Electronic Spin Alignment in Free Radical Reactions#

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Classical spin alignment in radical reactions is studied by the GSF-HF wave function in H_3 model system. The GSF-HF wave function introduces a simple classical picture of electronic spins directly and leads to the classical Heisenberg model. The instability of various spin alignments is studied on the GSF-HF electronic energy surface. In compensation for the classical spin freedom, the GSF-HF method does not satisfy quantum mechanical spin-symmetry. The GSF-HF wave function is analyzed with a projection operator constructed by a full-CI wave function.

The electronic spin alignment in molecules takes an important role in free radical reactions. Its dynamic behavior is also studied by the CIDEP in spin exchange reactions.[1] The spin structure is one of the typical quantum mechanical properties and it is difficult to have a simple classical picture. Interesting theoretical investigations have been carried out by Yamaguchi et al.[2—4] They discussed the spin alignment in the radical reaction with a simple spin picture based on the classical[2] and quantum[3] Heisenberg models. Koutecky et al. also discussed the change of spin alignments in reactions by the VB-CI wave function.[5] Both of these theoretical studies, however, employed exchange integrals as parameters and the ratio of exchange integrals was taken as a reaction coordinate. The change of spin alignments was discussed along this ratio which was not evaluated explicitly.

In this paper we study the electronic spin alignment in radical reactions using the generalized spin function[6,7] HF (GSF-HF) and the full-CI wave function. The GSF-HF wave function introduces a simple classical freedom about the spin alignment in molecules and leads directly to the classical Heisenberg model. The mechanism of spin alignment in classical picture is studied along the explicit change of molecular structure with an ab initio calculation. The stationary and instability conditions of the spin alignment are also investigated on the GSF-HF energy surface. The GSF-HF wave function, which does not satisfy the quantum mechanical spin-symmetry, is analyzed by the projection onto the full-CI manifold.

1. GSF-HF Wave Function

1.1. GSF-HF Wave Function and Spin Angle. The electronic wave function is represented as an antisymmetrized product of spin orbitals. For each spin orbital ϕ_i, we adopt a simple direct product of a spatial orbital φ_i and a spin function σ_i as

$$\phi_i = \varphi_i \sigma_i. \tag{1}$$

The spatial orbitals are orthonormalized. σ_i is a generalized spin function (GSF)[6,7] defined as

$$\sigma_i = \{\cos(\eta_i/2)\}\alpha + \{\sin(\eta_i/2)\}\beta, \tag{2}$$

where η_i is a mixing parameter of α- and β-spin components. Here the coefficients of linear combination are constrained to be real. The GSF-HF wave function can be obtained by optimizing the spatial and spin mixing parameters variationally:

$$\Psi^{\text{GSF-HF}} = \|\phi_1(1)\phi_2(2)\cdots\phi_N(N)\|. \tag{3}$$

The electronic energy of the GSF-HF wave function is

$$\begin{aligned} E &= \langle \Psi^{\text{GSF-HF}} | \hat{H} | \Psi^{\text{GSF-HF}} \rangle \\ &= \sum_i^N h_i + (1/2)\sum_{i\neq j}^N\sum^N [J_{ij} - (1/2)K_{ij} \\ &\quad \{1+\cos(\eta_i - \eta_j)\}], \end{aligned} \tag{4}$$

where $\hat{H}$ is the total electronic Hamiltonian. h_i is the one-electron integral and J_{ij} and K_{ij} are the Coulomb and exchange integrals.[6] In Eq. 4, the energy term which depends on the spin mixing parameters is

$$E\left(\{\eta_i\}_{i=1,N}\right) = -(1/4)\sum_{i\neq j}^N\sum^N K_{ij}\cos(\eta_i - \eta_j). \tag{5}$$

This has an exactly analogous form to the classical two-dimensional Heisenberg model[8] and $(\eta_i - \eta_j)$ can be considered as the relative angle between classical electronic spin vectors at the i- and j-sites. in such a case, the spin mixing freedom η_i in the GSF may be considered as a tilted angle from the α-spin. We call η_i as a spin angle hereafter. To obtain this classical picture about the spin structure, we should admit the following restrictions for the GSF-HF wave function. First, the spatial orbitals are required to be localized to individual atomic sites and each of these orbitals should be occupied by only one electron. This is necessary to keep a simple picture of one-electron on one-site model. Second, the exchange integrals in Eq. 4 are always positive because of the orthogonality of spatial orbitals[6] which is also necessary to derive a simple energy expression. So the most stable electronic state which the GSF-HF wave function can describe is the high-spin excited state where each orbital is occupied by one electron as described by Eq. 3.

1.2. Instability of Spin Alignments. Based on

#This paper is dedicated to the late Professor Hiroshi Kato.

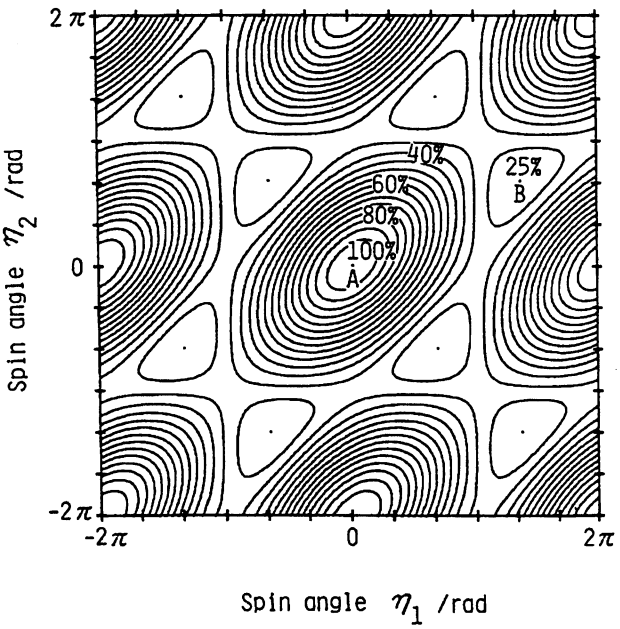

Fig. 1. Contour map of the weight for the quartet state of H_3 system in the GSF-HF wave function. The spin angle η_3 is fixed to zero. The pure quartet state is assigned as A. B is the minimum (maximum) weight of the quartet (doublet) state.

