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Heisenberg Models of Radical Reactions

II. Conservation of the Local Spin-Permutation Symmetry in Reactions of Biradical Species

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Interactions between a pair of two-electron (singlet or triplet) systems undergoing abstraction, insertion, exchange and association reactions are treated on the basis of the quantum Heisenberg model. The local spin-permutation-symmetry properties of these reactions can well be visualized from the continuous or discontinuous variations of Penney's bond orders for the interacting electron pairs. In reactions where such a local permutation symmetry is not conserved, there is an apparent transition between two distinct valence-bond structures. It is shown that the concept of the local spin-permutation-symmetry conservation is useful for understanding the nature of the electron pairing requirement inherent in reactions of biradical species.

Key words: Heisenberg model – Local permutation-symmetry conservation – Radical reactions – Biradical species

1. Introduction

Group theories which treat the orbital, spin (magnetic) and permutation symmetries are often useful for the analysis of symmetry requirements imposed on chemical reactions. A typical example of the outcomes of such analysis is the so-called Woodward-Hoffmann rule; the orbital symmetry is conserved in concerted reactions [1]. The point-group symmetry of orbitals thus plays an essential role in the classification of nonradical reactions. Likewise, it has been pointed out that the local spin-permutation symmetry is conserved in the courses of favourable radical reactions [2, 3] when considered on the basis of the magnetic point-group [4].

The purpose of the present article is to analyze the local spin-symmetry conservations in various modes of interactions between a pair of two-electron (singlet or triplet) systems on the basis of the quantum-mechanical Heisenberg model. The interaction modes investigated include those that may lead to abstraction, insertion, exchange and association reactions. In considering the Heisenberg Hamiltonian, the interaction $\mathfrak{S}_i \cdot \mathfrak{S}_j$ between spins on sites i and j can be replaced by the permutation operator $\mathfrak{P}^{\sigma}_{ij}$, which is the transposition of spin coordinates σ_i and σ_j. Consequently, the problem of the local spin symmetry can be reduced to that of the local permutation symmetry.

Penney's bond order b_{ij} [5] is also related with $\mathfrak{P}^{\sigma}_{ij}$, thus being possessed of the property of local permutation symmetry. Therefore, its variation with the progress of reaction can clearly display whether the interchange of the electron pairings (or exchange interactions [6]) would be an allowed or forbidden process in nature. It will be shown that the bonding property of a reaction system can be represented most conveniently by the resonance of the valance-bond (VB) structures corresponding to the bases of the irreducible representation of a permutation group.

2. Method of Calculation

2.1. Heisenberg Model and Penney's Bond Order

Derivation of the Heisenberg Hamiltonian from the ordinary spin-free Hamiltonian for a permutation group S_N has been performed by a number of workers [7–10]. It is expressed as

$$H = -2 \sum_{i<j} J_{ij} \mathfrak{S}_i \cdot \mathfrak{S}_j \tag{1}$$

where J_{ij} is the exchange interaction, which can be related to the elements of S_N. By using the Dirac identity [11]

$$\mathfrak{S}_i \cdot \mathfrak{S}_j = -(1 - 2\mathfrak{P}^{\sigma}_{ij})/4, \tag{2}$$

Eq. (1) can be rewritten into

$$H = \frac{1}{2} \sum_{i<j} J_{ij}(1 - 2\mathfrak{P}^{\sigma}_{ij}) \tag{3}$$

where $\mathfrak{P}^{\sigma}_{ij}$ is the spin permutation operator whose parity is -1 and 1 for singlet and triplet spin pairs, respectively. Since

$$[\mathfrak{P}^{\sigma}, \mathfrak{S}^2] = [\mathfrak{P}^{\sigma}, \mathfrak{S}_z] = 0, \quad \mathfrak{P}^{\sigma} \in S_N \tag{4}$$

the eigenstates to H should automatically be eigenstates to $\mathfrak{S}^2$ and $\mathfrak{S}_z$ with the eigenvalues $S(S+1)$ and M, respectively. Thus, the eigenstates can be classified according to the irreducible representations of the permutation group S_N.

We now consider the eigenfunctions of H explicitly. Let $\{\theta^M_q\}$ be a set of linearly independent basis spin functions which are simple products of the α- and β-spin functions and provide a common eigenvalue M of $\mathfrak{S}_z$. The eigenfunctions in question can be expressible as a linear combination of these basis spin functions:

$$\Psi^M_k = \sum_q c_{kq} \theta^M_q . \tag{5}$$

However, because H and $\mathfrak{S}^2$ also mutually commute, the eigenstate functions of our search should better be expanded by the simultaneous spin eigenfunctions $\{{}^{2S+1}\Theta_p^M\}$ of $\mathfrak{S}^2$ and $\mathfrak{S}_z$. Thus,

$$
{}^{2S+1}\Psi_k^M = \sum_p {}^S d_{kp}\, {}^{2S+1}\Theta_p^M. \tag{6}
$$

The expansion coefficients ${}^S d_{kp}$ are given by

$$
{}^S d_{kp} = \sum_q c_{kq} \langle \theta_q^M \,|\, {}^{2S+1}\Theta_p^M \rangle. \tag{7}
$$

In this paper, we will use the Serber-type spin functions for ${}^{2S+1}\Theta_p^M$ [12, 13]:

$$
{}^{2S+1}\Theta_p^M(N) = \sum_{m_n} C(S', M-m_n, S_n, m_n \,|\, S, M)\, {}^{2S'+1}\Theta_p^{M-m_n}(N-2)\, w_n(S_n, m_n) \tag{8}
$$

Here, $C(S', M-m_n, S_n, m_n \,|\, S, M)$ are the Clebsch-Gordan coefficients [14, 15]; $N = 2n$ is the total number of electrons; ${}^{2S'+1}\Theta_p^{M-{}^n}n(N-2)$ is the spin function for an $(N-2)$-electron system of the spin angular momentum S' and its z-component $M-m_n$; and $w_n(S_n, m_n)$ is the spin function for the nth geminal pair. Since S_n, which is the spin angular momentum of the nth geminal pair, should be either 0 or 1, S' can only be $S+1$, S *or* $S-1$. Correspondingly, the geminal spin functions $w_n(S_n, m_n)$ of our concern are:

$$
\begin{aligned}
w_n(1, 1) &= \alpha(2n-1)\alpha(2n) \\
w_n(1, 0) &= [\alpha(2n-1)\beta(2n) + \beta(2n-1)\alpha(2n)]/\sqrt{2} \\
w_n(1, -1) &= \beta(2n-1)\beta(n) \\
w_n(0, 0) &= [\alpha(2n-1)\beta(2n) - \beta(2n-1)\alpha(2n)]/\sqrt{2}
\end{aligned} \tag{9}
$$

The spin functions, Eq. (8) are constructed by a genealogical procedure of coupling the subsets with the geminal pair of two electrons. In the case of four-electron systems, in which two two-electron pairs (1, 2) and (3, 4) are regarded as the subsets (or molecules), construction of such functions is quite an easy task.

