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Extended Hartree–Fock (EHF) Theory in Chemical Reactions

II. Symmetry Properties of the EHF Wavefunctions Constructed by the Magnetically Ordered General Spin Orbitals

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The roles of orbital, spin and permutation symmetries in the extended Hartree–Fock (EHF) wavefunction are investigated in relation to the applications of group theory to chemical reactions. The utility of the magnetically ordered set for an extended HF calculation is pointed out. The relative stabilities among linear Hückel and Möbius three-center three-electron (3,3) systems are investigated by the generalized Hartree–Fock (GHF) and EHF methods in order to confirm the reliability of the valence-bond (VB) selection rule for free radical reactions.

Key words: Extended Hartree–Fock orbital, spin and permutation symmetries

1. Introduction

The correlation and spin correlation effects play an essential role to determine the chemical behaviour of reacting systems, i.e., the electronic mechanisms of chemical reactions. Previously it has been shown that the orbital and spin degeneracy problems are very important to elucidate the free radical reaction mechanisms on the basis of the Heisenberg models [1] and the Hartree–Fock methods [2, 3]. Although the Hartree–Fock method provides useful information concerning the electronic structures of reacting molecules, it has intrinsic deficiencies such as symmetry-breaking properties. Then it seems important and interesting to investigate the electronic structures of reacting molecules by using the symmetry-adapted wavefunctions such as the extended Hartree–Fock (EHF) wavefunction [4].

The spin-free Hamiltonian $\mathscr{H}_{\mathrm{SF}}$ commutes with the symmetry elements of time-reversion (T), permutation (S_N) spin rotation (SR) and point group (P_n):

$$[\mathscr{H}_{\mathrm{SF}}, \mathscr{X}]=0, \quad \mathscr{X} \in T, S_N, SR, P_n \tag{1}$$

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Since the wavefunction of a system is not a physical observable, it is therefore not necessarily required to be invariant under the symmetry operations of that system. But the symmetry of the system imposes some restrictions on the behaviour of the wavefunction. Thus the group theories treating the orbital (P_n), spin (magnetic) ($T \times SR$) and permutation (S_N) symmetries are very important to derive the group-theoretical selection rules of chemical reactions. In the previous paper [4] which is referred to as the Part I of this series, we have briefly discussed the utility of the group theoretical approach in the case of the equilateral H_3 radical. Thus the above success suggests the utility of the extended Hartree–Fock formalism by use of the magnetically ordered general spin orbitals (GSO).

Generally speaking, there are spin-free approach [5] and space-spin formalism which involve the generalized Hartree–Fock (GHF) approximation [2, 3, 6–8]. The permutation (S_N) and magnetic ($T \times SR$) symmetries are closely related to the former and latter approaches, respectively. The former approach is familiar in relation to the simple valence-bond (VB) approach [4, 5] for molecules. The latter method is used to elucidate the magnetism of solids [9]. However these approaches are independently developed in the fields of molecular and solid-state physics, respectively. Thus a theoretical approach to combine the spin-free and spin-dependent formalisms is of importance and interest. The approach can be applied to elucidate the electronic mechanisms of chemical reactions. For example, the electronic mechanisms of ion and radical reactions are closely related to the ionic and antiferromagnetic phases of solids, respectively [9]. Thus the primary interest of this series of papers lies in the theoretical investigation of the interrelationships between the electronic mechanisms of chemical reactions and electronic correlations on the basis of the symmetry-adapted, i.e., extended Hartree–Fock, wavefunctions.

In the present paper, as a first step to the purpose, we wish to investigate generally the behaviour of the wavefunctions constructed by the generalized Hartree–Fock solutions by using the permutation operator. Simple EHF wavefunctions by use of the magnetically ordered GSO's will be constructed to elucidate the electronic structures of linear, Hückel and Möbius three-center three-electron (3,3) systems.

2. Permutation Symmetry and Spin-Symmetry Adapted Wavefunctions

The wavefunction of a N-electron system is expressed by the natural orbital (NO) set $\{\phi_i\}$ which belongs to the irreducible representation of the point group of the system. In the present paper we construct the wavefunctions in the HF type orbital approximation. The one-electron orbitals are generally expressed by orthonormalized two-component spinors [6–9]:

$$\psi_A = \psi_{1A}\eta_+ + \psi_{2A}\eta_- = \begin{pmatrix} \psi_{1A} \\ \psi_{2A} \end{pmatrix} \qquad (2)$$

$$\langle \psi_A \mid \psi_B \rangle = \delta_{AB}$$

The orbital components are given by the natural orbitals as

$$\psi_{1A}=\sum_i a_{1i}\phi_i, \qquad \psi_{2A}=\sum_i a_{2i}\phi_i \tag{3}$$

The Hartree product of N orbitals is given by

$$\phi_{\mathrm{H}}=\psi_1\,\psi_2\,\psi_3\ldots\psi_N \tag{4}$$

Since the above wavefunction has not the pure S_z component, the projection operator $\mathscr{P}_{\mathscr{S}_z}$ is necessary as

$$\mathscr{P}_{\mathscr{S}_z}=\prod_{k\pm M}(\mathscr{S}_z-k)\,/\,(M-k) \tag{5}$$

where

$$\hat{\mathscr{S}}_z=\sum_i\frac{1}{2}\boldsymbol{\sigma}_z(i), \quad \boldsymbol{\sigma}_z(i)=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{6}$$

Then the $\mathscr{S}_z$ projected wavefunction is given by

$$\Phi_{\mathrm{H}}(M)=\sum_l \Phi_l\,\Theta_l(M) \tag{7}$$

where

$$\Phi_l=\sum_\beta d_{l\beta}\,(\phi_i(i)\,\phi_j(j)\ldots\phi_k(k))_\beta \tag{8}$$

$$\Theta_l(M)=\eta(i)\,\eta(j)\ldots\eta(k)\ (\eta=\eta_+\text{ or }\eta_-) \tag{9}$$

Each Φ_l involves natural orbital products arranged in ascending numerical order. The above $\mathscr{S}_z$ projected wavefunction however involves the wavefunctions with various $\mathscr{S}^2$ components. Then the projection with $\mathscr{S}^2$ is necessary to obtain the pure spin symmetry. From the Pauli principle, the allowed partition of N electrons are given by

$$[\tilde{\alpha}]=[2^p,1^{\mathrm{N}-2p}] \tag{10}$$

The spin quantum number to be associated with the partition $\tilde{\alpha}$ is

$$S=N/2-p \tag{11}$$

The projection operator to obtain the total spin components S is given by the structure basis [5, 10, 11] or the matric basis [12–19]. From the latter it is given by

$$\mathscr{P}_{\hat{\mathscr{S}}^2}=\frac{1}{f^\alpha}\sum_i C_i\mathscr{Y}_i^\alpha=\frac{1}{f^\alpha}\sum_i C_i\sum_j \boldsymbol{e}_{ij}^{\tilde{\alpha}}\,\boldsymbol{e}_{ij}^{\tilde{\alpha}} \tag{12}$$

where f^α is the dimension of the irreducible representation matrix of the partition α. The operators $\boldsymbol{e}_{ij}^{\alpha}$ and $\boldsymbol{e}_{ij}^{\tilde{\alpha}}$ act on the spin and space parts, respectively, and select the pure symmetry components. The coefficients C_i are related with the so-called spin degeneracy problem. The spin symmetry adapted wavefunction therefore is given by

$$\Phi_{\mathrm{H}}(S,M)=\mathscr{P}_{\mathrm{spin}}\,\Phi_{\mathrm{H}}=\sum_j D_j\,\Phi_j(S,M) \tag{13}$$

where $\Phi_j(S, M)$ is given by the Slater determinants and the spin symmetry projection operator is given by

$$\mathscr{P}_{\text{spin}} = \mathscr{P}_{\hat{\mathscr{S}}^2} \; \mathscr{P}_{\hat{\mathscr{S}}^2} \tag{14}$$

The coefficients D_j are the functions of a_{ij} and C_i which are determined by the SCF procedures [13–15, 19].

3. Time-Reversal Symmetry and Spin Moment Inversion

The time-reversal operation $\mathscr{T}$ is defined by

$$\mathscr{T} = \prod_j [i\sigma_y(j)] \, \mathscr{K} \tag{15}$$

where $\mathscr{K}$ is the operation of the complex conjugation. In order to satisfy Wigner's theorem, if Φ_{E} is an eigenfunction of $\mathscr{H}_{\mathrm{SF}}$ then $\mathscr{T}\Phi_{\mathrm{E}}$ is also an eigenfunction of $\mathscr{H}_{\mathrm{SF}}$ which has the same energy E as Φ_{E}:

$$\int \Phi_{\mathrm{E}}^{\star} \mathscr{H}_{\mathrm{SF}} \Phi_{\mathrm{E}} \, d\tau = \int (\mathscr{T}\Phi_{\mathrm{E}})^{\star} \mathscr{H}_{\mathrm{SF}} (\mathscr{T}\Phi_{\mathrm{E}}) \, d\tau = \mathrm{E} \tag{16}$$

Then the projected HF wavefunction should have the above property.