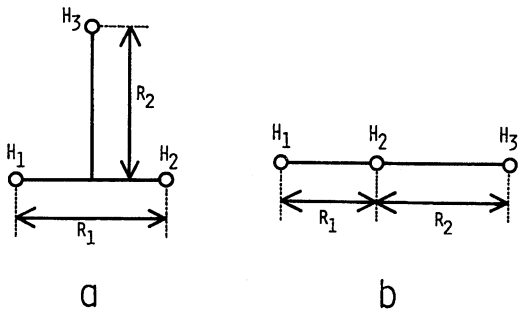

Fig. 2. Geometry of H_3 reaction system. a: The isosceles triangular approach in C_{2v} conformation; b: the colinear approach.

the electronic energy formula [Eq. 4], the stationary and instability conditions of the spin alignments are studied. The stationary condition for the spin angle η_i is

$$\partial E/\partial \eta_i = (1/2) \sum_{j(\neq i)} K_{ij} \sin(\eta_i - \eta_j) = 0. \quad (6)$$

The second derivative of Eq. 4 constructs the Hessian matrix whose components are

$$\partial^2 E/\partial {\eta_i}^2 = (1/2) \sum_{j(\neq i)} K_{ij} \cos(\eta_i - \eta_j), \quad (7)$$
$$\partial^2 E/\partial \eta_i \partial \eta_j = -(1/2) K_{ij} \cos(\eta_i - \eta_j), \quad (i \neq j)$$

and the instability of the spin alignments at stationary states is studied by solving the eigenvalue equation for this matrix. For the N-spin system, we have N spin angles. The electronic energy given by Eq. 4, however, depends only on the relative spin angles and the Hessian matrix has at least one zero-eigenvalue whose eigenvector does not change the relative angles between the electronic spins.

1.3. Spin-Symmetry of GSF-HF Wave Function. The classical spin freedom of the GSF breaks the $\hat{S}^2$ and $\hat{S}_z$ spin-symmetry in the GSF-HF wave function. The mixed spin-symmetry is analyzed by the spin projection operators with the closure relation:

$$1 = \sum_i^{2^N} |\Theta_i\rangle\langle\Theta_i|, \quad (8)$$

where $|\Theta_i\rangle$ is the orthogonalized N-spin eigenfunction and satisfies

$$\hat{S}^2|\Theta_i\rangle = S_i(S_i+1)|\Theta_i\rangle, \quad (9)$$

$$\hat{S}_z|\Theta_i\rangle = S_{z_i}|\Theta_i\rangle, \quad (10)$$

in unit of $\hbar$. The GSF-HF wave function is decomposed into each spin state by Eq. 8 as

$$|\Psi^{\text{GSF-HF}}\rangle = \sum_i^{2^N} |\Theta_i\rangle\langle\Theta_i|\Psi^{\text{GSF-HF}}\rangle, \quad (11)$$

where the integration is carried out over the spin. The expectation value of $\hat{S}^2$ in the state described by the GSF-HF wave function is

$$\langle\hat{S}\rangle^2 = \sum_i^{2^N} S_i(S_i+1)\langle\Theta_i|\Psi^{\text{GSF-HF}}\rangle^2. \quad (12)$$

For a particular case of 3-spin system, $<\hat{S}^2>$ is

$$\begin{aligned}\langle\hat{S}\rangle^2 &= (3/2)\{(3/2)+1\} \\ &\times \left[\cos^2\{(\eta_1-\eta_2)/2\} + \cos^2\{(\eta_2-\eta_3)/2\}\right. \\ &+ \left.\cos^2\{(\eta_3-\eta_1)/2\}\right]/3 \\ &+ (1/2)\{(1/2)+1\} \\ &\times \left[\sin^2\{(\eta_1-\eta_2)/2\} + \sin^2\{(\eta_2-\eta_3)/2\}\right. \\ &+ \left.\sin^2\{(\eta_3-\eta_1)/2\}\right]/3, \end{aligned} \quad (13)$$

and the doublet and quartet states are mixed. The mixing weight of these two states in the expectation value $<\hat{S}^2>$ depends on the spin angles. The contribution from the quartet state is maximized when the spin angle satisfies

$$\eta_1 = \eta_2 = \eta_3, \quad (14)$$

for instance, and there is no contribution from the doublet state. The pure double state, however, can not be constructed in the GSF-HF wave function. One of the spin angles which lead to the maximum weight (75%) of the doublet state or the minimum weight (25%) of the quartet state is

$$\eta_1 = (4/3)\pi, \ \eta_2 = (2/3)\pi, \text{ and } \eta_3 = 0. \quad (15)$$

Figure 1 shows the weight for the quartet state in Eq. 13 along the spin angle coordinate when η_3 is fixed to zero.

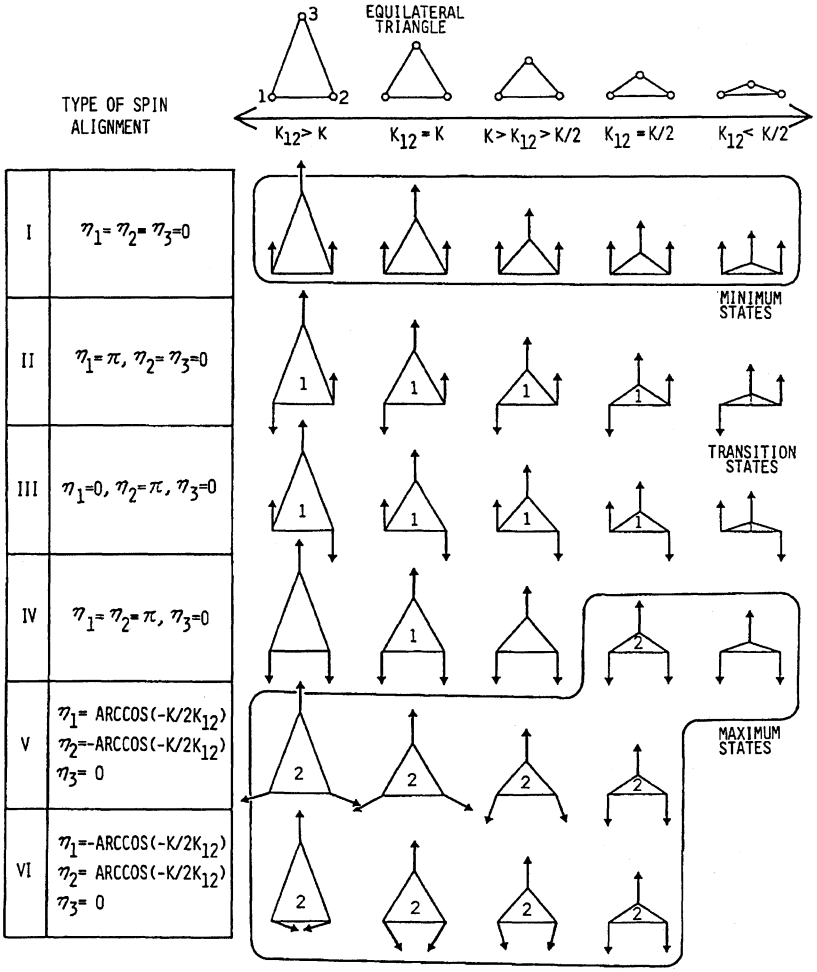

Fig. 3. Spin alignments at stationary states in the isosceles triangular approach. The states assigned with the same numbers (1 or 2) are degenerate energetically at each geometry. Exchange integral is $K=K_{13}=K_{23}$ from C_{2v} symmetry.