In connection with the eigenstate functions, it is advantageous to consider the bond order b_{ij} between sites i and j. Penney [5] defined the bond order operator $\hat{b}_{ij}$ for two spins $\mathfrak{S}_i$ and $\mathfrak{S}_j$ as follows:

$$
\hat{b}_{ij} = -\tfrac{4}{3}\mathfrak{S}_i \cdot \mathfrak{S}_j \quad (i<j) \tag{10}
$$

Obviously, the $\hat{b}_{ij}$ is directly related to the local permutation symmetry just as is the case with the Heisenberg Hamiltonian, Eq. (3). The bond orders b_{ij} in given states are calculated as

$$
b_{ij} = \langle {}^{2S+1}\Psi_k^M \,|\, \hat{b}_{ij} \,|\, {}^{2S+1}\Psi_k^M \rangle = \sum_{pp'} {}^S d_{kp}\, {}^S d_{kp'} \langle {}^{2S+1}\theta_p^M \,|\, \hat{b}_{ij} \,|\, {}^{2S+1}\theta_{p'}^M \rangle \tag{11}
$$

In practice, the state functions of $M=0$ and 1 are utilized for singlet $(S=0)$ and triplet $(S=1)$ states, respectively.

2.2. *Serber-Type Spin Functions and the VB Structures in Four-Electron Systems*

In four-electron systems, there are six and four linearly independent basis spin functions for $M=0$ and $M=1$, respectively:

$M=0$

$$\begin{aligned} &\theta_1^0=\alpha(1)\beta(2)\alpha(3)\beta(4) && \theta_2^0=\alpha(1)\beta(2)\beta(3)\alpha(4) \\ &\theta_3^0=\beta(1)\alpha(2)\alpha(3)\beta(4) && \theta_4^0=\beta(1)\alpha(2)\beta(3)\alpha(4) \\ &\theta_5^0=\alpha(1)\alpha(2)\beta(3)\beta(4) && \theta_6^0=\beta(1)\beta(2)\alpha(3)\alpha(4) \end{aligned} \tag{12}$$

$M=1$

$$\begin{aligned} &\theta_1^1=\alpha(1)\alpha(2)\alpha(3)\beta(4) && \theta_2^1=\alpha(1)\alpha(2)\beta(3)\alpha(4) \\ &\theta_3^1=\alpha(1)\beta(2)\alpha(3)\alpha(4) && \theta_4^1=\beta(1)\alpha(2)\alpha(3)\alpha(4) \end{aligned} \tag{13}$$

The matrix elements $\langle\theta_q^M|H|\theta_{q'}^M\rangle$ are summarized in Tables 1 and 2 for the cases of $M=0$ and 1, respectively. The energies E_k and coefficients c_{kq} are determined by diagonalization of this matrix.

Serber's spin functions, Eq. (8) are given by

$$\begin{aligned} {}^1\Theta_1^0({}^1X\,{}^1Y)&=\frac{1}{2}(\theta_1^0-\theta_2^0-\theta_3^0+\theta_4^0) \\ {}^1\Theta_2^0({}^3X\,{}^3Y)&=\frac{1}{2\sqrt{3}}[2(\theta_5^0+\theta_6^0)-(\theta_1^0+\theta_2^0+\theta_3^0+\theta_4^0)] \\ {}^3\Theta_1^0({}^1X\,{}^3Y)&=\frac{1}{2}(\theta_1^0+\theta_2^0-\theta_3^0-\theta_4^0) \\ {}^3\Theta_2^0({}^3X\,{}^1Y)&=\frac{1}{2}(\theta_1^0-\theta_2^0+\theta_3^0-\theta_4^0) \\ {}^3\Theta_3^0({}^3X\,{}^3Y)&=\frac{1}{\sqrt{2}}(\theta_5^0-\theta_6^0) \\ {}^5\Theta^0({}^3X\,{}^3Y)&=\frac{1}{\sqrt{6}}(\theta_1^0+\theta_2^0+\theta_3^0+\theta_4^0+\theta_5^0+\theta_6^0) \end{aligned} \tag{14}$$

$$\begin{aligned} {}^3\Theta_1^1({}^1X\,{}^3Y)&=\frac{1}{\sqrt{2}}(\theta_3^1-\theta_4^1) \\ {}^3\Theta_2^1({}^3X\,{}^1Y)&=\frac{1}{\sqrt{2}}(\theta_1^1-\theta_2^1) \\ {}^3\Theta_3^1({}^3X\,{}^3Y)&=\frac{1}{2}(\theta_1^1+\theta_2^1-\theta_3^1-\theta_4^1) \\ {}^5\Theta^1({}^3X\,{}^3Y)&=\frac{1}{2}(\theta_1^1+\theta_2^1+\theta_3^1+\theta_4^1) \end{aligned} \tag{15}$$

where ${}^1\Theta_2^0({}^3X\,{}^3Y)$, for instance, is the singlet spin function constructed by the coupling of triplet molecules ${}^3X$ and ${}^3Y$ (i.e. the singlet-coupled triplet-triplet

Table 1. Matrix elements $\langle \theta_q | H | \theta_{q'} \rangle$ for the spin functions with $M=0$

Diagonal elements:

$$\langle \theta_1 | H | \theta_1 \rangle = \tfrac{1}{2}(J_{12} - J_{13} + J_{14} + J_{23} - J_{24} + J_{34})$$
$$\langle \theta_2 | H | \theta_2 \rangle = \tfrac{1}{2}(J_{12} + J_{13} - J_{14} - J_{23} + J_{24} + J_{34})$$
$$\langle \theta_3 | H | \theta_3 \rangle = \langle \theta_2 | H | \theta_2 \rangle$$
$$\langle \theta_4 | H | \theta_4 \rangle = \langle \theta_1 | H | \theta_1 \rangle$$
$$\langle \theta_5 | H | \theta_5 \rangle = \tfrac{1}{2}(-J_{12} + J_{13} + J_{14} + J_{23} + J_{24} - J_{34})$$
$$\langle \theta_6 | H | \theta_6 \rangle = \langle \theta_5 | H | \theta_5 \rangle$$

Off-diagonal elements:

	θ_2	θ_3	θ_4	θ_5	θ_6
θ_1	$-J_{34}$	$-J_{12}$	0	$-J_{23}$	$-J_{14}$
θ_2		0	$-J_{12}$	$-J_{24}$	$-J_{13}$
θ_3			$-J_{34}$	$-J_{13}$	$-J_{24}$
θ_4				$-J_{14}$	$-J_{23}$
θ_5					0

structure). Other spin functions may be termed likewise. The elements $\langle {}^{2S+1}\Theta_p^M | \hat{b}_{ij} | {}^{2S+1}\Theta_{p'}^M \rangle$ of Penney's bond-order matrices for singlet and triplet states are summarized in Tables 3 and 4, respectively.