The projection operator $\mathscr{P}_{\mathscr{S}^2}$ of the total spin component S commutes with the time-reversal operation:

$$[\mathscr{P}_{\mathscr{S}^2}, \mathscr{T}] = 0 \tag{17}$$

The projection operator $\mathscr{P}_{\mathscr{S}_z}$, on the other hand, does not commute with the $\mathscr{T}$ operation since it involves the $\boldsymbol{\sigma}_z$ operator. Generally speaking, the wavefunction for the spin-free Hamiltonian thus cannot be the simultaneous eigenstate of $\mathscr{S}_z$ and $\mathscr{T}$ operators. In the present spin-symmetry adapted formulation, the $\boldsymbol{\sigma}_z$ operator transforms as

$$[i\boldsymbol{\sigma}_y(j)\mathscr{K}] \, \boldsymbol{\sigma}_z(j) \, [i\boldsymbol{\sigma}_y(j)\mathscr{K}]^{-1} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \tag{18}$$

Thus the inversion of the spin moment occurs under the time-reversion.

The projection operator $\mathscr{P}_{\mathscr{S}_z}$ is also converted as

$$\mathscr{P}_{\mathscr{S}^2} = \mathscr{T}\mathscr{P}_{\mathscr{S}_z}\mathscr{T}^{-1} = \prod_{k \mp M} (- \;\hat{\mathscr{S}}_z - k) \,/\, (M - k) \tag{19}$$

where $\mathscr{P}'_{\hat{\mathscr{S}}_z}$ extracts the $-M$ component of $\mathscr{S}_z$. The orbitals transform as

$$i\boldsymbol{\sigma}_y \mathscr{K} \psi_A = -\psi_{1A}^{\star} \eta_- + \psi_{2A}^{\star} \eta_+ = \begin{pmatrix} \psi_{2A}^{\star} \\ -\psi_{1A}^{\star} \end{pmatrix} \tag{20}$$

Since the down spin components should be added up instead of up spin parts (vice versa) to obtain the $-M$ value, the projected HF wavefunction therefore transforms as

$$\mathscr{T}\Phi_{\mathrm{H}}(S, M) = \mathscr{T}_{\mathscr{S}^2}\mathscr{P}_{\hat{\mathscr{S}}_z}\Phi_{\mathrm{H}} = \mathscr{P}_{\mathscr{S}^2}\mathscr{T}\mathscr{P}_{\hat{\mathscr{S}}_z}\mathscr{T}^{-1}\mathscr{T}\Phi_{\mathrm{H}} = (-1)^{\mathrm{N}/2+\mathrm{M}}\Phi_{\mathrm{H}}^{\star}(S, -M) \tag{21}$$

The time-reversal operation $\mathscr{T}$ thus causes the spin inversion. However the energy E remains invariant as shown in Eqs. (16) and (21), satisfying Wigner's theorem. Thus the time-reversal symmetry operation itself is independent of the energy calculation by the spin-symmetry adapted wavefunction.

The time-reversal symmetry is closely related to the stability of the Hartree–Fock solutions [2, 3, 7, 20–22] and the so-called complex molecular orbital method [23–25]. The spatial parts of spinors in Eq. (2) are decomposed into real and complex parts as

$$\psi_A = (\psi'_{1A} + i\psi''_{1A})\eta_+ + (\psi'_{2A} + i\psi'_{2A})\eta_- \tag{22}$$

Then the spin symmetry adapted wavefunctions are also decomposed into two parts:

$$\Phi_{\mathrm{H}}(S, M) = \Phi_{\mathrm{H}}(S, M)_{\mathrm{R}} + i\Phi_{\mathrm{H}}(S, M)_{\mathrm{C}} \tag{23}$$

The real and complex parts can be extracted by using the time-reversal operator as

$$\begin{aligned} \Phi_{\mathrm{H}}(S, M) &= \mathscr{P}^{\pm}_{\mathrm{time}} \Phi_{\mathrm{H}}(S, M) \\ &= \begin{cases} 1/2\,[\Phi_{\mathrm{H}}(S, M)_{\mathrm{R}} + (-1)^{\mathrm{N}/2+\mathrm{M}} \Phi_{\mathrm{H}}(S, M)_{\mathrm{R}}] \\ i/2\,[\Phi_{\mathrm{H}}(S, M)_{\mathrm{C}} + (-1)^{\mathrm{N}/2+\mathrm{M}} \Phi_{\mathrm{H}}(S, M)_{\mathrm{C}}] \end{cases} \end{aligned} \tag{24}$$

where

$$\mathscr{P}^{\pm}_{\mathrm{time}} = 1/2(1 \pm \mathscr{T}) \tag{25}$$

The transformation properties of the above operators are as follows:

$$\begin{aligned} &\mathscr{T}\mathscr{P}^{\pm}_{\mathrm{time}} = \pm\mathscr{P}^{\pm}_{\mathrm{time}},\ (\mathscr{P}^{\pm}_{\mathrm{time}})^2 = \mathscr{P}^{\pm}_{\mathrm{time}},\ \mathscr{T}^2 = 1 \text{ for } N = 2m \text{ (even)} \\ &\mathscr{T}\mathscr{P}^{\pm}_{\mathrm{time}} = \mp\mathscr{P}^{\pm}_{\mathrm{time}},\ (\mathscr{P}^{\pm}_{\mathrm{time}})^2 \neq \mathscr{P}^{\pm}_{\mathrm{time}},\ \mathscr{T}^2 = -1 \text{ for } N = 2m+1 \text{ (odd)} \end{aligned} \tag{26}$$

Then the wavefunctions can be constructed to be the simultaneous eigenstates of $\mathscr{T}$ and $\mathscr{P}_{\mathscr{S}_z}$ in the case of even electron systems with $M = 0$ where $\mathscr{P}^{+}_{\mathrm{time}}$ and $\mathscr{P}^{-}_{\mathrm{time}}$ are the projection operators which extract the time-reversal symmetric and antisymmetric components, respectively. However such procedures do not exist in the case of odd-electron systems (Kramers degeneracy).

The real and complex components can also be extracted by means of the projection operators as

$$\begin{aligned} \mathscr{P}^{+}_{\mathrm{alter}} \Phi_{\mathrm{H}}(S, M) &= \Phi_{\mathrm{H}}(S, M)_{\mathrm{R}} \\ \mathscr{P}^{-}_{\mathrm{alter}} \Phi_{\mathrm{H}}(S, M) &= i\Phi_{\mathrm{H}}(S, M)_{\mathrm{C}} \end{aligned} \tag{27}$$

where $\mathscr{P}^{\pm}_{\mathrm{alter}}$ are defined by the complex conjugation operator $\mathscr{K}$ as

$$\mathscr{P}^{\pm}_{\mathrm{alter}} = 1/2(1 \pm \mathscr{K}) \tag{28}$$

These projection operators are closely related with the alternancy symmetry breaking [26] and parity mixing [23–25] procedures which lead to the complex molecular orbitals. Although many variational parameters can be introduced by using the complex MO's, a general study of the above symmetry breaking modes is very difficult in the case of the extended HF method [23–25, 26, 27].

In the case of the HF theory, the complex charge-density wave (CCDW) solutions for even-electron systems are the typical complex molecular orbitals. The CCDW solutions arise from the singlet instability breaking the time-reversal symmetry and have the closed-shell forms, i.e., $N/2$ pair orbitals, as

$$\psi_A^{\pm} = \psi_A \eta_{\pm} (A = 1, \ldots, N/2), \quad \psi_A \neq \psi_A^{*} \tag{29}$$

The utility of the CCDW-type solutions for the extended HF calculations has been shown in some papers [23–25, 28].

4. Local Spin (Magnetic) Symmetry and Magnetic Orderings in Spinors

There are three different symmetry operations for orthogonal spinors: 1) time-reversion (T), 2) spin rotation (SR) and 3) spatial symmetry (P_n) operations. The role of the time-reversal operation was already discussed in Sect. 3. The spin rotation operation $u(\boldsymbol{e}, \Theta)$ around the axis $\boldsymbol{e}$ by the angle Θ are expressed by the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ which are the generators of the so-called $SU(2)$ group:

$$\begin{aligned} u(\boldsymbol{e}, \Theta) &= \exp(-\Theta/2\, \boldsymbol{\sigma}\cdot\boldsymbol{e}) \\ &= \cos\Theta/2 - i(\boldsymbol{\sigma}\cdot\boldsymbol{e})\sin\Theta/2 \end{aligned} \tag{30}$$

The spatial symmetry operations are familiar. Then any orbital set belongs to a subgroup of the direct product group, i.e., the magnetic double point group $M_n = T \times SR \times P_n$ [4, 9, 29]. The most symmetry breaking orbitals set involves no symmetry element of the group M_n. The restricted Hartree–Fock (RHF) orbital set of the ground singlet state, on the other hand, has all the elements of M_n. There are various levels of the symmetry-breaking orbital sets as well as the above specific cases. In the case of the HF theory, the forms of the ground HF solutions are determined by the stability conditions [2, 3].