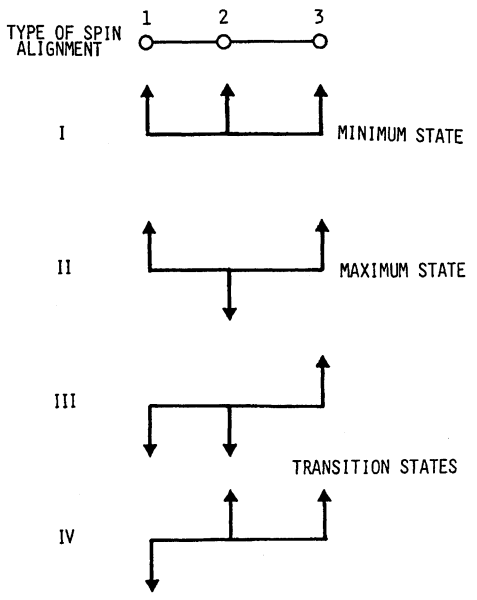

Fig. 4. Spin alignments at stationary states in the colinear approach with the approximation $K_{13}=0$.

Table 1. Electronic Energy of Stationary States in Isosceles Triangular Approach[a] (in au)

Type of stationary state	R_2/Å				
	2.0	1.0	$\sqrt{3}/2$	0.5	0.0
I[b]	−2.26181	−2.54085	−2.57627	−2.57471	−1.80155
II,III[c]	−2.25200	−2.52570	−2.55979	−2.55483	−1.78271
IV[d]	−2.26000	−2.52728	−2.55979	−2.54959	−1.76611
V,VI[e]	−2.25198	−2.52432	−2.55773	−2.54944	—

a) R_1 is fixed to 1.0 Å. b) Minimum state. c) Transition state. d) If $K_{12}<K/2$, the spin alignment is the maximum state. If $K_{12}=K/2$, we have one positive eigenvalue and two zero-eigenvalues. If $K_{12}>K/2$, the spin alignment is the transition state. e) If $K_{12}=K/2$, we have one positive eigenvalue and two zero-eigenvalues. If $K_{12}>K/2$, the spin alignment is the maximum state.

2. Spin Alignments and Energy Surfaces in H_3 System by GSF-HF Wave Function

The insertion and abstraction reactions are typical free radical reactions[5] and we investigate the spin align-

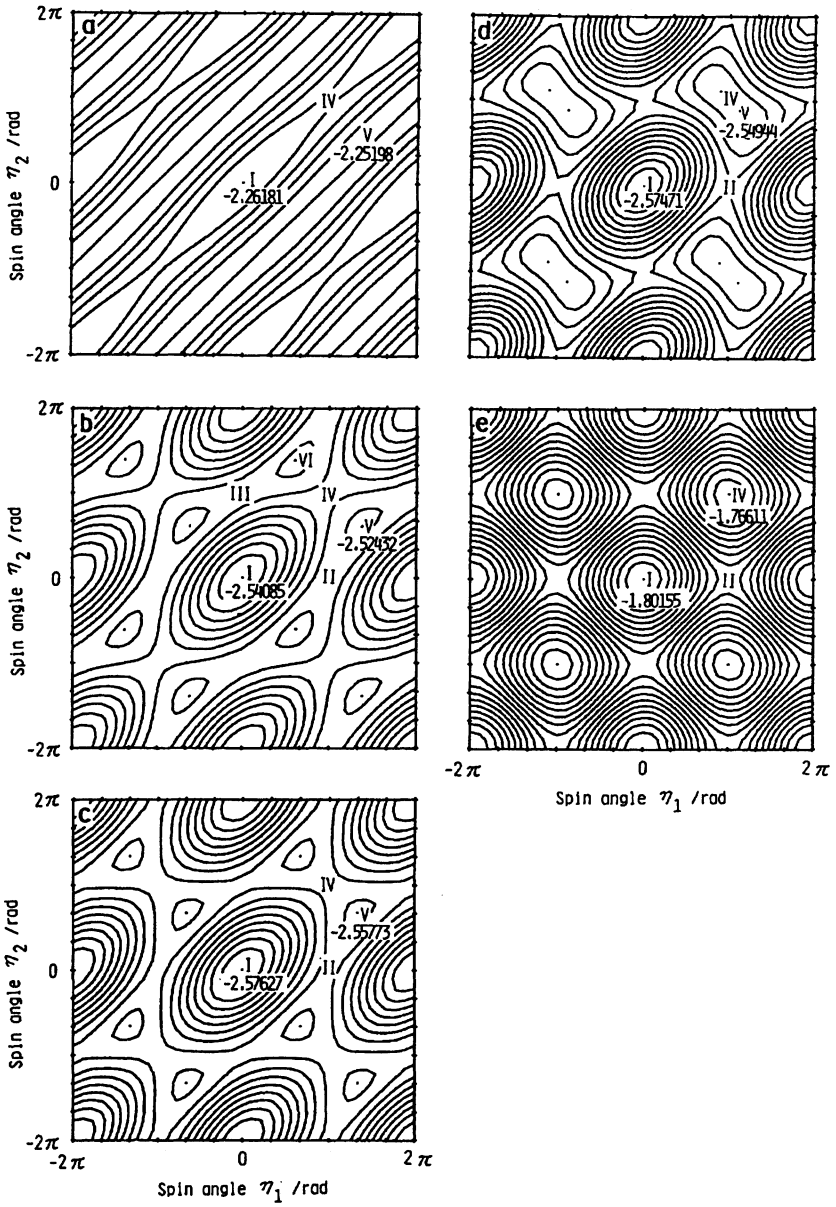

Fig. 5. Contour map of the electronic energy of H_3 system by the GSF-HF wave function in the isosceles triangular approach. Spin angle η_3 is fixed to zero and $R_1=1.0$ Å. The unit of the energy is au and the spacing of contour lines is 0.002 au. a: $R_2=2.0$ Å; b: $R_2=1.0$ Å; c: $R_2=\sqrt{3}/2$ Å; d: $R_2=0.5$ Å; e: $R_2=0.0$ Å.

