 0.0031$ by 6-311G and L_{ij} value $= 0.0139$. However, generally, there is a strong proportional relationship between the ΔE and L_{ij} values.

To conclude, in all systems, there is proportional relationship between the ΔE and L_{ij} values with little dependence on basis set. Therefore, the L_{ij} value can be an effective tool for evaluating high-spin stabilities without performing heavy calculations with large basis sets.

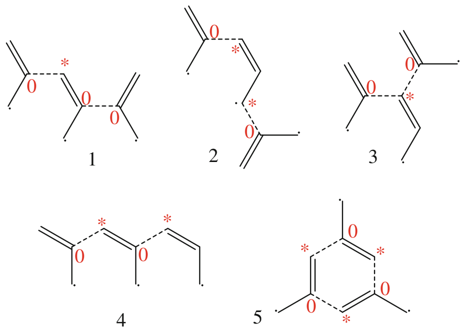

Fig. 15 (Color online) Calculated triradical molecules consisting of three allyl radicals

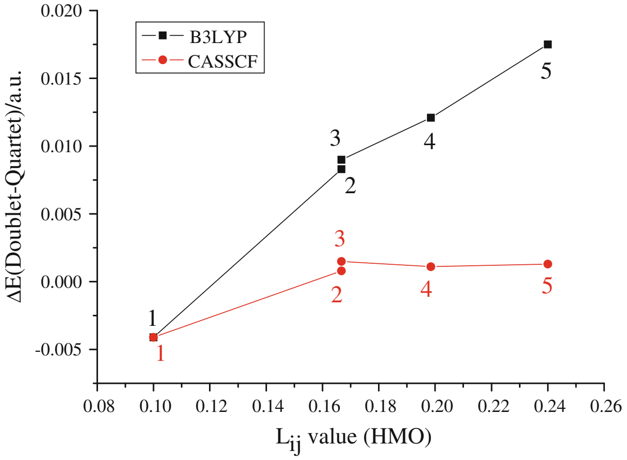

Fig. 16 (Color online) Plots of ΔE (doublet–quintet)/a.u. by B3LYP and CASSCF/6-311G(d, p) methods for the molecules in Fig. 15 versus L_{ij} values (HMO)

3.6 Toward polyradical systems

In order to examine the effectiveness of the 0–* rule and the L_{ij} value for polyradical systems, DFT and the CASSCF calculations were performed for several model molecules. Allyl radicals were selected as an element of polyradicals for this paper. In polyradical systems, the L_{ij} value is defined as the way that all the $L_{ij}^{\min}$ values are added to among all NBMO pairs. For example, considering a triradical system, one obtains three NBMOs and three L_{ij} values for all the pairs. The L_{ij} value of the system is defined as the total of the three L_{ij} values.

We examined the triradical system in this paper. The triradical molecules calculated are shown in Fig. 15 in which three allyl radicals are included. Molecule **1** contains one 0–0 bonding and the others **2**–**5** are combined by only 0–* bonding. For geometry optimization, we used the unrestricted DFT calculations with the B3LYP functional and the 6-31G(d, p) basis sets for high- and low-spin states (i.e., the quartet and doublet states). The geometries are constrained to be planar in the same way as a diradical system. Using the geometries obtained, CASSCF calculations were performed for each state. All the π-orbitals were selected as the active space that corresponds to implementing the full-CI calculations between π-orbitals.

The ΔE and L_{ij} values of each molecule are plotted in Fig. 16. ΔE indicates the energy difference between quartet and doublet states, i.e., $\Delta E = E(\text{doublet}) - E(\text{quartet})$. If the ΔE value of a molecule is positive, the molecule is energetically stable in the quartet ground state. It can clearly be seen that molecule **1** has the doublet ground state, while the others have the quartet ground state for each method. For instance, molecule **4** has $\Delta E = 0.0121$ by the B3LYP calculation and the ground spin state is quartet. Molecule **1** has 0–0 bonding and the others have only 0–* bondings. Therefore, the 0–* rule seems to also be useful for triradical systems, although the number of molecules examined is inadequate. From Fig. 16, it is found that a proportional connection exists between the ΔE values by DFT calculations and the L_{ij} values, whereas a similar tendency cannot be found in CASSCF calculations. Although the ΔE value of molecule **3** by the

CASSCF method is the largest of the molecules calculated, molecule **3** does not give the largest L_{ij} value. With the exception of molecule **3**, the relationships between the ΔE values and the L_{ij} values tend to be the same by both methods. It would be necessary to define an L_{ij} value appropriate for polyradical systems that possesses many spin states in excited states between the lowest singlet and the highest high-spin state.

4 Conclusion

In this work, we generalized the 0–* rule to systems including heteroatoms and carried out highly accurate ab initio calculations for several model molecules in order to examine the reliability of the 0–* rule and the L_{ij} value, as well as that of DFT calculations. With regard to the methodological comparison between DFT and CASSCF calculations, there are differences in the evaluation of the ΔE values. However, it can be seen in Figs. 2, 6, and 8 that, overall, triplet stability increases with increasing L_{ij} values. That is, the larger the L_{ij} value becomes, the larger the ΔE value becomes positive. Therefore, we can conclude that the index is conveniently obtained in the framework of the simple Hückel method and the ROHF method, and the values obtained indicate the degree of energetic stability in the high-spin state and, furthermore, can be a useful index for designing organic ferromagnetic materials. Additionally, all the 0–* model molecules (non-disjoint type molecules) have positive ΔE values, while all the 0–0 model molecules (disjoint type molecules) have negative ΔE values. That is, the 0–* rule can be expected to be appropriate even for heteroatom-included systems. In the design of organic ferromagnetic substances using the 0–* rule enables easier molecular design than performing highly accurate quantum chemical calculations. Actually, it is difficult to calculate gigantic molecules by ab initio methods, which include electron correlation effects, especially using the CASSCF method in which sufficient active space should be included. Therefore, the L_{ij} value will be an efficient tool for evaluating high-spin stability of organic ferromagnetic polyradical systems. The reliability of the L_{ij} value for organic ferromagnetic polyradical systems that have over three NBMOs is now being systematically examined in our laboratory.

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