The single Slater determinant built from the spinors gives the second-order reduced density matrices for parallel and antiparallel spin pairs as

$$P_2^f(1,2) = \tfrac{1}{2}[P_1(1)P_1(2) - P_1^2(1,2)] + \tfrac{1}{2}[S_i(1)S_i(2) - S_i^2(1,2)] \tag{31}$$

$$P_2^c(1,2) = \tfrac{1}{2}[P_1(1)P_1(2) - S_i(1)S_i(2)] - \tfrac{1}{2}[S_j^2(1,2) + S_k^2(1,2)] \tag{32}$$

where P_1 is the density and $S_m (m = x, y, z)$ is the spin density matrix of the m-direction. The pair function P_2^f of the parallel spin disappears for 2 → 1, indicating the so-called Fermi-hole. The pair function P_2^c of the opposite spin, on the other hand, is reduced for 2 → 1 to

$$P_2^c(1) = 1/2\,[P_1^2(1) - \sum_m S_m^2(1)] \tag{33}$$

Thus the spin densities are closely related to the decrease of pair function of opposite spin in the case of the HF solution, indicating the healing of the Coulomb repulsion. The total pair function is given by

$$P_2(1,2) = P_2^f(1,2) + P_2^c(1,2) = P_1(1)P_1(2) - 1/2\,[P_1^2(1,2) + \sum_m S_m^2(1,2)] \tag{34}$$

Thus the off-diagonal parts of the spin density matrices are related to the exchange correlations. Therefore the structures of pair functions can be characterized by the density and spin density matrices in the HF scheme.

The characteristic of the exchange phenomena can be directly extracted from the scalar product of two spins $\mathscr{S}(1)\cdot\mathscr{S}(2)$ because of the remarkable relation due to Dirac:

$$\mathscr{S}(1)\cdot\mathscr{S}(2)=1/4[2\mathscr{P}_{12}-1] \tag{35}$$

where $\mathscr{P}_{12}$ is the permutation operator of two spins. Then the so-called spin correlation function K_2 [2, 9] can be introduced as

$$\begin{aligned} K_2(r_1, r_2) &= \iint \mathscr{S}(1)\cdot\mathscr{S}(2)\, \rho_2(r_1, r_2, r_1', r_2')\, dS_1\, dS_2 \\ &= \tfrac{1}{4}\sum S_m(r_1)S_m(r_2)+\tfrac{1}{8}\sum S_m^2(r_1, r_2)-\tfrac{3}{8}P_1^2(r_1, r_2) \end{aligned} \tag{36}$$

where ρ_2 is the second-order density matrix.
Thus the spin correlation function is isotopic and involves the product of the diagonal parts of spin density matrix which is related to the spin exchange phenomena. The classical (K_2^c) and quantum (K_2^q) parts of the K_2-function are defined by

$$\begin{aligned} K_2^c(r_1, r_2) &= \tfrac{1}{4}\sum_m S_m(r_1)S_m(r_2) \\ K_2^q(r_1, r_2) &= \tfrac{1}{8}\sum_m S_m^2(r_1, r_2)-\tfrac{3}{8}P_1^2(r_1, r_2) \end{aligned} \tag{37}$$

The classical precession picture of spin correlation can be directly expressed by the K_2^c-function. For example, an antiparallel spin arrangement can be regarded as a pictorial expression of the singlet type spin correlation. The quantum part, on the other hand, comes from the quantum mechanical exchange phenomena of electrons and cannot be explained classically.

The above results indicate the importance of the spin-symmetry breaking for the incorporation of correlation effects [2, 3, 26] in the case of the HF approximation. The familiar DODS solution has only the *i*-component of the spin density. The helical SDW solution, on the other hand, has two components of spin density. These conditions on the spin density are satisfied by the orbital pairings in the HF approximation [7]. Since the spin rotations are expressed by the Pauli matrices, the orbital set must be invariant under the σ_i operation in order to retain the axial symmetry for the axis *i*. The S_x modulate SDW (ASDW) [2, 3, 7] solution ($S_z=S_y=0$) is closely related to the spin-flipping (SF) instability of the restricted HF solution:

$$\begin{aligned} &\boldsymbol{\sigma}_x\psi_A^{\pm}=\psi_A^{\pm} \quad \text{or} \quad \psi_A^{\mp} && (A=1, 2, \,..p) \\ &\boldsymbol{\sigma}_x\psi_A=\psi_A && (A=2p+1, \,..) \end{aligned} \tag{38}$$

The planar symmetry operation, on the other hand, is expressed by the π rotation around the *i*-axis followed by the time reversion $\boldsymbol{t}=i\boldsymbol{\sigma}_y\mathscr{K}$

$$\boldsymbol{\sigma}_i'=\boldsymbol{t}\boldsymbol{\sigma}_i \; (i=x, z) \tag{39}$$

Then the HSDW orbitals with σ'_z symmetry, i.e., $s_z=0$, transform as

$$\begin{aligned} &\sigma'_z\psi_A^{\pm}=\psi_A^{\pm} \quad \text{or} \quad \psi_A^{\mp} && (A=1,2,\ldots p) \\ &\sigma'_z\psi_A=\psi_A && (A=2p+1,\ldots) \end{aligned} \tag{40}$$

The stability analyses [2, 3, 7] indicate that the singlet or spin-unflipping instability does not occur in the ground HF solution in most cases. The spatial symmetry-breaking is thus not so effective for the Coulomb-hole healing in the HF approximation. Then the spatial parts in Eqs. (2), (38) and (40) are reduced into the simple forms which involve one natural orbital. This leads frequently to the full magnetic ordering in the ground HF solution. The magnetically ordered ASDW solution is given by

$$\begin{aligned} &\psi_{1A}=\phi_i\cos\lambda/2, \quad \psi_{2A}=\phi_j\sin\lambda/2 && (A=1,2,\ldots p) \\ &\psi_{1A}=\psi_{2A}=\phi_k && (A=2p+1,\ldots) \end{aligned} \tag{41}$$

Similarly the magnetically ordered HSDW solution is given in the natural orbital form [2, 3, 7] as

$$\begin{aligned} &\psi_{1A}=\phi_i\cos\lambda/2, \quad \psi_{2A}=\phi_j^*\sin\lambda/2 && (A=1,2,\ldots p) \\ &\psi_{1A}=\phi_k, \quad \psi_{2A}=\phi_k^* && (A=2p+1,\ldots) \end{aligned} \tag{42}$$

There are various spatial symmetry-nonadapted ASDW (NASDW) [3] and HSDW (NHSDW) solutions with higher energies. The spatial parts of these solutions involve the various natural orbitals as shown in Eq. (2).

5. Simple Extended Hartree–Fock Wavefunctions

The present results indicate that the extended HF wavefunction can be constructed by any orbital set if the necessary projections are performed [4, 10–19, 24–26] before the SCF procedure:

$$\Phi_\text{E}(S,M)=\mathscr{P}_\text{space}\mathscr{P}_\text{alter}\mathscr{P}_\text{spin}\Phi_\text{H} \tag{43}$$

where $\mathscr{P}_\text{space}$ is the projection operator relating with the spatial symmetry projection. We also utilize the variational parameters coming from the spin degeneracy in the spin-optimized SCF scheme [13–19] in contrast to the PHF scheme [16, 30].

Generally speaking, the more symmetry-breaking orbitals are the more useful to incorporate the dynamical correlation effects in the extended Hartree–Fock scheme because of the variational principle. Then the spatial-symmetry non-adapted orbitals are important to incorporate dynamical correlation effects as much as possible on the basis of the EHF scheme. The spatial-symmetry breakings, however, lead to the non-orthogonality of trial orbitals in many cases. The non-orthogonality makes the construction of determinantal matrix elements much more time-consuming than orthogonal orbital set. This is likely to cause serious trouble if the method is to be used for large systems. Then the ortho-normalized spinors are utilized in the present EHF calculations.

The other problem lies in the fact that simple criterions to select the effective variational parameters are not presented in the case of the EHF method. For this purpose one can conveniently use the results of the stability analyses of the HF solutions. In fact, the eigenvectors belonging to the lowest roots of the stability conditions directly suggest the form of the orbitals to be used. The previous stability analyses [2, 3] indicate that the ground HF solutions change as: RHF → ASDW → HSDW → HSW, according to the complexity of correlation effects where the helical spin wave (HSW) has no symmetry property concerning spin density. Thus the ground HF solutions are closely related to the modulations of spin density as can be recognized in Eqs. (34) and (36). Then it seems useful enough to construct the relatively simple EHF wavefunction from the HF-like orbital set for applications to molecular calculations as shown in Table 1. The present EHF scheme is a direct extension of the HF method which has a wrong spin property [2, 3, 7]. Although the dynamical correlation cannot be incorporated by using the HF-type magnetically ordered spinors, the method, however, can sufficiently incorporate the static (non-dynamical) correlations coming from the orbital and spin degeneracies which play an essential role to determine the chemical behaviours of reacting molecules, i.e., the mechanisms of chemical reactions. In the present paper we discuss the simple two- and three-electron systems as illustrations.