Table 2. Electronic Energy of Stationary States in Colinear Approach[a] (in au)

Type of stationary state	R_2/Å			
	2.0	1.5	1.0	0.5
I[b]	−2.18556	−2.26725	−2.32299	−2.15791
II[c]	−2.17489	−2.25321	−2.30304	−2.13125
III[d]	−2.18384	−2.26225	−2.31261	−2.14229
IV[d]	−2.17647	−2.25781	−2.31261	−2.14437

a) R_1 is fixed to 1.0 Å. b) Minimum state. c) Maximum state. d) Transition state.

ment in these reactions by the GSF-HF wave function. As a simple model of three-electron three-site system, H_3 molecule is studied. The STO-6G minimal basis set[9] is used with the scale factor 1.24. Three atomic orbitals are orthogonalized by the symmetric orthogonalization procedure and localized well to each atomic site. The spatial orbitals φ_i in the GSF-HF wave function are fixed to these orthogonalized atomic orbitals. The stationary and instability conditions of the electronic energy are studied in terms of the spin angles.

2.1. Reaction Path. The geometry of the model system for the insertion reaction is shown in Fig. 2a. H_1 and H_2 constitute a single chemical bond and H_3 comes down vertically in C_{2v} conformation. This reac-

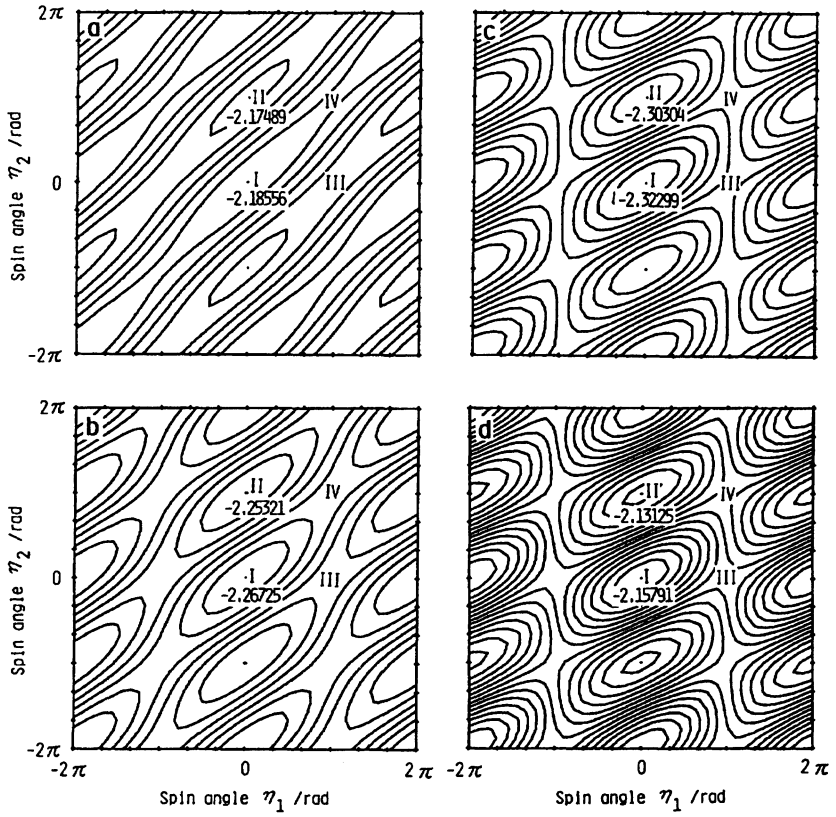

Fig. 6. Contour map of the electronic energy of H_3 system by the GSF-HF wave function in the colinear approach. Spin angle η_3 is fixed to zero and $R_1=1.0$ Å. The unit of the energy is au and the spacing of contour lines is 0.002 au. a: $R_2=2.0$ Å; b: $R_2=1.5$ Å; c: $R_2=1.0$ Å; d: $R_2=0.5$ Å.

tion path is called as an isosceles triangular approach hereafter. Figure 2b shows the abstraction reaction and H_3 attacks the hydrogen molecule along the H_1–H_2 molecular axis. The reaction path in Fig. 2b is called as a colinear approach.

2.2. Classification of Spin Alignments in Radical Reactions. Along the isosceles triangular approach, the instability of spin alignments is studied. The model system has C_{2v} symmetry and the exchange integral is $K_{13}=K_{23}=K$. The spin angles which satisfy the stationary condition are determined by

$$\sin(\eta_1-\eta_2)=\sin(\eta_2-\eta_3)=\sin(\eta_3-\eta_1)=0. \quad (16)$$

When $K\leqq 2K_{12}$, the following spin angles also satisfy the stationary condition,

$$\begin{aligned}\cos(\eta_1-\eta_2)&=(1/2)(K/K_{12})^2-1,\\ \cos(\eta_2-\eta_3)&=-K/(2K_{12}),\\ \cos(\eta_3-\eta_1)&=-K/(2K_{12}).\end{aligned} \quad (17)$$

The instability conditions at these stationary states are obtained by the diagonalization of Eq. 7. They are summarized in Appendix A1. Figure 3 shows the spin structures which satisfy the stationary condition Eq. 16 or Eq. 17. The spin alignments are classified from type I to VI. Type I, which is a high-spin state, is always the most stable state because of the positive exchange integrals. Types V and VI are torsional spin states and the most unstable states. They are degenerate energetically. Types II and III are transition states and they are also degenerate. The spin structures of V and VI depend on the exchange integrals and these stationary states disappear when K becomes larger than the twice of K_{12}.

The stationary condition for the electronic energy in the colinear approach is

$$\sin(\eta_1-\eta_2)=\sin(\eta_2-\eta_3)=0, \quad (18)$$

with the approximation $K_{13}=0$. The instability condition is also summarized in Appendix A2. In Fig. 4, type I (the high-spin state) is again the most stable state. Type II has the maximum energy and types III and IV are transition states. In comparison with the isosceles triangular approach, the spin structure is rather simple and there is no large change of spin alignments along the reaction.

2.3. Electronic Energy Surface of GSF-HF Wave Function. The states which satisfy the stationary condition for the electronic energy were analyzed in the previous section. Here we show global electronic energy surfaces of the GSF-HF wave function.