Each of Serber's spin functions uniquely corresponds to a VB structure written by the coupling of geminal spin pairs:

$$ {}^1\Theta_1^0 \leftrightarrow \left(\begin{array}{cc} 2 & 3 \\ | & | \\ 1 & 4 \end{array} \right) \qquad {}^1\Theta_2^0 \leftrightarrow \left(\begin{array}{c} 2-3 \\ \\ 1-4 \end{array} + \begin{array}{cc} 2 & 3 \\ \multicolumn{2}{c}{\times} \\ 1 & 4 \end{array} \right)$$

$$ {}^3\Theta_1^1 \leftrightarrow \left(\begin{array}{cc} 2 & 3\cdot \\ | & \\ 1 & 4\cdot \end{array} \right) \qquad {}^3\Theta_2^1 \leftrightarrow \left(\begin{array}{cc} 2\cdot & 3 \\ & | \\ 1\cdot & 4 \end{array} \right)$$

$$ {}^3\Theta_3^1 \leftrightarrow \left(\begin{array}{c} 2-3 \\ \\ 1\cdot\ 4\cdot \end{array} + \begin{array}{c} 2\cdot\ 3\cdot \\ \\ 1-4 \end{array} \right) \qquad {}^5\Theta_1^2 \leftrightarrow \left(\begin{array}{cc} 2\cdot & 3\cdot \\ & \\ 1\cdot & 4\cdot \end{array} \right)$$

where ${}^1\Theta_2^0({}^3X{}^3Y)$ and ${}^3\Theta_3^1({}^3X{}^3Y)$ are represented by the resonance of two structures, however. In all these VB structures, full lines indicate the singlet spin coupling of the two sites while the unlinked sites have no spin coupling. In singlet states each site is linked with another, but there remain two points unlinked in triplet states.

Table 2. Matrix elements $\langle \theta_q | H | \theta_{q'} \rangle$ for the spin functions with $M=1$

Diagonal elements:

$$\langle \theta_1 | H | \theta_1 \rangle = \tfrac{1}{2}(-J_{12} - J_{13} + J_{14} - J_{23} + J_{24} + J_{34})$$
$$\langle \theta_2 | H | \theta_2 \rangle = \tfrac{1}{2}(-J_{12} + J_{13} - J_{14} + J_{23} - J_{24} + J_{34})$$
$$\langle \theta_3 | H | \theta_3 \rangle = \tfrac{1}{2}(J_{12} - J_{13} - J_{14} + J_{23} + J_{24} - J_{34})$$
$$\langle \theta_4 | H | \theta_4 \rangle = \tfrac{1}{2}(J_{12} + J_{13} + J_{14} - J_{23} - J_{24} - J_{34})$$

Off-diagonal elements:

	θ_2	θ_3	θ_4
θ_1	$-J_{34}$	$-J_{24}$	$-J_{14}$
θ_2		$-J_{23}$	$-J_{13}$
θ_3			$-J_{12}$

Table 3. Bond order matrix elements for the singlet states

$\langle {}^1\Theta_1^0 | \hat{b}_{ij} | {}^1\Theta_1^0 \rangle$

$i \diagdown j$	2	3	4
1	1	0	0
2		0	0
3			1

$\langle {}^1\Theta_2^0 | \hat{b}_{ij} | {}^1\Theta_2^0 \rangle$

$i \diagdown j$	2	3	4
1	$-1/3$	$2/3$	$2/3$
2		$2/3$	$2/3$
3			$-1/3$

$\langle {}^1\Theta_1^0 | \hat{b}_{ij} | {}^1\Theta_2^0 \rangle$

$i \diagdown j$	2	3	4
1	0	$1/\sqrt{3}$	$-1/\sqrt{3}$
2		$-1/\sqrt{3}$	$1/\sqrt{3}$
3			0

2.3. Interaction Models

The spin interactions in the four-electron system which we intend to examine are as shown in Fig. 1. Models A and B correspond to the linear abstraction processes of a pair of two-electron species. Models C and D are for cyclic approaches with isosceles conformations, which are responsible for the insertion or migration process. Models E, F and G represent the rectangular approaches which are the models of exchange, addition and association reactions. Models H and I express the staggered approaches corresponding to exchange and addition reactions.

In the present model systems, each pair of reaction sites, (1, 2) or (3, 4), represents one molecular system. In a given molecular system, the energies for the singlet and triplet spin couplings are given as $3J^S/2$ and $-J^T/2$, respectively. For the sake of simplicity, we assume $J^S = J^T = J$ throughout this paper. J can be taken to be negative in sign without loss of generality [16–19]. Thus, the ground singlet and triplet reactants are characterized by negative (J) and positive ($-J$) exchange

Table 4. Bond order matrix elements for the triplet states

$\langle {}^3\Theta_1^1 | \hat{b}_{ij} | {}^3\Theta_1^1 \rangle$

$i \backslash j$	2	3	4
1	1	0	0
2		0	0
3			$-1/3$

$\langle {}^3\Theta_2^1 | \hat{b}_{ij} | {}^3\Theta_2^1 \rangle$

$i \backslash j$	2	3	4
1	$-1/3$	0	0
2		0	0
3			1

$\langle {}^3\Theta_3^1 | \hat{b}_{ij} | {}^1\Theta_3^1 \rangle$

$i \backslash j$	2	3	4
1	$-1/3$	$1/3$	$1/3$
2		$1/3$	$1/3$
3			$-1/3$

$\langle {}^3\Theta_1^1 | \hat{b}_{ij} | {}^3\Theta_2^1 \rangle$

$i \backslash j$	2	3	4
1	0	$-1/3$	$1/3$
2		$1/3$	$-1/3$
3			0

$\langle {}^3\Theta_1^1 | \hat{b}_{ij} | {}^3\Theta_3^1 \rangle$

$i \backslash j$	2	3	4
1	0	$\sqrt{2}/3$	$\sqrt{2}/3$
2		$-\sqrt{2}/3$	$-\sqrt{2}/3$
3			0