Table 1. Interrelationships between various effective Hamiltonians

Classical Heisenberg model (spin arrangement)	Hartree–Fock (HF)	Projected Hartree–Fock (PHF)	Spin-optimized SCF (SO SCF)
Axial (one dimension)	ASDW	ASDW PHF	ASDW SO SCF
Planar (two dimension)	HSDW	HSDW PHF	HSDW SO SCF
Random (three dimension)	HSW	HSW PHF	HSW SO SCF

5.1. Homopolar Two-Center Two-Electron System

The homopolar two-center two-electron system is first examined. The natural orbitals are given by the orthogonalized atomic orbitals (OAO) as

$$\phi_{\pm 1} = 1/\sqrt{2}(\chi_1 \pm \chi_2) \tag{44}$$

where the signs + and − denote the bonding and antibonding orbitals, respectively. The spin- and time-reversal symmetry breaking occupied MO's are given, respectively, by

$$\begin{aligned} \psi_s^{\pm} &= \phi_1 \cos \lambda/2\eta_{\pm} + \phi_{-1} \sin \lambda/2\eta_{\mp} \\ \psi_t^{\pm} &= (\phi_1 \cos \lambda/2 + i\phi_{-1} \sin \lambda/2)\eta_{\pm} \end{aligned} \tag{45}$$

The S_x modulate ASDW [2, 3, 7] and complex charge-density wave (CCDW) solutions [22, 23] are given by the above orbitals as

$$\Phi_{\text{ASDW}} = |\psi_s^+ \psi_s^-| = D_1|\phi_1 \bar{\phi}_1| + D_2/2\{|\bar{\phi}_1 \bar{\phi}_{-1}| + |\phi_1 \phi_{-1}|\} - D_3|\phi_{-1} \bar{\phi}_{-1}| \tag{46}$$

$$\Phi_{\text{CCDW}} = |\psi_t^+ \bar{\psi}_t^-| = D_1|\phi_1 \bar{\phi}_1| + iD_2/2\{|\phi_1 \bar{\phi}_{-1}| + |\bar{\phi}_1 \phi_{-1}|\} - D_3|\phi_{-1} \bar{\phi}_{-1}| \tag{47}$$

where

$$D_1 = 1/2(1+\cos\lambda), \quad D_2 = \sin\lambda \quad \text{and} \quad D_3 = 1/2(1-\cos\lambda) \tag{48}$$

These solutions are reduced to the restricted HF solution when $\lambda = 0$. The normalized energies of these solutions are given on the basis of the Hubbard-like parametrization as:

$$\tilde{E}_{\mathrm{ASDW}} = -2x + 1/2(x \geqslant 0.5) \quad \text{and} \quad -2x^2(x<0.5) \tag{49}$$

$$\tilde{E}_{\mathrm{CCDW}} = -2x + 1/2(x \geqslant 0.25) \quad \text{and} \quad -4x^2 + 1/4(x<0.25) \tag{50}$$

where

$$x = -\beta/\gamma \tag{51}$$

Functional dependences of the normalized energies on x are depicted in Fig. 1.

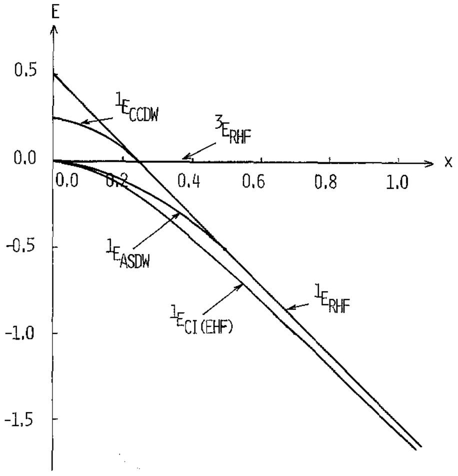

Fig. 1. Functional dependences of the total energies of the ASDW, CCDW and extended HF (EHF) solutions of homopolar two-center two-electron system on x

As is apparent from Eq. (45), the CCDW solution satisfies the spin symmetry but breaks the time-reversal symmetry. Fig. 1 shows that the CCDW solution gives the lower energy than the RHF solution in the molecular-orbital crossing region since the Coulomb repulsion between biradical electrons is removed by the doubly excited configuration introduced by the coupling of the singlet monoexcitations. However, since the singlet mono-excitation energy is larger than that of the triplet one, the CCDW solution is higher in energy than the spin-density wave (SDW) solution involving the triplet mono-excitation [23]. This is compatible with the fact that the triplet instability precedes the singlet instability breaking the time-reversal symmetry [31]. Fig. 1 clearly shows that the ASDW solution gives the reliable potential surface in the dissociation region ($x \simeq 0$). The CCDW solution, on the other hand, gives $1/4\,\gamma$ at $x = 0$, indicating the wrong behaviour at the dissociation limit. Thus the spin-symmetry breaking procedure is very important in order to incorporate the static correlation effect coming from the orbital degeneracy in the case of the HF method.

The spin- and time-reversal symmetry projected solutions are given by

$$\Phi_{\mathrm{H}}(0,0)=\mathscr{P}_{\mathrm{spin}}\psi_s^+\psi_s^-=\mathscr{P}_{\mathrm{time}}^+\psi_t^+\psi_t^-=N\{D_1|\phi_1\bar{\phi}_1|-D_3|\phi_{-1}\bar{\phi}_{-1}|\}\tag{52}$$

where N is the normalizing factor. Thus the projected HF solutions have the same full CI form in the present simple case. Then the spin- and time-reversal symmetry breaking procedures play the same role to heal the Coulomb repulsion in the extended HF scheme. This implies that the symmetry-breaking modes to incorporate the correlation effects are not uniquely determined in the minimal basis approximation. Functional dependences of the variational parameter on x are depicted in Fig. 2. As is apparent from Fig. 2, the ASDW solution is a good trial orbital set for the EHF calculation at small x-region. The potential surface of the ASDW solution is also similar to that of the EHF solution. Thus the present result indicates the utility of the ASDW-type spin-symmetry breaking orbital set as a trial set of the EHF calculation.

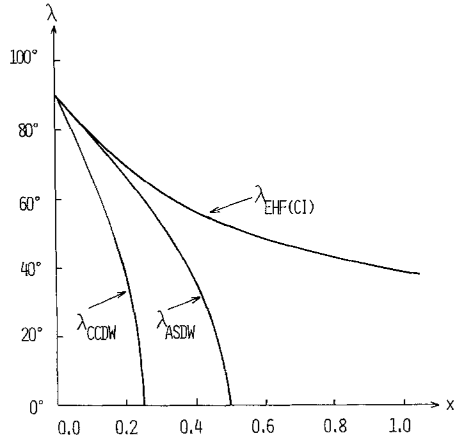

Fig. 2. Variations of the orbital mixing parameters of the ASDW, CCDW and EHF solutions of the homopolar two-center two-electron system with x

5.2. Linear Symmetric Three-Center Three-Electron L (3,3) System

Next, let us consider the linear symmetric (3,3) system with C_{2v} symmetry as shown in Fig. 3a. The natural orbitals are given by the OAO basis as

$$\begin{pmatrix}\phi_1^l\\ \phi_0^l\\ \phi_{-1}^l\end{pmatrix}=\frac{1}{2}\begin{pmatrix}1 & 1 & \sqrt{2}\\ \sqrt{2} & -\sqrt{2} & 0\\ 1 & 1 & -\sqrt{2}\end{pmatrix}\begin{pmatrix}\chi_1\\ \chi_2\\ \chi_3\end{pmatrix}\tag{53}$$

where $\phi_{\pm 1}^l$ and ϕ_0^l has A_1 and B_2 symmetries, respectively. The ground HF solution is given by the ASDW form [3] as

$$\begin{aligned}\psi_{\pm 1}^l&=\phi_1^l\cos\lambda/2\eta_{\pm}+\phi_{-1}^l\sin\lambda/2\eta_{\mp}\\ \psi_0^l&=\phi_0^l\,1/\sqrt{2}(\eta_++\eta_-)\end{aligned}\qquad (54$$

Table 2. Transformation properties of the M_x-modulate axial spin density wave (ASDW) orbitals with m′m2′ symmetry for the linear H_3 radical and the M_{xz}-modulate helical SDW (HSDW) orbitals with 2′ symmetry for the equilateral H_3 radical[a]

	E	$(C_{2z})^t$	$(\sigma_y)^t$	σ_x
ψ^l_1	ψ^l_1	$-i\psi^l_{-1}$	ψ^l_1	$-i\psi^l_{-1}$
ψ^l_{-1}	ψ^l_{-1}	$-i\psi^l_1$	ψ^l_{-1}	$-i\psi^l_1$
ψ^l_0	ψ^l_0	$i\psi^l_0$	$-\psi^l_0$	$-i\psi^l_0$
ψ'_1	ψ'_1	ψ'_1	*	*
ψ'_{-1}	ψ'_{-1}	$-\psi'_{-1}$	*	*
ψ'_0	ψ'_0	ψ'_0	*	*

[a] t = time reversion: $i\sigma_y\mathscr{K}$.