Figure 5 shows the electronic energy surface of the GSF-HF wave function against the spin angle coordi-

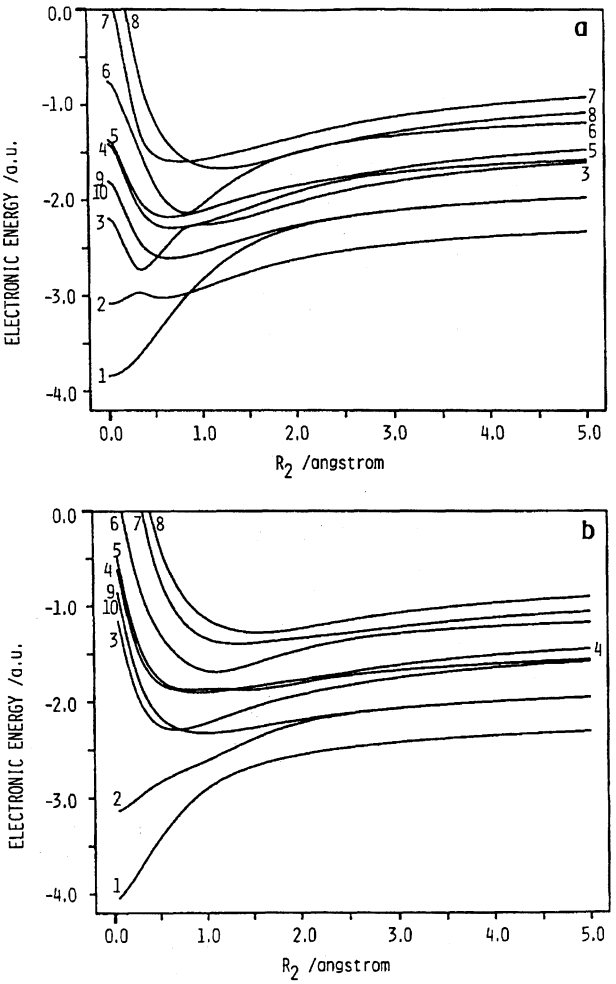

Fig. 7. Electronic energy curves of H_3 system by the full-CI wave function with $R_1=1.0$ Å. The numbers I in the figure represent the indices for the full-CI eigenvectors ${\Psi_I}^{CI}$. a: The isosceles triangular approach; b: the colinear approach.

nate. The bond length R_1 between H_1 and H_2 is fixed to 1.0 Å and the spin angle at the approaching H_3 site is also fixed to zero for simplicity. The spin types in Fig. 3 are again assigned in Fig. 5 and their electronic energies are give in Table 1. When H_3 is far from the H_1–H_2 molecule, the energy is determined by the relative spin angle between η_1 and η_2. In Fig. 5a, the energy changes as a function of $(\eta_1-\eta_2)$ approximately. Type IV has a local triplet-spin structure at H_1–H_2 site and is more stable than the spin types II and III as shown in Fig. 5b. Figure 5c shows the case of the equilateral triangle. Types II, III, and IV are degenerate energetically. Here, types V and VI correspond to the spin angles which have the maximum weight of the doublet state as shown in Fig. 1. In Fig. 5d, types II and III become more stable than type IV and the energy crossing occurs at the equilateral triangle geometry. In Fig. 5e, the stationary states which have the torsional spin alignments (types V and VI) have disappeared.

The GSF-HF energy surface in the colinear approach is shown in Fig. 6. The bond length R_1 of H_1–H_2 molecule is fixed to 1.0 Å and the spin angle at the approaching H_3 site is fixed to zero again. Here K_{13} integral is not neglected. The electronic energies at stationary states are given in Table 2. Figure 6a is the case of $R_2=2.0$ Å and the energy is determined mainly by $(\eta_1-\eta_2)$ as in Fig. 5a. As H_3 site approaches, the feature of the energy surface does not change so largely in comparison with Fig. 5 and there is no large spin rearrangement in the colinear approach.

3. Full-CI Wave Function

3.1. Full-CI Wave Function and Electronic Energy. In Sect.2, we studied the electronic energy surfaces of H_3 system by the GSF-HF wave function. The GSF-HF wave function, however, does not satisfy the quantum mechanical spin-symmetry. Moreover, we required the spatial orbitals to be localized at individual atomic sites. In this section, a full-CI wave function for H_3 system is studied. The full-CI wave function satisfies the pure spin-symmetry and does not have a unitary dependence in the mixing of orbitals, although it is difficult to have a simple classical spin picture. Here, H_3 system is treated again with STO-6G minimal basis.[9] In this case, the full-CI wave function is equivalent to the extended HF wave function.[4] The full-CI manifold consists of 20 spin-symmetry-adapted CSF's. In the following, 10 CSF's which have positive $\hat{S}_z$ eigenvalues are given explicitly:

$$
\begin{aligned}
\Phi_1 &= \|\varphi_1\varphi_2\varphi_3\{2\alpha\alpha\beta-(\alpha\beta+\beta\alpha)\alpha\}/\sqrt{6}\|,\\
\Phi_2 &= \|\varphi_1\varphi_2\varphi_3(\alpha\beta-\beta\alpha)\alpha/\sqrt{2}\|,\\
\Phi_3 &= \|\varphi_1\varphi_1\varphi_2\alpha\beta\alpha\|,\\
\Phi_4 &= \|\varphi_1\varphi_1\varphi_3\alpha\beta\alpha\|,\\
\Phi_5 &= \|\varphi_2\varphi_2\varphi_1\alpha\beta\alpha\|,\\
\Phi_6 &= \|\varphi_2\varphi_2\varphi_3\alpha\beta\alpha\|,\\
\Phi_7 &= \|\varphi_3\varphi_3\varphi_1\alpha\beta\alpha\|,\\
\Phi_8 &= \|\varphi_3\varphi_3\varphi_2\alpha\beta\alpha\|,\\
\Phi_9 &= \|\varphi_1\varphi_2\varphi_3(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)\sqrt{3}\|,\\
\Phi_{10} &= \|\varphi_1\varphi_2\varphi_3\alpha\alpha\alpha\|,
\end{aligned}
\tag{19}
$$

where φ_1, φ_2, and φ_3 are orthogonal spatial orbitals localized to individual atomic sites. The CSF's from Φ_1 to Φ_8 belong to the doublet spin state and the CSF's Φ_9 and Φ_{10} are the quartet state. Other 10 CSF's $\{{\Phi'}_I\}_{I=1,10}$ are constructed by the interchanging the α- and β-spin components in $\{\Phi_I\}_{I=1,10}$. Then we have 20 CI eigenvectors in total, $\{{\Psi_I}^{CI}\}_{I=1,10}$ for positive $\hat{S}_z$ eigenvalues and $\{{{\Psi'}_I}^{CI}\}_{I=1,10}$ for negative $\hat{S}_z$ eigenvalues. ${\Psi_I}^{CI}$ and ${{\Psi'}_I}^{CI}$ are degenerate energetically. Figures 7a and 7b show the electronic energy curves for the isosceles triangular approach and the colinear approach, respectively. The H_1–H_2 length R_1 is fixed to 1.0 Å as in the GSF-HF case. The numbers assigned to CI