$\langle {}^3\Theta_2^1 | \hat{b}_{ij} | {}^3\Theta_3^1 \rangle$

$i \backslash j$	2	3	4
1	0	$-\sqrt{2}/3$	$\sqrt{2}/3$
2		$-\sqrt{2}/3$	$\sqrt{2}/3$
3			0

interactions, respectively. The intermolecular exchange interactions (J') are incorporated only for neighbouring pairs. In the analyses of reactions, we express the ratio J'/J by the symbol x as the only variable parameter. That $x=0$ indicates that two molecular systems are far away. The larger absolute value of x implies the closer

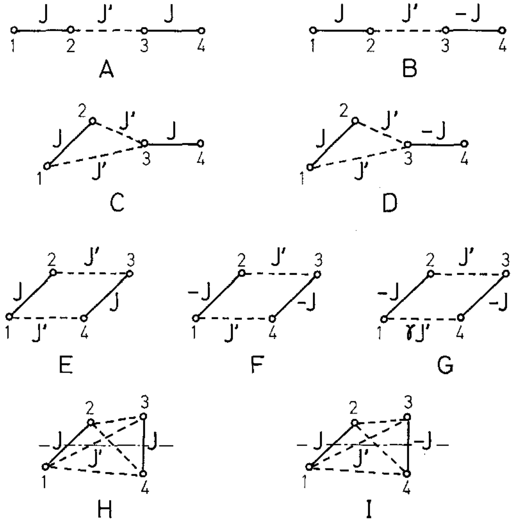


Fig. 1 A–I. Interaction models in four-electron systems. J and J' denote the intramolecular and intermolecular exchange integrals, respectively

approach of the two molecular systems. Eigenvalues of H expressed in units of $-J$ will be referred to as the reduced energies:

$$^{2S+1}E_k=\langle {}^{2S+1}\Psi_k^M|H|{}^{2S+1}\Psi_k^M\rangle/(-J) \tag{16}$$

The reduced energies $^{2S+1}E_k$ are the functions of x, and so are Penney's bond orders b_{ij}.

3. Conservations of the Local Permutation Symmetry

3.1. Linear Abstraction Models A and B

We will first examine model A. The functional dependences of the reduced energies on x are depicted in Fig. 2.

As is apparent from Fig. 2, the ground state is singlet in both the positive and negative x-regions. The spin function corresponding to the ground singlet state is given by

$$^{1}\Psi_1=\frac{\sqrt{3}(\sqrt{\alpha}+2)}{2\alpha^{1/4}(2\sqrt{\alpha}+x+2)^{1/2}}\cdot\frac{x-2}{|x-2|}\left\{{}^1\Theta_1^0-\frac{\sqrt{\alpha}+2x-2}{\sqrt{3}(\sqrt{\alpha}+2)}\,{}^1\Theta_2^0\right\} \tag{17}$$

where $\alpha=x^2-2x+4$. When $x=0$, the ground spin function reduces to $-{}^1\Theta_1^0$. As $|x|$ increases, the singlet-coupled bitriplet component $^1\Theta_2^0$ is mixed with the singlet-coupled bisinglet one $^1\Theta_1^0$. Therefore, no intersection occurs between the energy surfaces of the two singlet states.

Variations in Penney's bond orders with x are illustrated in Fig. 3. When $x=0$, the intramolecular and intermolecular bond orders are 1 and 0, respectively. As the

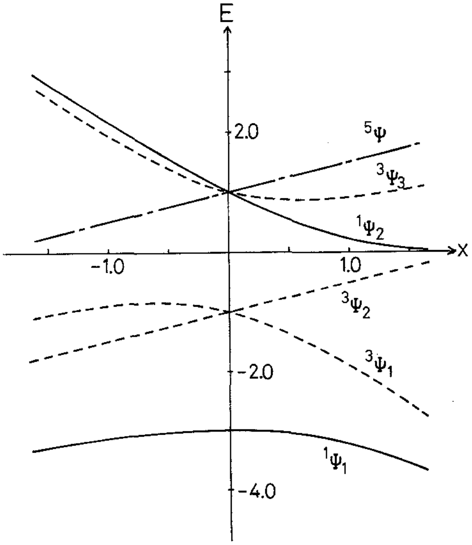


Fig. 2. Variations in the reduced energies with x in the course of the linear abstraction process of singlet species (model A). (——) singlet, (– – –) triplet, and (— — —) quintet

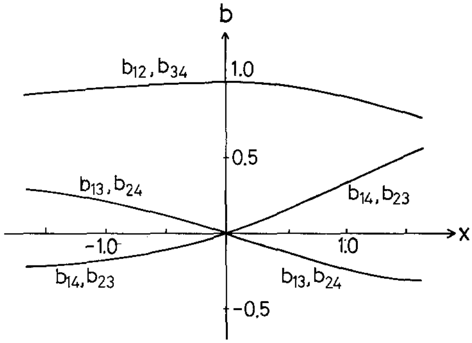


Fig. 3. Functional dependences of Penney's bond orders on x in the course of the linear abstraction process of singlet species (model A)

reaction proceeds ($x>0$), the spin coupling between sites 2 and 3 increases its singlet character ($b_{23}>0$) until a bond is formed between the reactants. For $x<0$, on the other hand, the intermolecular spin coupling is of the triplet type ($b_{23}<0$). Each bond order varies continuously, indicating no sudden interchange of the local permutation symmetry. Thus, the process can be characterized as a *local spin-permutation-symmetry allowed process*. The entire system can be represented by the resonance of the VB structures:

$$(1-2\quad 3-4)+(\overline{1\quad 2-3\quad 4}+\overline{1\quad \underline{2\quad 3}}\underline{\quad 4})$$

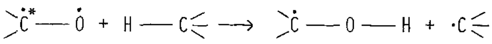
The spin functions of the lowest excited triplet states are given by

$$^3\Psi_1=\frac{x+1+\sqrt{\alpha}}{2\sqrt{2}\alpha^{1/4}(\sqrt{\alpha}+x)^{1/2}}\left\{{}^3\Theta_1^1+{}^3\Theta_2^1-\sqrt{2}\left(\frac{x-1+\sqrt{\alpha}}{x+1+\sqrt{\alpha}}\right){}^3\Theta_3^1\right\} \tag{18}$$

and

$$^3\Psi_2=-\frac{1}{\sqrt{2}}({}^3\Theta_1^1-{}^3\Theta_2^1), \tag{19}$$

where $\alpha=x^2+1$. As can be seen in Fig. 2, the excited triplet reaction proceeds without surface crossing in either of the negative and positive x-regions because of the smooth mixing among the triplet spin components. Consequently, the linear abstraction process of lowest excited triplet species can also be characterized as a local permutation-symmetry allowed process. It will be because of its local permutation-symmetry allowed character that the hydrogen abstraction reaction by $^3(n-\pi^*)$ excited ketone readily takes place.