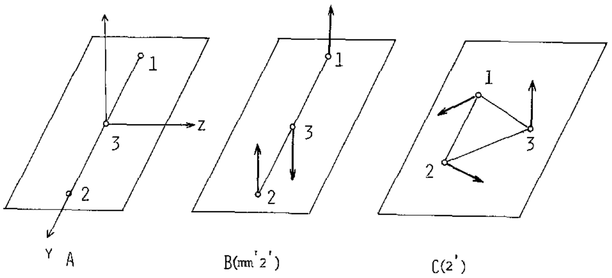

Fig. 3. Symmetry axes (A), and spin structures (B and C) of the linear symmetric and equilateral H_3 radicals, respectively

This orbital set has the $m'm2'$ magnetic symmetry [1] as shown in Table 2 and Fig. 3b. The normalized energy of the ASDW solution is given on the basis of the Hubbard-like model as

$$\tilde{E}_{\mathrm{ASDW}} = -2\sqrt{2}\,x \cos\lambda + \tfrac{1}{4}(1-\sin\lambda) + 3/8 \cos^2\lambda \tag{55}$$

where the energy of the RHF solution corresponds to the case where $\lambda = 0$. Functional dependences of the energies on x are depicted in Fig. 4. Fig. 4 shows that the ASDW solution gives the reliable potential surface even in the dissociation limit.

The $\mathscr{S}_z$ projected ASDW wavefunction is given by

$$\Phi(1/2) = \mathscr{P}_{\mathscr{S}_z} \psi^l_1 \psi^l_{-1} \psi^l_0 = \Phi_1\Theta_1 + \Phi_2\Theta_2 + \Phi_3\Theta_3 \tag{56}$$

where

$$\begin{aligned} \Phi_1 &= d_1 \phi^l_1(1)\phi^l_1(2)\phi^l_0(3), \qquad \Theta_1 = \eta_+(1)\eta_-(2)\eta_+(3), \\ &\quad d_1 = 1/2\sqrt{2}\,(1+\cos\lambda) \\ \Phi_2 &= d_2 \phi^l_1(1)\phi^l_{-1}(2)\phi^l_0(3), \qquad \Theta_2 = \eta_+(1)\eta_+(2)\eta_-(3), \\ &\quad d_2 = 1/2\sqrt{2}\,\sin\lambda \\ \Phi_3 &= d_3 \phi^l_{-1}(1)\phi^l_{-1}(2)\phi^l_0(3), \qquad \Theta_3 = \eta_-(1)\eta_+(2)\eta_+(3), \\ &\quad d_3 = 1/2\sqrt{2}\,(1-\cos\lambda) \end{aligned} \tag{57}$$

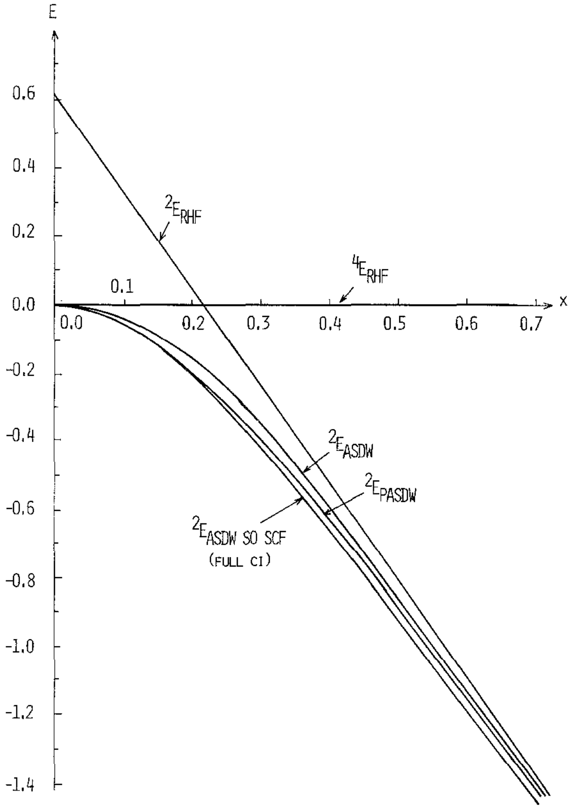

Fig. 4. Functional dependences of the total energies of the ASDW SO SCF and spin-projected ASDW solutions of the linear symmetric H_3 radical on x as those of various HF solutions

The $\hat{\mathscr{S}}^2$-projection is performed by using the unitary matric basis as

$$\begin{aligned}\mathscr{P}_{\mathscr{S}^2}\Phi_1\Theta_1&=\mathscr{A}\sum_i C_i e_{ii}^{[2,1]}\Phi_1\Theta_1=\mathscr{A}\Phi_1\sum_i C_i e_{ii}^{[2,1]}\Theta_1\\&=\mathscr{A}\phi_1^l(1)\phi_1^l(2)\phi_0^l(3)\,[C_1/6\,(2\Theta_1+2\Theta_3-\Theta_1-\Theta_2-\Theta_3-\Theta_2)\\&\quad+C_2/6\,(2\Theta_1-2\Theta_3+\Theta_1+\Theta_2-\Theta_3-\Theta_2)]\\&=d_1C_2\Phi_G\end{aligned}\tag{58}$$

where $\mathscr{A}$ is the antisymmetrizer and the ground configuration is given by $\Phi_G=|\phi_1^l\bar{\phi}_1^l\phi_0^l|$. Other terms are similarly given by

$$\begin{aligned}&\mathscr{A}e_{11}^{[2,1]}\Phi_2\Theta_2=-d_2/3\,\Phi_{C\beta}, &&\mathscr{A}e_{22}^{[2,1]}\Phi_2\Theta_2=0\\&\mathscr{A}e_{11}^{[2,1]}\Phi_3\Theta_3=0 &&\mathscr{A}e_{22}^{[2,1]}\Phi_3\Theta_3=-d_3\,\Phi_{E\alpha}\end{aligned}\tag{59}$$

where $\Phi_{C\beta}$ and $\Phi_{E\alpha}$ denote the spin-polarization and doubly excited configurations as

$$\Phi_{C\beta}=1/\sqrt{6}\{|\phi_1^l\bar{\phi}_{-1}^l\phi_0^l|+|\bar{\phi}_1^l\phi_{-1}^l\phi_0^l-2|\phi_1^l\phi_{-1}^l\bar{\phi}_0^l|\},\qquad \Phi_{E\alpha}=|\phi_1^l\bar{\phi}_{-1}\phi_0^l|\tag{60}$$

Thus the spin-symmetry adapted ASDW solution is given by

$$\Phi(1/2,\, 1/2) = \mathscr{P}_{\text{spin}} \phi_1^l \bar{\phi}_{-1}^l \phi_0^l = D_1 \Phi_{\text{G}} + D_2 \Phi_{\text{C}\beta} + D_3 \Phi_{\text{E}\alpha} \tag{61}$$

where the weights of the configurations are given by using the normalizing factor N as

$$D_1 = N\, d_1\, C_2, \qquad D_2 = -\sqrt{2/3}\, N\, d_2\, C_1, \qquad D_3 = -N\, d_3\, C_2 \tag{62}$$

The spatial and alternancy symmetry projections are not necessary since the above solution has the ${}^2B_2$ symmetry. The ASDW SO SCF wavefunction is equivalent to the full CI wavefunction in a minimal basis approximation when the spin-symmetry breaking (λ) and spin-coupling (ω) parameters are determined variationally where the latter is defined by

$$\sigma = \tan^{-1} \omega, \quad \omega = C_1/C_2 \tag{63}$$

The normalized total energy is given by

$$\tilde{E}_{\text{EHF}}(L) = -2\sqrt{2}\, x\, (D_1^2 - D_3^2) + \tfrac{5}{8} + \tfrac{3}{4} D_1 D_2 + \sqrt{3/8}\, (D_1 D_2 - D_2 D_3) \tag{64}$$

Figure 5 illustrates how the total energy changes with variations of the λ- and ω-parameters, assuming that $x = 0.5$. Then Löwdin's PHF solution corresponds to the case where $\omega = 1.0$. As is apparent from Fig. 5, the SO SCF wavefunction gives the local minimum in the hypersurface. The optimized λ- and ω-parameters for