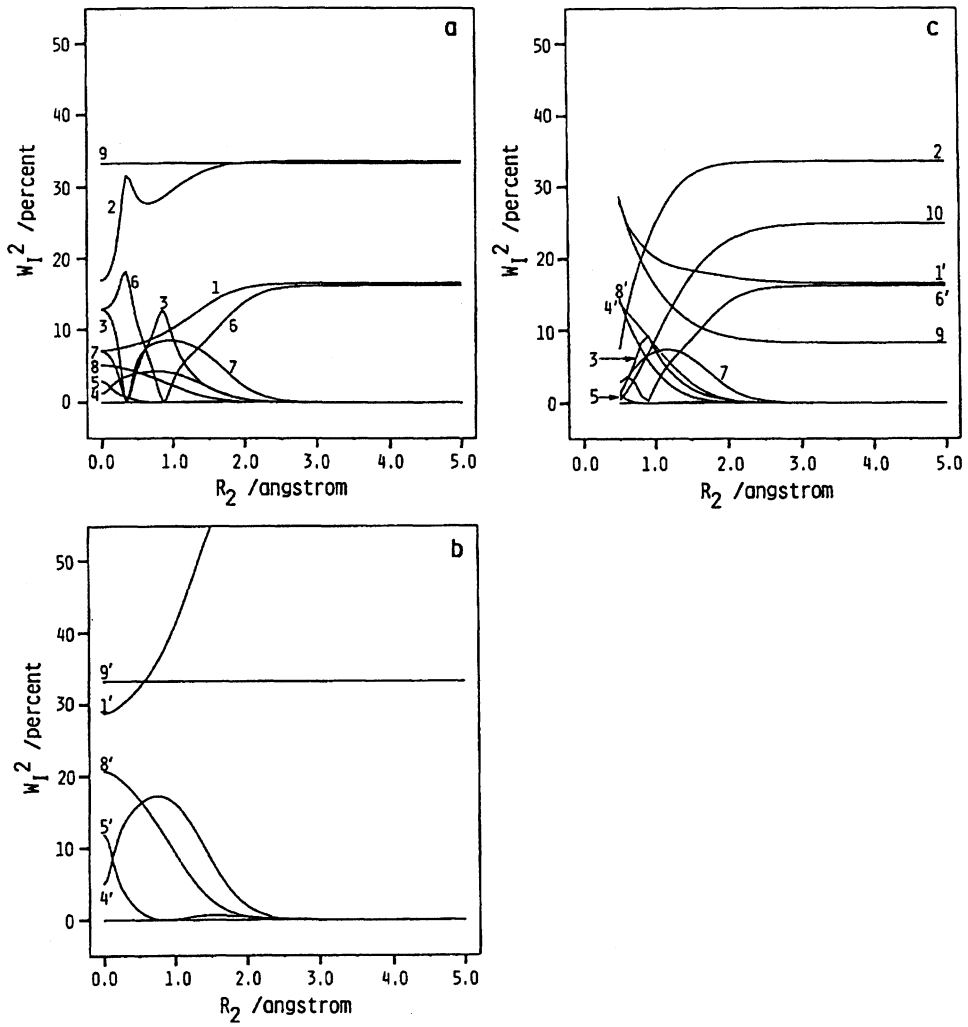

Fig. 8. Weight of the full-CI eigenvectors in the GSF-HF wave function for the isosceles triangular approach. The numbers I and I' in the figure represent the indices for the full-CI eigenvectors ${\Psi_I}^{\mathrm{CI}}$ and ${\Psi'_I}^{\mathrm{CI}}$, respectively. a: Spin alignment Type II; b: Type IV; c: Type V.

eigenvectors are also shown for states with positive $\hat{S}_z$ values. In Fig. 7a, there are crossings of energy curves at the equilateral triangle geometry and interchanges of electronic states occur. In Fig. 7b, the energy curves are rather simple compared to Fig. 7a. The small electronic energy barrier along the colinear approach in the ground state, estimated by the VB-CI with effective exchange parameter,[5] is not found in this case and our result is consistent with Yamaguchi's work.[3]

3.2. Analysis of GSF-HF Wave Function. A projection operator is constructed by the full-CI wave function. The GSF-HF wave function is partitioned to correct quantum mechanical states. The closure relation for the 20 CI eigenvectors is

$$1 = \sum_I^{10} |{\Psi_I}^{\mathrm{CI}}\rangle\langle{\Psi_I}^{\mathrm{CI}}| + \sum_I^{10} |{\Psi'_I}^{\mathrm{CI}}\rangle\langle{\Psi'_I}^{\mathrm{CI}}|. \quad (20)$$

The GSF-HF wave function is partitioned as

$$\begin{aligned} |\Psi^{\mathrm{GSF\text{-}HF}}\rangle &= \sum_I^{10} |{\Psi_I}^{\mathrm{CI}}\rangle\langle{\Psi_I}^{\mathrm{CI}}|\Psi^{\mathrm{GSF\text{-}HF}}\rangle \\ &\quad + \sum_I^{10} |{\Psi'_I}^{\mathrm{CI}}\rangle\langle{\Psi'_I}^{\mathrm{CI}}|\Psi^{\mathrm{GSF\text{-}HF}}\rangle, \quad (21) \\ &= \sum_I^{10} W_I |{\Psi_I}^{\mathrm{CI}}\rangle + \sum_I^{10} W'_I |{\Psi'_I}^{\mathrm{CI}}\rangle, \end{aligned}$$

where W_I and W'_I are the weight of the CI eigenvectors. From the normalization, we have

$$\sum_I^{10} {W_I}^2 + \sum_I^{10} {W'_I}^2 = 1. \quad (22)$$

In the isosceles triangular approach, we have six stationary spin alignments as discussed in Sect.2.2. The GSF-HF wave function with type I spin alignment corresponds correctly to the pure quartet spin state and is identical with the CSF Φ_{10}. It does not mix with other CSF's from the spin-symmetry and constitutes one of the CI eigenvectors by itself. Spin alignments II–III and V–VI are degenerate sets, respectively. Then the GSF-