Next, model B for the linear abstraction by a ground triplet biradical species is examined. As can be seen in Fig. 4, the ground state is always triplet in both the positive and negative x-regions. The ground triplet energy surface does not intersect other triplet surfaces in the course of reaction.

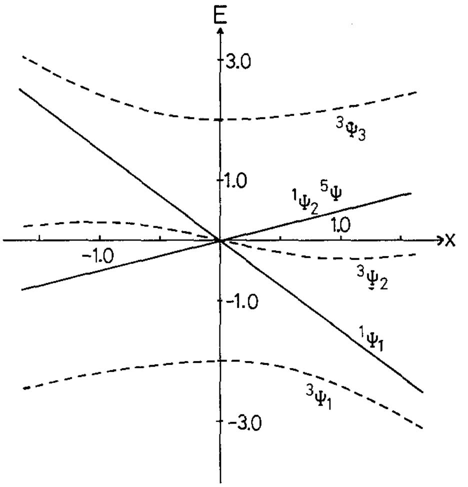
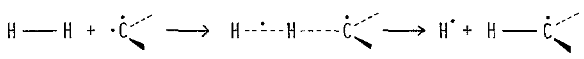


Fig. 4. Variations in the reduced energies with x for the linear abstraction by triplet biradicals (model B)

It was ascertained that the bond order b_{23} changes continuously with x, keeping the same sign as that of x. Consequently, the linear abstraction of ground triplet biradical species is characterized as a permutation-symmetry allowed process. The hydrogen abstraction from the H_2 molecule by triplet methylene may be regarded as one example of such cases:



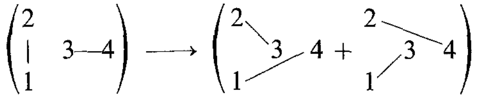
3.2. *Insertion Models C and D*

Fig. 5 illustrates how the reduced energies vary with the change in x in the course of the insertion process C. Two distinct energy surfaces, whose spin functions are

$${}^1\Psi_1 = {}^1\Theta_1^0 \quad \text{and} \quad {}^1\Psi_2 = {}^1\Theta_2^0, \tag{20}$$

intersect each other at $x=2$.

Penney's bond orders (Appendix B) calculated for the ground spin functions are discontinuous accordingly. The spin coupling between the pairs (1, 2) and (3, 4), which is of the singlet type at the initial stage of reaction, changes into the triplet type at the crossing point $x=2$. Intermolecular bond orders also suddenly change from 0 to 2/3 at this point. Thus, the local spin-permutation symmetry is not conserved in this particular case. The ground-state VB structure changes as follows:



The insertion reaction of singlet biradical species should therefore be characterized as a *local spin-permutation-symmetry forbidden process*.

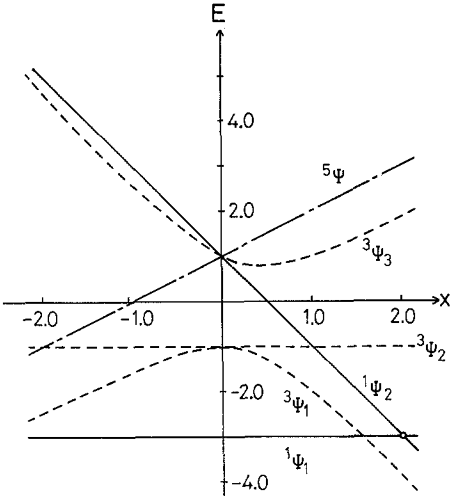


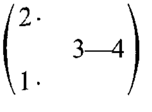
Fig. 5. Variations in the reduced energies with x for the insertion process (C_{2v}) of singlet biradical into singlet pair bond (model C)

The above results are similar to those for the insertion of a doublet radical [2]. The similarity is no doubt due to the irrelevance of the fourth electron at site 4 to the bond formation. In fact, in the addition of $^1(n-\pi^*)$ excited carbonyl compounds toward hydrocarbons, the π^* electron formally remains intact [20].

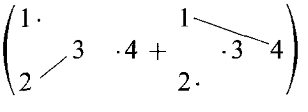
The spin function corresponding to the lowest excited triplet state is given by

$$^3\Psi_1=\frac{3x+\sqrt{\alpha}+2}{\sqrt{2}\,\alpha^{1/4}(3\sqrt{\alpha}+9x-2)^{1/2}}\left\{{}^3\Theta_2^1-\sqrt{2}\left(\frac{3x+\sqrt{\alpha}-2}{3x+\sqrt{\alpha}+2}\right){}^3\Theta_3^1\right\} \tag{21}$$

where $\alpha=9x^2-4x+4$. At the initial stage of reaction ($x=0$), the spin function is ${}^3\Theta_2^1$, which corresponds to the following VB structure:



The energy surface does not intersect other triplet surfaces at $x>0$. As x increases, the ${}^3\Theta_3^1$ component to be represented by the VB structure



mixes in progressively to permit a smooth bond interchange between the reactants. It may be concluded that the insertion reaction of singlet biradical species is rendered permutation-symmetry allowed on the photochemical triplet excitation of its reaction partner.