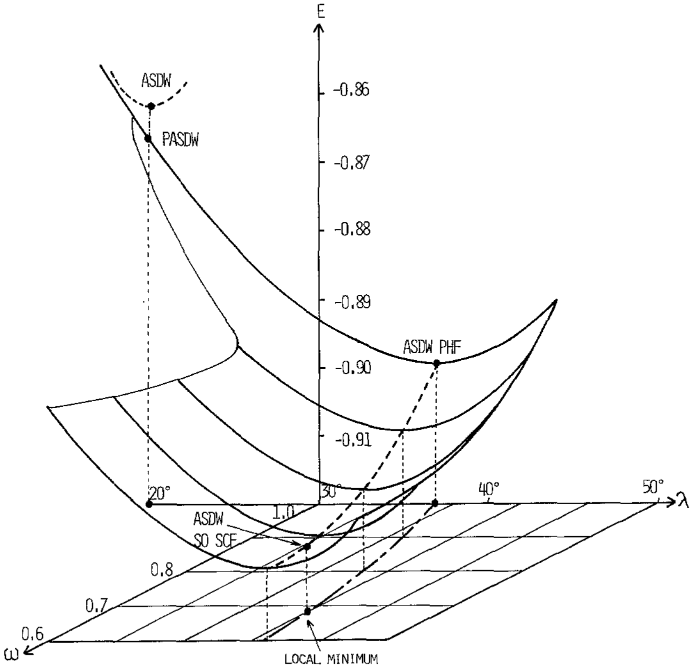

Fig. 5. Interrelationships among the energies of the spin-projected HF (SP-HF), projected HF (PHF) and spin-optimized SCF (SO-SCF) solutions of the linear symmetric H_3 radical on the basis of the Hubbard-like model at $x = 0.5$

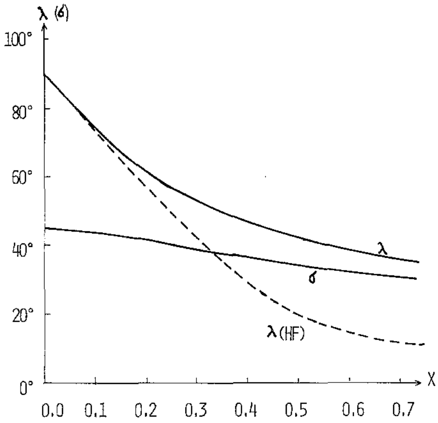

Fig. 6. Variations of the orbital mixing λ and spin-coupling σ parameters with x in the case of the ASDW SO SCF calculation of the linear symmetric H_3 radical. The λ-values of the ASDW solution are illustrated by the dotted line

varying x-values are illustrated in Fig. 6. Functional dependences of the total energies of the ASDW SO SCF and spin-projected ASDW solutions on x are also depicted in Fig. 4 as those of the HF solutions [3]. Figures 4–6 show that the ASDW solution is a good trial set for the SCF calculation and the spin-projected ASDW wavefunction gives a good energy surface.

The full CI wavefunction of the linear symmetric (3,3) system can be given by the spatial (v) and spin (λ) symmetry breaking parameters in the case of the projected HF (PHF) calculation by Laforge, Čižek and Paldus [26] as

$$\Phi_E(\tfrac{1}{2},\tfrac{1}{2}) = \mathcal{P}_{\text{space}}\mathcal{P}_{\text{spin}}\psi_1\psi_{-1}\psi_0 \tag{65}$$

where

$$\begin{aligned} \psi_\pm &= \cos\lambda/2\{(1-a)\phi_1 + b\phi_0 - a\phi_{-1}\}\eta_\pm \\ &\quad + \sin\lambda/2\{-a\phi_1 + b\phi_0 + (1-a)\phi_{-1}\}\eta_\mp \\ \psi_0 &= \{-b\phi_1 + (1-2a)\phi_0 - b\phi_{-1}\}1/\sqrt{2}\,(\eta_+ + \eta_-) \\ a &= \tfrac{1}{2}(1-\cos v), \qquad b = 1/2\sin v \end{aligned} \tag{66}$$

The spatial part of the trial function in the above approach has not the full symmetry of the C_{2v} group. Then their orbital set is referred to as the spatially symmetry non-adapted ASDW (NASDW) solution [3]. The spatial-symmetry projection is necessary to obtain the B_2 symmetry in this case. The above examples indicate that the NASDW PHF wavefunction is equivalent to that of the ASDW SO SCF method in the linear symmetric (3,3) system.

The mode of symmetry breaking to incorporate the correlation effects is, thus, not unique in the EHF scheme in the minimal basis approximation. In fact there are four different combinations in the case of the linear symmetric H_3 radical [26], i.e., (I) spatial plus spin symmetry breaking, (II) spin plus alternancy symmetry breaking, (III) spatial plus alternancy symmetry breaking, and (IV) spin-symmetry breaking plus spin-coupling variation. In the case of set (I), the spin-symmetry breaking parameter in the EHF calculation is considerably different from that of the ASDW solution. This implies that the ASDW solution cannot be utilized for the trial orbital set for the EHF calculation of the type (I). The last combination (IV) used in the present calculation, on the other hand, indicates the utility of the ASDW solution.

5.3. Hückel Three-Center Three-Electron H (3,3) System

The ground HF solution of the Hückel (3,3) system is given by the helical spin density wave (HSDW) orbitals which are defined by using the real natural orbitals as

$$\begin{aligned} \psi'_1 &= (\cos \lambda/2\ \phi^h_1 + 1/\sqrt{2} \sin \lambda/2\ \phi^h_{-1})\eta_+ + 1/\sqrt{2} \sin \lambda/2\ \phi^h_0 \eta_- \\ \psi'_{-1} &= (\cos \lambda/2\ \phi^h_1 - 1/\sqrt{2} \sin \lambda/2\ \phi^h_{-1})\eta_- + 1/\sqrt{2} \sin \lambda/2\ \phi^h_0 \eta_+ \\ \psi'_0 &= 1/\sqrt{2}\ (\phi^h_0 \eta_+ + \phi^h_{-1} \eta_-) \end{aligned} \tag{67}$$

where

$$\begin{pmatrix} \phi^h_1 \\ \phi^h_0 \\ \phi^h_{-1} \end{pmatrix} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 & 1 & 2 \\ \sqrt{3} & -\sqrt{3} & 0 \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \end{pmatrix} \tag{68}$$

This orbital set has the 2′ magnetic symmetry as shown in Table 2 and Fig. 3c. The normalized energy of the HSDW solution is given on the basis of the Hubbard-like model as

$$\tilde{E}_{\mathrm{HSDW}}(H) = -3x \cos \lambda + 1/3\ (2 - \sin \lambda - \sin^2 \lambda) \tag{69}$$

where the energy of the RHF solution corresponds to the case $\lambda = 0$. Functional dependences of the energies on x are depicted in Fig. 7. Fig. 7 shows that the HSDW solution gives the reliable potential surface even in the dissociation limit.

The S_z projected HSDW wavefunction is given by

$$\Phi'_{\mathrm{H}}(1/2) = \mathscr{P}_{\mathscr{S}_z} \psi'_1 \psi'_{-1} \psi'_0 = \Phi'_1 \Theta_1 + \Phi'_2 \Theta_2 + \Phi'_3 \Theta_3 \tag{70}$$

where the spin function Θ_i are the same in Eq. (57) and the spatial parts are given by

$$\begin{aligned} \Phi'_1 &= d_1\ \phi^h_1(1) \phi^h_1(2) \phi^h_0(3) + 1/\sqrt{2}\ d_2\ \{\phi^h_{-1}(1) \phi^h_1(2) \phi^h_0(3) - \phi^h_1(1) \phi^h_{-1}(2) \phi^h_0(3)\} \\ &\quad - 1/2\ d_3\ \phi^h_{-1}(1) \phi^h_{-1}(2) \phi^h_0(3) \\ \Phi'_2 &= 1/\sqrt{2}\ d_2\ \phi^h_1(1) \phi^h_0(2) \phi^h_{-1}(3) + \tfrac{1}{2}\ d_3\ \phi^h_{-1}(1) \phi^h_0(2) \phi^h_{-1}(3) \\ \Phi'_3 &= \tfrac{1}{2}\ d_3\ \phi^h_0(1) \phi^h_0(2) \phi^h_0(3) \end{aligned} \tag{71}$$