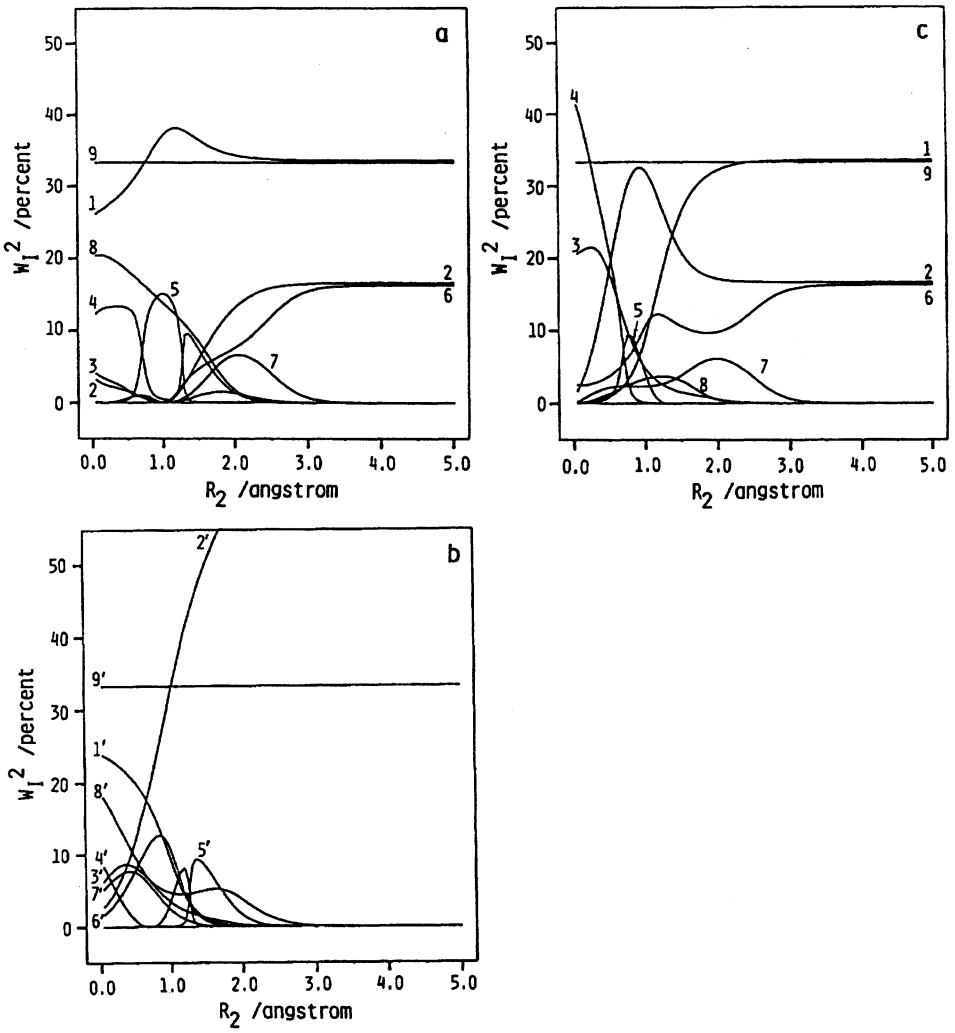

Fig. 9. Weight of the full-CI eigenvectors in the GSF-HF were function for the colinear approach. The numbers I and I' in the figure represent the indices for the full-CI eigenvectors ${\Psi_I}^{\mathrm{CI}}$ and ${\Psi'_I}^{\mathrm{CI}}$, respectively. a: Spin alignment Type II; b: Type III; c: Type IV.

HF wave functions with spin alignments II, IV, and V, are analyzed. Their ${W_I}^2$ are shown in Figs. 8a, 8b, and 8c, respectively. The variation of the weight in Fig. 8a or Fig. 8b is rather complicated and it is hard to assign the GSF-HF electronic structure to a specific CI vector. The spin alignment type II corresponds to $\beta\alpha\alpha$ spin function and IV corresponds to $\beta\beta\alpha$. These are parallel to the change of the CI coefficients for the CSF's Φ_1, Φ_2, Φ_9, ${\Phi'}_1$, and ${\Phi'}_9$ as shown in Appendix A3. Figure 8c is the case of the torsional spin alignment type V and the GSF-HF wave function again represents heavily mixed state. Figures 9a, 9b, and 9c are the case of the spin alignment types II, III, and IV, respectively, in the colinear approach. These figures show again the difficulty to extract the dominant character of the GSF-HF wave function from the CI vectors.

4. Summary

The GSF-HF wave function gives a classical picture for spin freedom and its energy expression leads to the classical Heisenberg model. From the first and the second derivatives of the GSF-HF energy along the classical spin freedom, the stationary and instability conditions of spin alignments are studied. As typical radical reactions, the isosceles triangular and colinear approaches in H_3 system are studied by the ab initio method. In the isosceles triangular approach, the torsional spin alignment state disappears as the reaction proceeds. In the colinear approach, there is no large change in the spin alignments. The partition of the GSF-HF wave function with the full-CI wave functions, however, shows that it is difficult to find a specific CI vector which has the dominant character of the GSF-HF wave function except for the high-spin state. The GSF-HF wave function is therefore a highly mixed state of quantum mechanical states although it provides a bridge between the simple spin picture in the classical Heisenberg model and the quantum mechanical wave function straightforwardly.

Table 3. Instability Analysis in Isosceles Triangular Approach

Type	Eigenvalue	Eigenvector
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$
I[a]	$\lambda_2=K_{12}+K/2$	$u_2=(1/\sqrt{2},\ -1/\sqrt{2},\ 0)$
	$\lambda_3=3K/2$	$u_3=(1/\sqrt{6},\ 1/\sqrt{6},\ -2/\sqrt{6})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $A=(K_{12}^2+3K^2)^{1/2}$
II[b]	$\lambda_2=(-K_{12}+A)/2$	$u_2=(\mathrm{sgn}^{e)}\{1/3-(K_{12}+3K)/6A\}^{1/2},\ \{1/3+(3K-K_{12})/6A\}^{1/2},\ -(1/3+K_{12}/3A)^{1/2})$
	$\lambda_3=(-K_{12}-A)/2$	$u_3=(-\{1/3+(K_{12}+3K)/6A\}^{1/2},\ \{1/3+(K_{12}-3K)/6A\}^{1/2},\ (1/3-K_{12}/3A)^{1/2})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $A=(K_{12}^2+3K^2)^{1/2}$
III[b]	$\lambda_2=(-K_{12}+A)/2$	$u_2=(\{1/3+(3K-K_{12})/6A\}^{1/2},\ \mathrm{sgn}^{e)}\ \{1/3-(K_{12}+3K)/6A\}^{1/2},\ -(1/3+K_{12}/3A)^{1/2})$
	$\lambda_3=(-K_{12}-A)/2$	$u_3=(\{1/3+(K_{12}-3K)/6A\}^{1/2},\ -\{1/3+(K_{12}+3K)/6A\}^{1/2},\ (1/3-K_{12}/3A)^{1/2})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$
IV[c]	$\lambda_2=K_{12}-K/2$	$u_2=(1/\sqrt{2},\ -1/\sqrt{2},\ 0)$
	$\lambda_3=-3K/2$	$u_3=(1/\sqrt{6},\ 1/\sqrt{6},\ -2/\sqrt{6})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$
V,VI[d]	$\lambda_2=K^2/4K_{12}-K_{12}$	$u_2=(1/\sqrt{2},\ -1/\sqrt{2},\ 0)$
	$\lambda_3=-3K^2/4K_{12}$	$u_3=(1/\sqrt{6},\ 1/\sqrt{6},\ -2/\sqrt{6})$

a) Minimum state. b) Transition state. c) If $K_{12}<K/2$, the spin alignment is the maximum state. If $K_{12}=K/2$, we have one positive eigenvalue and two zero-eigenvalues. If $K_{12}>K/2$, the spin alignment is the transition state. d) If $K_{12}=K/2$, we have one positive eigenvalue and two zero-eigenvalues. If $K_{12}>K/2$, the spin alignment is the maximum state. e) If $K_{12}\geqq K$, sgn=1. In other case, sgn=−1.