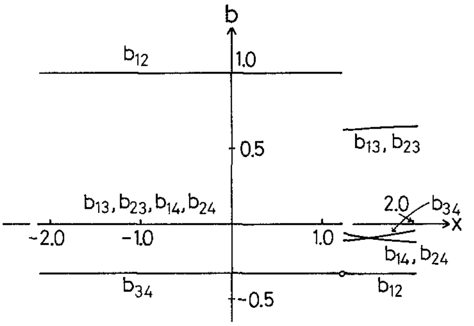
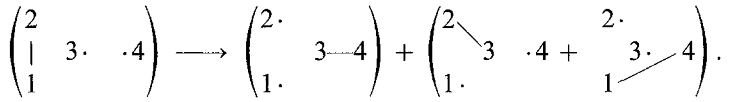


Fig. 6. Functional dependences of Penney's bond orders on x of the insertion process (C_{2v}) of triplet biradical into singlet pair bond (model D)

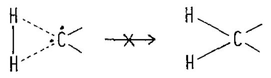
In the insertion reaction model D for triplet biradicals, lower triplet states are given by

$$
\begin{aligned}
{}^3\Psi_1 &= {}^3\Theta_1^1 \\
{}^3\Psi_2 &= \frac{2+3x+\sqrt{\alpha}}{\alpha^{1/4}(3\sqrt{\alpha}+9x+2)^{1/2}}\left\{\frac{2-3x-\sqrt{\alpha}}{\sqrt{2}(2+3x+\sqrt{\alpha})}\,{}^3\Theta_2^1+{}^3\Theta_3^1\right\}
\end{aligned}
\tag{22}
$$

where $\alpha=9x^2+4x+4$. The excited triplet state ${}^3\Psi_2$ is stabilized by the mixing between the spin functions ${}^3\Theta_2^1$ and ${}^3\Theta_3^1$. The ground state changes from ${}^3\Psi_1$ to ${}^3\Psi_2$ at $x=\sqrt{5}-1$ (Appendix A). The (1, 2)-pair is converted from singlet to triplet at the crossing point. Intermolecular pairs (1, 3) and (2, 3), on the other hand, become singlet-coupled after the crossing. Thus, variations of Penney's bond orders are discontinuous in the course of reaction, as can be seen in Fig. 6. In accordance with the discontinuity of the bond orders, the VB structure is also varied as follows:



After all, the insertion reaction of triplet biradical species must be a permutation-symmetry forbidden process. For example, insertion of triplet methylene into H_2 should be forbidden [20].



3.3. *Addition or Exchange Reaction Models E, F and G in the D_{2h} Conformation*

Model E of addition or exchange reaction of singlet species is first examined. Variations of the reduced energies with x are illustrated in Fig. 7.

Fig. 7 shows that the ground state is singlet, exhibiting no surface intersection. The ground spin function is given by

$$
{}^1\Psi_1=\frac{\sqrt{3}(\sqrt{\alpha}+1)}{2\alpha^{1/4}(2\sqrt{\alpha}+x+1)^{1/2}}\left\{{}^1\Theta_1^0-\frac{2x-1+\sqrt{\alpha}}{\sqrt{3}(\sqrt{\alpha}+1)}\,{}^1\Theta_2^0\right\},
\tag{23}
$$

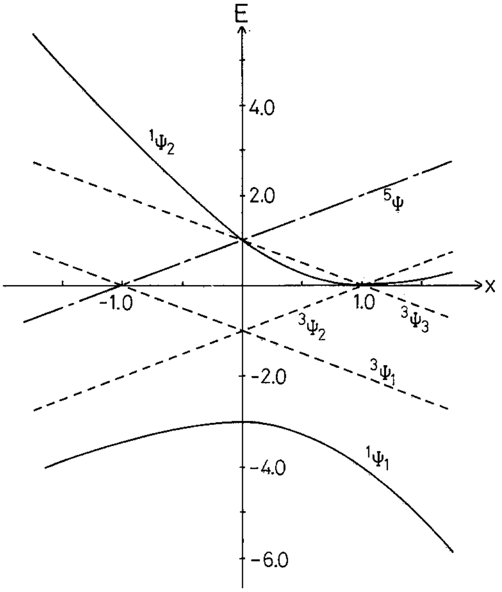
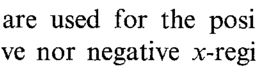


Fig. 7. Variation in the reduced energies with x for the exchange or addition process (D_{2h}) of singlet biradicals (model E)

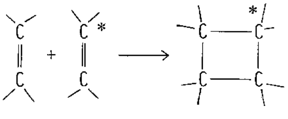
where $\alpha = x^2 - x + 1$. There is no transition between different VB structures because of the above mixing. Correspondingly, the intermolecular bond orders b_{14} and b_{23} both increase continuously, retaining the singlet spin coupling which is responsible for the bond formation. Therefore, both the addition and exchange reactions of singlet species proceeding in a planar $(2_s + 2_s)$ conformation are regarded as permutation-symmetry allowed processes, even though they are obviously forbidden in the orbital symmetry criterion [1]. The exchange reaction $H_2 + D_2 \rightarrow 2HD$ is a typical example of such reactions. Insertion of the singlet oxygen atom $O(^1D)$ into a bond also falls in this category.



The spin function corresponding to the lowest excited triplet state is given by

$$^{3}\Psi_{\pm} = \frac{1}{\sqrt{2}}\left(^{3}\Theta_{1}^{1} \pm {}^{3}\Theta_{2}^{1}\right), \tag{24}$$

where the signs + and − are used for the positive and negative x-regions, respectively. In neither positive nor negative x-region, is there surface crossing present. The bond interchange is also smooth, indicating the local spin-permutation-symmetry allowed character. This is well consistent with the facile $(2_s + 2_s)$ photochemical cycloaddition between ground singlet and excited triplet olefins.



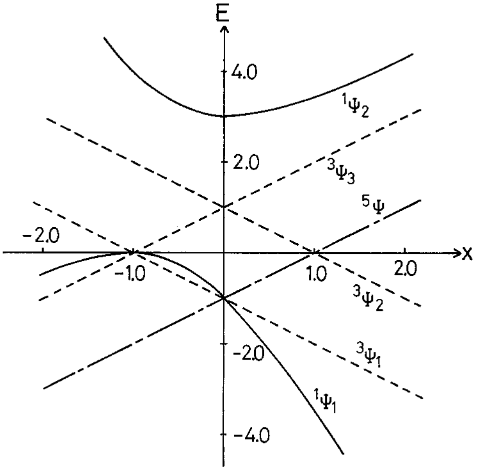
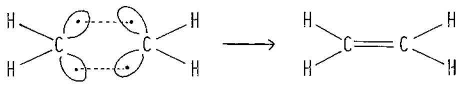


Fig. 8. Variations in the reduced energies with x for the exchange or addition process (D_{2h}) of triplet biradicals (model F)

The insertion model F of addition or exchange reaction between two triplet biradicals can be treated in a similar manner. The singlet-coupled bitriplet spin function is dominant in the course of reaction ($x>0$)

$$^1\Psi_1=\frac{\sqrt{3}(\sqrt{\alpha}+1)}{2\alpha^{1/4}(2\sqrt{\alpha}-x+1)^{1/2}}\left\{\frac{2x-\sqrt{\alpha}+1}{\sqrt{3}(\sqrt{\alpha}+1)}\,{}^1\Theta_1^0-{}^1\Theta_2^0\right\} \tag{25}$$

where $\alpha=x^2+x+1$. The surface crossing does not take place (Fig. 8), and the bond interchange is smooth (Appendix B). Thus the singlet coupling of ground triplet species is a permutation-symmetry allowed process. The dimerization of triplet methylenes in the D_{2h} conformation could be mentioned as an example.