The $\mathscr{S}^2$-projections are performed similarly as shown in Eqs. (58) and (59), and results are as follows:

$$\begin{aligned} \mathscr{P}_{\mathscr{S}^2} \Phi'_1 \Theta_1 &= d_1 C_2 \Phi'_{\mathrm{G}} - 1/\sqrt{3}\ \Phi'_{\mathrm{C}\beta} - \tfrac{1}{2}\ d_3 C_2 \Phi'_{\mathrm{E}\alpha} \\ \mathscr{P}_{\mathscr{S}^2} \Phi'_2 \Theta_2 &= -d_2 C_1 \{\tfrac{1}{2}\sqrt{3}\, \Phi'_{\mathrm{C}\beta} + \tfrac{1}{2} \Phi'_{\mathrm{C}\alpha}\} - \tfrac{1}{2}\ d_3 C_1 \Phi'_{\mathrm{E}\alpha} \\ \mathscr{P}_{\mathscr{S}^2} \Phi'_3 \Theta_3 &= 0 \end{aligned} \tag{72}$$

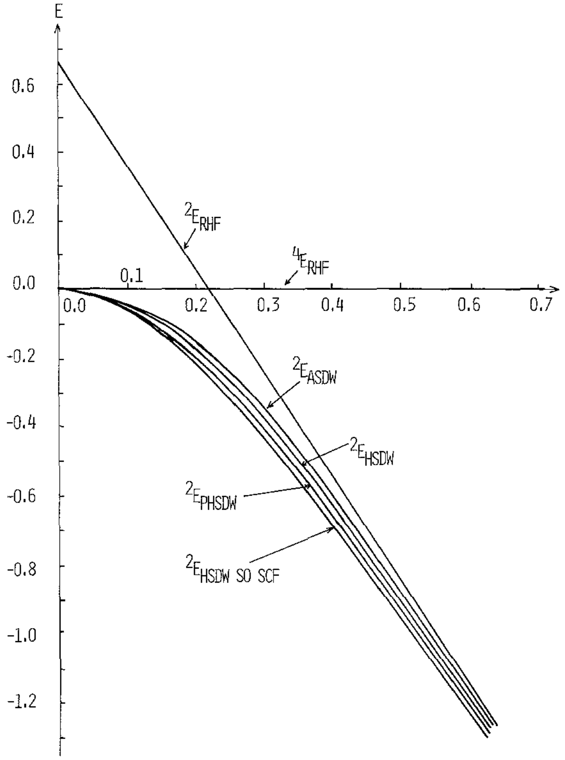

Fig. 7. Functional dependences of the total energies of the HSDW SO SCF and spin-projected HSDW solution of the equilateral H_3 radical on x as those of various HF solutions

where the configurations are similarly defined as in the case of the linear H_3 radical by replacing ϕ_i^l with ϕ_i^h. These configurations are schematically illustrated in Fig. 8. The spin-symmetry projected HSDW wavefunction is given by

$$\Phi_{\mathrm{H}}(\tfrac{1}{2},\tfrac{1}{2})(^2B_2)=D_1'\Phi_{\mathrm{G}}'+D_2'\{\sqrt{3}/2\,\Phi_{\mathrm{C}\beta}'+\tfrac{1}{2}\Phi_{\mathrm{C}\alpha}'\}-D_3'\Phi_{\mathrm{E}\alpha}' \tag{73}$$

where the CI coefficients D_i' and the singlet mono-excited configuration $\Phi_{\mathrm{C}\alpha}$ are given, respectively, by

$$D_1'=N'd_1C_2,\ D_2'=N'd_2C_1,\ D_3'=N'\tfrac{1}{2}(C_1+C_2)d_3$$

$$(N':\text{normalizing factor}) \tag{74}$$

$$\Phi_{\mathrm{C}\alpha}'=1/\sqrt{2}\{|\phi_1^h\bar{\phi}_{-1}^h\phi_0^h|-|\bar{\phi}_1^h\phi_{-1}^h\phi_0^h|\} \tag{75}$$

The above wavefunction (72) has the $^2B_2$ symmetry. The wavefunction with the $^2A_1$ symmetry, on the other hand, can be obtained in a similar manner as follows:

$$\begin{aligned}\Phi_{\mathrm{H}}(\tfrac{1}{2},\tfrac{1}{2})(^2A_1)&=\mathscr{P}_{\mathrm{spin}}(\psi_1')^t(\psi_{-1}')^t(\psi_0')^t\\&=D_1'\Phi_b+D_2'1/\sqrt{2}(\Phi_{\mathrm{a}}-\Phi_{\mathrm{E}\beta})-D_3'\Phi_{\mathrm{d}}\end{aligned} \tag{76}$$

where $\boldsymbol{t}$ is the time-reversal operation and the weights D_i' are defined by Eq. (74).

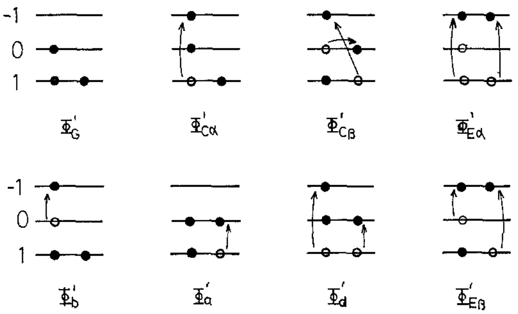

Fig. 8. The ground and excited doublet configurations constructed of the natural orbitals of the equilateral H_3 radical. The notations of the configurations are given in the text

The configurations with ${}^2A_1$ symmetry are given by

$$\Phi_b = |\phi_1^h \bar{\phi}_1^h \phi_{-1}^h|, \qquad \Phi_a = |\phi_0^h \bar{\phi}_0^h \phi_1^h|, \qquad \Phi_d = |\phi_0^h \bar{\phi}_0^h \phi_{-1}^h|,$$
$$\Phi_{E\beta} = |\phi_{-1}^h \bar{\phi}_{-1}^h \phi_1^h| \tag{77}$$

where Φ_a and Φ_b, Φ_d and $\Phi_{E\beta}$ are the mono-excited (internal), semi-internal and doubly excited (external) configurations [32], respectively, assuming that the ground configuration is given by $|\phi_1^h \bar{\phi}_1^h \phi_0^h|$. They are schematically illustrated in Fig. 8.

The ${}^2B_2$ and ${}^2A_1$ states are degenerate in energy at the D_{3h} conformation, compatible with the ${}^2E'$ state of the equilateral H_3 radical. The wavefunction with ${}^2E'$ symmetry is given by the complex molecular orbitals [4] as

$$\Phi_H(\tfrac{1}{2},\tfrac{1}{2})({}^2E') = \mathscr{P}_{\text{spin}} \psi_1^h \psi_{-1}^h \psi_0^h = 1/\sqrt{2}\{\Phi_H(\tfrac{1}{2},\tfrac{1}{2})({}^2A_1) + i\Phi_H(\tfrac{1}{2},\tfrac{1}{2})({}^2B_2)\}$$
$$= D_1' |\phi_1^h \bar{\phi}_1^h \phi_e^h| + D_2' |\phi_1^h \phi_{-e}^h \bar{\phi}_{-e}^h| + D_3' |\phi_e^h \bar{\phi}_e^h \phi_{-e}^h| \tag{78}$$

where the complex molecular orbitals are given [4] by

$$\phi_{\pm e}^h = -1/\sqrt{2}(\phi_{-1}^h \mp i\phi_0^h) \tag{79}$$

Thus the present results indicate that the spatial symmetry projections are not necessary if the magnetically ordered spinors are utilized as trial orbitals for the extended HF (EHF) calculations in the case of the $H(3,3)$ radical. This property is very important since the surface crossing between two states with different spatial symmetries can be correctly described in the present EHF scheme in contrast to the HF scheme [2, 3]. Thus the present results suggest the utility of the magnetically ordered spinors in the EHF approach.

The HSDW SO SCF wavefunction is equivalent to the full CI wavefunction in a minimal basis approximation when the spin-symmetry breaking (λ) and spin-coupling (ω) parameters defined by Eq. (63) are determined variationally. The normalized total energy is given by

$$E'_{\text{EHF}}(\text{H}) = -3x(D_1'^2 - D_3'^2) + \tfrac{2}{3}(1 - D_1'D_2' - D_2'D_3' - D_3'D_1') \tag{80}$$

Figure 9 illustrates how the total energy changes with variations of the λ- and ω-parameters, assuming that $x = 0.5$. As is apparent from Fig. 9, the SO SCF wave-