Table 4. Instability Analysis in Colinear Approach

Type	Eigenvalue	Eigenvector
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $A=(K_{12}^2-K_{12}K_{23}+K_{23}^2)^{1/2}$
I[a]	$\lambda_2=(K_{12}+K_{23}-A)/2$	$u_2=(\{1/3+(2K_{23}-K_{12})/6A\}^{1/2},\ \mathrm{sgn}^{d)}\ \{1/3-(K_{12}+K_{23})/6A\}^{1/2},\ -\{1/3+(2K_{12}-K_{23})/6A\}^{1/2})$
	$\lambda_3=(K_{12}+K_{23}+A)/2$	$u_3=(\{1/3+(K_{12}-2K_{23})/6A\}^{1/2},\ -\{1/3+(K_{12}+K_{23})/6A\}^{1/2},\ \{1/3+(K_{23}-2K_{12})/6A\}^{1/2})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $A=(K_{12}^2-K_{12}K_{23}+K_{23}^2)^{1/2}$
II[b]	$\lambda_2=-(K_{12}+K_{23}-A)/2$	$u_2=(\{1/3+(2K_{23}-K_{12})/6A\}^{1/2},\ \mathrm{sgn}^{d)}\ \{1/3-(K_{12}+K_{23})/6A\}^{1/2},\ -\{1/3+(2K_{12}-K_{23})/6A\}^{1/2})$
	$\lambda_3=-(K_{12}+K_{23}+A)/2$	$u_3=(\{1/3+(K_{12}-2K_{23})/6A\}^{1/2},\ -\{1/3+(K_{12}+K_{23})/6A\}^{1/2},\ \{1/3+(K_{23}-2K_{12})/6A\}^{1/2})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $B=(K_{12}^2+K_{12}K_{23}+K_{23}^2)^{1/2}$
III[c]	$\lambda_2=(K_{12}-K_{23}-B)/2$	$u_2=(\{1/3-(K_{12}+2K_{23})/6B\}^{1/2},\ \{1/3+(K_{23}-K_{12})/6B\}^{1/2},\ -\{1/3+(2K_{12}+K_{23})/6B\}^{1/2})$
	$\lambda_3=(K_{12}-K_{23}+B)/2$	$u_3=(-\{1/3+(K_{12}+2K_{23})/6B\}^{1/2},\ \{1/3+(K_{12}-K_{23})/6B\}^{1/2},\ \{1/3-(2K_{12}+K_{23})/6B\}^{1/2})$
	$\lambda_1=0$	$u_1=(1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$ $B=(K_{12}^2+K_{12}K_{23}+K_{23}^2)^{1/2}$
IV[c]	$\lambda_2=(-K_{12}+K_{23}+B)/2$	$u_2=(\{1/3-(K_{12}+2K_{23})/6B\}^{1/2},\ \{1/3+(K_{23}-K_{12})/6B\}^{1/2},\ -\{1/3+(2K_{12}+K_{23})/6B\}^{1/2})$
	$\lambda_3=(-K_{12}+K_{23}-B)/2$	$u_3=(-\{1/3+(K_{12}+2K_{23})/6B\}^{1/2},\ \{1/3+(K_{12}-K_{23})/6B\}^{1/2},\ \{1/3-(2K_{12}+K_{23})/6B\}^{1/2})$

a) Minimum state. b) Maximum state. c) Transition state. d) If $K_{12}\geqq K_{23}$, sgn=1. In other case, sgn=−1.

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Appendix

A1. Instability Analysis in Isosceles Triangular Approach. The eigenvalues and eigenvectors of the Hessian matrix Eq. 7 are summarized in Table 3. Each of spin alignments has one zero-eigenvalue at least. The minimum state has two positive eigenvalues and the maximum state has two negative eigenvalues. The transition state has one negative and one positive eigenvalues.

A2. Instability Analysis in Colinear Approach. The eigenvalues and eigenvectors of the Hessian matrix Eq. 7 are summarized in Table 4 for the colinear approach with the approximation $K_{13}=0$.

A3. W_I and CI Coefficients. When each of the spin angles in $n\pi$ (n is an integer), the classical spin alignment corresponds to a simple product of spin functions, α and β. For the case of three spins, the spin alignments (π, 0, 0) and (π, π, 0) correspond to the spin functions $\beta\alpha\alpha$ and $\beta\beta\alpha$, respectively. The non-zero overlap integrals between these spin functions and CSF's given in Eq. 19 are

$$\langle\|\varphi_1\varphi_2\varphi_3\beta\alpha\alpha\|\|\Phi_1\rangle = -1/\sqrt{6},$$
$$\langle\|\varphi_1\varphi_2\varphi_3\beta\alpha\alpha\|\|\Phi_2\rangle = -1/\sqrt{2},$$

$$\langle\|\varphi_1\varphi_2\varphi_3\beta\alpha\alpha\|\|\Phi_9\rangle = 1/\sqrt{3},$$

and

$$\langle\|\varphi_1\varphi_2\varphi_3\beta\beta\alpha\|\|\Phi'_1\rangle = 2/\sqrt{6},$$
$$\langle\|\varphi_1\varphi_2\varphi_3\beta\beta\alpha\|\|\Phi'_9\rangle = 1/\sqrt{3}.$$

Then the weight of these classical spin alignments changes in parallel with the coefficients C_{IJ} or C'_{IJ} for these CSF's in CI eigenvectors as

$$\begin{aligned} W_I &= \langle\|\varphi_1\varphi_2\varphi_3\beta\alpha\alpha\|\|\Psi_I{}^{CI}\rangle \\ &= -(1/\sqrt{6})C_{I1} - (1/\sqrt{2})C_{I2} + (1/\sqrt{3})C_{I9} \end{aligned}$$

and

$$\begin{aligned} W'_I &= \langle\|\varphi_1\varphi_2\varphi_3\beta\beta\alpha\|\|\Psi'_I{}^{CI}\rangle \\ &= (2/\sqrt{6})C'_{I1} + (1/\sqrt{3})C'_{I9}. \end{aligned}$$

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