Model G is a modification of model F such that the two intermolecular exchange interactions are taken to be different. By assuming that the ratio γ of these two interactions is negative in sign, we may deal with the triplet coupling of two triplet species. The ground spin function is given as

$$\begin{aligned}^3\Psi_1=&\frac{1}{2\alpha^{1/4}}[\sqrt{\alpha}+(\gamma-1)x]^{1/2}\left\{\frac{1}{\sqrt{2}}[1+(\gamma-1)x-\sqrt{\alpha}]({}^3\Theta_1^1+{}^3\Theta_2^1)\right.\\&\left.+[1+\sqrt{\alpha}-(\gamma-1)x]\,{}^3\Theta_3^1\right\},\end{aligned} \tag{26}$$

where $\alpha=(\gamma-1)^2x^2+1$.

Variations of the reduced energies and Penney's bond orders for the case of $\gamma=-0.5$ as an example are depicted in Figs. 9 and 10, respectively. It is apparent from Fig. 9 that the ground state is indeed triplet. It does not intersect other triplet states.

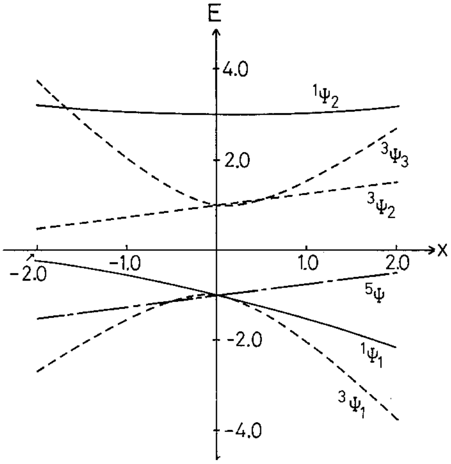
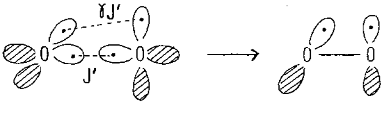


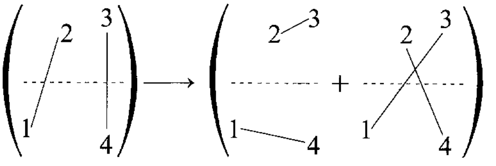
Fig. 9. Variations in the reduced energies with x for the trapezoidal association process of triplet biradicals (model G). $\gamma = -0.5$

Variations of the bond orders are all continuous. The intermolecular bond order b_{23} increases with increasing x, indicating an intermolecular bond formation. The continuous decrease of b_{14} from positive down to negative values indicates that a triplet spin coupling is induced between sites 1 and 4. Since the bond interchange is smooth, the overall process should be permutation-symmetry allowed in nature. The association reaction of triplet O atoms forming the triplet O_2 molecule corresponds to this reaction model.



3.4. Exchange or Association Reaction Models H and I with D_{2d} Symmetry

Model H is a $(2_s + 2_a)$ version of model E. As Fig. 11 shows, the surface crossing takes place between singlet states at $x = 1$. The VB structure of the ground state also changes as follows:



The bond interchanges occur suddenly in accord with this transition (Fig. 12). Thus, the association or exchange reaction of singlet species in the D_{2d} conformation is to be characterized as a permutation-symmetry forbidden process.

The above prototype reaction is forbidden with respect to the orbital symmetry also. As has been mentioned in Section 3.3, the $(2_s + 2_s)$ exchange reaction in the D_{2h}

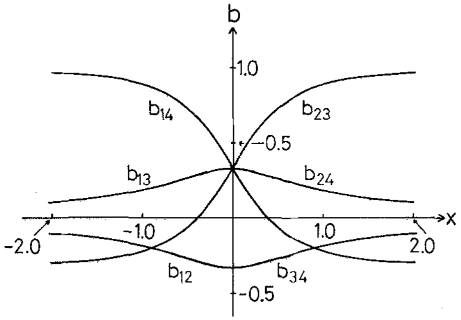


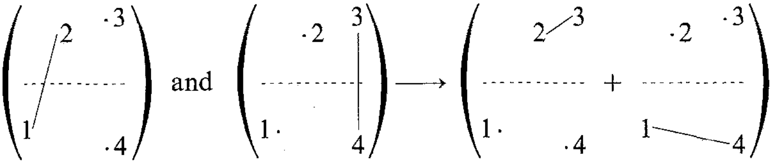
Fig. 10. Functional dependences of Penney's bond orders on x for the trapezoidal association process of triplet biradicals (model G). $\gamma=-0.5$

conformation is orbital-symmetry forbidden but local spin-permutation-symmetry allowed. The difference between the D_{2h} and D_{2d} paths lies in the local spin-permutation symmetry. This is one of the reasons why both the orbital and spin-permutation symmetries are necessary to fully characterize the chemical reactions. From the viewpoint of local spin-permutation-symmetry conservation, the D_{2h} path is considered to be more favourable than the D_{2d} path. Detailed calculations [22] support this conclusion.