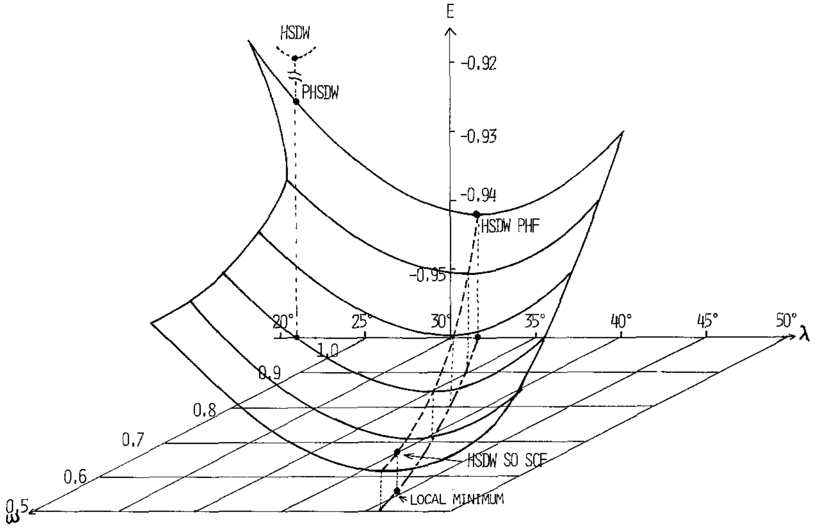

Fig. 9. Interrelationships among the energies of the spin projected HF (SP-HF), projected HF (PHF) and spin-optimized SCF (SO SCF) solutions of the equilateral H_3 radical on the basis of the Hubbard-like model at $x=0.5$

function gives the local minimum in the hypersurface. The optimized λ- and σ-parameters for varying x-values are illustrated in Fig. 10. Functional dependences of the total energies of the HSDW SO SCF and spin-projected HSDW solutions on x are also depicted in Fig. 7 as those of the HF solutions [3]. Figs. 7, 9 and 10 show that the HSDW solution is a good trial set for the SCF calculation and the spin-projected HSDW wavefunction gives a good energy surface. Thus the present EHF solution can be used to confirm the reliability of the HF calculations for organic molecules [2, 3] and clarify the characteristic of the HF approximation.

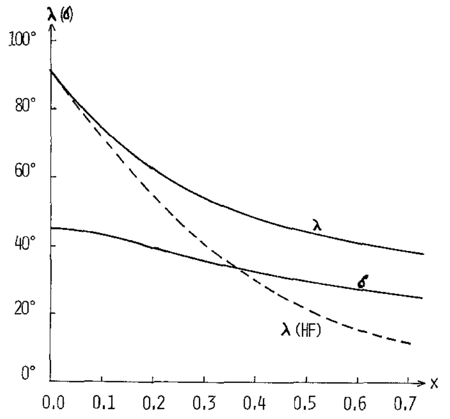

Fig. 10. Variations of the orbital mixing λ and spin-coupling σ parameters with x in the case of the HSDW SO SCF calculation of the equilateral H_3 radical. The λ-values of the HSDW solution are illustrated by the dotted line

5.4. *Möbius Three-Center Three-Electron M(3,3) System*

The natural orbitals of the Möbius (3,3) system can be easily obtained by the spatial symmetry as

$$\begin{pmatrix} \phi^m_e \\ \phi^m_{-e} \\ \phi^m_{-1} \end{pmatrix} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & \kappa & \kappa^2 \\ 1 & -\kappa^2 & -\kappa \\ 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \end{pmatrix} \quad (\kappa = e^{\pi i/3}) \tag{81}$$

The ground HF solution of the Möbius (3,3) system is given by the HSDW orbital as the Hückel (3,3) system [4].

$$\begin{aligned} \psi^m_{\pm 1} &= \cos \lambda/2 \; \Phi^m_{\pm e}\eta_{\pm} + \sin \lambda/2 \; \phi^m_{-1}\eta_{\mp} \\ \psi^m_0 &= 1/\sqrt{2}(\phi^m_{-e}\eta_{+} + \phi^m_e \eta_{-}) \end{aligned} \tag{82}$$

The EHF wavefunction of the pure doublet state can be easily obtained as

$$\begin{aligned} \Phi_M(\tfrac{1}{2},\tfrac{1}{2}) &= \mathscr{P}_{\text{spin}} \psi^m_1 \psi^m_{-1} \psi^m_0 \\ &= D'_1 |\phi^m_{-e}\phi^m_{-e}\phi^m_e| + D'_2 |\phi^m_e \phi^m_e \phi^m_{-1}| + D'_3 |\phi^m_{-1}\phi^m_{-1}\phi^m_e| \end{aligned} \tag{83}$$

where D'_j is given by Eq. (74). The normalized total energy of the M(3,3) system is equivalent to that of the H(3,3) system in both the HF and EHF cases.

$$\tilde{E}'_{\text{HSDW}}(H) = \tilde{E}'_{\text{HSDW}}(M), \; \tilde{E}'_{\text{EHF}}(H) = \tilde{E}'_{\text{EHF}}(M) \tag{84}$$

Since the same situations as those of the H(3,3) system appear in the case of the M(3,3) system, there is no need to repeat them here.

6. Energy Foundations of the Selection Rules of Free Radical Reactions

The linear, Hückel and Möbius conformations of homopolar systems have been utilized as the models of transition states of organic reactions. The Hückel MO approaches have been extensively performed to evaluate the resonance energies of the systems. However the more general approaches such as HF and EHF methods have not been performed to elucidate the relative stabilities among them. The three-center three-electron (3,3) system is one of the most simple systems where the EHF and HF wavefunctions can be obtained by using the Hubbard-like parametrization as shown in the preceding section. Then it seems important and interesting to examine the foundations of the selection rules based on the orbital- and permutation (spin)-symmetry conservation criteria [1–3] from the relative stabilities of the transition states in the case of the system. Figure 11 illustrates the variations of the electronic energies of the linear and cyclic (Hückel or Möbius) systems on x.

Figure 11 shows that the RHF energy lines for linear and cyclic conformations cross at $x = 0.265$. The energy lines of the HF solutions, on the other hand, do not cross, compatible with the EHF results which are equivalent to those of the full CI approaches in this case. Thus the same results are derived from the HF and EHF methods. This fact is very important since the construction of the EHF wave-

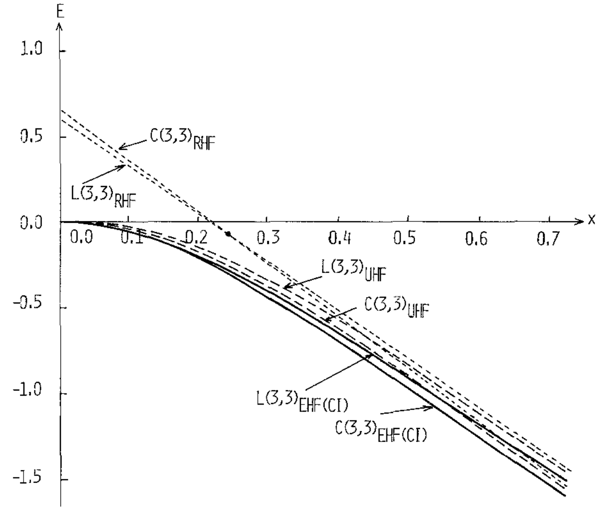

Fig. 11. Schematic illustrations of the relative stabilities between the linear and cyclic (Hückel or Möbius) conformations on the basis of the RHF, UHF and EHF approximations

functions is very difficult in the case of many-electron systems and HF solutions are alternately utilized in many cases. The present results also indicate that one can hardly derive the reliable stability–instability relationship unless the correlation effect is taken into account in the small x-region, i.e., weak resonance interaction region. The RHF solution, on the other hand, gives the reliable result in the strong resonance interaction region: $x > 0.5$. Thus Hückel and RHF solutions can be utilized to examine the relative stabilities of considerably stable free radicals.

The Hückel and Möbius (3,3) systems are only a little more stable in the electronic energy than the linear one in contrast to the even electron systems [1]. The nuclear repulsion term may cancel the excess stabilization energy of the cyclic conformation. For example, it has already been shown that the linear conformation is more stable than the Hückel one in the case of the H_3 radical [2]. It is also noteworthy that the effective exchange interaction J in the Heisenberg model involves the nuclear repulsion terms as the exchange interaction of the VB model of H_2 molecule by Heitler–London. The model can correctly predict the greater stability of the linear form [1, 33].

The correlation and spin correlation effects incorporated by the various wavefunctions obtained in the present paper can be analyzed systematically on the basis of the pair and spin correlation functions. They will be discussed in relation to the MO and VB selection rules in the succeeding paper.

7. Concluding Remarks

The results presented here are summarized as 1) the spin-symmetry adapted wavefunction can be constructed from the Hartree–Fock type orbital set by using the permutation operator and it satisfies Wigner's theorem, 2) there are axial (ASDW), planar (HSDW) and random (HSW) spin arrangements in the trial orbital sets of the present extended Hartree–Fock scheme as the Hartree–Fock approach, and

3) one of the ground EHF wavefunctions can be obtained by use of the magnetically ordered set which is similar to that of the ground HF solution, indicating the utility of the magnetic double point group.

The merit of the present EHF scheme lies in the group-theoretical approach which can clarify the interrelationships among the Heisenberg model, Hartree–Fock and simple extended HF methods [4]. The present method will be used to investigate the chemical reaction mechanisms in the case of the ground states of organic molecules as the three-center three-electron systems discussed in the present paper. The application of the present method to the four-electron systems are easy. This will be shown elsewhere [34].

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