The spin functions corresponding to the lowest excited triplet state are given by

$$^{3}\Psi=\begin{cases}{}^{3}\Theta_{1}^{1} \text{ and } {}^{3}\Theta_{2}^{1}, & 0\leqslant x<1\\ {}^{3}\Theta_{3}^{1}, & x\geqslant 1\end{cases} \tag{27}$$

Here also, a surface crossing occurs at $x=1$, the transition being



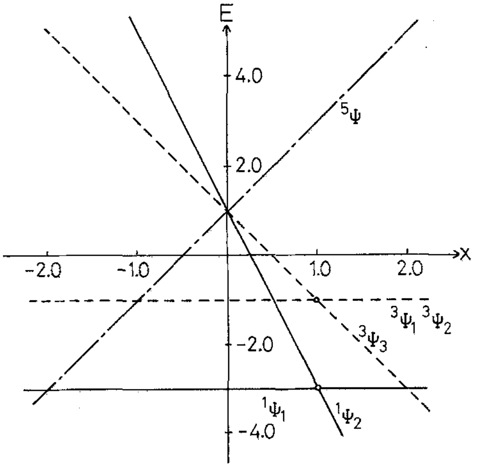


Fig. 11. Variations in the reduced energies with x for the exchange or addition process (D_{2d}) between singlet species (model H)

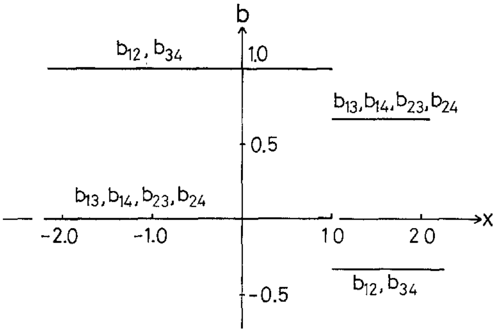
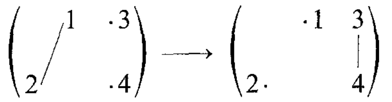


Fig. 12. Functional dependences of Penney's bond orders on x for the exchange or addition process (D_{2d}) between singlet species

Thus the reaction is also permutation-symmetry forbidden even in the excited triplet state. This implies that the exchange reaction with a D_{2d} conformation would hardly take place by photochemical excitation of a reactant.

Finally, model I of association or exchange reaction between ground singlet and triplet biradicals is examined. As can be seen from Appendices A and B, two triplet energy surfaces intersect at $x=1$, leading to the transition of the VB structure:



The association or exchange reaction is therefore a permutation-symmetry forbidden process. Thus the D_{2d} conformation is an unfavoured path in the case of radical reactions.

4. Concluding Remarks

As has been shown in the preceding section, the quantum-mechanical Heisenberg model describes reliably the bond interchange processes in which open-shell species such as singlet and triplet biradicals participate. In particular, the model is useful for the elucidation of the principal role of the local spin-permutation symmetry in these reactions in relation to Penney's bond order between reaction sites. The relationships of the energy levels of various spin states obtained by the Heisenberg model are also in good agreement with the results of *ab initio* calculations reported by some workers [22, 23]. Thus, the nature and location of the surface crossing points in radical reactions can be inferred reasonably by the simple and visual concept based on the present model.

The main points brought out in the present treatments are summarized as follows:

1) Linear abstraction processes of singlet and triplet biradicals are local spin-permutation-symmetry allowed reactions. Linear abstraction in the lowest excited triplet state is also permutation-symmetry allowed.
2) Insertions of atoms in the ^1D state are local spin-permutation-symmetry allowed processes, whereas insertions of triplet biradicals are forbidden. The insertion of

singlet biradical toward excited triplet species should be a permutation-symmetry allowed process.

3) The exchange (or addition) reactions in conformations of the D_{2h} and D_{2d} symmetries of ground singlet species are permutation-symmetry allowed and forbidden, respectively. The same generalization can be made for reactions of the lowest excited triplet states.
4) Association reactions of triplet biradicals such as the oxygen atom and triplet methylene are permutation-symmetry allowed.

In short, radical reactions of open-shell species proceed in such a manner that the bond interchanges occur smoothly, retaining the bonding characters expressed by Penney's bond orders. The local spin-permutation-symmetry is conserved in favourable radical reactions of closed- as well as open-shell species.

Appendix A

The reduced energies of reaction models B, D, and I are as follows:

Model B

Singlet states

$$^0E_1 = -3x/2, \qquad {}^0E_2 = x/2.$$

Triplet states

The energies are given as the roots of the secular equation

$$\begin{vmatrix} E+x/2-2 & -x-1 & -1 \\ -x & E+x/2+1 & -1 \\ 0 & 0 & E-x/2+1 \end{vmatrix} = 0.$$

Quintet state

$$^2E = x/2.$$

Model D

Singlet states

$$^0E_1 = -2x, \qquad {}^0E_2 = 0.$$

Triplet states

$$^1E_1 = -2, \qquad {}^1E_2 = 1 - x/2 - \sqrt{\alpha}/2,$$

$$^1E_3 = 1 - x/2 + \sqrt{\alpha}/2, \qquad \alpha = 9x^2 + 4x + 4.$$

Quintet state

$$^2E = x.$$

Model I

Singlet states

$$^{0}E_1 = -4x, \qquad ^{0}E_2 = 0.$$

Triplet states

$$^{1}E_1 = -2, \qquad ^{1}E_2 = -2x, \qquad ^{1}E_3 = 2.$$

Quintet state

$$^{2}E = 2x.$$

Appendix B

Penney's bond orders for models C, E, F and I are as follows:

Model C

$$b_{12} = b_{34} = \begin{cases} 1 & x < 2 \\ -1/3 & x \geqslant 2 \end{cases}$$

$$b_{13} = b_{23} = b_{14} = b_{24} = \begin{cases} 0 & x < 2 \\ 2/3 & x \geqslant 2 \end{cases}$$

Model E

$$b_{12} = b_{34} = \frac{\sqrt{\alpha} - x + 2}{3\sqrt{\alpha}}$$

$$b_{13} = b_{24} = \frac{\sqrt{\alpha} - x - 1}{3\sqrt{\alpha}}$$

$$b_{14} = b_{23} = \frac{2x + \sqrt{\alpha} - 1}{3\sqrt{\alpha}} \qquad \alpha = x^2 - x + 1$$

Model F

When $x > 0$

$$b_{12} = b_{34} = \frac{\sqrt{\alpha} - x - 2}{3\sqrt{\alpha}}$$

$$b_{13} = b_{24} = \frac{\sqrt{\alpha} - x + 1}{3\sqrt{\alpha}}$$

$$b_{14} = b_{23} = \frac{2x + \sqrt{\alpha} + 1}{3\sqrt{\alpha}} \qquad \alpha = x^2 + x + 1$$

When $x<0$

$$b_{12}=b_{13}=b_{14}=b_{23}=b_{24}=b_{34}=-1/3$$

Model I

$$b_{12}=\begin{cases}1 & x<1\\ -1/3 & x\geqslant 1\end{cases},\qquad b_{34}=-1/3$$

$$b_{13}=b_{14}=b_{23}=b_{24}=\begin{cases}0 & x<1\\ 1/3 & x\geqslant 1\end{cases}$$

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